**Iminopyrrolidine Ligand Design and Novel Group Four Precursors
for Chemical Vapour and Atomic Layer Deposition**

by

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Abstract

Consistent downsizing of microelectronics due to Moore's law scaling of integrated circuits has pushed traditional design techniques to their micro-scale limitations. When approaching the nano-scale, the electrical properties of the widely used poly-silicon based metal-oxide-semiconductor field-effect transistor (MOSFET) change drastically and render the devices un-useable. For this reason, the development of new materials that maintain favourable electrical properties on a nano-scale, such as titanium, aluminum, and zirconium based metals, metal-nitrides and metal-oxides, have been of growing interest in research. Future circuit design will require an efficient means for controlled and uniform coating of ultra-thin films of next-generation microelectronic materials. Two interesting candidates for depositing thin films are atomic layer deposition (ALD) and chemical vapour deposition (CVD).

The ability to control the uniformity of thin films using ALD and CVD depends on locating effective precursors for deposition. An effective precursor should be thermally stable, volatile, chemically reactive and self-limiting. Compounds with guanidinate and amidinate ligands make promising precursors due to their facile tunability, their volatility and their self-limiting properties. In this work amidinate and guanidinate precursors for ALD and CVD are developed and characterized.

This work includes the synthesis of a novel iminopyrrolidine ligand and characterization to determine its potential as an ALD precursor ligand. The ligand showed thermal stability and a tunable melting point trend demonstrating potential as an effective ligand for ALD and CVD precursors. In addition, once the iminopyrrolidinate

ligand was reacted with aluminum and titanium species, tunable melting points were observed for the resulting metal containing precursor species, offering potential flexibility in ALD process design.

The synthesis and thermal chemistry of other novel heteroleptic titanium and zirconium species are also presented. The most promising precursors include the heteroleptic titanium +3 guanidinate and amidinate species for the deposition of TiN/TiO₂ films. One of the guanidinate species was chosen for an exposure experiment on high surface area silica to study and determine the precursor chemistry with respect to nucleation between titanium and the substrate. The novel heteroleptic zirconium species presented in this work demonstrated two different bonding arrangements within the guanidinate family.

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List of Abbreviations

ALD – Atomic Layer Deposition

C₆D₆ – Benzene

CDI – Carbodiimide

CMOS – Complimentary Metal-Oxide-Semiconductor

CVD – Chemical Vapour Deposition

DEPT – Distortionless Enhancement by Polarization Transfer

DFT – Density Functional Theory

dimdip – dimethylamide diisopropyl guanidinate

DSC – Differential Scanning Calorimetry

EDS – Electron Diffraction X-ray Spectroscopy

ibip – iso-butyl iminopyrrolidine

IC – Integrated Circuit

ip – iminopyrrolidine

ipip – iso-propyl iminopyrrolidine

MAS-NMR – Magic Angle Spinning Nuclear Magnetic Resonance

MOCVD – Metal Organic Chemical Vapour Deposition

MOSFET – Metal-Oxide-Semiconductor Field-Effect Transistors

MS – Mass Spectroscopy

nbip – n-butyl iminopyrrolidine

NMR – Nuclear Magnetic Resonance

npip – n-propyl iminopyrrolidine

PVD – Physical Vapour Deposition

sbip – sec-butyl iminopyrrolidine

SEM – Scanning Electron Microscopy

SSP – Single Source Precursor

tbip – tert-butyl iminopyrrolidine

TEA – Triethyl aluminum

TG – Thermal Gravimetric

THF – Tetrahydrofuran

TMA – Trimethyl aluminum

TMS – Tetramethylsilane

tripyl – triisopropyl guanidinate

UHP – Ultra High Pure

VT NMR – Variable Temperature Nuclear Magnetic Resonance

List of Publications

Yamile Ana-Maria Wasslen, Agnieszka Kurek, Paul A. Johnson, Taylor C. Pigeon, Wesley H. Monillas, Glenn P. A. Yap, Seán T. Barry; Heteroleptic Iminopyrrolidines of Aluminum, *Dalton Trans.*, **2010**, DOI: 10.1039/C0DT00267D.

Yamile Ana-Maria Wasslen, Eva Tois, Suvi Haukka, Kevin A. Kreisel, Glenn P.A. Yap, Mathew D. Halls, Seán T. Barry; A Family of Heteroleptic Titanium Guanidines: Synthesis, Thermolysis, and Surface Reactivity, *Inorg. Chem.*, **2010**, 49, 1976.

Yamile Ana-Maria Wasslen, Seán T. Barry, Antti Rahtu, Suvi Haukka; A Novel Titanium Precursor for Atomic Layer Deposition, *U.S. patent*, **2006**, No. 11/588,595.

Chapter 1: Introduction

1.1 Atomic Layer Deposition

As nanotechnology becomes increasingly prevalent, the desire to make smaller scale architectures and thinner films is a mounting challenge. One method for developing thin films in a controlled manner can be accomplished using chemical vapour deposition techniques known as metal organic chemical vapour deposition (MOCVD) and atomic layer deposition (ALD).¹ Both techniques involve gas-phase introduction of reactants and require a chemical change to occur at the deposition surface. MOCVD and ALD are close cousins for the fabrication of thin films. They differ in the way in which the precursor is handled, which greatly affects the surface chemistry of the process. MOCVD introduces both precursors into the reaction chamber simultaneously where they react at the substrate to form a thermodynamically determined film.² ALD on the other hand has more control over the uniformity and the thickness of the film by introducing the precursors in intervals to the reaction chamber separated by purges to remove any volatile by-products.^{1,2} This process allows a monolayer of chemisorbed precursor with self-limiting behaviour to form at the substrate, which subsequently allows greater control of the film. Self-limiting monolayer formation occurs when the surface reactions are limited by the number of reactive surface sites and no further reactions occur on the surface once these sites are occupied.^{1,2} This complete monolayer saturation prevents continual growth of the film by inhibiting further reactions on the surface.^{1,2}

The step-wise introduction of the precursors help to attain the control that is achieved during ALD.² In the **first step** a metallic species for the desired target film is introduced to the reaction chamber and allowed to saturate the surface. During saturation, the metallic species chemisorbs to the surface via an anchoring ligand forming a new surface functional group and volatile by-products.

The **second step** is the removal of any unreacted metallic species and volatile by-products through purging with an inert gas, evacuating the chamber or by a combination of the two.

In the **third step** the second precursor, commonly referred to as the reactant gas, is introduced to the reaction chamber where it reacts with the chemisorbed metallic species to form a monolayer of the target film.

The resulting volatile by-products, this time the protonated ligands from the metallic species, and any excess second precursor is removed through purging with an inert gas, evacuating the chamber or by a combination of the two. This is the **fourth and final step** of a binary ALD cycle. Typical monolayer thicknesses are measured in Angstroms (Å), varying anywhere from a fraction of an Angstrom to several Angstroms.¹

An example of the step-wise growth of ALD is shown in Figure 1-1 using trimethyl aluminum (TMA) as the metallic precursor and water as the second precursor. The target film in this example is Al_2O_3 . a) is the introduction of the organometallic precursor, b) is the removal of unused volatile species and by-products, c) the introduction of the second precursor and d) removal of unused volatile species and by-products.

Figure 1-1. Step-wise growth of Al_2O_3 film using ALD.

These four steps are repeated until the desired thickness of the target film is achieved. In an ideal ALD process a full monolayer is formed after each cycle.³ In practice, however, due to steric hindrance caused by the precursor molecules, one cycle will usually produce only a partial monolayer.^{1d} This does not decrease the atomic level control that an ALD process can achieve as film thickness is dependent on the number of deposition cycles.^{1d}

There are two types of film growth that can occur through gas-phase reactions; continuous growth and self-limiting growth. One method of differentiating the type of growth that occurs during deposition is by collecting a saturation curve.⁴ A saturation

curve is a plot of the film growth rate as a function of precursor concentration and can be seen in Figure 1-2.

Figure 1-2. Saturation curve demonstrating a) ALD growth by self-limiting monolayer formation and b) continuous growth for a CVD process.

The precursor concentration can be determined by the pulse length, typically measured in seconds. When the pulse length is long, more precursor is introduced into the reaction chamber, thus increasing the exposure of the surface to the precursor. When self-limiting behaviour is reached (Figure 1-2a), all the surface sites have been fully saturated by a monolayer of precursor and no further reaction will occur on the surface, regardless of the amount of precursor introduced into the reaction chamber.⁴ At such a concentration the growth rate will reach a plateau as any further increase in precursor concentration will not affect the growth rate. In order for a process to be considered ALD, **both** precursors must exhibit self-limiting behaviour. This can be accomplished by collecting saturation curves for both precursors demonstrating a growth rate plateau with respect to precursor concentration. Saturation curves not only demonstrate the type of

growth occurring during deposition but it is also a useful tool in optimizing growth conditions such that precursor waste and process times are kept to a minimum.

If self-limiting monolayer formation is not accomplished during deposition, continuous growth can be seen in the saturation curve (Figure 1-2b). In a continuous growth deposition, no plateau of the growth rate is reached and the growth rate will increase with increasing precursor concentration. This type of growth is a chemical vapour deposition (CVD) process: the precursor is decomposing upon chemisorption to the surface.⁴ The thickness of the film cannot be controlled through number of pulses as film thickness will increase with increasing precursor concentrations.

Many different types of films can be produced via ALD or CVD process such as metal oxides, metal nitrides and metal films, to name a few. Metal oxides typically use water as the second precursor; however ozone⁵, hydrogen peroxide^{4,6} and oxygen^{1d} have also been used when the reactivity of water has not been sufficient.⁷ Metal nitride films are typically deposited using metal halide and ammonia as the two precursors.² Metal films can be deposited by ALD using either hydrogen reduction through thermal chemistry or enhanced by hydrogen plasma.⁸ The reactions that occur spontaneously at various temperatures are referred to as thermal ALD because films can be deposited through use of heat and without the aid of plasma assistance. However, for certain metallic films, thermal chemistry and hydrogen reduction is not reactive enough and so techniques such as plasma enhanced ALD can be used. Energetic species in the plasma can induce reactions that are otherwise not possible using thermal energy. Plasma sources can be used to produce hydrogen radicals that reduce the metal.^{2d}

ALD is not only limited to binary reaction sequences. Other types of films such as binary oxide films $\text{Zr}_x\text{Ti}_y\text{O}_z$,⁹ GdScO_3 ¹⁰ and SrTiO_3 ¹¹ can be deposited using this technique. The deposition temperature (also known as reaction temperature) for a self-limiting ALD process is very important. It is at these optimal temperatures that thermal decomposition of the precursor does not occur, but monolayer growth is achieved.^{1d} This temperature is typically above the temperature of chemisorptions, but below the temperature of thermal decomposition.

Additionally, when depositing a multi component film it is very important to know the vapour phase thermal stability of the precursors.¹² The reaction temperature of each precursor should overlap in such a manner that self-limiting growth is attained and condensation or insufficient precursor reactivity (reaction temperature too low) or decomposition or desorption of precursors (reaction temperature too high) does not occur.¹ Designing processes with lower reaction temperatures for ALD and CVD processes is an ongoing challenge in this field of chemistry. The drive for lower temperature processes is an effort to reduce energy consumption and (in some cases) prevent crystallization of the target film. One method of achieving this is by synthesizing precursors that are highly volatile and chemically active at lower temperatures.

ALD is becoming an important technique for depositing thin films for a variety of applications.^{1,2,4} The ability to control the deposition of thin films by an atomic layer stems from the stepwise addition of the precursors. However the design of the precursors also plays an important role in the uniform and controlled manner of this technique.^{8,13} In order for a precursor to be ideal for ALD it must follow certain criteria.^{3,4}

1.2 Precursor Design

The first design criterion is the production of a **volatile species**. The precursor must have a high vapour pressure in order to reach the reaction chamber in the gaseous state as ALD is a gas-phase reaction. This characteristic can be achieved by coordinatively saturating the metal centre to prevent oligomerization from occurring and by keeping the molecular weight of the species to a minimum.

The second design criterion that compliments the first is to design a precursor with a **low melting point**. A distillable liquid precursor would be ideal; however low melting solids are not detrimental.⁴ Heating a low melting solid at an elevated temperature forces the solid to melt. Once the solid has melted, the surface area of the liquid would allow production of a reproducible amount of gaseous precursor to enter the reaction chamber as the surface area will constantly replenish itself. High melting solids do not have a surface area that can replenish itself; as the solid sublimes, the surface area of the solid decreases. A precursor with a reproducible vapour pressure would allow a constant concentration to enter the reaction chamber at each cycle of an ALD run. This in turn would help to ensure complete and uniform monolayer formation and will help to make ALD a more efficient process for thin film deposition. This can be achieved by introducing branching and asymmetry in the ligand in order to frustrate crystallization.¹⁴

Thermal stability is an important design criterion for two reasons. Firstly, since ALD is a gas-phase reaction and a high vapour pressure is essential, the precursor of choice may be heated for long periods of time to maintain an acceptable vapour pressure during deposition. The precursor must be able to withstand such treatment to ensure that the species introduced to the reaction chamber in the first pulse is the same as the species

introduced in the last pulse. The second reason for thermal stability is to prevent thermal decomposition once in the gas-phase in order to obtain self-limiting film growth. Decomposition may occur during the deposition of a film without the reactant gas, (i.e. CVD-type growth). The rate of decomposition will increase exponentially with temperature as decomposition is thermally activated. Reaction chamber temperatures can range from room temperature to as high as 500°C¹⁵ and so a good precursor must be kinetically stable at these temperatures.

Chemical reactivity is another criterion for a good ALD precursor. The bonds being formed during deposition must be stronger than the bonds being broken within the precursor.^{1c} Both precursors must be reactive towards each other and should react completely to reduce cycle time and impurity levels.⁴ The organometallic precursor must react with the surface functional groups of the substrate by chemisorption and remain bonded during purging periods.³ One way of achieving this is by including an anchor ligand on the metal precursor. An anchor ligand is a small monodentate ligand that can reach, and thus react, with the surface species resulting in the formation and evolution of a stable volatile by-product. An example of an anchor ligand would be a methyl group from a precursor such as TMA, which, once reacted to the surface hydroxyl species, would produce methane for aluminum oxide depositions.

The production of **stable** and **volatile by-products** when the metal precursor reacts with the surface functional groups and when the reducing precursor reacts with the chemisorbed metal precursor is a subset to the latter criterion. This ensures that the metal films contain fewer impurities as the by-products can be easily and efficiently removed during the purging or evacuation step.

The most important criterion for ALD is **self-limiting behaviour**.^{1,2,3,4,8} This type of behaviour is accomplished by sterically protecting the metal centre through use of a ligand. This will prevent vapour phase molecules from reacting with the molecules chemisorbed to the surface as well as preventing the molecules from reacting with itself in the gas-phase. If this criterion is not met then continuous growth can occur as more than one monolayer can be deposited in each sequential pulse.

Meeting these simple criteria can afford a precursor that will help make the ALD process more efficient. In order to do so, the ligands of the metal precursor must be carefully considered.

1.3 Ligands

Previously, cyclopentadienyl groups have been used as ancillary ligands for ALD as they have been known to increase the deposition rates for certain films.¹⁶ Due to the reactive nature of these metallocene precursors, softer oxidizing precursors, such as water, are often used for oxide film deposition. The most common bonding arrangement of cyclopentadienyl to a metal ion is “side on”, where all five carbon atoms are equidistant from the metal ion and are thought to participate in a π -bonding fashion.¹⁷ The other less common bonding arrangement of cyclopentadienyl ligand is through a single C-M bond where it is considered to participate in a σ -bonding mode (Figure 1-3).

Figure 1-3. Bonding modes of cyclopentadienyl ligands; η^1 and η^5 .

ALD precursors with cyclopentadienyl ligands are attractive, however their reactive nature and troublesome handling (they can be very pyrophoric and air-sensitive) make them undesirable.¹⁸ There have been many advances in organometallic chemistry to find alternative ancillary ligands to the cyclopentadienyl ligands.¹⁹ Amidinate and guanidinate ligands are of particular interest for many reasons, one being their wide range of commercially available starting materials – carbodiimides and lithiated alkyl and amido groups (Figure 1-4) as well as their versatile nature.

Figure 1-4. Resonance structure of a) amidinate and b) guanidinate ligands.

Amidates and guanidates are interesting N-centred donor ligands in organometallic chemistry. They are especially important as they have been shown to behave similar to cyclopentadienyl ligands; their core angles and sterics are very similar.²⁰ They have an advantage over the latter ligands in that they are more versatile

and their electronic and steric properties can be altered more readily by varying the substituents on the N-atoms.²¹

1.3.1 Amidinates

Amidinate anions have been thoroughly studied in the past few decades.¹⁹ Their versatility makes them attractive ligands for ALD as they can be easily tuned to meet the specific criteria mentioned above. The nature of the ligand can vary depending on the steric bulk found on the sp^2 hybridized carbon and the chelating nitrogens. Amidinates are named according to these substituents. An amidinate with $R = H$ is known as a formamidinate. Where $R = Me$ the ligand is known as an acetamidinate, $R = Et$ the ligand is named ethylamidinate and so on. There are theoretically eight ways in which they can bond to metal centres based on their electronic and spatial structures^{19a} (Figure 1-5).

Figure 1-5. Theoretical bonding modes of the amidinate ligand.

Of these theoretical bonding modes, two have not been seen experimentally; A and E. The most commonly seen amidinate in ALD precursors is structure C and will be discussed further. The reason for its predominance is the stabilization of the metal centre through the resonance structure it possesses (Figure 1-6). In this mode, the four-membered MNCN metallocycle introduces steric strain and can lead to a distortion in N-C bond lengths and planarity of the ring.

Figure 1-6. Resonance structure of amidinate ligands.

The degree of pyramidalization of the nitrogens is determined by the sum of all bond angles around the nitrogen atom. The closer this number is to 360° , the less pyramidalized the nitrogen atom and the closer the metallocycle geometry is to planar. The amidinate ligand has a net charge of -1 and thus can displace one monodentate ligand at a time to form mono-substituted (four-coordinate) to tri-substituted (six-coordinate) species (Figure 1-7). Their stabilization is limited compared to guanidines as they do not have the ability to form a second resonance form like their guanidine cousins.

Figure 1-7. Bonding modes of a) mono-substituted (four-coordinate) and b) tri-substituted (six-coordinate) amidinate species.

1.3.2 Guanidines

Monoanionic guanidinate ligands have shown remarkable compatibility with a large range of metals in a variety of oxidation states.²¹ They differ from amidinates by the bonding of an amido group to the sp^2 hybridized carbon. This bonding arrangement can lead to an extra electronic flexibility of the system due to a unique resonance form that can place a formal negative charge to both nitrogens, resulting in a zwitterionic resonance (Figure 1-8). This resonance form can only occur if the exocyclic nitrogen is in a position where its lone pair electron density can be donated to the central carbon atom.²² With this resonance form, guanidines exceed the flexibility and π -donor ability of amidinates and allow them to bond to more electron deficient metals. It also increases their basicity as they are stronger donors, and for a given metal, replacement of an amidinate with a guanidinate would increase the electron density on the metal and reduce its oxidation potential.²¹

Figure 1-8. Zwitterionic resonance.

Dianionic guanidinate species can be synthesized by deprotonating the parent guanidine a second time in tetrahydrofuran (THF) at or below room temperature. This ligand is unique as it is isoelectronic with the carbonate anion and the trimethylenemethane dianions.^{21,23} Similar to the latter ligands, the dianionic guanidinate

ligand can have a Y-conjugation occurring, where the π delocalization of the lone pairs on the sp^2 hybridized nitrogen are shared with the sp^2 hybridized carbon centre as seen in Figure 1-9.²³ There are fewer cases of the dianionic species than monoanionic guanidinate species found in literature. This may be attributed to the fact that these ligands have been known to form dimers with complicated bonding modes.²⁴

R = alkyl

Figure 1-9. Y-conjugation.

Guanidinate anions are valuable ancillary ligands due to their steric and electronic flexibility, the variety of possible coordination modes, the availability of both monoanionic and dianionic forms and the ease with which they can be synthesized to bear many combinations of substituents.²¹ The monoanionic guanidinate has a net charge of -1 and can displace one to three monodentate ligands to form mono-substituted (four-coordinate) to tri-substituted (six-coordinate) species. The dianionic guanidinate ligand has a net charge of -2 and can displace two monodentate ligands to form a mono-substituted (four-coordinate) species depending on the metal centre used.

Figure 1-10. Bonding modes of a) mono-substituted (four-coordinate) and b) tri-substituted (six-coordinate) guanidinate species.

Each of the aforementioned ligands are volatile species when protonated, making their use in ALD and CVD attractive. The volatile by-products can be eliminated through purging or evacuation of the reaction chamber reducing the amount of impurities within the film.

1.4 Synthesis

There are several ways to synthesize metal complexes with amidinate and guanidinate ligands. The first synthetic method is an insertion reaction where an alkyl or amido group of an organometallic moiety (M-R) inserts into a C=N double bond of a carbodiimide (CDI). These reactions proceed under fairly mild conditions and can produce mono, bis, or tris substituted amidinate and guanidinate derivatives in high yields.²⁵ CDI insertion reactions have been thoroughly studied and a mechanism was established using density functional theory (DFT) calculations.^{25d}

Scheme 1-1. Insertion reaction of carbodiimide to metal alkyl or amido bond.

CDI insertion is an excellent synthetic pathway when the starting material contains only one type of ligand (homoleptic), however once there are different alkyls, amido or halogen ligands on the metal, CDI insertion can be problematic. Chang et al. have studied these systems and concluded that CDI insertion exhibits preferences over which ligand to insert depending on what type of CDI is used. One way to overcome such issues when synthesizing complexes that bear different ligands (heteroleptic) is by ligand exchange. Ligand exchange can occur between a six or five-coordinate metal species and a tri-substituted alkyl or amido homoleptic metal species (Scheme 1-2). This process was thoroughly studied using DFT calculations²⁶ but will not be expanded upon as no exchange reactions were conducted throughout this work.

Scheme 1-2. Ligand exchange from a five-coordinate species to a four-coordinate species.

Another approach involves deprotonation of an amidine or guanidine by an alkyl or amido organometallic compound.¹⁹ This method also proceeds under fairly mild conditions and tends to produce high yields due to the thermodynamic sink of an evolving gas.

Alkane or amine elimination is an attractive method in synthesizing organometallic compounds as the production of by-products is minimal. This method was used in this work for the synthesis of heteroleptic aluminum and one set of heteroleptic titanium precursors.

The most popular method of amidinate and guanidinate synthesis in transition metal and main group complexes (and metal compound synthesis generally) is salt metathesis.^{19a} This includes the reaction of anionic amidinate and guanidinate salts of alkali or alkaline-earth metals with halides of Group 3 – 15 elements. The driving force of this reaction is the precipitation of insoluble salts, forcing the reaction to push to the right.

Scheme 1-4. Salt metathesis reaction.

Four to six-coordinated amidinate and guanidinate species can be made using this synthetic pathway with overall decent yields. The majority of the compounds synthesized in this work were achieved through salt metathesis.

1.5 Thermal Characterization

One technique that is commonly used to determine the volatility of an ALD or CVD precursor is thermal gravimetric (TG) analysis. This technique measures weight changes in a material as a function of time or (most commonly) temperature under a controlled atmosphere. Such a technique can help to determine the thermal stability and volatility of a certain species.²⁷ The slope and the temperature at which the compound begins to volatilize can help determine whether the species would be fit for ALD or CVD processes. When the slope is steep, has only one feature and results in a low residual mass (< 15%) (Figure 1-11), the species is considered to have high volatility and thermal stability as the thermolysis is considered to be clean. If the slope is gradual or interrupted the species is considered to have poor volatility as thermal degradation has occurred (Figure 1-12).

Figure 1-11. TG demonstrating a clean volatilization accompanied with a derivative weight curve.

Figure 1-12. TG demonstrating an interrupted derivative weight curve and poor volatilization.

A derivative weight curve is used to aid in the determination of clean thermolyses. A single asymmetric peak with a slow on-set and a quick drop-off after a maximum is reached demonstrates one thermal event has occurred and that clean volatilization was achieved (Figure 1-11). If the derivative weight percent shows several features or has a symmetric peak the species is considered to have most likely undergone thermal degradation (Figure 1-12).

The temperature at which volatilization begins is termed the on-set of volatility and is defined (somewhat arbitrarily) as 5% weight loss. A desirable on-set of volatility for an ALD precursor would occur at low temperatures.

Another technique that is used simultaneously with TG is differential scanning calorimetry (DSC). DSC measures temperature and heat flow associated with the thermal transitions within a sample material. This is accomplished by measuring the difference in the amount of heat required to heat a sample and a reference as a function of temperature. This complementary technique measures endothermic or exothermic events which have no associated weight loss, such as melting, and can help to differentiate between events that do involve weight loss, such as thermal degradation.

1.6 References

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Chapter 2:

Iminopyrrolidine Ligand and Aluminum Complexes

2.1 Introduction

Amidates and guanidates have been widely used as alternative ligands to cyclopentadienyl ligands in organometallic chemistry.¹ These ligands have been used with many metals across the periodic table to make organometallic complexes for catalysis² as well as potential precursors for processes in material science and nanotechnology such as MOCVD and ALD.³

Amidate and guanidate anions of the general formula $[\text{RC}(\text{NR}')_2]^-$ and $[\text{R}_2\text{NC}(\text{NR}')_2]^-$ respectively (where $\text{R} = \text{H}$ or alkyl and $\text{R}' = \text{alkyl}$) are commonly found as ligands on precursors for ALD due to their tunable properties which allow control over volatility and melting point.⁴ The flexibility to change the steric and electronic properties of these ligands is highly attractive. However, mechanistic investigations of these ligands have revealed that deinsertion of CDI from the parent guanidinate or amidinate at elevated temperatures can occur (Scheme 2-1).⁴

Scheme 2-1. Deinsertion of CDI at elevated temperatures.

Thus the search for a ligand that does not allow the deinsertion of CDI has led to a novel alternative; iminopyrrolidine. The iminopyrrolidinate ligand is monoanionic like its amidinate counterpart; however the sp^2 carbon is tethered to one of the chelating nitrogens through a five membered ring (Figure 2-1). This type of structure would prevent CDI (Scheme 2-1) deinsertion because rearrangement to form CDI would be highly unfavourable. It is also viewed to be more stable than their oxazoline analogues as they are less likely to undergo ring opening decomposition.⁵

Figure 2-1. The similarity in chelating geometry of an amidinate, an iminopyrrolidinate and an aminooxazolidinate.

Iminopyrrolidinate based ligands, like amidinates, can be easily tuned to decrease melting point by increasing the length and controlling the branching of the alkyl chain bonded to the acyclic nitrogen. The asymmetry of the ligand is a desirable feature as it can increase volatility of organometallic complexes. This chapter will introduce a novel family of ligands and discuss their reactivity with TMA and triethyl aluminum (TEA) to make heteroleptic aluminum derivatives. Aluminum was used as an introductory metal as its chemistry is facile and well known. The thermal behaviour of the ligands and the aluminum compounds will also be examined. The advantage of these potential aluminum precursors would be the prevention of CDI deinsertion at elevated temperatures.

2.2 Results and Discussion

2.2.1 Ligand Synthesis and Thermolysis

A straightforward synthetic route (Scheme 2-2) for iminopyrrolidines was achieved after Amanda Kenney and Agnieszka Kurek tweaked the experimental from two previously reported syntheses^{5,6} and each reported their advances in their theses.^{7,8} Due to the low boiling point of isopropyl amine, the butyl amine family and n-propyl amine were used in hopes to increase the yield of this ligand. Thus, the synthetic procedure will be discussed in detail.

Scheme 2-2. Synthetic procedure for iminopyrrolidine ligands.

The molar ratio of the amine was increased compared to the literature preparation due to high volatility issues. The amount of amine was doubled and mixed with the pyrrolidinone then added through a reflux condenser to neat P_2O_5 . A longer reflux condenser was used to ensure that the amine would be contained during the reaction. Very importantly, the source of heat was changed from an oil bath to a sand bath. The sand bath proved to have less heat loss to the surroundings than the oil bath and so it was much easier to control and quicker to reach reflux temperatures. Keeping the time of heating short was crucial to improving the yield.

Once the reaction time of 2 hours was reached, the reaction was allowed to cool to a glassy solid. Instead of using ice to dissolve the solid,⁶ 40 mL of distilled water was used with the aid of a heat gun. The strength of the base was increased to 6 M NaOH to avoid the introduction of too high a volume of water: iminopyrrolidines are soluble in water.

By simply implementing these changes we were able to achieve excellent yields of the purified ligands. The n-propyl iminopyrrolidine, **1**, was sublimed under reduced pressure at 60°C to afford a colourless solid (Table 2-1).

Table 2-1. Yield and melting point for compounds **1** - **4**.

	Compound	Yield (%)	Melting Point (°C)
1	N-propyl iminopyrrolidine	72	72 - 74
2	AlMe ₂ npip	79	79 - 83
3	AlEt ₂ ipip	70	120 - 124
4	AlEt ₂ npip	72 ^a	liquid

^a Crude yield

The bench top melting point of the ligand **1** was comparable with the endothermic peak of the DSC results (Figure 2-2, Table 2-1). An endotherm at 79°C was achieved at a ramp rate of 10°C/min as well as what may be a boiling point at 255°C. The first endotherm was very close to the bench top melting point of 72 - 74°C. Five other iminopyrrolidine ligands were synthesized, purified and studied in previous reports, with **1** completing the series of the propyl derivatives.^{7,8,10} Thermolysis studies demonstrated a melting point trend associated with the alkyl moiety on the ligand (Table 2-2). N-propyl iminopyrrolidine (npip, **1**) has a lower melting point than its similar propyl iminopyrrolidine ligand; iso-propyl (ipip, **1.1**), 74°C compared to 100°C, respectively. The drop in melting point may be associated with the increase in the degree

of freedom of the longer chain from the n-propyl moiety of **1** compared to the branched iso-propyl moiety of **1.1**. This effect of lowering melting points was also evident when **1** was compared with the n-butyl iminopyrrolidine (nbip, **1.2**), where the longer chain lowered the melting point by roughly 18°C. The extra methyl group adds to the degree of freedom of **1.2** compared to **1**. As the branching increases, the degree of freedom decreases, from **1.2** to tert-butyl iminopyrrolidine (tbip, **1.5**) increasing the melting point. Notably, there is a decrease in the melting point for sec-butyl iminopyrrolidine (sbip, **1.4**). This can be attributed to the fact that there is asymmetric branching around the amine as well as the stereoisomer present due to the sec-butyl group.

Figure 2-2. Differential scanning calorimetry of **1**.

Table 2-2. Thermal parameters of iminopyrrolidine ligands.

Compound	R	Melting Point (°C)	On-set of Volatility (°C) ^a
1	N-propyl (npip)	72 – 74	84.91
1.1	Iso-propyl (ipip) ^b	99 – 100	76.48
1.2	N-butyl (nbip) ^c	55 – 56	95.30
1.3	Iso-butyl (ibip) ^c	102 -103	83.46
1.4	Sec-butyl (sbip) ^c	98 – 100	75.51
1.5	Tert-butyl (tbip) ^c	108 – 110	71.21

^a on-set of volatility was taken as 5% mass loss, ^b compound taken from reference [7], ^c compounds taken from reference [8].

Thermal gravimetric (TG) analyses of all six ligands were collected (Figure 2-3). Although **1.2** had the lowest melting point it is evident that it had the highest on-set of volatility, followed by **1**. The higher on-set of volatility suggests stronger hydrogen bonding between the molecules. This can be attributed to the lack of steric hindrance around the amide in the straight chained alkyl complexes. Even with a higher on-set of volatility compound **1** has a clean volatilization (only one feature in the TG), demonstrating that it did not decompose under heat. The residual mass of each ligand was zero, also indicating a clean thermolysis. The on-set of volatilization (i.e. 5% mass loss) for **1** occurred at 85°C and showed an uninterrupted weight loss to 0% residual mass. The differential curve for this weight loss (Figure 2-4) had the typical appearance of sublimation, an asymmetric curve with a slow on-set and a quick drop-off.

Figure 2-3. Thermal gravimetric analysis of iminopyrrolidine ligands.

Figure 2-4. Differential weight curve for iminopyrrolidine ligands.

A nuclear magnetic resonance (NMR) tube boil-up was performed on all six ligands since this thermolysis experiment was previously unreported for these compounds.¹⁰ Compounds **1** - **1.5** were dissolved in 0.25 ($\pm$ 6) mL of 1% v/v tetramethylsilane (TMS) in benzene (C_6D_6) solution in thick-walled NMR tubes under inert atmosphere. The tubes were immersed in liquid nitrogen and the glass tube was sealed under vacuum. Each tube was placed in a furnace at 125°C and the loss of the furthest methyl (CH_3) group peak of R was monitored relative to TMS using 1H NMR. Decomposition began for ligands **1**, **1.1**, **1.2**, and **1.3** after 6 days but did not progress further during the duration of the experiment. The decomposition of the ligands showed no production of CDI; however the formation of a small amount of the parent amine and a ring species was evident in each case. After 28 days at elevated temperatures ligands **1.4** and **1.5** showed no decomposition. This finding revealed that the ligand species **1** – **1.3** thermolyses by loss of the parent amine was perhaps due to some impurities found within the NMR tube as there was no progression of the decomposition for the duration of the study. Subjecting these ligands to such aggressive conditions for an extended period of time without decomposition demonstrated that they may be excellent ligands for ALD processes.

2.2.2 Synthesis of Heteroleptic Aluminum Species and Crystal Structure Data

TMA was used as the starting material for the synthesis of a heteroleptic aluminum complex containing **1** as the ligand. A one-to-one ligand-to-TMA mixture in hexanes at room temperature was used to synthesize the dimethyl aluminum iminopyrrolidinate complex **2** (Scheme 2-3). Methane elimination was the driving force of this reaction.

Scheme 2-3. Synthesis of complex **2**.

Compound **2** was a colourless solid and was purified by crystallization which produced cubic crystals of sufficient quality for a single crystal structure to be collected (Figure 2-5 and Figure 2-6, Table 2-3 and Table 2-4). The ^1H NMR for this compound was similar in its simplicity to the other bip/pip heteroleptic compounds^{7,8} suggesting a symmetric compound with no evidence of monomer – dimer equilibrium.

Figure 2-5. The single-crystal X-ray structure of **2**. The thermal ellipsoids are shown at 50% probability and the hydrogen centres are omitted for clarity.

Compound **2** was symmetrical existing in a P-1 space group with an S_2 symmetry axis and a centre of inversion residing at the molecular centre. The aluminum was in a distorted tetrahedral geometry with angles very close to ideal ranging from 105.7° to 114.7° with C1-Al-C2 being the largest angle. It was evident from the crystal structure that the π -system was localized within the chelate ring as the N1-C3 and N2-C3 bonds were shorter at approximately $1.33\text{\AA}$ than the N1-C6 and N2-C7 bonds at approximately $1.48\text{\AA}$, respectively. The latter C-N bonds were similar to ideal C-N single bond lengths of $1.479\text{\AA}$.⁹ The quaternary carbon, C3, was planar with a sum of angles of 360° indicating that it had an sp^2 hybridization, allowing the remaining p orbital to participate in the π -system. The nitrogen centres N1 and N2 were close to planar with sums of

angles at 355.5° and 356.6° , respectively. The N1-Al-N2' angle was 113.5° which was slightly larger than previously reported Al iminopyrrolidinate complexes.¹⁰ The pyrrole ring had a bite angle of 122.6° which was the same as the previously reported Al complexes. The eight membered ring from the dimer structure had a chair conformation as seen from the side view in Figure 2-6.

Figure 2-6. The single-crystal X-ray structure of **2** demonstrating chair conformation. The thermal ellipsoids are shown at 50% probability; the hydrogen centres and both aluminum methyls are omitted for clarity.

Table 2-3. Selected crystal data for compound **2**.

2	
Empirical Formula	C ₁₈ H ₃₈ AlN ₂
FW	364.48
Crystal System	Triclinic
Space Group	P-1
<i>a</i> (Å)	8.243(3)
<i>b</i> (Å)	8.424(3)
<i>c</i> (Å)	8.511(3)
α (deg)	94.333(5)
β (deg)	92.335(5)
γ (deg)	108.428(5)
<i>V</i> (Å ³)	557.8(4)
<i>Z</i>	1
<i>D</i> _c (kg/L)	1.085
μ (mm ⁻¹)	0.138
<i>T</i> (K)	200(2)
<i>R</i> , <i>wR</i>	0.0600, 0.1665
Goodness-of-fit on <i>F</i> ²	1.000

Table 2-4. Selected bond lengths and angles for compound **2**.

<i>Selected Bond Lengths (Å)</i>			
Al-C1	1.970(2)	N1-C6	1.483(2)
Al-C2	1.978(2)	C6-C5	1.495(3)
Al-N1	1.9219(16)	C5-C4	1.521(3)
N1-C3	1.332(2)	C4-C3	1.520(2)
C3-N2	1.326(2)	C7-C8	1.493(3)
N2-C7	1.477(2)	C8-C9	1.518(4)
N2-Al'	1.9285(17)		
<i>Selected Bond Angles (°)</i>			
C1-Al-C2	114.73(9)	C3-N2-Al'	120.95(12)
N2'-Al-N1	113.46(7)	C7-N2-C3	117.41(15)
C1-Al-N1	108.53(8)	N2-C3-C4	125.32(16)
C1-Al-N2'	108.38(9)	C3-C4-C5	103.07(16)
N1-Al-C2	105.67(8)	C4-C5-C6	105.48(18)
N2'-Al-C2	106.20(8)	C5-C6-N1	105.83(17)
Al-N1-C3	126.04(12)	C3-N1-C6	108.80(15)
N1-C3-N2	122.62(16)		
<i>Sum of Angles (°)</i>			
N1	355.50	C3	360
N2	356.56		

The n-propyl moiety of the iminopyrrolidine ligand was not large enough to prevent dimerization, so both iso-propyl and n-propyl ligands were reacted with TEA to try and force monomer formation through steric crowding by the aluminum alkyl groups. A one-to-one ligand-to-TEA reaction in hexanes at room temperature was used to synthesize the diethyl aluminum iminopyrrolidinate complexes (Scheme 2-4). Ethane elimination was the driving force of this reaction.

Scheme 2-4. Synthesis of AlEt_2 iminopyrrolidinate complexes.

This reaction was also attempted with the sbip and tbip ligands⁸ and a crystal was collected from the sbip reaction demonstrating the formation of a dimer. Compound **3** formed a colourless solid in excellent yield (Table 2-1) and the diethyl aluminum n-propyl iminopyrrolidinate, **4**, formed a liquid. This liquid appeared to consist of several components according to the ^1H NMR, but the desired product was indeed present. Distillation at 86°C was attempted several times, however, no enhanced purity was seen by ^1H NMR. The reaction was repeated at lower temperatures (-78°C) and the dissolved ligand was added dropwise. The ^1H NMR from these reactions were cleaner however, it was evident that there were still several by-products present. Distillation from these

lower temperature reactions did not produce a purer compound. Further investigation of the purification of this compound is needed. If compound **4** is indeed a liquid, it would be very interesting to compare the thermolysis and the stability of this compound with an existing aluminum oxide precursor that was developed in our lab.¹¹

Figure 2-7. Analogous aluminum amidinate precursors.

This previously developed aluminum amidinate precursor is a colourless liquid that distils at 36°C at 85mTorr with a yield of 77%. The thermolysis of this compound has been thoroughly studied and an ALD process for Al₂O₃ films has been developed and is currently in use. Studying the thermolysis of the analogous amidinate ligand would provide a better understanding of how useful such a ligand would be for ALD processes.

2.2.3 Thermolysis of Heteroleptic Organometallic Compounds

The trend in the melting point of the ligands was reflected in the melting points of the heteroleptic aluminum complexes, as seen in Table 2-5. For instance, **2** (npipAlMe₂) had a lower melting point than **2.1** (ipipAlMe₂). As the length of the alkyl chain increased by one carbon the melting point decreased. Increasing the branching from **2.2** (nbipAlMe₂)

to **2.5** (tbipAlMe₂) increased the melting point with the exception of the stereocentre and asymmetry of **2.4** (sbipAlMe₂).

Table 2-5. Melting points for aluminum dimethyl iminopyrrolidinate complexes.

Compound	R	Melting Point (°C)
2	N-propyl (npip)	79 – 83
2.1	Iso-propyl (npip) ^a	87 – 91
2.2	N-butyl (nbip) ^b	68 – 70
2.3	Iso-butyl (ibip) ^b	111 – 113
2.4	Sec-butyl (sbip) ^b	62 – 65
2.5	Tert-butyl (tbip) ^b	116 – 118

^a compound taken from reference [7], ^b compounds taken from reference [8].

The TG analysis of the heteroleptic aluminum complex **2** can be seen in Figure 2-8. The TG had one major thermal event with two smaller events. The first small event occurred in the temperature range 60 - 98°C with a 1% weight loss which most likely corresponded to loss of incidental solvent. The second event occurred at temperature range 103 - 163°C a 5% weight loss which can be attributed to a slow thermal degradation of the compound. The major thermal event occurred at 167 - 315°C with a weight loss of 82%. This feature had a shape that was characteristic of volatilization and was thought to be due to the volatilization of the decomposed aluminum complex. The curve was non-symmetrical in shape, which is commonly associated with the volatilization of a compound, where there is a slow on-set and a rapid drop-off when the maximum is reached. The final mass of **2** was approximately 8 mg, 10% residual mass, most likely corresponding to the residual mass of a decomposed species. This is a reasonable residual mass for a vapour deposition precursor. Although there is no real need for additional aluminum-containing precursors for the deposition of traditional aluminum targets (Al₂O₃ and AlN), this does lend credibility to these ligands to fulfill a

similar role as guanidines and amidines to aid in the volatility of other potential precursors.

Figure 2-8. Thermal gravimetric analysis of **2**.

The TG analysis of **3** had two thermal events (Figure 2-9). The on-set of volatility occurred at 109°C and the slope continued to 180°C with a weight loss 73%. The second feature occurred at a temperature range of 180 - 280°C with a weight loss of 19%. The major feature had a shape that was similar in character to volatilization and was thought to be due to the volatilization of the aluminum complex. The curve was non-symmetrical in shape, common to volatilization of a compound, with a slow on-set and a rapid drop-off when the maximum is reached. The second feature was characteristic of decomposition; a gradual on-set and drop-off. The residual mass of this complex was 1.8% which may correspond to residual decomposed material.

Figure 2-9. Thermal gravimetric analysis of **3**.

A sealed NMR tube thermolysis experiment was conducted for two of the methyl derivatives **2** and **2.1** as well as the ethyl derivative **3**. They were dissolved in $0.35 (\pm 6)$ mL 1% v/v TMS in C_6D_6 solution in thick-walled NMR tubes under inert atmosphere. The tubes were immersed in liquid nitrogen and the glass tube was sealed under vacuum. Each tube was placed in a furnace at $78^\circ C$ and the decomposition of the dimethyl peak or the ethyl peak (as appropriate for the compound) was monitored relative to the TMS peak. Following the decomposition of these compounds, the ring feature designed to prevent CDI deinsertion had proven effective. No CDI peaks were seen by 1H NMR and the ligands appeared to have stayed intact, possibly forming bis or tris iminopyrrolidinate aluminum species through the formation of a isomer from the iminopyrrolidinate ligand.

After 5 days at $78^\circ C$, the 1H NMR signals associated with compound **2** had shown the development of a new ligand environment with signals at δ 3.39, 3.24 (m, 4H,

$\text{NCH}_2\text{CH}_2\text{CH}_2\text{C}$), 3.00 (m, 4H, $\text{CH}_3\text{CH}_2\text{CH}_2\text{N}$), 1.96 (m, 4H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{C}$), 1.42 (m, 4H, $\text{CH}_3\text{CH}_2\text{CH}_2\text{N}$), 1.29 (br. m, 4H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{C}$), 0.82 (dblt t, 6H, $\text{CH}_3\text{CH}_2\text{CH}_2\text{N}$), 0.15, -0.16, -1.01 (s, 6H, $\text{Al}(\text{CH}_3)_2$). The change in the NMR suggests that a formation of a dimerised ligand occurred. It may be possible that the parent dimer molecule broke apart forming a monomer that could then easily isomerise during the thermolysis creating a new bonding mode to the aluminum.

Scheme 2-5. Speculation of isomerization followed by dimerization of the ligand.

There were several shifts visible in the ^1H NMR that indicated the possibility that isomerization did indeed occur. The sextet of the n-propyl moiety of **2** showed a chemical shift from 1.39 ppm to 1.42 ppm. Also the quintet of the pyrrole ring shifted

from 1.32 ppm to 1.29 ppm. The methyl signal from the aluminum at -0.34 ppm began to diminish and a new singlet grew in at -0.16 ppm. The ^{13}C NMR also showed the development of new quaternary carbons at 179.7 and 179.5 ppm (labelled “a” and “b” in Scheme 2-5). Neither peak represented the original quaternary carbon of **2** at 181.9 ppm. Additional NMR experiments such as DEPT-135 showed these carbons to be quaternary.

Figure 2-10. First order decomposition of the dimethyl and diethyl peak at 78°C.

Compound **2.1** had shown almost complete transformation to the assumed dimerized species after 5 days at 78°C. The ^1H NMR signal associated with the aluminum methyl for compound **2.1**, had completely disappeared with the growth of a new methyl aluminum signal. A new ligand environment was also seen with signals at δ 3.46, 3.09 (m, 4H, $\text{N}(\text{CH}_2)(\text{CH}_2)(\text{CH}_2)\text{C}$), 3.21 (quin, 2H, $\text{NCH}(\text{CH}_3)_2$), 2.00, 1.88 (m, 4H, $\text{N}(\text{CH}_2)(\text{CH}_2)(\text{CH}_2)\text{C}$), 1.31, 1.23 (m, $\text{N}(\text{CH}_2)(\text{CH}_2)(\text{CH}_2)\text{C}$), 1.28, 1.11 (d, 12H, $\text{NCH}(\text{CH}_3)_2$), -0.060, -1.027 (s, 12H, $\text{Al}(\text{CH}_3)_2$). The ^{13}C NMR of the thermal product

supported the formation of an isomer as the quaternary carbon signal underwent a significant shift (from 179.0 ppm to 177.9 ppm in the thermal product) suggesting that the bonding environment had changed.

The ^1H NMR of compound **3** was very clean with the only change associated with the experiment – an increase in the noise of the base line. The ^{13}C NMR was also unchanged after 4 days.

From this study it was clear that the diethyl aluminum complex **3** was the most stable with a half-life of 21.7 days (Table 2-6). Each heteroleptic aluminum compound had a first order decomposition with respect to the loss of the dimethyl or diethyl group on the aluminum (Figure 2-10).

Table 2-6. R^2 value, rate constant and half-lives of heteroleptic aluminum complexes.

Compound	R^2 value	k	τ (days)
2	0.982	0.123	5.6
2.1	0.975	0.449	1.5
3	0.9286	0.032	21.7

2.3 Conclusions

A new iminopyrrolidine ligand was synthesized in good yield, 72%. Low sublimation temperatures suggested volatility which was confirmed by DSC and TG analyses. These types of iminopyrrolidine ligands have proven to be more stable than their oxazoline analogues as ring opening decomposition⁵ did not occur as seen by ^1H NMR tube boil-ups.

Two novel heteroleptic aluminum complexes were synthesized and purified with great yields; 70 and 79%, respectively. Some trends in melting points emerged reflecting

that of the ligands. This suggests that thermal properties of the aluminum species may be controlled by variation of the R-group on the chelating ligand. Therefore, the synthesis of other organometallic compounds with these ligands may prove to be advantageous for ALD processes. Thermolyses of these heteroleptic compounds showed the stability of the ligands and were found to follow first order decomposition. The half-lives of the dimethyl aluminum complexes **2** and **2.1** were 5.6 and 1.5 days, respectively. The half-life of the diethyl aluminum complex, **3**, was higher at 21.7 days showing its stability to be higher than the dimethyl aluminum complexes.

2.4 Methods and Materials

All manipulations were performed in a nitrogen filled dry box unless otherwise specified. The chemicals: 2-pyrrolidinone, n-propyl amine, phosphorous pentoxide, TMA and TEA were purchased from Aldrich Chemical Company and used as received. All solvents used were reagent grade and purified from an MBraun Solvent Purifier System. Nuclear Magnetic Resonance was done on either a 300MHz Avance III or a 400MHz AMX Bruker. Mass spectra were obtained using the electron impact method on a VG ZAB-2HF triple-focusing spectrometer. Guelph Chemical Laboratories performed combustion analysis. Thermal gravimetric analyses were performed on a TA Instruments Q50 apparatus located in an MBraun Labmaster 130 Dry box under a nitrogen atmosphere. Differential Scanning Calorimetry was performed on a TA Instruments Q10 apparatus. Single crystal XRD was conducted on a Bruker-AXS APEX CCD Diffractometer located at Delaware University with the help of Glenn P. Yap.

2.4.1 N-propyl iminopyrrolidine, 1

A mixture of 2-pyrrolidinone (3.0 g, 35.2 mmol) and n-propyl amine (4.4 g, 70.5 mmol) was prepared in a 20 ml vial in the dry box, capped and brought out of the dry box. This mixture was added 1 mL at a time through a reflux condenser to a 100 mL round bottom flask that contained neat phosphorous pentoxide (5.0 g, 35.2 mmol). As the pyrrolidinone mixture reached the reaction flask, vapour began to rise up the reflux condenser. The reaction mixture was heated over one hour to 220°C and then refluxed with stirring for two hours in a sand bath. The reaction was cooled to room temperature and it became a hard glassy substance. 40 mL of distilled water was added to the flask and the compound dissolved with the aid of a heat gun. Using a Pasteur pipette 50 mL of 6 M aqueous NaOH was added until a pH of 11 was obtained. The aqueous phase was extracted with 3 X 70 mL of diethyl ether. Volatiles were removed under reduced pressure to afford a brown solid (3.6 g, 28.5 mmol, 81%). The brown solid sublimed at 60°C under reduced pressure to afford needle like white crystals (3.2 g, 25.4 mmol, 72%). mp (72 - 74°C). ¹H NMR (300 MHz, C₆D₆): δ 3.780 (t, 2H, NCH₂CH₂CH₂C), 3.44 (s, 1H, NCNH), 3.22 (t, 2H, CH₃CH₂CH₂N), 1.92 (t, 2H, NCH₂CH₂CH₂C), 1.63 (quintet, 2H, NCH₂CH₂CH₂C), 1.41 (sextet, 2H, CH₃CH₂CH₂N), 0.77 (t, 3H, CH₃CH₂CH₂N). ¹³C NMR (300 MHz, C₆D₆): δ 165.5 (NCN), 56.6 (NCH₂CH₂CH₂C), 44.9 (CH₃CH₂CH₂N), 32.5 (NCH₂CH₂CH₂C), 23.5 (CH₃CH₂CH₂N), 23.1 (NCH₂CH₂CH₂C), 11.4 (CH₃CH₂CH₂N). Mass spectral data (EI, *m/z*) (rel. intensity, %): 126.1 (92.0, M⁺). Combustion analysis; found (calculated), C: 66.43 (66.62), H: 10.92 (11.18), N: 22.44 (22.20).

2.4.2 Dimethyl aluminum n-propyl iminopyrrolidinate, **2**

N-propyl iminopyrrolidine (1.5 g, 11.8 mmol) was suspended in approximately 40 ml of hexanes and slowly added to a solution of TMA (5.9 ml, 12.5 mmol, 2M) dissolved in about 80 ml of hexanes. The reaction was allowed to proceed for 18 hours at room temperature. Volatiles were removed under reduced pressure to afford a colourless solid. The solid was dissolved in about 8 mL of diethyl ether and allowed to recrystallize at -30°C. Colourless cubic crystals were collected (1.7 g, 9.3 mmol, 79%). mp (79 - 83°C). ¹H NMR (300 MHz, C₆D₆): δ 3.27 (t, 2H, NCH₂CH₂CH₂C), 3.05 (t, 2H, CH₃CH₂CH₂N), 1.92 (t, 2H, NCH₂CH₂CH₂C), 1.39 (sextet, 2H, CH₃CH₂CH₂N), 1.32 (quintet, 2H, NCH₂CH₂CH₂C), 0.77 (t, 3H, CH₃CH₂CH₂N), -0.34 (s, 6H, Al(CH₃)₂). ¹³C NMR (300 MHz, C₆D₆): δ 181.9 (NCN), 51.043 (CH₃CH₂CH₂N), 51.0 (NCH₂CH₂CH₂C), 31.1 (NCH₂CH₂CH₂C), 25.8 (CH₃CH₂CH₂N), 21.8 (NCH₂CH₂CH₂C), 11.5 (CH₃CH₂CH₂N). Mass spectral data (EI, *m/z*) (rel. intensity, %): 349.2 (38.5, (M-Me)⁺). Combustion analysis; found (calculated), C: 59.15 (59.31), H: 10.80 (10.51), N: 15.33 (15.37).

2.4.3 Diethyl aluminum iso-propyl iminopyrrolidinate, **3**

Same reaction procedure as **2** was used substituting the previous aluminium complex with TEA (15.85 ml, 15.8 mmol, 1M) and the previous ip ligand with ipip (1.99g, 15.8 mmol). The solution was clear and colourless. Volatiles were removed under reduced pressure to afford a colourless solid. The solid was dissolved in about 14 mL of diethyl ether and allowed to recrystallize at -30°C. Colourless cubic crystals were collected (2.3 g, 11.1 mmol, 70%). mp (120 - 124°C). ¹H NMR (300 MHz, C₆D₆): δ 3.35 (m, 1H, NCH(CH₃)₂), 3.25 (t, 2H, NCH₂CH₂CH₂C), 2.06 (t, 2H, NCH₂CH₂CH₂C), 1.42 (quintet,

2H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{C}$), 1.30 (t, 6H, $\text{Al}(\text{CH}_2\text{CH}_3)_2$), 1.15 (d, 6H, $\text{NCH}(\text{CH}_3)_2$), 0.24 (q, 4H, $\text{Al}(\text{CH}_2\text{CH}_3)_2$). ^{13}C NMR (300 MHz, C_6D_6): δ 181.5 (NCN), 50.1 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{C}$), 49.8 ($\text{NCH}(\text{CH}_3)_2$), 32.5 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{C}$), 23.1 ($\text{NCH}(\text{CH}_3)_2$), 22.4 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{C}$), 10.2 ($\text{Al}(\text{CH}_2\text{CH}_3)_2$), 1.2 ($\text{Al}(\text{CH}_2\text{CH}_3)_2$). Combustion analysis; found (calculated), C: 63.11 (62.82), H: 11.28 (11.02), N: 13.72 (13.32).

2.4.4 Diethyl aluminum n-propyl iminopyrrolidinate, 4

Same reaction procedure as **2** was used substituting the previous aluminium complex with TEA (11.88ml, 11.8 mmol, 1M). The solution changed to clear yellow. Volatiles were removed under reduced pressure to afford a thick yellow wax. A distillation was attempted starting with an oil bath at 30°C and slowly increasing to 170°C throughout the day. At this point the vapour temperature increased to 86°C and 0.2 g (1.0 mmol, 9%) clear colourless solution was obtained. ^1H NMR (300 MHz, C_6D_6): δ 3.28 (t, 2H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{C}$), 3.02 (t, 2H, $\text{CH}_3\text{CH}_2\text{CH}_2\text{N}$), 2.06 (t, 2H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{C}$), 1.43 (m, 2H, $\text{CH}_3\text{CH}_2\text{CH}_2\text{N}$ and $\text{NCH}_2\text{CH}_2\text{CH}_2\text{C}$), 1.25 (t, 6H, $\text{Al}(\text{CH}_2\text{CH}_3)_2$), 0.76 (t, 3H, $\text{CH}_3\text{CH}_2\text{CH}_2\text{N}$), 0.20 (q, 4H, $\text{Al}(\text{CH}_2\text{CH}_3)_2$). ^{13}C NMR (400 MHz, C_6D_6): δ 180.4 (NCN), 50.0 ($\text{CH}_3\text{CH}_2\text{CH}_2\text{N}$), 49.6 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{C}$), 30.0 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{C}$), 25.0 ($\text{CH}_3\text{CH}_2\text{CH}_2\text{N}$), 22.2 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{C}$), 11.1 ($\text{CH}_3\text{CH}_2\text{CH}_2\text{N}$), 9.45 ($\text{Al}(\text{CH}_2\text{CH}_3)_2$), -0.9 ($\text{Al}(\text{CH}_2\text{CH}_3)_2$).

2.5 Structural Determination for Compound 2

A suitable crystal was mounted with viscous oil on a plastic mesh and cooled to the data collection temperature. Unit cell parameters were determined using data frames from four different sections of the Ewald sphere. SADABS multi-scan absorption corrections were applied. No symmetry higher than triclinic was observed. Solution in the centrosymmetric space group option, P-1, yielded chemically reasonable and computationally stable results of refinement. The structure was solved using direct methods and refined with full matrix least squares procedures of F^2 data. The dimeric molecule was located at an inversion centre. All hydrogen atoms were treated as idealized contributions and all non-hydrogen atoms were refined with anisotropic displacement coefficients. Atomic scattering factors are contained in the SHELXTL program library.

2.6 References

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Chapter 3:

Heteroleptic Cyclopentadienyl Titanium (III) Guanidinate

3.1 Introduction

Titanium-containing precursors used for the deposition of pure metal, nitride and oxide films have a variety of applications in microelectronics. Titanium as a metal can be used as an electrode in microelectronic devices. However, due to a high tendency towards oxidation, titanium itself is typically not used. Instead titanium-nitride (TiN) is often deposited as a capping layer.¹ Some important examples of TiN in the microelectronic space include gate metals in metal-oxide-semiconductor field-effect transistors (MOSFETs) as well as metal electrodes in various capacitor applications.² In these applications, extreme down-scaling of size of electronic components cannot be supported by traditional poly-silicon based techniques.³ When gate sizes approach 1 nm in thickness, thin-film metal gates such as TiN are required to obtain favourable electrical properties.⁴ In addition to applications in microelectronics, thin films of TiN have been used in solar cells,⁵ as hard and decorative coatings, and in optics.⁶ In addition to gate metals, down-scaling the size of electronics requires high-k dielectrics.⁷ To this end, there is an increasing interest in titanium oxide (TiO₂).⁸ Titanium oxide offers a high-k value (80 - 110)⁹ and can be deposited either as the pure oxide, or in combination with other oxides to achieve desired properties.^{7,10} For instance, with strontium oxide it will form the ultra high-permittivity ternary material SrTiO₃, with a k value that may exceed 300.

Titanium based materials can be deposited by several known methods such as physical vapour deposition (PVD),¹¹ CVD¹² and ALD.¹³ ALD for titanium based materials is promising because it offers control and scalability to a nanoscale. This chapter focuses on novel guanidinate precursors for the ALD of titanium based materials.

An ALD precursor should meet several design criteria: the compound should have a low molecular weight and the metal centre should be sterically congested. This promotes volatility as well as self-limiting behaviour when the chemisorbed monolayer is formed on the surface. The compound should be thermally stable to resist decomposition in the gas-phase and on the surface at process temperatures, yet be chemically reactive to allow formation of the target film.

A well known titanium precursor for ALD of TiN and TiO₂ is TiCl₄. It is highly volatile and thermally stable. However, TiCl₄ cannot be used to deposit TiN layers near copper interconnects because of the formation of hydrogen chloride as a by-product, which etches the copper.¹⁴ Furthermore, TiCl₄ can induce the formation of a very stable SrCl₂ phase when employed in the deposition of SrTiO₃ by ALD, which contaminates the film and alters the electrical properties. Titanium alkyl amides have also been widely studied for the deposition of TiN via ALD. However, these precursors have low thermal stability and decompose above 150°C limiting their applications.¹⁵ Alkoxides have been used for TiO₂ deposition but they too have low thermal stability, with a temperature limit of approximately 250°C.¹⁶ Despite the large number of titanium precursors available for ALD, there is need for development of thermally stable metal organic titanium precursors for both TiN and TiO₂ deposition.

Chapters 3 to 6 of this thesis introduces the synthesis of novel titanium (III) and titanium (IV) compounds that were synthesized to use as TiN or TiO₂ precursors in ALD or CVD. This chapter introduces a new class of volatile and thermally stable titanium precursors for ALD: cyclopentadienyl titanium guanidines; Cp₂Ti(NⁱPr)₂CNRR' (where R, R' = H, Me, ⁱPr or ^tBu). Guanidine ligands were used in this chapter to increase the stability of the heteroleptic titanium precursors by increasing ligand saturation.¹⁷ The resonant structure of guanidine ligands have been known to increase the stability of the compound (compared to metal alkyl amides) as well as prevent oligomerization of the organometallic species.¹⁸ They are also known for minimizing the amount of impurities found within deposited thin films; metal-nitrogen bonds within a precursor can help to eliminate potential halide and carbon contamination within the film.¹⁹ The advantage of these potential precursors is the increased stability the bidentate ligands offer compared to other monodentate cyclopentadienyl complexes.²⁰

The volatility and thermal chemistry of these compounds will be discussed with the goal of assessing their suitability as ALD precursors. Finally, surface reactivity on high surface area silica will be shown for the selected candidate [ⁱPrN(H)C(NⁱPr)₂]TiCp₂ to determine how the precursor might dissociatively adsorb to an oxide substrate. This experiment will give insight on how these types of metallic precursors react to form the first monolayer in an ALD process. High surface area silica is an ideal material for this experiment due to the abundance of surface hydroxyls, which in turn lead to a high enough concentration of surface species to use solid-state nuclear magnetic resonance to characterize the end result.

3.2 Results and Discussion

3.2.1 Synthesis and Crystal Structure Data

Generally, Ti(III) compounds of the formulation (guan)TiCp₂ (where guan is any guanidinate) can be made in very low yields from Cp₂TiCl₂ and a dianionic guanidinate at room temperature with stirring over night. An *in situ* reduction of the titanium centre and the reaction mixture resulted in several unidentifiable side products. This reaction is highlighted here by using the compound Cp₂Ti[(NⁱPr)₂CN(H)ⁱPr] (**5**) as an example. When following equation 1 using Li₂(ⁱPrN)₃C as a ligand, compound **5** was isolated in 15% yield, while the rational synthesis of **5** using [Cp₂TiCl]₂ (from reduction of Cp₂TiCl₂ and zinc dust, equations 2 and 3) and Li(ⁱPrN)₂C(N(H)ⁱPr) produced **5** in a 58% yield.

In general, compounds **5** - **8** (Table 3-1, Figure 3-1 and Figure 3-2) were easily synthesized in moderate yields from the [Cp₂TiCl]₂ starting material and appropriate lithium guanidinate. It was found that the compounds formed slowly at room temperature with the starting titanium species changing from a characteristic yellow-green to a solution ranging from grey-green to blue, depending on the guanidinate. In every case, blue crystals were isolated and this colour change was used to gauge the

completeness of the reaction. Compounds **5**, **6**, and **8** produced crystals of sufficient quality for single crystal structures to be collected (Figure 3-1 and Table 3-1).

R = H, Me, Et, ⁱPr

R' = Me, Et, ⁱPr, ^tBu

Figure 3-1. Heteroleptic titanium species.

Table 3-1. Guanidinate species and percent yield of compounds **5** - **9**.

	Compound (Guanidinate)	Percent Yield (%)
5	Cp ₂ Ti triisopropyl	58
6	Cp ₂ Ti dimethyl diisopropyl	39
7	Cp ₂ Ti diethyl diisopropyl	40
8	Cp ₂ Ti tetra isopropyl	30
9	Cp ₂ Ti tert-butyl diisopropyl	7

Figure 3-2. The single-crystal X-ray structure of (a) **5**, (b) **6**, and (c) **8**. The thermal ellipsoids are shown at 50% probability and the hydrogen centres are omitted for clarity. N.B.: Only one of two orientations of **6** is shown (see text).

A fourth crystal structure was obtained: compound **9**, bis(cyclopentadienyl) titanium (III) tert-butyl diisopropyl guanidinate (Figure 3-4, Table 3-2 and Table 3-4). The tert-butyl diisopropyl guanidinate ligand was prepared in a similar fashion as the other ligands used in this chapter: CDI insertion over a lithium-amido complex (Scheme 3-1). The organometallic compound was prepared similarly to the other compounds: a room temperature reaction with the addition of a lithiated guanidinate ligand. It was originally thought that the guanidinate ligand would bond to the titanium in a manner similar to the other guanidinate ligands: the isopropyl groups of the chelate nitrogens in the

metallocycle and the tert-butyl moiety in the exocyclic position (Figure 3-3). However, the tert-butyl moiety was found in the chelate position forming an asymmetric guanidinate ligand (Figure 3-3 and Figure 3-4). A variety of by-products were isolated and – due to the paramagnetic nature of the solids – were unidentifiable by ^1H NMR. The synthesis was repeated several times both at room temperature and at lower temperatures in hopes to increase the yield. Even when the reaction was controlled at -78°C no heteroleptic complexes were isolated and further thermolysis studies could not be conducted.

Scheme 3-1. Lithium amide insertion over CDI bond.

Figure 3-3. Asymmetric coordination of guanidinate ligand.

Figure 3-4. The single-crystal X-ray structure of **9**. The thermal ellipsoids are shown at 50% probability and the hydrogen centres are omitted for clarity.

Table 3-2. Selected crystal data for compounds **5**, **6**, **8**, and **9**.

	5	6	8	9
Empirical Formula	C ₂₀ H ₃₁ N ₃ Ti	C ₁₉ H ₃₀ N ₃ Ti	C ₂₃ H ₃₈ N ₃ Ti	C ₂₁ H ₃₄ N ₃ Ti
FW	361.38	348.36	404.46	376.41
Crystal System	Monoclinic	Tetragonal	Monoclinic	Orthorhombic
Space Group	P2 ₁ /n	P4 ₂ /ncm	P2 ₁ /n	Pbca
<i>a</i> (Å)	14.870	8.1809	8.8431	10.6679(19)
<i>b</i> (Å)	8.449	8.1809	29.036	14.750(3)
<i>c</i> (Å)	16.922	28.121	9.0884	26.043(5)
α (deg)	90	90	90	90
β (deg)	111.68	90	110.82	90
γ (deg)	90	90	90	90
<i>V</i> (Å ³)	1976	1882	2181	4097.8(13)
<i>Z</i>	4	4	4	8
<i>D_c</i> (kg/L)	1.215	1.229	1.232	1.220
μ (mm ⁻¹)	0.439	0.458	0.405	0.426
<i>T</i> (K)	120(2)	120(2)	120(2)	120(2)
<i>R</i>	0.0666	0.0792	0.0555	0.0576
<i>wR</i>	0.1379	0.2128	0.1159	0.1427
Goodness-of-fit on <i>F</i> ²	1.015	1.055	1.068	1.075

Table 3-3. Selected bond lengths and angles for compounds **5** and **6**.

C ₂₀ H ₃₁ N ₃ Ti (5)				C ₁₉ H ₃₀ N ₃ Ti (6)	
Selected Bond Lengths (Å)					
Ti-N1	2.154(2)	N3-C7	1.405(3)	Ti-N1	2.172(3)
Ti-N2	2.147(2)	Ti-Ct01	1.743	N1-C4	1.335(4)
N1-C7	1.339(3)	Ti-Ct02	1.751	N2-C4	1.409(6)
N2-C7	1.341(3)			Ti-Ct	1.723
Selected Bond Angles (°)					
N1-Ti-N2	61.81(7)	N1-C7-N2	111.07(18)	N1-Ti-N1'	61.58(14)
Ct01-Ti-N1	110.14	N1-C7-N3	122.4(2)	Ct01-Ti-N1	111.4
Ct02-Ti-N2	108.35	N2-C7-N3	126.54(19)	N1-C4-N1'	112.7(4)
Ct01-Ti-Ct02	133.24			N1-C4-N3	123.6(2)
				Ct01-Ti-Ct01'	129.67
Sum of Angles (°)					
N1	360	N2	359	N1	356
				N2	360

Table 3-4. Selected bond lengths and angles for compounds **8** and **9**.

C ₂₃ H ₃₈ N ₃ Ti (8)		C ₂₁ H ₃₄ N ₃ Ti (9)	
Selected Bond Lengths (Å)			
Ti-N1	2.1710(17)	Ti-N1	2.136(2)
Ti-N2	2.1730(17)	Ti-N2	2.145(2)
N1-C11	1.326(3)	N1-C11	1.333(3)
N2-C11	1.328(3)	N2-C11	1.328(3)
N3-C11	1.433(3)	N3-C11	1.402(4)
Ti-Ct01	1.737	N2-C15	1.477(3)
Ti-Ct02	1.741	Ti-Ct01	2.093
		Ti-Ct02	2.099
Selected Bond Angles (°)			
N1-Ti-N2	60.91(6)	N1-Ti-N2	61.66(8)
Ct01-Ti-N1	109.5	Ct01-Ti-N1	108.5
Ct02-Ti-N2	109.5	Ct02-Ti-N2	109.1
Ct01-Ti-Ct02	133.45	Ct01-Ti-Ct02	134.5
N1-C11-N2	112.14(17)	N1-C11-N2	111.0(2)
N1-C11-N3	121.82(17)	N1-C11-N3	122.5(4)
N2-C11-N3	126.04(18)	N2-C11-N3	126.5(2)
Sum of Angles (°)			
N1	360	N1	360
N2	360	N2	360
N3	354		

For compounds **5**, **6** and **8**, the titanium was in a four-coordinate distorted tetrahedral environment, considering the centroids of the cyclopentadienyl rings. Not surprisingly,

the angle between the centroids was much larger than ideal ($130 - 133^\circ$) and the bite angle of the guanidinate was correspondingly smaller ($61.0 - 61.8^\circ$). The centroid-titanium-nitrogen angles were closer to ideal for **5** (108.4° and 109.8°) and **8** (109.5°) and somewhat distorted for **6** (111.4°). The guanidinate ring was very close to planar in each case with torsion angles ranging from $0 - 1.3^\circ$. As is typical for guanidates, the exocyclic amido moieties were rotated from the plane of the guanidinate ring in all cases. However, π -overlap follows a $\cos^2\theta$ relationship for twisted systems like this, thus the exocyclic group participated significantly in the delocalized π -bonding of the guanidinate.²¹ In every structure, the C-N bond to the exocyclic amide was longer than the C-N bonds to the chelate nitrogens. This indicated a higher contribution to the π -system from the metallocycle nitrogens compared to the exocyclic nitrogen. This can be seen in the sum of angles around the chelate nitrogens on **5** and **8** (N1 at 360° and N2 at 359° for **5**, 360° for **8**), whose planarity indicated an sp^2 hybridization and thus participation in the π -system. Interestingly, compound **6** was defined by two planes of symmetry: one in the C1-Ti-C4 plane and one in the Ti-N1-C4 plane. This gave rise to two orientations of the isopropyl groups where they bend 14° above or below the Ti-N1-C4 plane 50% of the time. Likewise, the exocyclic amido group tilts 36° in either direction out of the C1-Ti-C4 plane 50% of the time. This symmetry is likely enforced by the crystal's $P4_2/nm$ space group and forces the chelating nitrogen out of planarity.

In these structures, the bond lengths to the centroids were somewhat shorter than a typical four-coordinate Cp-titanium compound ($Cp_2Ti(NSO)_2$ reported by Roesky et al., $Cp-Ti = 2.06 \text{ \AA}$).²² The bond lengths were longer than those of the starting material $[Cp_2TiCl]_2$ ²³ at a range of $1.72 - 1.75 \text{ \AA}$ compared to $1.31 - 1.38 \text{ \AA}$. The Cp-Ti-Cp angle

was similar to the starting material $[\text{Cp}_2\text{TiCl}]_2$ at a range of $129.7 - 133.4^\circ$ ($\text{Cp-Ti-Cp} = 131.2 - 133.4^\circ$).²³ The Ti-N bond lengths were slightly longer than a typical bonding distance for a monoanionic guanidinate at titanium²⁴ at a range of $2.14 - 2.17\text{\AA}$ compared to $2.09 - 2.11\text{\AA}$.²⁴ The lengths fell within range reported by Hagadorn and Arnold for their prototypical titanium (III) amidinate ($2.05 - 2.16\text{\AA}$).²⁵

Complex **9** was also a four-coordinate distorted tetrahedron. The Ti-N bond lengths differed due to the sterically hindering t-butyl species found on one side of the ligand; Ti-N1 at $2.136\text{\AA}$ and Ti-N2 at $2.145\text{\AA}$ (Figure 3-4). The bite angle of the guanidinate was found to be 61.6° with a corresponding centroid-titanium-centroid angle of 134.5° . The guanidinate ring deviated slightly from planarity with a torsion angle of 3.1° . The exocyclic amido species was found to be rotated from the Ti-N2-C11 plane of the guanidinate ring by 53.7° showing partial participation in the delocalized π -bonding of the metallocycle. Similar to the other titanium (III) structures, the C-N bond to the exocyclic amide (C11-N3) was longer ($1.40\text{\AA}$) than the C-N bonds to the chelate nitrogens (N1-C11 and N2-C11) at $1.33\text{\AA}$, respectively. This length indicated a higher contribution to the π -system from the chelate ring nitrogens compared to the exocyclic amide. The participation of the metallocycle nitrogens in the π -system was complimented by the sum of angles around the chelate nitrogens (N1 and N2) at 360° .

3.2.2 Thermolysis

Thermal data for compound **9** was not studied due to difficulty in reproducing the ligand and the complex. The melting points for compounds **5** - **8** fell in a wide range, from 147°C for **5** to decomposition at $>180^\circ\text{C}$ for **8**. TG analyses showed all compounds

to decompose with small residual masses and similar on-sets of volatility (Figure 3-5, Table 3-5). The thermal data showed no clear predominant candidate as an ALD precursor from these compounds, so compound **5** was selected due to its higher yield, lower melting point and generally less problematic synthesis.

Thermal analyses was undertaken for compounds **5** - **8**. For compound **5** there was a small initial weight loss in the TG of < 1% (highlighted in the derivative curve, Figure 3-6) that was due to residual solvent in the sample. The on-set of volatilization (i.e. 5% mass loss) occurred at 149°C and showed an uninterrupted weight loss to 10.5% of the original mass. The differential curve (Figure 3-6) for this weight loss had the typical appearance of sublimation; a slow on-set and a quick drop-off with an additional small feature centred at 155°C. This interruption in the otherwise smooth volatilization corresponded to the melting point of the sample and was likely caused by a change in surface area upon melting. From the residual mass, after volatilization, there was a second weight loss of approximately 5%. This could be the volatilization of an impurity that was present in **5** but the more likely explanation is a subsequent thermal decomposition of the remaining mass.

Table 3-5. Thermal parameters for compounds **5** - **8**.

Exocyclic Amido		Melting point (°C)	On-set of Volatility ¹ (°C)	Residual Mass (%)
5	R = ⁱ Pr, R' = H	147 - 150	149	10.5
6	R = R' = Me	163 - 165	127	0.0
7	R = R' = Et	155 - 157	142	12.8
8	R = R' = ⁱ Pr	Decomposes > 180	168	1.3

¹on-set of volatility was taken as 5% mass loss

The TG for compound **6** showed one thermal event that occurred at a temperature range of 127 - 382°C with a residual mass of 0%. The derivative weight curve (Figure 3-6) displayed characteristic volatility as there was no interruption in the curve. This demonstrated that the compound had a clean volatilization with no decomposition occurred throughout the experiment.

The derivative weight curve (Figure 3-6) for compound **7** showed three minor thermal events ranging from 142 - 168°C, 168 - 185°C and 185 - 292°C. The three events were considered to be caused by thermal degradation of the compound as the derivative weight curve (Figure 3-6) was symmetric. The curve demonstrated a gradual on-set and drop-off once the maximum was reached. The final residual mass of this compound was 12.8%. The results of this experiment lead to the conclusion that this compound would not be an ideal candidate for ALD processes.

Compound **8** had one thermal event that occurred at the temperature range of 168 - 340°C with a residual mass of 1.3%. The derivative weight curve (Figure 3-6) demonstrated characteristic volatilization as the curve had a slow on-set and quick drop-off without interruption.

The DSC data for compound **5** suggested that the volatilization occurred while the material was in the liquid state. An initial endotherm at 152.5°C corresponded to the melting point of **5** as corroborated by bench-top methods. The second broad endotherm corresponded to the major weight loss in the TG and can thus be assigned to the volatilization of the compound. Although the on-set of volatilization was at a relatively high temperature with respect to ALD process temperatures, the lack of thermal

decomposition during the volatilization event suggested that this material could be used as a vapour precursor.

Figure 3-5. Thermal gravimetric analysis of 5 - 8.

Figure 3-6. Differential weight curve for compounds 5 - 8.

Figure 3-7. Differential scanning calorimetry of 5.

In potential ALD growth of TiN films using **5** as a precursor, the initial nucleation pathway would involve nucleation on the interfacial oxide layer of a silicon substrate creating a bound titanium complex. High surface area silica is the most often used material support for metallocene catalysts²⁶ and is a useful model to lend insight into the nucleation products at the interfacial oxide layer. High surface area silica is an ideal material for investigating the surface reactivity of **5** due to the abundance of surface hydroxyls, which in turn, leads to a high enough concentration of surface species to use traditional characterization techniques such as elemental analysis and solid-state nuclear magnetic resonance.

3.2.3 Exposure Experiments

Upon reactive exposure of the silica to a gas-phase metal precursor the number of product surface species is directed by details of the surface structure. Pre-heating the substrate decreases the density of surface hydroxyl sites²⁷ limiting the coordination number of the bound product complex (Figure 3-8). Previous experimental work by Leskelä and co-workers²⁸ using NMR and elemental analysis demonstrated that the silica surface bonding mode of a zirconocene precursor depended on the level of substrate pre-heating.

Figure 3-8. Hydroxyl group density as a function of temperature pre-treatment (adapted from Gunter²⁹).

Each exposure experiment was preformed on a commercial F-120 ALCVDTM reactor manufactured by ASM Microchemistry Ltd. (Figure 3-9). The reactor was equipped with a reaction chamber for processing porous materials. In the test exposures, 3 to 5g of porous high surface area SiO₂ and Al₂O₃ powder (Table 3-6) were heat treated in a muffle furnace for 16h at 350, 950 and 600°C, respectively, to control the number of surface hydroxyl groups. These were subsequently used as substrates. Before the introduction of the titanium precursor to the surface, the substrates were further preheated in the reaction chamber at the reaction temperatures for 3 to 5 h to remove any possible moisture adsorbed to the surface during storage. After pre-treatment, the titanium precursor was vaporized and transported with the help of nitrogen flow through the silica particles where it reacted. Just one exposure of the precursor was carried out per test on the oxide surface. The precursor amount was varied from 1.8 g to 2.0 g and the reaction time was 4 hours to ensure surface saturation. After the reaction, the reaction chamber was purged with nitrogen. The samples were handled inertly by storing them in a glove box.

Figure 3-9. Schematic of F-120 ALCVD™ reactor.

Table 3-6. Physical properties of high surface area substrates.

Oxide	Type	Surface area (m ² /g)	Pore volume (cm ³ /g)	Pore size (nm)	Mean particle diameter (μm)
SiO ₂	INEOS silicas EP10X	300	1.8	24	100
Al ₂ O ₃	Akzo Nobel Alumina 000-1.5E	180 - 195	0.5	10	1600 - 1800

High surface area silica was pre-treated at two different temperatures: 350°C and 900°C and alumina extrudate pre-treated to 600°C, labelled SiO₂-350, SiO₂-900 and Al₂O₃-600, respectively. In order to optimize the surface exposure experiment SiO₂-350 was exposed to the titanium precursor in N₂ carrier gas for 5 hours using 0.4 - 1.0 g of compound **5** at a variety of reaction temperatures. In these cases the precursor was completely volatilized from the bubbler. It was determined that 240°C was the optimal reaction temperature for the exposure experiments based on the latter exposure experiment results obtained by ASM Microchemistry Ltd. When the reactions were

repeated at 240°C using an excess of precursor with substrates pre-heated at either 350°C or 900°C, complete saturation was visually evident from the complete change in colour of the silica (Figure 3-10, Table 3-7). However, for the alumina substrate pre-treated to 600°C, only partial saturation was achieved (Figure 3-10) as demonstrated by the patchy colour change.

Figure 3-10. Resulting colour change of SiO₂-350, SiO₂-900 and Al₂O₃-600 after exposure experiments.

Table 3-7. Exposure experiment data for pre-heated silica at 350°C (SiO₂-350) and 900°C (SiO₂-900) and alumina 600°C (Al₂O₃-600).

Substrate	Reaction Temperature (°C)	Ti Density (at·nm ⁻²)	C/Ti ratio
SiO ₂ -350	180	0.53	8.8
SiO ₂ -350	210	0.31	7.45
SiO ₂ -350	240	0.25	8.0
SiO ₂ -350	270	0.71	6.8
SiO ₂ -350	300	0.54	5.0
SiO ₂ -350	330	0.72	4.9
SiO ₂ -350	240	1.47	6.6
SiO ₂ -900	240	1.02	7.0
Al ₂ O ₃ -600	240	1.67	8.4

SiO₂-350 turned uniformly bright orange, a colour that persisted on air exposure. Solid state magic angle spinning (MAS) NMR showed two ¹³C resonances: a broad complex peak in the aliphatic region centred at 23.8 ppm and a broad peak in the aromatic region at 115.3 ppm (Figure 3-11). Elemental analysis yielded a C/Ti ratio of 6.6. This suggested that **5** may have decomposed on the SiO₂-350 silica surface to yield both a guanidinate containing as well as a Cp containing surface species, suggesting that the surface enthalpies for equations **a**) and **b**) are similar.

Figure 3-11. Solid state ¹³C NMR of SiO₂-350 depicting aromatic and aliphatic carbons.

The lower pre-treatment temperature resulted in a larger hydroxyl density located on the surface causing the silica to be somewhat acidic.²⁹ The acidity may have allowed the hydroxyl groups to participate in hydrogen bonding with the exocyclic nitrogen of the guanidinate, resulting in a stabilized guanidinate-titanium species.

SiO₂-900 was uniformly dark orange-brown (Figure 3-10) and this colour faded to light yellow when the silica was exposed to atmosphere after several hours. Solid state ¹³C-MAS NMR showed one resonance at 115.0 ppm (Figure 3-12), in the aromatic region, as well as a C/Ti ratio of 7.0. This suggested a mixture containing one to two cyclopentadienyl titanium surface complexes remained. With higher pre-treatment temperature the surface had less hydroxyl density. The lack of hydroxyl groups present on the surface decreased the chance for hydrogen bonding thus the guanidinate-titanium species could not be preserved during the reaction.

Figure 3-12. Solid state ¹³C NMR of SiO₂-900 depicting aromatic carbons.

Al_2O_3 -600 was not fully saturated demonstrated by the patchy brown colour (Figure 3-10). Solid state ^{13}C -MAS NMR showed the presence of both aliphatic and aromatic resonances at 22.5 and 114.9 ppm, respectively (Figure 3-13). The C/Ti ratio was found to be 8.4 suggesting a possible mixture of one guanidinate-titanium species to one or two cyclopentadienyl containing titanium species. It can be speculated that hydrogen bonding also occurred as the pre-treatment temperature resulted in a higher concentration of hydroxyl density on the alumina as in the SiO_2 -350 example.

Figure 3-13. Solid state ^{13}C NMR of Al_2O_3 -600 depicting aromatic and aliphatic carbons.

One interesting observation from these exposure experiments was that the titanium species found on the surface of the silica and alumina was likely in an oxidation state of +4. This can be seen by the characteristic colour of +4 oxidation state titanium species (orange/red) as well as the diamagnetic ^{13}C NMR signals. No special experiments were

conducted while collecting the solid state MAS NMRs, which would have been an issue if the samples were paramagnetic. It was evident that the bound species were very stable as it took several hours for a colour change to occur when the coated silica was exposed to air. These observations would explain the inertness this monolayer showed while attempting ALD reactions with both ammonia and water as the second precursor.

3.2.4 Isolated Zinc By-product

The reduction of Cp_2TiCl_2 with zinc dust produced *in situ* ZnCl_2 . It was difficult to remove the ZnCl_2 from solution, even though it has been reported that $[\text{Cp}_2\text{TiCl}]_2\text{-ZnCl}_2$ is less soluble in polar solvents, such as ether.³⁰ When the $[\text{Cp}_2\text{TiCl}]_2$ dimer crystallized out of solution, some ZnCl_2 precipitated out as well forming the less soluble $[\text{Cp}_2\text{TiCl}]_2\text{-ZnCl}_2$ species. Purification of the parent titanium species would have increased the yield of the cyclopentadienyl guanidinate species, however, this was experimentally difficult to achieve, thus the Ti^{+3} species was used *in situ*. When further reaction of the $[\text{Cp}_2\text{TiCl}]_2\text{-ZnCl}_2$ species with lithiated triisopropyl guanidinate (tripyl) ligand was undertaken, a zinc guanidinate dimer was produced. Crystals of this compound (**10**) were isolated as colourless needles. The dimer contained two zinc centres with three tripyl ligands bound to them in a Chinese lantern fashion and a lone chlorine bound to one zinc (Figure 3-14, Table 3-8 and Table 3-9). The rational synthesis of this compound was further studied by a co-worker.³¹

Compound **10** had two zincs in two different coordination environments. Zn1 was three coordinate with a trigonal planar geometry with respect to the nitrogens. The sum of angles around Zn1 in the nitrogen plane was 359.8° indicating planarity at the bottom

half of the dimer. The distance to Zn2 was almost at a right angle with respect to the nitrogen-Zn plane at an average of 88.6° , respectively. The angles of the three nitrogens around Zn1 were very close to ideal at 119.4° , 120.0° and 120.4° , respectively. Zn2 on the other hand was four coordinate in a slightly distorted tetrahedral geometry. The tetrahedral angles around Zn2 were very close to ideal at 110.2° , 110.4° , 112.6° and 107.3° , respectively. The Zn2-Cl1 bond length was $2.29\text{\AA}$, which was found to be similar to previously reported Zn-Cl bonds of length $2.22\text{\AA}$.³² The Zn1-Zn2 distance of $2.71\text{\AA}$ was longer than a previously reported Zn-Zn bond at $2.33\text{\AA}$.³³ The Zn1-N2, N4, and N8 bond lengths were all smaller than the Zn2-N1, N5, and N7 at an average of $1.93\text{\AA}$ compared to an average of $2.04\text{\AA}$, respectively. Lengthening of the Zn2-N bonds may be caused by the steric bulk or the electron donating nature of the chlorine atom.

Each guanidinate bite angle was similar at 119.2° , respectively, which was quite large and unsurprisingly attributed to the dimer structure. The sum of angles around the chelate nitrogens, N1, N2, N4, N5, N7 and N8 were all very close to 360° deviating by $<0.50^\circ$ indicating very good planarity around the nitrogens. The C-N bond lengths of the chelate nitrogens (N1, N2, N4, N5, N7, and N8) to the quaternary carbons (C3, C4, C10) were also very similar and shorter than an ideal single C-N bond length ($1.479\text{\AA}$)³⁴ at $1.33 - 1.35\text{\AA}$. The shortened bond lengths demonstrated the participation of the chelate nitrogens to the π -system. The quaternary carbons (C3, C4, C10) and exocyclic nitrogens (N3, N6, and N9) bond lengths were longer at 1.38 to $1.40\text{\AA}$, respectively, however still shorter than an ideal single C-N bond.³⁴ This demonstrated that the exocyclic nitrogens were somewhat involved in the extended π -bonding of the guanidinate ring. The steric bulk of the isopropyl groups caused the guanidinate ligands to twist above and below the

Cl1-Zn2-Zn1 plane (Figure 3-15a). The twist forced the chelate nitrogens to be above and below the plane with the quaternary carbon in the Cl1-Zn2-Zn1 plane. The twisting of the guanidinate ligands allowed C_3 symmetry of the compound to occur as seen when looking at the complex through the Cl1-Zn2-Zn1 axis (Figure 3-15b).

Figure 3-14. The single-crystal X-ray structure of **10**. The thermal ellipsoids are shown at 50% probability and the hydrogen centres are omitted for clarity.

Figure 3-15. The single-crystal X-ray structure of **10**. The thermal ellipsoids are shown at 50% probability and the hydrogen centres are omitted for clarity. (a) demonstrating guanidinate twist across the Cl1-Zn2-Zn1 plane with one isopropyl moiety omitted for clarity, (b) looking down Cl1-Zn2-Zn1 axis.

Table 3-8. Selected crystal data for compound **10**.

10	
Empirical Formula	$C_{30}H_{66}N_9ClZn_2$
FW	719.11
Crystal System	Monoclinic
Space Group	$P2_1/c$
a (Å)	10.725(3)
b (Å)	34.697(10)
c (Å)	10.581(3)
α (deg)	90
β (deg)	104.206(4)
γ (deg)	90
V (Å ³)	3816.8(18)
Z	4
D_c (kg/L)	1.251
μ (mm ⁻¹)	1.358
T (K)	120(2)
R, wR	0.0614, 0.1135
Goodness-of-fit on F^2	1.029

Table 3-9. Selected bond lengths and angles for compound **10**.

<i>Selected Bond Lengths and Distances (Å)</i>			
Cl1-Zn2	2.2876(8)	N3-C10	1.385(3)
N1-Zn2	2.040(2)	N4-C4	1.336(3)
N5-Zn2	2.038(2)	N5-C4	1.347(3)
N7-Zn2	2.054(2)	N6-C4	1.384(3)
N2-Zn1	1.932(2)	N7-C3	1.337(3)
N4-Zn1	1.928(2)	N8-C3	1.333(3)
N8-Zn1	1.931(2)	N9-C3	1.394(3)
N1-C10	1.338(3)	Zn1-Zn2	2.7093(6)
N2-C10	1.334(3)		
<i>Selected Bond Angles (°)</i>			
N1-Zn2-N5	110.22(8)	N7-C3-N8	119.4(2)
N1-Zn2-N7	110.36(8)	Zn2-N1-C10	125.48(16)
N5-Zn2-N7	112.64(8)	C10-N2-Zn1	113.39(16)
N2-Zn1-N4	119.42(8)	Zn1-N4-C4	114.21(15)
N2-Zn1-N8	119.96(8)	C4-N5-Zn2	125.12(16)
N4-Zn1-N8	120.45(8)	Zn2-N7-C3	125.01(16)
N1-C10-N2	119.2(2)	C3-N8-Zn1	113.38(16)
N4-C4-N5	119.0(2)		
<i>Sum of Angles (°)</i>			
N1	359.81	N5	359.90
N2	359.50	N7	359.88
N4	359.37	N8	359.63
Zn1	359.83	Zn2	333.21

3.3 Conclusions

This chapter presented the synthesis, structural characterization and thermolysis of new monomeric heteroleptic titanium (III) gas-phase precursors of type $\text{Cp}_2\text{Ti}[(\text{N}^i\text{Pr})_2\text{CNRR}']$ where $\text{R} = \text{H}, \text{Me}, \text{Et}$ or ^iPr and $\text{R}' = \text{Me}, \text{Et}, ^i\text{Pr}$ or ^tBu . Compounds **5** to **9** were synthesized using salt metathesis at room temperature after reducing the parent Cp_2TiCl_2 complex with zinc dust. Five crystal structures were obtained; four for the heteroleptic titanium (III) complexes and one for a zinc by-product. Melting points and TG analyses were obtained for complexes **5** to **8** which fell in a wide

range, from 147°C for **5** to decomposition at >180°C for **8**. Each TG analysis produced a smooth volatilization curve with low residual mass.

Compound **5** was used to study the interfacial oxide layer of a silicon substrate through an exposure experiment. High surface area silica and alumina extrudate were the substrate of choice and were pre-treated at different temperatures. The resultant exposed silica and alumina were then studied further using solid state ^{13}C -MAS NMR and elemental analysis to observe how the complex bound to the nucleation sites.

Both pre-treated silica were fully saturated as demonstrated by complete colour change. The alumina extrudate was only partially saturated as a patchy colour change occurred. The C/Ti ratio for SiO_2 -350 was 6.6 and the ^{13}C NMR showed the presence of both aliphatic and aromatic carbons. It was concluded that the acidity of Si-350 allowed for hydrogen bonding to occur between the hydroxyl groups present on the surface and the exocyclic nitrogen allowing the guanidinate ligand to be preserved during the exposure. The C/Ti ratio for SiO_2 -900 was 7.0 and the ^{13}C NMR demonstrated solely aromatic carbons. It was concluded that with less hydroxyl species present the guanidinate ligand could not be stabilized through hydrogen bonding. The partially saturated Al_2O_3 -600 had a C/Ti ratio of 8.4 and the ^{13}C NMR had both aliphatic and aromatic carbons present. With the lower pre-treatment temperature the extrudate surface acidity allowed for stabilization of the guanidinate species.

From the exposure experiments it was noted that the titanium species did not maintain the oxidation state of +3 but instead was oxidized to +4. This was determined by both the colour of the exposed surface and the clear solid state ^{13}C -MAS NMR. This result was a little off-putting as it would be very advantageous to have a Ti(III) precursor for

ALD applications of TiN film deposition. Conserving oxidation state would allow for more facile ALD reactions as no oxidation or reduction would be necessary to obtain the desired TiN film.

3.4 Methods and Materials

All reactions were performed in a nitrogen-filled dry box, unless otherwise stated. The bis(cyclopentadienyl)titanium (IV) dichloride was purchased from Strem Chemicals and used as received. All solvents used were reagent grade purified from an MBraun Solvent Purifier System. The chemicals: diisopropyl amine, diethyl amine, tert-butyl amine, isopropyl amine, lithium dimethyl amide, 1,3-diisopropyl carbodiimide and zinc dust were purchased from Aldrich Chemical Company and used as received. Preparation of N,N',N''- triisopropyl guanidinate followed a literature procedure.³⁵ Preparation of $[\text{Cp}_2\text{TiCl}]_2$ followed literature procedure.³⁰ Mass spectra were obtained using electron impact on a VG ZAB-2HF triple-focusing spectrometer. Thermal gravimetric analysis was performed on a TA Instruments Q50 apparatus located in an MBraun Labmaster 130 Dry box under a nitrogen atmosphere. Differential scanning calorimetry analysis was performed on a TA Instruments Q10 apparatus. Guelph Chemical Laboratories performed combustion analysis. Single crystal XRD was conducted on a Bruker-AXS APEX CCD Diffractometer located at Delaware University with the help of Glenn P. Yap.

3.4.1.1 Synthesis of $\text{Cp}_2\text{Ti}[\text{PrN}(\text{H})\text{C}(\text{PrN})_2]$ (**5**) from Cp_2TiCl_2

In a 60 mL round bottom flask 4.20 g (16.9 mmol) of bis(cyclopentadienyl)titanium (IV) dichloride was allowed to stir in 40 mL of diethyl ether. 3.33 g (16.9 mmol) of dianionic ligand was slowly added to the red solution. The solution changed from bright red to a dark maroon, almost brown colour and was left to stir over night. The resulting blue solution was then filtered and placed in the freezer and allowed to sit for 24 hours. 0.916 g (2.53 mmol, 15% yield) dark blue needle like crystals of **1** were collected. Combustion analysis: found (calculated). C: 65.97 (66.29), H: 9.21 (8.90), N: 11.52 (11.59). Mass Spectral data: 248 (M^+).

3.4.1.2 Synthesis of $\text{Cp}_2\text{Ti}[\text{PrN}(\text{H})\text{C}(\text{PrN})_2]$ (**5**) from $[\text{Cp}_2\text{TiCl}]_2$

2.82 g (10 mmol) of $[\text{Cp}_2\text{TiCl}]_2$ was placed in a 60 mL round bottom flask and dissolved in ether. To this solution, an *in situ* solution of $\text{Li}(\text{PrN})_2\text{C}(\text{N}(\text{H})\text{Pr})$ (1.92 g, 10 mmol) was slowly added. As the reaction proceeded, the solution changed from light green to dark blue. The reaction was allowed to stir overnight. It was then filtered to remove LiCl, evacuated to dryness and redissolved in approximately 10 mL of diethyl ether, then placed in a freezer at $-30\text{ }^\circ\text{C}$ overnight. Thick dark blue needle-like crystals were collected (58% yield, 1.76 g, 4.9 mmol). Combustion analysis; found (calculated). C: 65.87 (66.29), H: 9.23 (8.90), N: 11.65 (11.59). Mass Spectral data: 248 (M^+).

3.4.2 Bis(cyclopentadienyl) titanium dimethylamide diisopropyl guanidinate,

6

Same reaction procedure as **5** from $[\text{Cp}_2\text{TiCl}]_2$ was used substituting the previous guanidinato ligand with $[\text{Me}_2\text{NC}(\text{N}^i\text{Pr})_2]\text{Li}$ (0.44 g, 2.48 mmol). The reaction was allowed to stir overnight at room temperature. The resulting baby blue solution was then filtered, evacuated to dryness, redissolved in approximately 5 mL of diethyl ether and placed into a freezer at -30°C . After 16 hours in the freezer, 0.34 g (0.98 mmol) of a baby blue solid was collected resulting in 39% yield. Mass spectral data (EI, m/z) (rel. intensity, %): 348, (37.3, M^+). Combustion analysis; found (calculated). C: 65.85 (65.51), H: 9.00 (8.68), N: 11.64 (12.06).

3.4.3 Bis(cyclopentadienyl) titanium diethylamide diisopropyl guanidinate, 7

Same reaction procedure as **5** from $[\text{Cp}_2\text{TiCl}]_2$ was used substituting the previous guanidinato ligand with $[\text{Et}_2\text{NC}(\text{N}^i\text{Pr})_2]\text{Li}$ (0.72 g, 3.50 mmol). The reaction was allowed to stir overnight at room temperature. The light blue solution was then filtered to remove LiCl , evacuated to dryness, redissolved in approximately 5 mL of diethyl ether and placed into a freezer at -30°C . The next morning 0.53 g (1.4 mmol) of a dark blue solid was collected resulting in 40% yield. Mass spectral data (EI, m/z) (rel. intensity, %): 376.2, (100, M^+). Combustion analysis; found (calculated). C: 67.20 (67.01); H: 9.33 (9.11); N: 11.00 (11.16).

3.4.4 Bis(cyclopentadienyl) titanium tetrakis isopropyl guanidinate, **8**

Same reaction procedure as **5** from $[\text{Cp}_2\text{TiCl}]_2$ was used substituting the previous guanidinato ligand with $[\text{}^i\text{Pr}_2\text{NC}(\text{N}^i\text{Pr})_2]\text{Li}$ (4.14 g, 17.8 mmol). The solution changed to a dark army green colour. The reaction was allowed to stir overnight at room temperature. The resulting green solution was then filtered to remove LiCl. The blue mother liquor was evacuated to dryness, redissolved in diethyl ether and placed into a freezer at -30°C . Blue crystals were collected (2.12 g, 5.24 mmol) yielding 30%. Mass spectral data (EI, m/z) (rel. intensity, %): 404.3, (100, M^+). Combustion analysis; found (calculated). C: 68.40 (68.30), H: 9.56 (9.47), N: 10.35 (10.39).

3.4.5 Bis(cyclopentadienyl) titanium t-butylamide diisopropyl guanidinate, **9**

Same reaction procedure as **5** from $[\text{Cp}_2\text{TiCl}]_2$ was used substituting the previous guanidinato ligand with $[\text{}^t\text{BuN}(\text{H})\text{C}(\text{N}^i\text{Pr})_2]\text{Li}$ (1.71 g, 8.0 mmol). The reaction was allowed to stir overnight at room temperature. The midnight blue solution was then filtered to remove LiCl, evacuated to dryness, redissolved in diethyl ether and placed into a freezer at -30°C . Baby blue crystals were collected, 0.21 g (0.56 mmol) resulting in 7 % yield.

3.5 Structural Determination for Compounds **5**, **6**, **8**, **9**, and **10**

Suitable crystals were mounted with viscous oil on a plastic mesh and cooled to the data collection temperature. Unit cell parameters were determined using data frames from four different sections of the Ewald sphere. SADABS multi-scan absorption

corrections were applied. No symmetry higher than monoclinic was observed for compounds **5**, **8** and **10**. Compound **6** showed no higher symmetry than tetragonal and compound **9** showed no higher symmetry than orthorhombic. Solution in the space group option, $P2_1/n$, yielded chemically reasonable and computationally stable results of refinement for compounds **5** and **8**, and $P2_1/c$ for **10**. For compounds **6** and **9** space group option $P4_2/nm$ and $Pbca$ yielded chemically reasonable and computationally stable results of refinement. The structures were solved using direct methods and refined with full matrix least squares procedures of F^2 data. All hydrogen atoms were treated as idealized contributions and all non-hydrogen atoms were refined with anisotropic displacement coefficients. Atomic scattering factors are contained in the SHELXTL program library.

3.6 References

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Chapter 4:

Heteroleptic Cyclopentadienyl Titanium (III) Amidinates

4.1 Introduction

It was found that the bis(cyclopentadienyl) titanium (III) guanidinate complexes¹ reported in Chapter 3 were not as reactive as were expected for thin film deposition, thus the amidinate analogues were synthesized and tested for their thermal reactivity. It has been reported that guanidinate anions are stronger donors (more basic) than amidinate anions since the lone pair on the exocyclic amido group can donate into the ligand system, thus increasing the electron-density of the metal.² Replacement of a guanidinate by an amidinate ion could increase the reactivity of the metal by reducing the electron-density on the metal centre.³ Multidentate ligands, such as amidinates, have allowed researchers to produce volatile monomeric complexes of Group 2 metals,⁴ transition metals⁵ and lanthanides.⁶ The advantage to using bidentate ligands as opposed to monodentate ligands (such as alkylamido species) is that oligomerization can be suppressed. Amidinates have the ability to shield the metal centre from inter-molecular interactions.⁵ Additionally, introducing the bidentate amidinate ligand to these cyclopentadienyl titanium species might increase the stability – making them easier to handle. As heteroleptic cyclopentadienyl complexes that have monodentate ligands within the complex are known to be highly reactive towards air and moisture, thus harder to handle.⁷

Four heteroleptic titanium amidinate precursors were synthesized and their thermal properties were studied. Thermolyses of these compounds were encouraging by TG analysis and DSC. The amidinate analogue ligand ip⁸ was included in these studies to compare the thermal stability of the four compounds.

4.2 Results and Discussion

4.2.1 Synthesis and Crystal Structure Data

Four heteroleptic titanium (III) compounds were synthesized in reasonable yields from the [Cp₂TiCl]₂ starting material and appropriate lithium amidinate (Figure 4-1 and Figure 4-2). It was found that the compounds formed slowly at room temperature, with the starting titanium species changing from a characteristic yellow-green to a solution ranging from light blue to dark blue, depending on the amidinate used. In the case of compounds **11**, **12**, and **14** the solution was removed under vacuum; the blue solid was redissolved in diethyl ether and placed in the freezer to promote crystallization. Blue crystals were isolated and further characterization was undertaken. Compound **13** formed green plate-like crystals after volatiles were removed under vacuum. The solid was redissolved in a minimal amount of diethyl ether and placed in the freezer for purification. Compound **11** produced crystals of sufficient quality for a single crystal structure to be collected (Figure 4-2, Table 4-1 and Table 4-2).

Figure 4-1. Heteroleptic titanium amidinate species.

Figure 4-2. The single-crystal X-ray structure of 11. The thermal ellipsoids are shown at 50% probability and the hydrogen centres are omitted for clarity.

Compound **11** was a four coordinate distorted tetrahedral considering the centroids of the cyclopentadienyl rings with an acetamidinate bite angle of 61.5° . The amidinate bite angle fell within range of the titanium guanidinate bite angles.¹ The centroid angle was correspondingly larger than ideal at 134° similar to the previously reported titanium guanidinate complexes.¹ The centroid-metal-nitrogen angles were closer to ideal tetrahedral angles at 110.7° and 108.7° , respectively. The acetamidinate ring was very close to planar with a torsion angle of only 1.1° across the metallocycle. The titanium-centroid bond lengths were much smaller than a previously reported bis(cyclopentadienyl) bis(thionyl)imide titanium (IV) complex ($\text{Cp-Ti} = 2.06\text{\AA}$)^{9,10} and similar in length to compounds **8**, **9**, and **11** from Chapter 3 ($\text{Ct01-Ti} = 1.74$ and $\text{Ct02-Ti} = 1.73\text{\AA}$). Due to the short centroid bond lengths the titanium-nitrogen bond lengths were longer than reported acetamidinate complexes¹¹ ($\text{Ti-N1} = 2.146$ and $\text{Ti-N2} = 2.152\text{\AA}$). Interestingly, the methyls of both isopropyl groups point in the same direction, angled toward the metal centre unlike compounds **8**, **9**, and **11** from Chapter 3. The exocyclic carbon (C12) was slightly out of plane from the chelate ring (Ti-N1-C11) by 2.7° , correspondingly C13 is 3° and C16 is 1.6° out of plane.

The carbon-nitrogen bonds of the chelate ring (N1-C11 and C11-N2) were shorter at $1.33\text{\AA}$ than the carbon-nitrogen bonds of the exocyclic isopropyl moieties (N1-C13 and N2-C16) at $1.46\text{\AA}$, respectively. The bond length and the sum of angles around the chelate nitrogens (N1 and N2 both at 360°) and the sum of angles around the sp^2 carbon (C11 at 360°) corroborated with the planarity of the system indicating an sp^2 hybridization, and thus participation in the π -system.

Table 4-1. Selected crystal data for compound **11**.

11	
Empirical Formula	C ₁₈ H ₂₇ N ₂ Ti
FW	319.32
Crystal System	Monoclinic
Space Group	Cc
<i>a</i> (Å)	9.5692(14)
<i>b</i> (Å)	15.311(2)
<i>c</i> (Å)	11.7080(17)
α (deg)	90
β (deg)	91.569(2)
γ (deg)	90
<i>V</i> (Å ³)	1714.7(4)
<i>Z</i>	4
<i>D_c</i> (kg/L)	1.237
μ (mm ⁻¹)	0.495
<i>T</i> (°C)	120(2)
<i>R</i> , <i>wR</i>	0.0477, 0.0893
Goodness-of-fit on <i>F</i> ²	1.028

Table 4-2. Selected bond lengths and angles for compound **11**.

<i>Selected Bond Lengths (Å)</i>			
Ti-N1	2.1459(19)	C11-C12	1.502(3)
Ti-N2	2.1517(18)	N2-C11	1.327(3)
N1-C11	1.329(3)	N2-C16	1.462(3)
N1-C13	1.455(3)		
<i>Selected Bond Angles (°)</i>			
Ct01-Ti-Ct02	134.23	N1-C11-N2	111.64(19)
Ct01-Ti-N1	108.74	Ti-N1-C11	93.51(13)
Ct02-Ti-N2	110.72	C11-N2-Ti	93.32(14)
N1-Ti-N2	61.51(7)		
<i>Sum of Angles (°)</i>			
N1	360	N2	360

4.2.2 Thermolysis

The melting points of these compounds fell in a wide range, from 65°C for **11** to 181°C for **14**. TG analysis showed all compounds to decompose with low residual masses with a wide range of on-sets of volatility (Figure 4-3, Table 4-3). Compound **11**

had the second highest on-set of volatilization at 141°C. The curve was characteristic of volatilization with the asymmetric curve due to a slow weight loss until the maximum of the curve was reached at which point the compound had completely volatilized away. The TG showed one major thermal event in the derivative weight curve (Figure 4-4) that occurred at a temperature range of 141 - 270°C with a residual mass of 3%. The TG demonstrated that **11** may be a good candidate for ALD or CVD. This would be a great finding as the acetamidinate ligand is very easy to synthesize and thus the production of large amounts of the titanium precursor would be possible.

Compound **12** had the lowest on-set of volatilization at 118°C. The TG showed one major thermal event that occurred from 118 - 249°C. This major thermal event had a shape that was characteristic of volatilization. The derivative curve (Figure 4-4) was non-symmetrical in shape which is commonly associated with the volatilization of a compound, where there is a slow on-set and a rapid drop-off when the maximum is reached. A residual mass of 6% was achieved. Such a low residual mass could be attributed to the complete volatilization of the titanium species.

Table 4-3. Thermal parameters for compounds **11 - 14**.

	Compound	Percent Yield (%)	Melting Point (°C)	Onset of Volatility¹ (°C)	Residual Mass (%)
11	Cp ₂ Ti acetamidinate	43	65 - 66.5	140.55	3.0
12	Cp ₂ Ti ethyl amidinate	36	99 - 104	117.88	5.5
13	Cp ₂ Ti iso-propyl iminopyrrolidinate	42	111 - 115	126.91	6.0
14	Cp ₂ Ti dicyclohexyl acetamidinate	26	179 - 181	187.89	2.8

¹on-set of volatility was taken as 5% mass loss

Compound **13** was found to have the second lowest on-set of volatilization at 127°C. The derivative weight curve (Figure 4-4) had a non-symmetrical shape which is commonly associated with the volatilization of a compound, a slow on-set and a rapid drop-off when the maximum is reached. The TG had one major thermal event that occurred from 127 - 230°C with a residual mass of 6%. The TG was very clean and indicated that this compound has potential as a CVD or ALD candidate as complete volatilization occurred. However the synthesis of this compound is a little more tedious than compounds **11**, **12**, and **14** because the ipip ligand synthesis is somewhat longer.

Figure 4-3. Thermal gravimetric analysis of 11 - 14.

Figure 4-4. Differential weight curve for compounds **11** - **14**.

The thermal data for compound **14** showed that it would be less likely a candidate for ALD or CVD of the four compounds discussed as it had the highest on-set of volatilization at 188°C and melting point at 181°C. The TG had one thermal feature as seen in the derivative weight curve (Figure 4-4). The thermal event occurred at a temperature range of 188 - 297°C with a weight loss of 92% resulting in a residual mass of 3%. The low yielding residual mass and the uninterrupted volatilization curve demonstrated that this compound had a clean volatilization. The large on-set of volatility may be attributed to the large molecular mass of the compound as it possesses cyclohexyl groups on the chelating nitrogens rather than iso-propyl groups as compounds **11** and **12**.

An NMR tube boil up was performed on each compound. They were each dissolved in 0.25 ($\pm$ 6) mL of 1% v/v TMS in C₆D₆ solution in thick-walled NMR tubes under inert atmosphere. The tubes were immersed in liquid N₂ and the glass tube was sealed under

vacuum. Each tube was placed in a furnace at 125°C and the decomposition of peaks was monitored to observe CDI growth. It was clear that CDI deinsertion did not occur for compounds **11**, **13**, and **14** under these extreme conditions as no CDI peaks were observed by ^1H NMR. This was not a surprise for compound **13** as it contained a ligand that was synthesized to prevent CDI deinsertion. As no CDI deinsertion occurred for compounds **11** and **14** their thermal stability in solution was demonstrated to be a success. After seven days there was a metallic precipitate that collected at the bottom of the NMR tubes for each compound.

By contrast, after three days at 125°C compound **12** showed the presence of CDI by ^1H NMR as well as a precipitation at the bottom of the NMR tube. The presence of CDI was not a surprise as it has been known to deinsert from amidinate or guanidinate ligands at elevated temperatures.¹² It may be possible that the deinsertion occurred on the titanium species leaving behind an alkyl group instead of forming the parent amidine and subsequently deinserting CDI, as there were a broad peaks growing in that region of the NMR throughout the experiment.

4.2.3 Preliminary ALD reactions

An attempt at depositing TiO_2 films was undertaken using compound **11** as the metallic precursor and water as the second precursor. Compound **11** was chosen for two reasons; the thermolysis studies done on this compound showed it to be stable and the synthesis of this compound was easiest. A starting mass of 0.9 g of $\text{Cp}_2\text{Ti}[\text{MeC}(\text{N}^i\text{Pr})_2]$ was placed in the bubbler and a N_2 flow of 20 sccm was used. The substrates used were mechanical grade N-doped Si(100) with a resistance of 1-10 Ω and a native SiO_2 layer.

The deposition apparatus used was a hot-walled ALD reactor (Angstrom Engineering Inc.) consisting of an automated valve array of five pneumatic valves (Figure 4-5).

The reaction chamber was a stainless steel tube with a 1 inch diameter encased in a furnace which leads to a vacuum pump. Bubbler 1 was independently heated and connected to the reactor by a manual valve. Bubbler 2 was held at room temperature. Ultra high pure nitrogen (UHP, 5.0) was used as the carrier and purging gas. The base pressure of the reactor was less than 1×10^{-3} Torr and the typical operating pressure was in the range of 0.08 to 0.09 Torr.

Figure 4-5. Schematic diagram of hot-walled ALD reactor.

The Si(100) substrates were fractured from three inch diameter wafers into strips of ~ 1 cm by use of a diamond tipped glass cutter. The edges were scored with the cutter and broken by hand along the scored line. The substrates were cleaned and prepared by an HF dip and UV/O₃ method that a previous student had reported in her thesis.¹³ The pulse sequence for one cycle in the ALD deposition experiment was:

1. 5.0 s N₂, evacuate for 5.0 s
2. 5.0 s fill Cp₂Ti[MeC(NⁱPr)₂] bubbler with N₂, 0.5 s evacuate
3. 5.0 s Cp₂Ti[MeC(NⁱPr)₂], 0.5 s evacuate
4. 5.0 s N₂, 5.0 s evacuate
5. 5.0 s fill H₂O bubbler with N₂, 0.5 s evacuate
6. 3.0 s H₂O, 10.0 s evacuate

The first experiment was conducted for 300 cycles with bubbler 1 set to 100°C with a gradual temperature gradient throughout the reactor to prevent condensation of the precursor. The precursor delivery line was set to 110°C, the valve array was set to 120°C, line E (Figure 4-5) was set to 130°C and the furnace was set to 200°C. The slides were placed on a stainless steel holder and placed at the centre of the furnace, where the temperature of the furnace was more precisely controlled. The slides retrieved from this experiment (**S1**) did not show any deposition.

The furnace temperature for the second experiment was decreased to 175°C because from the TG it was thought that perhaps at 200°C decomposition of the precursor was occurring in the reaction chamber. The slides from this experiment (**S2**) appeared dusty, as though a thermalization occurred in the gas phase and compound snowed onto the slide.

The third experiment used the same temperatures and parameters as the second experiment with the only exception being an increase in the cycles; from 300 to 1000. These slides (**S3**) again appeared to have undergone no deposition.

The composition of the surface of **S2** and **S3** was analyzed by energy dispersive x-ray spectroscopy (EDS) (Cameca Camebox) that was concomitant with the scanning electron microscope (SEM) (Joel 840). This experimental technique removes an electron from the inner shell of an atom by means of an electron or photon beam. This in effect, leaves an empty space which is then filled with an electron from an outer shell, higher in energy, which releases the excess energy as a characteristic X-ray. This technique can be used to characterize composition as the spectral lines of the X-ray are specific to an element. The dusty film **S2** had some copper particles scattered throughout with a small amount of

titanium present (Figure 4-6). The residual copper (from a different ALD experiment) that was present in the reactor was thermalized and snowed out onto the substrate. The K energies of copper, titanium, oxygen and silicon are 8.982 keV, 4.966 keV, 0.532 keV and 1.838 keV, respectively.¹⁴

Figure 4-6. SEM image showing the surface morphology of S2 deposited at 175°C over 300 cycles.

The composition of S3 showed no titanium present and consisted solely of silicon and oxygen.

ywD13f
Figure 4-7. EDS spectrum of S2 deposited at 175°C over 300 cycles.

After the attempt at ALD was completed, the precursor vial was weighed and a mass of 0.4 g of $\text{Cp}_2\text{Ti}[\text{MeC}(\text{N}^i\text{Pr})_2]$ was collected demonstrating a 55% weight loss. The material appeared to have melted as it had conformed to the shape of the vial. The substance was analyzed by MS and the parent peak was observed. From this it can be deduced that the problem with these failed experiments was not due to volatility and thermal stability but perhaps with reactivity of the compound to the substrate, reactivity of the compound to water, or transportation of the volatilized species. As seen in Chapter 3, the titanium species bound to the high surface area silica were very stable. Water may

not have been a strong enough oxidizer to promote TiO_2 film growth. Acquiring optimized parameters for deposition experiments is very tedious and time consuming. With only one ALD reactor time was very limited thus optimization experiments were unable to be performed. As well, the lab is not equipped to handle stronger oxidizing agents as they require proper ventilation throughout the experiment.

4.2.4 Isolated Zinc By-product

The reduction of Cp_2TiCl_2 with zinc dust produced *in situ* ZnCl_2 . It was difficult to entirely remove the ZnCl_2 from solution, so when the $[\text{Cp}_2\text{TiCl}]_2$ dimer crystallized out of solution, ZnCl_2 precipitated as well. Since the Ti^{+3} species was used *in situ*, further reaction of the $[\text{Cp}_2\text{TiCl}]_2\text{-ZnCl}_2$ species with lithiated acetamidinate ligand produced a zinc amidinate dimer. Colourless cubic crystals of compound **15** were isolated and single crystal XRD was undertaken. The dimeric species contained two zinc centres with three acetamidinate ligands and one chlorine atom (Figure 4-8, Table 4-4 and Table 4-5). Interestingly the amidinate ligands had three different bonding arrangements; one bridged, one shared chelate and one normally chelating amidinate.

Figure 4-8. The single-crystal X-ray structure of **15**. The thermal ellipsoids are shown at 50% probability and the hydrogen centres are omitted for clarity.

Both Zn1 and Zn2 were found in distorted tetrahedral geometries. The angles around Zn1 ranged from 64.5° to 122.5° with the smallest angle corresponding to the bite angle of the N3, N4 amidinate ring and the largest angle corresponding to the Cl1-Zn1-N1 angle. The Cl1-Zn1 bond length was $2.21\text{\AA}$ which was similar to previously reported Zn-Cl bond lengths at $2.22\text{\AA}$.¹⁵ The nitrogen-Zn1 bond lengths varied from 1.98 to $2.15\text{\AA}$, with Zn1-N1 being the shortest and Zn1-N4 the longest. The lengthening of the Zn1-N4 bond length could be a result of the $\mu, \eta^2:\eta^1$ -coordination mode of the second amidinate ligand where Zn1-N4 was a dative bond.

The bridging N1, N2 amidinate had a bite angle of 119.9° which was very similar to a previously reported guanidinate Zn complex¹⁶ (119.3°) and a little smaller than another

amidinate Zn complex¹⁷ (120.8°). The C-N bond lengths of the chelate nitrogens (N1 and N2) to the quaternary carbon C7 were shorter than an ideal single C-N bond length (1.479Å),¹⁸ at 1.35 and 1.32Å, respectively. The shortening of the bond lengths demonstrated the participation of the chelate nitrogens and sp² carbon in the π -system. The sum of angles around the chelate nitrogens (N1 and N2) were found to be 355.4° and 357.4°, showing partial pyramidalization of the nitrogens. The quaternary carbon C7 had a sum of angles of 360°. The bond length from C7-C8 was 1.52Å, which is similar to C-C single bond lengths of 1.54Å.

The N3, N4 amidinate had a complicated $\mu, \eta^2: \eta^1$ -coordination mode. The bite angle was 113.0° (N3-Zn1-N4) which was comparable to other shared amidinate bite angles¹⁶ on zinc at 112.2°. The Zn1-N4-Zn2 angle was found to be 92.2° with a Zn2-N4 bond length of 2.04Å similar to a previously reported complex¹⁶ at 2.10Å. The C-N bond lengths of the chelate nitrogens (N3 and N4) to the quaternary carbon C15 were shorter than ideal single C-N bond lengths (1.479Å)¹⁸ at 1.29 and 1.40Å, respectively. Interestingly, the N4-C15 bond length was much longer than the N3-C15 bond length. The sum of angles around N3 and N4 were 360° and 332.7°, respectively. The bond length and the sum of angles around N4 make it clear that it was not participating fully in the π -system. The lone pair of N4 was involved in the Zn2-N4 bond thus making the N4-C15 bond longer than the N3-C15 bond. The bond length of N3-C15 was very similar to the bond lengths of imines at 1.28Å.¹⁸ The quaternary carbon C15 had a sum of angles of 360° demonstrating the participation in the resonance structure. The bond length of C15-C16 was a little shorter than C7-C8 at 1.51Å.

Zn2 was in a distorted tetrahedral arrangement with angles ranging from 64.8° to 126.2° with the smallest angle corresponding to the bite angle of the amidinate ring and the largest angle corresponding to the N4-Zn2-N6 angle. The N-Zn2 bond lengths varied from 2.00 to 2.09 Å with Zn2-N2 being the shortest and Zn2-N5 the longest.

The normally chelating amidinate (N5, N6) had a ligand angle of 113.3° which was very similar to previously reported zinc amidinate complex¹⁷ at 113.0°. The C-N bond lengths of the chelate nitrogens (N5 and N6) to the quaternary carbon C23 were shorter than an ideal single C-N bond length (1.479 Å)¹⁸ at 1.33 and 1.31 Å, respectively. The shortening of the bond lengths demonstrated the participation of the chelate nitrogens and sp² carbon to the π -system. The sum of angles around N5 and N6 were both 360° as well as the sum of angles around the quaternary carbon C23. The shortening of the bond lengths and the sum of angles corroborated the participation of the chelate nitrogens and sp² carbon to the π -system. The bond length of C23-C24 was 1.52 Å which was similar to C-C single bond lengths of 1.54 Å.

Figure 4-9. The single-crystal X-ray structure of **15**, looking down Zn2-Zn1 axis. The thermal ellipsoids are shown at 50% probability; the hydrogen centres and all isopropyl groups are omitted for clarity.

Table 4-4. Selected crystal data for compound **15**.

15	
Empirical Formula	C ₂₄ H ₅₁ N ₆ ClZn ₂
FW	589.90
Crystal System	Monoclinic
Space Group	P2 ₁
<i>a</i> (Å)	10.028(4)
<i>b</i> (Å)	10.595(4)
<i>c</i> (Å)	29.245(11)
α (deg)	90
β (deg)	96.308(6)
γ (deg)	90
<i>V</i> (Å ³)	3088(2)
<i>Z</i>	4
<i>D</i> _c (kg/L)	1.269
μ (mm ⁻¹)	1.661
<i>T</i> (K)	120(2)
<i>R</i> , <i>wR</i>	0.0319, 0.0685
Goodness-of-fit on <i>F</i> ²	1.037

Table 4-5. Selected bond lengths and angles for compound **15**.

<i>Selected Bond Lengths and Distances (Å)</i>			
Zn1-Cl1	2.2125(9)	N3-C9	1.467(2)
Zn1-N1	1.9754(17)	N3-C15	1.291(2)
Zn1-N3	2.0556(16)	N4-C12	1.477(2)
Zn1-N4	2.1485(17)	N4-C15	1.401(2)
Zn2-N2	2.0014(18)	N5-C17	1.467(3)
Zn2-N4	2.0412(16)	N5-C23	1.329(3)
Zn2-N5	2.0866(18)	N6-C20	1.469(3)
Zn2-N6	2.0323(19)	N6-C23	1.312(3)
N1-C1	1.490(3)	C7-C8	1.523(3)
N1-C7	1.346(3)	C15-C16	1.507(3)
N2-C4	1.480(3)	C23-C24	1.518(3)
N2-C7	1.317(3)	Zn1-Zn2	3.0201(7)
<i>Selected Bond Angles (°)</i>			
N1-Zn1-N3	112.51(7)	N1-C7-N2	119.94(19)
N1-Zn1-N4	116.15(7)	C7-N2-Zn2	119.14(13)
N3-Zn1-N4	64.51(6)	Zn1-N3-C15	94.59(11)
Zn1-N4-Zn2	92.21(6)	N3-C15-N4	112.95(16)
N2-Zn2-N4	106.43(7)	C15-N4-Zn1	87.51(11)
N2-Zn2-N6	113.15(7)	C15-N4-Zn2	109.80(12)
N4-Zn2-N5	117.03(7)	Zn2-N5-C23	89.54(13)
N5-Zn2-N6	64.76(8)	N5-C23-N6	113.27(19)
Zn1-N1-C7	118.13(14)	C23-N6-Zn2	92.41(14)
<i>Sum of Angles (°)</i>			
N1	355.35	N6	360
N2	357.41	C7	360
N3	360	C15	360
N4	332.68	C23	360
N5	360		

4.3 Conclusions

This work presented the synthesis, structural characterization, and thermolysis of new monomeric heteroleptic titanium (III) gas-phase amidinate precursors. Two crystal structures were obtained; one of the heteroleptic titanium (III) complexes and one zinc by-product. Preliminary thermolyses (TG and melting points) of the new precursors showed good volatility and thermal stability satisfying important requirements for

application as a titanium-containing precursor for chemical deposition techniques such as ALD. Further thermal investigations were conducted for each compound using sealed NMR tubes to study the decomposition of the compounds using ^1H NMR. It was found that compounds **11**, **13**, and **14** were thermally stable at 125°C for 7 days, after which a grey metallic precipitate was observed in the NMR tubes. Compound **12** was not as stable at elevated temperatures as CDI peaks were observed by ^1H NMR after three days as well as precipitation of a black solid out of solution.

Preliminary film deposition was attempted with compound **11** as the metallic precursor and water as the second precursor. Titanium was observed on **S2** however a film was not deposited. The titanium species was volatilizing and may have entered the reaction chamber, however the reactivity of the second precursor may have deterred film deposition from occurring. Further tests should be conducted on this species to determine whether it could be used in ALD applications.

4.4 Methods and Materials

All manipulations were performed in a nitrogen filled drybox unless otherwise stated. The chemicals: methyl lithium, ethyl lithium, 1,3-diisopropyl carbodiimide, 1,3-dicyclohexyl carbodiimide, 2-pyrrolidinone, isopropyl amine, phosphorous pentoxide and zinc dust were purchased from Aldrich Chemical Company and used as received. Bis(cyclopentadienyl) titanium dichloride was purchased from StremChemicals and used without further purification. All solvents used were reagent grade purified from an MBraun Solvent Purifier System. The monoanionic ligand synthesis of $[\text{MeC}(\text{N}^i\text{Pr})_2]\text{Li}$,

[MeC(NCy)₂]₂Li and [EtC(N^{*i*}Pr)₂]₂Li followed literature procedures.¹⁹ Iminopyrrolidine synthesis followed literature procedure.⁸ The iminopyrrolidinate [N(CH₂)₃C(N^{*i*}Pr)]Li synthesis followed Aeilts et. al. procedure for monoanionic ligands.¹⁹ The bis(cyclopentadienyl) titanium dichloride complex was reduced following literature procedure.²⁰ Mass spectra were obtained using the electron impact method on a VG ZAB-2HF triple-focusing spectrometer. Guelph Chemical Laboratories performed combustion analysis. TG analysis was performed on a TA Instruments Q50 apparatus located within a Labmaster 130 Dry box. Differential Scanning Calorimetry was performed on a DSC Instruments Q10 apparatus. Single crystal XRD was conducted on a Bruker-AXS APEX CCD Diffractometer located at Delaware University with the help of Glenn P. Yap.

4.4.1 Bis(cyclopentadienyl) titanium acetamidinate, 11

In a 60 mL round bottom flask 2.62 g (12.2 mmol) of [Cp₂TiCl]₂ was allowed to dissolve in about 30 mL of diethyl ether for about 10 min. An *in situ* solution of [MeC(N^{*i*}Pr)₂]₂Li (1.82 g, 12.2 mmol) in diethyl ether was slowly added to the yellowish green titanium solution. The reaction was allowed to stir overnight at room temperature. The light blue solution was filtered, evacuated to dryness, redissolved in approximately 10 mL of diethyl ether and placed into a freezer at -30°C. 1.13 g (3.5 mmol) of light blue solid was collected resulting in 43% yield. mp 65 - 66.5°C. ¹H NMR (300 MHz, C₆D₆): δ 3.47 (m, 2H, NCH(CH₃)₂), 1.58 (s, 3H, NCCH₃), 1.14 (d, 12H, CH(CH₃)₂) Mass spectral data (EI, *m/z*) (rel. intensity, %): 319.2 (M⁺, 100). Elemental analysis (calculated) experimental; C: (67.71), 67.60; H: (8.52), 8.21; N: (8.77), 8.57.

4.4.2 Bis(cyclopentadienyl) titanium ethyl amidinate, 12

Same reaction procedure as **11** was used substituting the previous amidinato ligand with $[\text{EtC}(\text{N}^i\text{Pr})_2]\text{Li}$ (0.568 g, 3.5 mmol). The reaction was allowed to stir overnight at room temperature. The blue solution was then filtered to remove LiCl, evacuated to dryness with a 65% crude yield, redissolved in approximately 5 mL diethyl ether and placed into a freezer at -30°C . 0.42 g (1.26 mmol) of a baby blue solid was collected resulting in a 36% yield. mp $99 - 104^\circ\text{C}$. Mass spectral data (EI, m/z) (rel. intensity, %): 333.2 (M^+ , 21.7). Elemental analysis (calculated) experimental; C: (68.46), 68.13; H: (8.77), 8.39; N: (8.40), 7.94.

4.4.3 Bis(cyclopentadienyl) titanium iso-propyl iminopyrrolidinate, 13

Same reaction procedure as **11** was used substituting the previous amidinato ligand with $[\text{N}(\text{CH}_2)_3\text{C}(\text{N}^i\text{Pr})]\text{Li}$ (0.416 g, 3.5 mmol). The reaction was allowed to stir overnight at room temperature. The green solution was then filtered, evacuated to dryness, redissolved in approximately 5 mL of diethyl ether and placed into a freezer at -30°C . 0.4 g (1.3 mmol) of a light green solid was collected resulting in a 42% yield. mp $111 - 115^\circ\text{C}$. Mass spectral data (EI, m/z) (rel. intensity, %): 303.1 (M^+ , 18.7). Elemental analysis (calculated) experimental; C: (67.33), 66.97; H: (7.64), 7.38; N: (9.24) 8.85.

4.4.4 Bis(cyclopentadienyl) titanium biscyclohexyl acetamidinate, 14

Same reaction procedure as **11** was used substituting the previous amidinato ligand with $[\text{MeC}(\text{NCy})_2]\text{Li}$ (0.80 g, 3.5 mmol). The reaction was allowed to stir overnight at

room temperature. The light blue solution was then filtered, evacuated to dryness, redissolved in approximately 5 mL of diethyl ether and placed into a freezer at -30°C. 0.311 g (0.90 mmol) of a blue solid was collected resulting in a 26% yield. mp 179 - 181°C. Mass spectral data (EI, m/z) (rel. intensity, %): 399.2 (M^+ , 100).

4.5 Structural Determination for Compounds **11** and **15**

Suitable crystals were mounted with viscous oil on a plastic mesh and cooled to the data collection temperature. Unit cell parameters were determined using data frames from four different sections of the Ewald sphere. SADABS multi-scan absorption corrections were applied. No symmetry higher than monoclinic was observed for compounds **11** and **15**. Solution in the space group option, Cc and $P2_1$, yielded chemically reasonable and computationally stable results of refinement for compounds **11** and **15**. The structures were solved using direct methods and refined with full matrix least squares procedures of F^2 data. All hydrogen atoms were treated as idealized contributions and all non-hydrogen atoms were refined with anisotropic displacement coefficients. Atomic scattering factors are contained in the SHELXTL program library.

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Chapter 5: Homoleptic Titanium (III) Compounds

5.1 Introduction

One issue that continues to arise in transition metal nitride film deposition is the lack of reactivity the commonly used nitrogen source ammonia (NH_3) has. Finding a suitable reducing agent to reduce titanium metal to the +3 oxidation state is a constant challenge. One method of avoiding such an issue is by developing a single source precursor (SSP) that contains both titanium and nitrogen in a single molecule.¹ The search for SSPs for TiN films began in the mid seventies.² The majority of these compounds, however, have been volatile homoleptic tetrakis(dialkylamido) titanium complexes in the +4 oxidation state.^{3,4} Other heteroleptic bis(dialkylamido) titanium species have been studied in SSP process by Carmalt et. al. and Winters et. al., these compounds, however, contained chlorine.^{5,6} Synthesizing a SSP that is chlorine free would be advantageous in improving the halide contamination of the deposited TiN film. To the best of our knowledge, the development of SSPs consisting of titanium in the +3 oxidation state has not been reported. It would be advantageous to synthesize a +3 oxidation state titanium SSP for TiN thin film deposition so that the surface reduction of the titanium would be unnecessary within the reaction chamber.

It has been reported that tetrakis(dialkylamido) titanium complexes undergo thermal decomposition at elevated temperatures and prolonged evacuation leaving behind high carbon impurities.⁴ As most CVD and ALD processes are conducted under such

environments, a compound that thermally decomposes with high impurities is highly undesirable.

It was predicted that by fully saturating the titanium centre with bulky bidentate ligands, such as guanidates, the vapour phase thermal stability may increase. This chapter focuses on the synthesis of homoleptic titanium (III) guanidinate compounds, their thermolysis and their reactivity towards N-doped Si(100) films.

5.2 Results and Discussion

5.2.1 Synthesis and Crystal Structure Data

Two homoleptic titanium (III) guanidinate species were synthesized in low yields from the $\text{TiCl}_3 \cdot 3\text{THF}$ starting material and the appropriate lithiated guanidinate. It was found that the compounds formed slowly at room temperature with the starting titanium species changing from a characteristic yellow-green to a solution ranging from dark green to brown, depending on the lithiated guanidinate used. In every case, the solution was removed under vacuum, the solid was redissolved in diethyl ether and placed in the freezer to promote crystallization. Dark green, red and black crystals were isolated, and further characterization was undertaken. Compounds **16** and **18** produced crystals of sufficient quality for a single crystal structure to be collected (Figure 5-1 and Figure 5-2, Table 5-1 and Table 5-2).

where R = NMe_2 or NH^iPr

The salt metathesis reaction for compound **16** was a success and the compound was characterized by MS, NMR and XRD with a crystallized yield of 59%. The reaction was a ratio of one $\text{TiCl}_3 \cdot 3\text{THF}$ to three lithiated dimethylamide diisopropyl guanidinate (dimdip). The ligand was made two hours prior to the reaction and used *in situ*. The reaction was carried out overnight at room temperature. The collected crystal structure was very symmetric with an I-43d space group. Compound **16** was a six coordinate distorted octahedral considering the arrangement of the dimdip ligands. The bite angle of the ligand was 62.4° which was slightly larger than previously reported heteroleptic titanium (III) guanidinate species at 61.6° .⁷ The increase in bite angle may be due to the fact that this compound is homoleptic and there is no competition between the electronic and steric properties of a single type of ligand⁸ as there would be if there were two different ligands present. The ligand angle (N1-C7-N2) was 112.8° which was the same as the previously reported heteroleptic dimdip species.⁷

Figure 5-1. The single-crystal X-ray structure of **16**. The thermal ellipsoids are shown at 50% probability and the hydrogen centres are omitted for clarity.

The titanium-nitrogen bond lengths of compound **16** were slightly smaller than previously reported heteroleptic guanidinate complexes⁷ at 2.14Å as compared to 2.17Å. This may also be attributed to the fact that **16** was a homoleptic species (as described above). The C-N bond lengths within the CN₃ core of the coordinated ligand were found to contain the π -system within the metallocycle with carbon-nitrogen bond lengths of 1.33Å for both N1-C7 and N2-C7. The bond length of the exocyclic nitrogen was found to be longer at 1.40Å, however, it was still shorter than single C-N bond lengths.^{9,10} The shorter than single C-N bond lengths of the exocyclic moiety led to the inclination that

the exocyclic nitrogen was participating slightly in the π -system of the ring. A torsion angle of 41.7° was found for (C8-N3-C7-N2) with a sum of angles around N3 of 357.8° . These results gave validation to the inclination that N3 was participating in the π -system. The guanidinate ring was planar with a torsion angle of 0.0° .

Table 5-1. Selected crystal data for compounds **16** and **18**.

	16	18
Empirical Formula	C ₂₇ H ₆₀ N ₉ Ti	C ₂₀ H ₄₄ N ₆ ClTi
FW	558.74	451.96
Crystal System	Cubic	Monoclinic
Space Group	I-43d	P2 ₁ /c
<i>a</i> (Å)	23.739(4)	9.6420(11)
<i>b</i> (Å)	23.739(4)	14.1909(17)
<i>c</i> (Å)	23.739(4)	19.236(2)
α (deg)	90.00	90.00
β (deg)	90.00	99.354(2)
γ (deg)	90.00	90.00
<i>V</i> (Å ³)	13378(4)	2597.0(5)
<i>Z</i>	16	4
<i>D_c</i> (Mg/m ⁻³)	4912	1.156
μ (mm ⁻¹)	0.285	0.449
<i>T</i> (K)	120(2)	120(2)
<i>R</i> , <i>wR</i>	0.0327, 0.0810	0.1011, 0.1338
Goodness-of-fit on <i>F</i> ²	1.013	1.050

Table 5-2. Selected bond lengths and angles for compounds **16** and **18**.

C ₂₇ H ₆₀ N ₉ Ti (16)			C ₂₀ H ₄₄ N ₆ ClTi (18)		
Selected Bond Lengths (Å)					
N1-Ti	2.1424(12)	N1-Ti	2.147(2)	N4-Ti	2.027(2)
N1-C7	1.335(2)	N2-Ti	2.037(2)	N5-Ti	2.117(2)
N2-Ti	2.1432(13)	N1-C1	1.323(3)	N4-C11	1.355(3)
N2-C7	1.3303(19)	N2-C1	1.368(3)	N5-C11	1.336(3)
N3-C7	1.4055(18)	N3-C1	1.365(3)	N6-C11	1.362(3)
		Ti-Cl	2.3326(8)		
Selected Bond Angles (°)					
N1-Ti-N2	62.35(5)	N1-C1-N2	111.2(2)	N4-Ti-N5	64.58(8)
N1-C7-N2	112.70(12)	N1-Ti-N2	64.07(8)	N4-C11-N5	110.8(2)
Ti-N1-C7	92.42(8)	Ti-N1-C1	90.59(15)	Ti-N4-C11	93.91(15)
Ti-N2-C7	92.52(9)	Ti-N2-C1	94.08(15)	Ti-N5-C11	90.53(15)
Sum of Angles (°)					
N1	356.88	N1	355.22	N4	358.27
N2	356.83	N2	355.32	N5	356.68
N3	357.75				

Compound **18** was isolated from the salt metathesis reaction of a miscalculation for compound **17**. A ratio of one $TiCl_3 \cdot 3THF$ to two lithiated tripryl was used rather than the intended one to three equivalents.

Brownish-red rectangular crystals were isolated, which were different from any other crystals isolated from these types of reactions. A 1H NMR was taken to see if the product was oxidized to a +4 oxidation state. The NMR was not clear as the peaks were broad indicating that the compound may still be paramagnetic; +3 oxidation state. Due to the puzzling NMR and colour of the crystals, qualitative tests for lithium and chloride were performed. The compound was dissolved in dilute nitric acid solution and a flame test was conducted. If lithium were present in the compound a bright magenta colour would

have appeared when introduced to the flame of a propane torch. This test was negative; no lithium was present in the isolated crystal. Next, three drops of silver nitrate were introduced to the solution and cloudy white precipitate formed immediately, indicating the presence of a halide by silver halide precipitation. With these tests it was considered that perhaps a bis(tripyl) titanium(III) mono chloride compound was synthesized. The crystal was sent for structural determination after a parent peak for the bis compound was seen by MS. A rational synthesis was performed in an attempt to increase the yield. From a rational synthesis, 0.3 g of brownish-red crystals were obtained (24% yield).

Figure 5-2. The single-crystal X-ray structure of **18**. The thermal ellipsoids are shown at 50% probability and the hydrogen centres are omitted for clarity.

There are two possible geometries for a five-coordinate species, trigonal-bipyramidal or square-pyramidal. Addison et al. suggested a geometric parameter, τ , that can be used to distinguish which geometry is dominant.¹¹ For square-pyramidal systems $\alpha = \beta = 180^\circ$

where α is the DME angle and β is the BMC angle with A as the axial ligand (Figure 5-3). In most square-pyramidal systems M is slightly displaced out of the BDCE plane, shifted towards A, this forces $\alpha = \beta < 180^\circ$. For perfectly trigonal-bipyramidal systems α and β angles differ with $\alpha = 120^\circ$ and $\beta = 180^\circ$. Thus the parameter τ is defined as equation 1:

$$\tau = \frac{(\beta - \alpha)}{60}, \text{ where } 0 \leq \tau \leq 1 \quad [1]$$

A square-pyramidal C_{4v} geometry has a value of 0 and trigonal-bipyramidal D_{3h} geometry has a value of 1.

Figure 5-3. Five-coordinate structures of a) square-planar and b) trigonal-bipyramidal geometries.

Compound **18** showed titanium to be in a five coordinate system that had $\alpha = 111.3^\circ$ and $\beta = 161.2^\circ$ giving a τ value of 0.83. With this high value it can be concluded that **18** was distinguishably more trigonal-bipyramidal in shape. The Ti-Cl bond length was $2.33\text{\AA}$ which was similar to previously reported titanocene monochloride species at $2.36\text{\AA}$ ¹² and monochloride bis(amidinate) Ti(III) species ($2.33\text{\AA}$) by Hagadorn et. al.¹³ The chlorine-titanium-nitrogen angles ranged from 98.8° to 125.9° with Cl-Ti-N1 being the smallest and Cl-Ti-N2 being the largest angle. Interestingly, the Cl-Ti-N5 angle was smaller than the Cl-Ti-N4 at almost the same values as for N1 and N2 at 100.0° and 122.8° , respectively. This difference in angles can be associated with the propeller like

structure the guanidinate ligands formed. This gave the structure a $P2_1/c$ space group with a C_2 symmetry on the Cl-Ti axis. The bite angle of the tripyl ligands were 64.1° and 64.7° , respectively. The angles were much larger than previously reported tripyl heteroleptic species at 61.8° ⁷ and similar to Hagadorn's monochloride species at 64.3° and 65.5° .¹³ The ligand angles (N1-C1-N2 and N4-C11-N5) were 111.2° and 110.3° which were similar to the previously reported tripyl heteroleptic species at 111.1° .⁷

The titanium-nitrogen bond lengths of compound **18** ranged from 2.03 to 2.15Å, with Ti-N4 being the shortest and Ti-N1 the longest bonds. Similarly the bond lengths mimic the Cl-Ti-N angles. The shortening of the N2 and N4 bond lengths was caused by their position in the equatorial plane.

The C-N bond lengths of both ligands were all relatively short at 1.32Å for N1-C1 and 1.37Å for N2-C1 with the exocyclic N3-C1 at 1.36Å.¹⁴ Similarly N4-C11 was 1.36Å, N5-C11 was 1.34Å and the exocyclic N6-C11 was 1.36Å. The shorter bond lengths led to the inclination that all three nitrogens were participating in the π -system of the ligand. The torsion angles within the guanidinate ring were 2.1° and 4.2° , far from planar. The iso-propyl groups on the exocyclic amido moieties of both ligands were rotated from the plane of the guanidinate ring by 30° for N2-C1-N3-C8 and 24° for N4-C11-N6-C18. However, π -overlap is known to follow a $\cos^2\theta$ relationship for twisted systems and with the lengths of the C-N bonds it was clear that the exocyclic groups participated significantly in the delocalized π -bonding of the guanidinate.¹⁵

R = NMe₂ or NH^{*i*}Pr

Figure 5-4. Homoleptic titanium (III) species.

Similarly, the synthesis of compound **17** was attempted at room temperature and solids were allowed to precipitate out of solution in the freezer; -30°C. The black needle like crystals were not easily isolated; they began to melt as the temperature began to approach room temperature.

This reaction was repeated several times at room temperature to attempt to collect the low melting solid previously seen. However, the colour of the solution (black) and the lack of precipitate led to believe that there were competing reactions, possibly β-hydride elimination from a guanidinate ligand occurring during synthesis. The reaction was attempted at lower temperatures outside the dry box, using Schlenk techniques. The lithiated tripryl was added slowly at -78°C over the period of an hour. The reaction was allowed to stir at low temperatures and slowly warm up to room temperature. The reaction was executed with careful control producing the same black solution. Volatiles

were removed under vacuum and the black paste was redissolved in minimal diethyl ether, filtered to remove any insoluble products and placed in the freezer for a long period of time. No solids were ever isolated.

5.2.2 Thermolysis

Only one melting point was obtained from the two paramagnetic homoleptic titanium precursors. TG analysis showed compound **16** to decompose with large residual mass and relatively low on-set of volatility (Figure 5-5 and Table 5-3). Compound **16** was found to have an on-set of volatility of 98°C. From the derivative weight curve it was clear that three thermal events occurred. These thermal events occurred at temperature ranges of 97.9 - 124.4°C, 124.4 - 163.3°C and 163.3 - 232.8°C which can be attributed to a slow thermal degradation of the compound. The residual mass was high, 15.1% at 232.8°C, which most likely corresponded to the mass of a decomposed species. The TG curve was not characteristic of volatilization as it had a very slow and gradual slope. The derivative weight curve did not show the characteristic asymmetry of a slow on-set and quick drop-off. The rather gradual drop-off led to believe that decomposition was occurring within the TG pan. It was suspected that one of the thermal events was the deinsertion of CDI and so an NMR tube boil-up experiment was performed.

Table 5-3. Yield and thermal parameters of compounds **16** - **18**.

Compound	R	Percent Yield (%)	Melting Point (°C)	On-set of Volatility (°C) ^a
16	NMe ₂	59	211-213	98
17	NH ⁱ Pr	N/A	Low melting solid	N/A
18	NH ⁱ Pr	24	N/A	N/A

^a on-set of volatility was taken as 5% mass loss

Figure 5-5. Thermal gravimetric analysis of **16**.

The complex was dissolved in $0.25 (\pm 6)$ mL of C_6D_6 solution in a thick-walled NMR tube under inert atmosphere. The tube was immersed in liquid N_2 and the glass tube was sealed under vacuum. The tube was placed in a furnace starting at $50^\circ C$ and the temperature increased to $160^\circ C$ over several days to observe possible CDI growth. On the third day at a temperature of $70^\circ C$ compound **16** demonstrated the presence of CDI by 1H NMR. The characteristic multiplet and doublet at 3.33 and 1.04 ppm was first observed at $70^\circ C$ and the intensity increased as the temperature increased for the duration of the experiment. The presence of CDI was not a surprise as it has been known to deinsert from amidinate or guanidinate ligands at elevated temperatures.¹⁶

5.2.3 Preliminary CVD Reactions

Even though compound **16** did not seem like the ideal candidate for ALD from the thermolysis studies, it was thought that it could be a suitable candidate for CVD of TiN films. Titanium nitride films have been produced by a single source method for over a decade using different alkyl amines and hydrazine-derived nitrogen sources.^{4,5,17} However, to this date there have not been TiN films deposited from guanidinate titanium (III) complexes. Thus it would be interesting to see if this tris(dimdip) guanidinate complex can be used as a SSP to deposit TiN thin films. The compound was sublimed at 110°C and used as the pure form. The same N-doped Si(100) substrates, cleaning procedures for the substrates, and ALD reactor were used as in Chapter 4 (Figure 4-5) with the exception of the pulse sequence used.

The pulse sequence of this experiment was:

1. 5.0 s fill $\text{Ti}[\text{Me}_2\text{NC}(\text{N}^i\text{Pr})_2]_3$ bubbler with N_2
2. 5.0 s $\text{Ti}[\text{Me}_2\text{NC}(\text{N}^i\text{Pr})_2]_3$ introduction to reaction chamber
3. 10.0 s evacuation

This cycle was repeated 1000 times. The starting mass of the titanium precursor was 0.9g.

All the temperatures within the reactor varied throughout the experiment as no film was observed after each run. The first experiment conducted had the bubbler set to 85°C with a gradual temperature gradient throughout the reactor to prevent condensation of the precursor within the reactor. Line C (Figure 4-5) was set to 95°C, the valve array system and line E were set to 105°C and the furnace was set to 300°C. The slides were placed on a stainless steel holder and positioned at the centre of the furnace where the temperature

of the furnace was seen to be more precise. After the first experiment was finished, the slides (**S4** and **S4.1**) were taken out of the furnace with no observable change.

The temperature was increased by 15°C throughout the system for the second deposition experiment. The pulse sequence, the furnace temperature and the placement of the slides remained the same with the only change being the addition of a glass substrate. The new substrate was cleaned using the same method as the Si(100) substrate. The Si(100) slide (**S5**) and the glass slide (**S5.1**) had undergone minimal change as evidence of contamination from the apparatus occurred and no obvious TiN was formed.

Increasing the temperature throughout the system by an extra 30°C with the furnace temperature constant produced no obvious films. The bare Si(100) substrates (**S6**) and the results from the previous two depositions (**S4** and **S5**) were taken to get the surface composition analyzed.

The lack of titanium on all three slides (**S4**, **S5**, and **S6**) was confirmed using an EDS (Cameca Camebox) that was concomitant with the SEM (Joel 840). The energies of oxygen and silicon at 0.532 keV and 1.839 keV, respectively^{9b} were the only signals observed.

When the bubbler was taken off the reactor and the vial with the titanium precursor weighed, a loss of 0.17 g was observed. The titanium precursor was no longer a dark green material but a black material. It appeared as though the material had melted as it conformed to the shape of the vial. The material was analyzed by MS and no parent peak was observed. The small weight loss throughout the experiment could have been associated with thermal decomposition. The deposition experiments performed were merely preliminary. A substantial amount of time and dedication would be necessary in

order to achieve a proper film; however this compound demonstrated that it was not an excellent candidate for such extensive studies as it was not volatile and its thermal stability was limited.

5.3 Conclusion

This work presented the synthesis, structural characterization and thermolysis of new monomeric homoleptic titanium (III) complexes in low yields. Two crystal structures were obtained; one for the tris(dimdip) titanium species **16** along with a serendipitous bis(tripyl) titanium mono chloride structure **18**. Preliminary thermolyses (TG) of compound **16** demonstrated that it decomposed slowly as the temperature increased. Further thermal investigations were conducted using a sealed NMR tube to study the decomposition of the compounds using ^1H NMR. It was found that **16** was not stable at elevated temperatures in solution as CDI peaks were observed by ^1H NMR after 3 days of the study, demonstrating CDI deinsertion. It was thought that **16** could decompose to make TiN films by means of a single source thus CVD was attempted. The results of the CVD experiments demonstrated that this compound showed poor volatility and thermal stability. These important requirements for CVD precursors were not satisfied and thus **16** would not be a likely titanium-containing precursor for chemical vapour deposition techniques.

5.4 Methods and Materials

All manipulations were performed in a nitrogen filled dry box, unless otherwise specified. The chemicals: isopropyl amine, lithium dimethyl amide, methyl lithium, 1,3-diisopropyl carbodiimide and titanium (III) chloride tetrahydrofuran complex (1:3) were purchased from Aldrich Chemical Company and used as received. All solvents used were reagent grade purified from an MBraun Solvent Purifier System. The monoanionic ligand synthesis of $[\text{Me}_2\text{NC}(\text{N}^i\text{Pr})_2]\text{Li}$ and $[\text{}^i\text{PrHNC}(\text{N}^i\text{Pr})_2]\text{Li}$ followed literature procedures.¹⁸ Nuclear Magnetic Resonance was done on a 300MHz Avance III. Mass spectra were obtained using the electron impact method on a VG ZAB-2HF triple-focusing spectrometer. Thermogravimetric analysis was performed on a TA Instruments Q50 apparatus located within a Labmaster 130 Dry box. Differential Scanning Calorimetry was performed on a DSC Instruments Q10 apparatus. Single crystal XRD was conducted on a Bruker-AXS APEX CCD Diffractometer located at Delaware University with the help of Glenn P. Yap.

5.4.1 Tris(dimethylamide diisopropyl guanidinate) titanium, 16

In a 60 mL round bottom flask, 0.50 g (1.35 mmol) of titanium (III) chloride tetrahydrofuran complex (1:3) was weighed and then suspended in 20 mL of diethyl ether. While this mixture was stirring at room temperature 0.72 g (4.05 mmol) of dimdip was added drop-wise. The ligand was made 2 hours prior to the reaction and was then added *in situ*. The suspended mixture was an opaque yellowish-green solution and as the ligand was added drop-wise the solution changed from an opaque yellowish-green to an army green colour. The reaction was allowed to stir at room temperature for 16 hours,

after which it was filtered to remove any LiCl that precipitated out. The green solution was evacuated to dryness in *vacuo* and then redissolved in about 1 mL of diethyl ether and placed in the freezer. After 1 hour dark green crystals precipitated out of solution. The crystals were allowed to grow over night in the freezer after which, 0.44 g (0.80 mmol) were collected in the morning. This resulted in a 59% yield. A melting point of 211-213°C was observed. The crystals were dissolved in deuterated benzene to take an NMR, however since the complex was paramagnetic, no clear spectra was collected. Mass spectral data (EI, *m/z*) (rel. intensity, %): 558 (M^+ , 19).

5.4.2 Tris(triisopropyl guanidinate) titanium, 17

The same reaction procedure as **16** was used substituting the previous guanidinate with triisopropyl guanidinate. The opaque black solution was evacuated to dryness in *vacuo* and then redissolved in about 3 mL of diethyl ether and placed in the freezer. Black needle like crystals were obtained after 16 hours. The crystals began to melt as the temperature approached room temperature while trying to isolate them on a kim wipe. The reaction was repeated at -78°C using solid CO₂ and acetone mixture. The lithiated guanidinate was slowly added through the use of an air free funnel. The reaction was allowed to proceed for 16 hours with an over pressure of nitrogen. Volatiles were removed under reduced pressure to afford a black paste. The black paste was dissolved in a minimal amount of diethyl ether, filtered to remove any insoluble substances and placed in the freezer. No solids were isolated.

5.4.3 Bis(triisopropyl guanidinate) titanium chloride, **18**

The same reaction procedure as **16** was used substituting the previous guanidinate with triisopropyl guanidinate and a decreased equivalence of the ligand. Ratios were 1.00 g (2.70 mmol) of titanium to 1.03 g (5.40 mmol) of lithiated ligand. Volatiles were removed and the remaining brownish-red solid was dissolved in a minimal amount of diethyl ether and placed in the freezer overnight. 0.3 g (0.66 mmol, 24% yield) of brownish-red crystals were isolated from the first batch of crystallization. Mass spectral data (EI, m/z) (rel. intensity, %): 451 (M^+ , 25).

5.5 Structural Determination for Compounds **16** and **18**

Suitable crystals were mounted with viscous oil on a plastic mesh and cooled to the data collection temperature. Unit cell parameters were determined using data frames from four different sections of the Ewald sphere. SADABS multi-scan absorption corrections were applied. No symmetry higher than cubic was observed for compound **16** and monoclinic for compound **18**. Solution in the space group option, I-43d, yielded chemically reasonable and computationally stable results of refinement for **16** and the centrosymmetric space group option $P2_1/c$ for **18**. The structures were solved using direct methods and refined with full matrix least squares procedures of F^2 data. All hydrogen atoms were treated as idealized contributions and all non-hydrogen atoms were refined with anisotropic displacement coefficients. Atomic scattering factors are contained in the SHELXTL program library.

5.6 References

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Chapter 6:

Heteroleptic Amido Iminopyrrolidinato Titanium (IV) Complexes

6.1 Introduction

The reactivity of an organometallic compound is controlled to a large extent by the ancillary ligands bound to it. Amidinates and guanidines have proven to be versatile supporting ligands in organometallic and coordination chemistry.¹ They have found use in many fields of chemistry including catalysis² and film deposition³. Iminopyrrolidinato ligands have been synthesized and used as spectator ligands for titanium half sandwich complexes which are known to be pre-catalysts for the inter- and intramolecular hydroamination of alkynes.⁴

Interestingly iminopyrrolidinate ligands have not been studied in thin film deposition as of yet. There are similarities between amidinates and iminopyrrolidines that make them an interesting avenue to explore. Both ligands are bidentate (capable of protecting the metal centre), highly volatile when protonated (great for reducing impurities within deposited films), and are versatile (the steric and electronic properties can be easily tuned). The ip ligands introduced in Chapter 2 have demonstrated an advantage over amidinates; a predictable melting point trend can be reached by altering the R-group. The ligand melting point trend can be carried through once introduced to a metal centre. This valuable quality can be very useful in the synthesis of precursors for thin film

deposition. This chapter introduces the synthesis of three heteroleptic titanium (IV) compounds along with their preliminary thermolyses.

6.2 Results and Discussion

6.2.1 Synthesis and Crystal Structure Data

Three heteroleptic amido iminopyrrolidinate titanium (IV) complexes were synthesized and isolated in reasonable yields (Table 6-1) from $\text{Ti}(\text{NMe}_2)_4$ and appropriate iminopyrrolidine starting materials. It was found that the compounds formed rather quickly (within four hours) at room temperature or at -20°C ; with the starting titanium species changing from a characteristic yellow solution to an orange/red solution. For each compound the volatiles were removed under vacuum; the orange/red solid was redissolved in diethyl ether and placed in the freezer to promote crystallization. Red crystals were isolated for each compound. Compound **19** produced crystals of sufficient quality for a single crystal structure to be collected (Figure 6-1, Table 6-2 and Table 6-3).

Table 6-1. Yield and thermal parameters for compounds **19 - 21**.

	R	Percent Yield (%)	Melting Point ($^\circ\text{C}$)	Residual Mass (%)
19	ipip	87	130 - 132	16.5
20	sbip	43	112 - 114	14.1
21	tbip	81	Decomposed > 120	17.5

Amine elimination was the driving force for these reactions (Scheme 6-1). An interesting result occurred while attempting to produce mono and tris ipip titanium complexes. Appropriate stoichiometric amounts of ipip (i.e. 1 or 3 equivalents) were

added to the starting titanium species and let to react overnight. The resultant pink solid was dissolved in minimal amounts of pentane and was then filtered to remove any insoluble solids. The resultant red solution was placed in the freezer and crystals of compound **19** were isolated from both reactions, demonstrating a thermodynamic preference for a bis-iminopyrrolidinate titanium species. This interesting result has occurred in the synthesis of similar iminopyrrolidinate titanium (IV) complexes by Gade et al.⁵

Scheme 6-1. Synthesis of heteroleptic titanium complexes.

A similar result occurred during the synthesis of compound **21**, when an excess amount of tbip ligand was added to the reaction. The resulting ¹H NMR showed the presence of the desired **21** along with excess tbip. The sample was placed in a sublimation apparatus and the ligand was removed under low temperature sublimation, 45°C. Pure tbip was isolated on the cold finger of the sublimation apparatus and pure **21** was left unsublimed.

The reaction for compound **20** was done at lower temperatures to prevent possible formation of a racemic mixture and was deemed to be a success as the NMRs were clean and the melting point was sharp. The ¹H and ¹³C NMR of compounds **19** and **21** were

similar in their simplicity. The ^1H and ^{13}C NMR for compound **20** was a little more complicated as the stereocentre of the ship ligand was evident.

Compound **19** was a six coordinate titanium species in a distorted octahedral geometry. It had a P-1 space group with a C_2 symmetry which explains the simplicity of the ^1H NMRs. The ip ligands were found cis to each other as was seen in other similar structures from Gade et al.⁵ The bite angle for the ip ligands were 61.9° for N1-Ti-N2 and 62.1° for N3-Ti-N4. These angles were a slightly larger than previously reported iminopyrrolidinate titanium structures ranging from 61.1° and 61.8° .⁵ The amido angle (N5-Ti-N6) was thus slightly smaller at 96.2° than the reported structures with angles of 97.4° and 101.1° . The ipip-titanium metallocycle was close to planar at 0.7° for Ti-N1-C4-N2 and 3.4° for Ti-N3-C11-N4.

Figure 6-1. The single-crystal X-ray structure of compound **19**. The thermal ellipsoids are shown at 50% probability and the hydrogen centres are omitted for clarity.

The Ti-N bonds varied from 1.92 - 2.27Å, with both amido (Ti-N5 and Ti-N6) lengths being the shortest at 1.92Å. The nitrogens trans to the amido species (N2 and N4) were the longest distances at 2.27 and 2.22Å. The lengthening of these bonds may be caused by the participation of the lone pair from the amido nitrogens to the titanium forcing the Ti-N bond lengths trans to the amido species to elongate.

The C-N bonds within the chelate ring showed participation in the π -system as their bond lengths were much shorter, ranging from 1.30 - 1.34Å compared to the C-N distance on the exocyclic nitrogen N2-C5 and N4-C12 at 1.48 and 1.46Å. The C-N lengths of the amido species were within range of single C-N distances of 1.479 Å and were nearly indistinguishable at values ranging from 1.44 - 1.45Å. These distances demonstrated that N1, N2, N3 and N4 were all participating in the π -system with C4 and C11; the distances were within C-N resonance bond lengths given by Allen et al.⁶

Table 6-2. Selected crystal data for compound **19**.

Empirical Formula	C ₁₈ H ₃₈ N ₆ Ti
FW	386.44
Crystal System	Triclinic
Space Group	P-1
<i>a</i> (Å)	8.732(2)
<i>b</i> (Å)	16.114(4)
<i>c</i> (Å)	17.358(4)
α (deg)	63.344(3)
β (deg)	83.829(4)
γ (deg)	83.848(4)
<i>V</i> (Å ³)	2165.4(9)
<i>Z</i>	4
<i>D_c</i> (kg/L)	1.185
μ (mm ⁻¹)	0.408
<i>T</i> (K)	200(2)
<i>R</i> , <i>wR</i>	0.0668, 0.1336
Goodness-of-fit on <i>F</i> ²	1.021

The sum of angles around the nitrogens were very close to planar (N1, N2, and N3 = 360° and N4 = 358°). The sum of angles around C4 and C11 were 360° also demonstrating planarity and thus participation in the π -system. The sum of angles around the amido nitrogens N5 and N6 were also 360° demonstrating the participation of the lone pairs of the nitrogens to the titanium species.

Table 6-3. Selected bond lengths and angles for compound **19**.

<i>Selected Bond Lengths (Å)</i>			
Ti-N1	2.0735(17)	N2-C5	1.457(2)
Ti-N2	2.2682(17)	N3-C11	1.335(3)
Ti-N3	2.0766(17)	N4-C11	1.304(3)
Ti-N4	2.2243(17)	N4-C12	1.463(2)
Ti-N5	1.9194(17)	N5-C15	1.448(3)
Ti-N6	1.9204(17)	N5-C16	1.445(3)
N1-C4	1.344(2)	N6-C17	1.453(3)
N2-C4	1.301(2)	N6-C18	1.453(3)
<i>Selected Bond Angles (°)</i>			
N1-Ti-N2	61.91(6)	N3-C11-N4	114.86(17)
N3-Ti-N4	62.17(6)	Ti-N3-C11	94.24(12)
N5-Ti-N6	96.25(8)	Ti-N4-C11	88.59(12)
N1-C4-N2	115.72(17)	Ti-N4-C12	148.46(14)
Ti-N1-C4	94.87(11)	C11-N4-C12	121.42(17)
Ti-N2-C4	87.49(12)	C15-N5-C16	111.27(18)
Ti-N2-C5	151.78(13)	C17-N6-C18	110.68(18)
C4-N2-C5	120.70(17)		
<i>Sum of Angles (°)</i>			
N1	359.88	N4	358.47
N2	359.97	N5	359.79
N3	359.96	N6	359.87

6.2.2 Thermolysis

Preliminary thermolyses (TGs) were conducted on each compound. Unfortunately, each experiment showed complicated and incomplete thermolysis as seen in Figure 6-2.

Compound **19** had two thermal events. The first event occurred at a temperature range of 151 - 193°C. This event may have been the thermal decomposition of the starting material into a compound that was more volatile, as the second thermal event had a characteristic volatilization curve as seen by the derivative weight curve (Figure 6-3). The second thermal event occurred at a range of 193 - 350°C resulting in a residual mass of 16%. With a rather high residual mass and a complicated volatilization curve this compound would not be a good candidate for either CVD or ALD.

Figure 6-2. Thermal gravimetric analysis of 19 - 21.

Figure 6-3. Differential weight curve for compounds 19 - 21.

Compound **20** had an on-set of volatility of 122°C and two thermal events observed in the derivative weight curve (Figure 6-3). The first thermal event occurred at a temperature range of 122 - 162°C. This event was characteristic of decomposition as the derivative weight curve (Figure 6-3) was broad and very symmetrical. The second thermal event occurred at a range of 162 - 350°C and showed a characteristic volatilization curve of the thermalized material, as it had an asymmetric peak demonstrating a slow on-set and a quick drop-off as the thermalized species volatilized off the pan. The residual mass for compound **20** was a little lower at 14%, resulting from a thermalized species volatilizing away and leaving behind a decomposed product.

Compound **21** had an on-set of volatility of 92°C and a complicated TG with three thermal events. The first feature occurred at a temperature range of 92 - 187°C, the second feature occurred at 187 - 244°C and the third event occurred at 244 - 377°C. Each

of these events were observed as thermal decompositions as neither of the events had a derivative weight curve (Figure 6-3) characteristic of volatilization.

An NMR tube boil up was performed on compound **19** to discern the nature of the thermolysis. The complex was dissolved in 0.25 ($\pm$ 6) mL of C₆D₆ solution in a thick-walled NMR tube under inert atmosphere. The tube was immersed in liquid N₂ and the glass tube was sealed under vacuum. The tube was placed in a furnace at 58°C to observe the stability of the complex. At this temperature a new amido peak was observed at 3.33 ppm as well as a new isopropyl doublet at 1.042 ppm along with new ring environments. The new peaks present may be attributed to a loss of symmetry, indicating a change in the geometry of the complex from cis to trans. After 2 days the temperature was increased to 94°C which increased the intensity of the amido singlet and the isopropyl doublet. This result along with the complicated TG demonstrated that **19** would not be a suitable compound for thin film deposition.

In Chapter 2, the iminopyrrolidine ligands were found to import their melting point trend to the heteroleptic aluminum family (Table 2-5). It was thought that the introduction of these ligands to titanium species would help to control thermal properties such as melting points by varying the R-group. This trend was arguably visible within the heteroleptic titanium species synthesized in this chapter as the ipip complex had a melting point of 130 - 132°C, the sbip complex had a melting point of 112 - 114°C and the tbip complex decomposed at >120°C. The ligands as well as the aluminum complexes demonstrated a dip in the melting point trend for sbip as it had a stereocentre and the tbip ligand had the highest melting point as seen in Table 2-2 and Table 2-5 in Chapter 2.

6.3 Conclusions

Three heteroleptic amido iminopyrrolidinate titanium (IV) complexes were synthesized in relatively high yields ranging from 50 to 87%. Compound **19** was isolated as red needle like crystals with a triclinic crystal system and a P-1 space group. The melting point trend present in the iminopyrrolidine ligands was visible within the heteroleptic titanium complexes. Preliminary thermolyses (TGs) were conducted on all three compounds and resulted in complicated stepwise thermal decomposition. Unfortunately these heteroleptic compounds would find no use in thin film deposition techniques; however they may find use in other branches of chemistry such as catalysis.

6.4 Methods and Materials

All manipulations were performed in a nitrogen filled drybox unless otherwise stated. The chemicals: 2-pyrrolidinone, phosphorous pentoxide, isopropyl amine, sec-butyl amine, tert-butyl amine, lithium dimethyl amide and titanium tetrachloride were purchased from Aldrich Chemical Company and used as received. All solvents used were reagent grade purified from an MBraun Solvent Purifier System. All iminopyrrolidine ligands were synthesized following literature procedures.⁷ Mass spectra were obtained using the electron impact method on a VG ZAB-2HF triple-focusing spectrometer. Thermal gravimetric analysis was performed on a TA Instruments Q50 apparatus located within a Labmaster 130 Dry box. Differential Scanning Calorimetry was performed on a DSC Instruments Q10 apparatus. Nuclear Magnetic Resonance was done on 300MHz Avance III or 400MHz AMX Bruker. Single crystal XRD was

conducted on a Bruker-AXS APEX CCD Diffractometer located at Delaware University with the help of Glenn P. Yap.

6.4.1 Bis(dimethyl amido) titanium bis(isopropyl iminopyrrolidinate), **19**

Both isopropyl iminopyrrolidine (0.93 g, 7.4 mmol) and $\text{Ti}(\text{NMe}_2)_4$ (0.83 g, 3.7 mmol) were dissolved in 20 mL diethyl ether. The dissolved ligand was added dropwise to the yellow Ti solution, as the reaction proceeded the solution changed to a dark red colour. The reaction was allowed to stir overnight at room temperature. Volatiles were removed under reduced pressure to afford a red solid (1.24 g, 3.21 mmol, 87%). The red solid was dissolved in minimal diethyl ether and placed in the freezer to afford needle like red crystals (1.10 g, 2.85 mmol, 77%). mp 130 - 132°C. ^1H NMR (300 MHz, C_6D_6): δ 3.79 (t, 4H, $\text{N}(\text{CH}_2)(\text{CH}_2)(\text{CH}_2)\text{C}$), 3.51 (s, 12H, $\text{Ti}(\text{N}(\text{CH}_3)_2)_2$), 3.34 (m, 2H, $\text{NCH}(\text{CH}_3)_2$), 1.99 (t, 4H, $\text{N}(\text{CH}_2)(\text{CH}_2)(\text{CH}_2)\text{C}$), 1.63 (m, 4H, $\text{N}(\text{CH}_2)(\text{CH}_2)(\text{CH}_2)\text{C}$), 1.16 (d, 12H, $\text{NCH}(\text{CH}_3)_2$). ^{13}C NMR (300 MHz, C_6D_6): δ 176.7 (NCN), 52.3 ($\text{N}(\text{CH}_2)(\text{CH}_2)(\text{CH}_2)\text{C}$), 50.8 ($\text{NCH}(\text{CH}_3)_2$), 47.5 ($\text{Ti}(\text{N}(\text{CH}_3)_2)_2$), 26.6 ($\text{N}(\text{CH}_2)(\text{CH}_2)(\text{CH}_2)\text{C}$), 25.3 ($\text{NCH}(\text{CH}_3)_2$), 23.9 ($\text{N}(\text{CH}_2)(\text{CH}_2)(\text{CH}_2)\text{C}$). Mass spectral data (EI, m/z) (rel. intensity, %): 386.40 ($(\text{M} - \text{NMe}_2)^+$, 66).

6.4.2 Bis(dimethyl amido) titanium bis(sec-butyl iminopyrrolidinate), **20**

Suspended 0.56 g (2.52 mmol) of $\text{Ti}(\text{NMe}_2)_4$ in 60 mL ether in a 250 mL Schlenk flask. Cooled the reaction flask to -78°C using an acetone/ $\text{CO}_{2(s)}$ bath. Sec-butyl iminopyrrolidine (0.71 g, 5.04 mmol) was dissolved in 20 mL ether. The dissolved

ligand was slowly added to the cooled titanium mixture by use of two 10 mL syringes. The reaction was stirred at low temperatures for 2 hours and then allowed to slowly reach room temperature for an additional 2 hours. After 4 hours of reaction time, volatiles were removed under reduced pressure to afford a red solid (0.453 g, 1.09 mmol, 43%). mp 112 – 114. ^1H NMR (400 MHz, C_6D_6): δ 3.87 (t, 4H, $\text{N}(\text{CH}_2)(\text{CH}_2)(\text{CH}_2)\text{C}$), 3.61 (s, 12H, $\text{Ti}(\text{N}(\text{CH}_3)_2)_2$), 3.14 (m, 2H, $\text{NCH}(\text{CH}_3)(\text{CH}_2\text{CH}_3)$), 2.14 (t, 4H, $\text{N}(\text{CH}_2)(\text{CH}_2)(\text{CH}_2)\text{C}$), 1.76 (m, 4H, $\text{N}(\text{CH}_2)(\text{CH}_2)(\text{CH}_2)\text{C}$), 1.68 (m, 4H, $\text{NCH}(\text{CH}_3)(\text{CH}_2\text{CH}_3)$), 1.26 (dd, 6H, $\text{NCH}(\text{CH}_3)(\text{CH}_2\text{CH}_3)$), 1.02 (dt, 6H, $\text{NCH}(\text{CH}_3)(\text{CH}_2\text{CH}_3)$). ^{13}C NMR (300 MHz, C_6D_6): δ 177.3 (NCN), 57.6 ($\text{NCH}(\text{CH}_3)(\text{CH}_2\text{CH}_3)$), 52.5 ($\text{N}(\text{CH}_2)(\text{CH}_2)(\text{CH}_2)\text{C}$), 46.5 ($\text{Ti}(\text{N}(\text{CH}_3)_2)_2$), 32.8 ($\text{NCH}(\text{CH}_3)(\text{CH}_2\text{CH}_3)$), 27.1 ($\text{N}(\text{CH}_2)(\text{CH}_2)(\text{CH}_2)\text{C}$), 23.8 ($\text{N}(\text{CH}_2)(\text{CH}_2)(\text{CH}_2)\text{C}$), 22.7 ($\text{NCH}(\text{CH}_3)(\text{CH}_2\text{CH}_3)$), 11.8 ($\text{NCH}(\text{CH}_3)(\text{CH}_2\text{CH}_3)$). Mass spectral data (EI, m/z) (rel. intensity, %): 370.3 ($(\text{M} - \text{NMe}_2)^+$, 100).

6.4.3 Bis(dimethyl amido) titanium bis(tert-butyl iminopyrrolidinate), 21

Same reaction procedure as **19** was used substituting the previous iminopyrrolidine with t-butyl iminopyrrolidine (0.50 g, 3.56 mmol). Volatiles were removed under reduced pressure to afford a red solid (0.60g, 1.45 mmol, 81%). Decomposed $> 120^\circ\text{C}$. ^1H NMR (300 MHz, C_6D_6): δ 3.753 (t, 4H, $\text{N}(\text{CH}_2)(\text{CH}_2)(\text{CH}_2)\text{C}$), 3.45 (s, 12H, $\text{Ti}(\text{NC}(\text{CH}_3)_2)_2$), 2.06 (t, 4H, $\text{N}(\text{CH}_2)(\text{CH}_2)(\text{CH}_2)\text{C}$), 1.62 (m, 4H, $\text{N}(\text{CH}_2)(\text{CH}_2)(\text{CH}_2)\text{C}$), 1.27 (s, 18H, $\text{N}(\text{CH}_3)_3$). ^{13}C NMR (300 MHz, C_6D_6): δ 175.4 (NCN), 152.1 ($\text{NC}(\text{CH}_3)_3$), 50.9 ($\text{N}(\text{CH}_2)(\text{CH}_2)(\text{CH}_2)\text{C}$), 47.2 ($\text{Ti}(\text{N}(\text{CH}_3)_2)_2$), 31.5 ($\text{NC}(\text{CH}_3)_3$), 30.4

(N(CH₂)(CH₂)(CH₂)C), 23.5 (N(CH₂)(CH₂)(CH₂)C. Mass spectral data (EI, *m/z*) (rel. intensity, %): 414.45 ((M- NMe₂)⁺, 100).

6.5 Structural Determination for Compound 19

A suitable crystal was mounted with viscous oil on a plastic mesh and cooled to the data collection temperature. Unit cell parameters were determined using data frames from four different sections of the Ewald sphere. SADABS multi-scan absorption corrections were applied. No symmetry higher than triclinic was observed. Solution in the centrosymmetric space group option, P-1, yielded chemically reasonable and computationally stable results of refinement. The structures were solved using direct methods and refined with full matrix least squares procedures of F² data. All hydrogen atoms were treated as idealized contributions and all non-hydrogen atoms were refined with anisotropic displacement coefficients. Atomic scattering factors are contained in the SHELXTL program library.

6.6 References

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Chapter 7: Heteroleptic Zirconium Complexes

7.1 Introduction

Group 4 guanidinate and amidinate compounds have been used in studies of polymerization reactions such as homogeneous Ziegler – Natta catalysis¹ as well as in advanced techniques for growth of high quality thin films; CVD and ALD.² Zirconium oxide thin films are of interest in thin film applications because they have excellent thermal, chemical and mechanical stability, as well as interesting optical and dielectric properties. This interesting group 4 metal oxide has an effective dielectric constant $k = 22$ ³, is thermodynamically stable on silicon,⁴ and has a band gap that ranges from 5 - 7 eV.⁵ Due to the downscaling of microelectronics silicon dioxide thin films are unable to cope as their dielectric constant is so low; 3.9.⁶ Zirconium oxide thin films are attracting attention as possible high-k gate oxide dielectrics in complementary metal-oxide semiconductor (CMOS) devices.²

Zirconium oxide thin films have been deposited using a variety of precursors such as inorganic salts of $ZrCl_4$ and $Zr(NO_3)_4$, as well as organometallic zirconium alkoxides ($Zr(OR)_4$) where $R = ^iPr$ or tBu .^{2a} These precursors have some disadvantages associated with them, such as chlorine contamination for $ZrCl_4$ and the zirconium alkoxides have tendencies to oligomerize. Zirconium amides have also been studied for thin film deposition however they have proven to be very reactive towards air and moisture and thus are difficult to handle.² Bidentate ligands such as amidinates and guanidinate have

proven to be more stable as they coordinatively saturate the metal complex. Guanidines also offer another mode of stabilization by allowing zwitterionic resonance to occur.

It is important for applications such as CVD and ALD that the precursors are thermally stable and easy to handle allowing for much research in the development of organometallic precursors. Amidines and guanidines are of interest for these processes mainly due to their versatility but also because they can minimize impurities that are found in thin films produced by other precursors, such as those containing halogens. A drawback of monoanionic guanidines (and amidines), however, is their ability to deinsert carbodiimide upon heating (Scheme 2-1).⁷ Indeed, many guanidine syntheses rely on carbodiimide insertion as a synthetic mechanism,⁸ however it has recently been shown to be reversible for group 13 metals.⁷

There are fewer examples of complexes containing dianionic guanidines than the previously mentioned monoanionic guanidines.⁹ Dianionic guanidines of the type $[\text{RN}=\text{C}(\text{NR}')_2]^-$ (where R and R' = alkyl) are chelating ligands that have the ability to fulfill the same favourable characteristics of monoanionic guanidines, however, deinsertion is far less favourable due to the necessary formation of a metal imide when carbodiimide is expelled (Scheme 7-1).

Scheme 7-1. Deinsertion less likely to occur for dianionic ligands.

This chapter will focus on the synthesis, characterization, and thermolysis of novel heteroleptic zirconium species using a mixture of guanidinate and amidinate ligands. Synthesizing heteroleptic zirconium species with solely bidentate ligands may help improve the stability of the species, as amides are known to be highly reactive towards air and moisture.¹⁰ Formation of a monomer would be ideal for ALD and CVD purposes as the molecular weight would be less; potentially allowing for a more volatile species. Dianionic guanidinates have been found to produce dimers when reacted to hafnium and zirconium species.¹¹ For this reason, the monoanionic ligands were reacted with the metal centre before reaction with the dianionic ligand. This was done in attempts to break the dimer; the process was found to be successful.

7.2 Results and Discussion

7.2.1 Synthesis and Characterization

Three heteroleptic zirconium compounds were synthesized in low yields (Table 7-1) from sequential salt metathesis reactions starting with ZrCl_4 , appropriate amidinate or guanidinate ligands and lithiated dianionic guanidinate species. It was found that the compounds formed slowly at room temperature with the reaction changing from colourless to yellow. In every case, the volatiles were removed under vacuum; the yellow solid was redissolved in diethyl ether and placed in the freezer to promote crystallization. Colourless crystals were isolated and further characterization was undertaken. Compound **22** produced crystals of sufficient quality for a single crystal structure to be collected (Figure 7-2, Table 7-2 and Table 7-3).

R = H^iPrN , NMe_2 , Me

Figure 7-1. Heteroleptic zirconium species.

Table 7-1. Percent yield and thermal data of compounds **22** - **24**.

	R	Percent Yield (%)	Melting Point (°C)
22	H^iPrN	35	96
23	NMe_2	25	126
24	Me	52	113

The ^1H NMR for these compounds were difficult to interpret. Due to the fluxional behaviour of monoanionic guanidinate and amidinate ligands and their ability to move about the metal centre within the time frame of the experiment, the NMRs were very complicated. A variety of isopropyl environments were observed along with the corresponding multiplets. A variable temperature (VT) NMR was undertaken for compound **24** to slow down the fluxionalization. Coalescence did not occur in the ^1H NMR as the solvent used (C_6D_6) could not reach the necessary low temperatures. It would have been advantageous to repeat this experiment with deuterated toluene (C_7D_8) to observe the change in NMR through a larger temperature range.

Compound **22** crystallized in a *Ccca* space group showing C_2 symmetry by ^1H NMR. The zirconium atom was found in a distorted octahedral position due to the strain introduced by the bite angles of the chelate rings at 61.5° for the dianionic ligand (N4-Zr-N5) and 60.7° for the monoanionic ligands (N1-Zr-N2 and N7-Zr-N8). The bite angles for the monoanionic ligands were slightly larger than in a similar compound reported by Richeson et. al. at 59.3° and 59.4° , respectively.¹² This can be attributed to a lower steric demand of the dianionic ligand compared to the two benzyl groups in the above reference. The bite angle of the dianionic ligand was only slightly larger than that of the monoanionic ligands. The N-C-N angles were similar, ranging from 108.0° - 111.3° ; the shortest angle being for the dianionic ligand (N4-C14-N6) at 108.0° as a compensation for the slightly larger bite angle. These were smaller than previously reported complexes.¹²

The sum of angles around the central carbon of the CN_3 core for each guanidinate (C4, C14, and C24) totalled 360.0° indicating delocalization of the π -system within the guanidinate. The sum of angles of the chelating nitrogens ranged from nearly planar at 360.0° for N7 to far from planar at 352.0° for N1. The guanidinate ring for each ligand had a torsion angle that ranged from 6.2° for the dianionic ligand (Zr-N4-C14-N5) to 7.0° for Zr-N1-C4-N2, showing partial participation of all three ligands in the π -system.

The nitrogen-zirconium bond lengths ranged from 2.17 to $2.23\text{\AA}$ with Zr-N4 being the shortest and Zr-N2 being the longest; which fell within range of previously reported zirconium guanidinate structures.¹² Interestingly, the dianionic guanidinate had the shortest Zr-N bond lengths at 2.17 and $2.19\text{\AA}$ (Zr-N4 and Zr-N5). The shorter Zr-N bond

Although the monoanionic and dianionic ligands were only differentiated in connectivity by the presence of a proton, they can easily be distinguished by the comparison of the C-N bond lengths within the CN₃ core of the coordinated ligand (Table 7-3).

Figure 7-2. The single crystal X-ray structure of compound **22**. The thermal ellipsoids are shown at 50% probability and the hydrogen centres are omitted for clarity.

Table 7-2. Selected crystal data for compound **22**.

Empirical Formula	C ₃₀ H ₆₅ N ₉ Zr
FW	643.13
Crystal System	Orthorhombic
Space Group	Ccca
a (Å)	26.876(3)
b (Å)	35.647(5)
c (Å)	15.144(2)
α (deg)	90
β (deg)	90
γ (deg)	90
V (Å ³)	145088(3)
Z	16
D _c (kg/L)	1.178
μ (mm ⁻¹)	0.334
T (K)	120(2)
R, wR	0.0473, 0.1135
Goodness-of-fit on F ²	1.063

Table 7-3. Selected bond lengths and angles for compound **22**.

<i>Selected Bond Lengths (Å)</i>			
Zr-N1	2.2134(15)	N3-C4	1.346(2)
Zr-N2	2.2260(13)	N4-C14	1.383(2)
Zr-N4	2.1711(14)	N5-C14	1.370(2)
Zr-N5	2.1871(15)	N6-C14	1.326(2)
Zr-N7	2.1925(15)	N7-C24	1.358(2)
Zr-N8	2.2246(15)	N8-C24	1.361(2)
N1-C4	1.358(2)	N9-C24	1.353(2)
N2-C4	1.358(2)		
<i>Selected Bond Angles (°)</i>			
N1-Zr-N2	60.71(5)	Zr-N8-C24	93.55(11)
N7-Zr-N8	60.65(6)	Zr-N4-C14	95.21(10)
N4-Zr-N5	61.47(5)	Zr-N5-C14	94.88(10)
Zr-N1-C4	93.96(10)	N1-C4-N2	111.38(15)
Zr-N2-C4	93.40(10)	N7-C24-N8	110.20(15)
Zr-N7-C24	95.06(11)	N4-C14-N5	107.99(14)
<i>Sum of Angles (°)</i>			
N1	351.6	C14	360
N2	355.76	N7	359.55
C4	360	N8	357.87
N4	352.7	C24	360
N5	357.28		

The exocyclic amide moieties on all three ligands were participating in the π -system to a certain extent as the C-N bond lengths are shorter than typical C-N single bond lengths of 1.479 Å and longer than C=N double bond lengths at 1.29 - 1.30 Å.¹³ The exocyclic nitrogen bond length of the dianionic guanidinate (N6-C14) was slightly smaller at 1.32 Å than for the two monoanionic guanidinate exocyclic C-N lengths (N3-C4 and N9-C24) at 1.35 Å, respectively. The C-N bond lengths within the chelate rings showed the opposite trend. The C-N bonds were longer in the dianionic ligand at 1.38 Å for N4-C14 and N5-C14, respectively, due to the deficiency of the π -system within the metallocycle. The monoanionic guanidinate C-N bonds were shorter at 1.36 Å for N1-C4, N2-C4, N7-C24 and N8-C24. The lengths of the C-N bonds within the CN₃ core of the monoanionic ligands were nearly indistinguishable indicating considerable delocalization of the nitrogen lone pair into the ligand π -system. From these results it can be concluded that the majority of the π -system for the dianionic ligand was localized at the exocyclic nitrogen while the monoanionic ligands displayed even distribution of the π -system throughout the CN₃ core.¹⁴

7.2.2 Thermolysis

No bench top melting point was collected for compound **23** as the sticky nature made it difficult to collect the sample at the bottom of the capillary tube. However, a DSC was collected at a ramp rate of 10°C/min and three endothermic peaks were observed (Figure 7-5). The first endotherm was at 126°C (associated with melting). The second endotherm observed at 264°C was thought to be associated with volatilization of a thermalized zirconium species and the third endotherm at 352°C was thought to be

decomposition given the complicated TG. TG analysis showed compound **23** to decompose with a large residual mass of 28% (Figure 7-3). There were 3 thermal events present in the TG demonstrated by the derivative weight curve (Figure 7-4). The first event corresponded to 1% weight loss which was most likely due to loss of incidental solvent. The second thermal event was the major feature which occurred at a temperature range of 130 - 279°C. This feature had the characteristic shape of volatilization; a slower on-set and a rapid drop-off. The volatilization of a thermalized zirconium species was apparent in this temperature range and a third thermal event occurred from 279 - 376°C indicative of decomposition. The residual mass was considered to be relatively high for a vapour deposition precursor.

Figure 7-3. Thermal gravimetric analysis of 22 - 24.

Figure 7-4. Differential weight curve for compounds **22** - **24**.

Compound **22** had a melting point of 95 - 96°C conducted on a bench top melting point apparatus. There were two major thermal events present as seen by the derivative weight curve (Figure 7-4). The first thermal event occurred at a temperature range of 126 - 285°C which was the major feature. It had the characteristic shape of volatilization, an asymmetric curve with a slow on-set and a quick drop-off. The second thermal event was observed at a temperature range of 285 - 392°C which was considered to be decomposition. The complicated TG curve and residual mass of 18.6% demonstrated that this compound decomposed leaving behind several non-volatile contaminants which is an undesirable characteristic for vapour deposition precursors.

Figure 7-5. Differential scanning calorimetry of **23**.

Compound **24** had a melting point of 110 - 113°C collected on a bench top melting point apparatus. The TG showed one major thermal event that ranged from 122 - 301°C with a residual mass of 7.6%. Thermal degradation was observed at the beginning of this experiment as shown by the initial gradual slope.

All three heteroleptic zirconium species had complicated TG curves resulting in high residual masses, with the exception of the residual mass of **24**. These results are undesirable when designing precursors for thin film deposition procedures; thus these complexes would not be considered as candidates for such procedures.

An NMR tube boil up was performed on compound **23**. The complex was dissolved in 0.25 ($\pm$ 6) mL of C₆D₆ solution in a thick-walled NMR tube under inert atmosphere. The tube was immersed in liquid N₂ and the glass tube was sealed under vacuum. The tube was placed in a furnace at 100°C to observe possible CDI growth. On the third day

compound **23** demonstrated the presence of CDI by ^1H NMR. The characteristic multiplet and doublet at 3.33 and 1.04 ppm was observed and the intensity increased for the duration of the experiment. The presence of CDI was not a surprise as it has been known to deinsert from amidinate or guanidinate ligands at elevated temperatures.⁷

7.3 Conclusions

This work presented the synthesis and thermolysis of three new heteroleptic zirconium complexes in reasonable to low yields. The ^1H NMRs collected were complicated in that many isopropyl environments were present and seemed to be fluxuating during the time frame of the experiment as the peaks were somewhat broad. One crystal structure was obtained for compound **23** displaying a Ccca space group. The crystal structure was novel as both monoanionic and dianionic guanidates were present and were distinguishable through C-N bond lengths found within the CN_3 core of the ligand. Preliminary thermolysis experiments such as TG were performed on all three compounds and they displayed complicated volatilization. The compounds synthesized in this chapter would not be good candidates for chemical vapour deposition techniques such as CVD or ALD as they were found to be thermally unstable. However, the isolation of a heteroleptic zirconium single crystal consisting of both monoanionic and dianionic guanidinate ligands was an interesting find.

7.4 Methods and Materials

All manipulations were performed in a nitrogen-filled drybox. The chemicals: isopropyl amine, zirconium tetrachloride, methyl lithium, lithium dimethyl amide and 1,3-diisopropyl carbodiimide were purchased from Aldrich Chemical Company and used as received. All solvents used were reagent grade purified from an MBraun Solvent Purifier System. The monoanionic ligand synthesis of $[\text{H}^i\text{PrNC}(\text{N}^i\text{Pr})_2]\text{Li}$, $[\text{Me}_2\text{NC}(\text{N}^i\text{Pr})_2]\text{Li}$ and $[\text{MeC}(\text{N}^i\text{Pr})_2]\text{Li}$ followed literature procedures.¹⁵ Dianionic ligand synthesis of $[\text{H}^i\text{PrN}=\text{C}(\text{N}^i\text{Pr})_2]\text{Li}_2$ followed literature procedures.¹⁶ ^1H and ^{13}C NMR spectra were collected on a Bruker 300 MHz or a Bruker 400 MHz spectrometer using the residual protons in the deuterated solvent for reference. Mass spectra were obtained using the electron impact method on a VG ZAB-2HF triple-focusing spectrometer. Thermal gravimetric analyses were performed on a TA Instruments Q50 apparatus located within a Labmaster 130 Dry box. Differential Scanning Calorimetry was performed on a DSC Instruments Q10 apparatus. Single crystal XRD was conducted on a Bruker-AXS APEX CCD Diffractometer located at Delaware University with the help of Glenn P. Yap.

7.4.1 Bis(triisopropyl monoguanidinate) zirconium mono(dianionic triisopropyl guanidinate), 22

In a 60 mL round bottom flask 3.57 g of $[\text{H}^i\text{PrNC}(\text{N}^i\text{Pr})_2]_2\text{ZrCl}_2$ (6.7 mmol) was mixed with 40 mL of ether and allowed to stir for 10 min. 1.33 g of $[\text{H}^i\text{PrNC}(\text{N}^i\text{Pr})_2]\text{Li}_2$ (6.7 mmol) was slowly added to the solution while stirring over 10 min, the solution

turned a beige colour. The reaction was allowed to stir over night at room temperature. The flask was then evacuated to dryness revealing a light brown powder and then redissolved in ether to separate the LiCl formed and the desired product. The mixture was then filtered and the brown mother liquor was evacuated to brown viscous oil and redissolved in ether and placed in the freezer at -30°C . The crystallized yield was found to be 35%. ^1H NMR (300 MHz, C_6D_6): δ 4.26 (sept, 2H, $(\text{CH}_3)_2\text{HCN}=\text{C}[\text{NCH}(\text{CH}_3)_2]_2$), 3.88 (sept, 1H, $(\text{CH}_3)_2\text{HCN}=\text{C}[\text{NCH}(\text{CH}_3)_2]_2$), 3.34 (sept, 2H, $(\text{CH}_3)_2\text{HCNC}-[\text{NCH}(\text{CH}_3)_2]_2$), 3.06 (m, 4H, $(\text{CH}_3)_2\text{HCNC}-[\text{NCH}(\text{CH}_3)_2]_2$), 1.30 (d, 12H, $(\text{CH}_3)_2\text{HCN}=\text{C}[\text{NCH}(\text{CH}_3)_2]_2$), 1.10 (d, 12H, $(\text{CH}_3)_2\text{HCNC}-[\text{NCH}(\text{CH}_3)_2]_2$), 1.02 (d, 6H, $(\text{CH}_3)_2\text{HCN}=\text{C}[\text{NCH}(\text{CH}_3)_2]_2$), 0.83 (d, 24H, $(\text{CH}_3)_2\text{HCNC}-[\text{NCH}(\text{CH}_3)_2]_2$).

7.4.2 Bis(dimethylamide diisopropyl guanidinate) zirconium mono(dianionic guanidinate), 23

In a 100 mL round bottom flask 7.00 g of $[(\text{Me})_2\text{NC}(\text{N}^i\text{Pr})_2]_2\text{ZrCl}_2$ (13.9 mmol) was mixed with 60 mL of ether and allowed to stir for 10 min. 2.75 g of $[^i\text{PrNC}(\text{N}^i\text{Pr})_2]\text{Li}_2$ (13.9 mmol) was slowly added to the solution while stirring over 10 min, the solution turned a pale orange colour. The reaction was allowed to stir over night at room temperature. The flask was then evacuated to dryness revealing a pale orange powder and then redissolved in tetrahydrofuran (THF) to separate the LiCl from the desired product. The mixture was then filtered and the orange mother liquor was evacuated to dryness. The crude yield was found to be 58 % from 4.95 g collected after filtering. From crystallization 2.12 g was collected a 25 % yield. ^1H NMR (300 MHz, C_6D_6): δ 4.58 (sept, 2H, $(\text{CH}_3)_2\text{HCN}=\text{C}[\text{NCH}(\text{CH}_3)_2]_2$), 4.39 (m, 1H, $(\text{CH}_3)_2\text{HCN}=\text{C}-$

[NCH(CH₃)₂]₂), 3.45 (m, 4H, (CH₃)₂NC[NCH(CH₃)₂]₂), 2.37 (s, 12H, (CH₃)₂NC[NCH(CH₃)₂]₂), 1.58 (d, 12H, (CH₃)₂HCN=C[NCH(CH₃)₂]₂), 1.55 (d, 6H, NCH(CH₃)₂), 1.41 (d, 6H, NCH(CH₃)₂), 1.32 (d, 6H, NCH(CH₃)₂), 1.29 (d, 6H, NCH(CH₃)₂), 1.03 (d, 6H, NCH(CH₃)₂). Mass spectrum (EI, m/z) (rel. intensity, %): 615, (6.0, M⁺).

7.4.3 Bis(acetamidinate) zirconium mono(dianionic guanidinate), 24

In a 100 mL round bottom flask 1.38 g of [MeC(N^{*i*}Pr)₂]₂ZrCl₂ (3.1 mmol) was mixed with 40 mL of diethyl ether and allowed to stir for 10 min. 0.67 g of [^{*i*}PrNC(N^{*i*}Pr)₂]₂Li₂ (3.1 mmol) was used *in situ* and was slowly added to the suspended solution while stirring at room temperature. The colour changed from a white solution to an iridescent yellow solution, the reaction was allowed to stir over night. The flask was then evacuated to dryness revealing a vibrant yellow powder and then redissolved in about 20 mL of tetrahydrofuran (THF) to separate the LiCl from the desired product. The mixture was then filtered and the yellow mother liqueur was evacuated to dryness to reveal 1.38 g of a yellow amorphous powder. The crude yield was found to be 72%. The yellow powder was dissolved in about 10 mL of diethyl ether and placed in the freezer overnight. The resultant colourless powder was filtered and weighed at 1.0 g, a percent yield of 52%. ¹H NMR (300 MHz, C₆D₆): δ 4.47 (m, 1H, NCH(CH₃)₂), 4.44 (m, 1H, NCH(CH₃)₂), 4.30 (m, 1H, NCH(CH₃)₂), 3.57 (m, 2H, NCH(CH₃)₂), 3.24 (m, 2H, NCH(CH₃)₂), 1.57 (d, 6H, NCH(CH₃)₂), 1.52 (s, 6H, CCH₃), 1.46 (d, 6H, NCH(CH₃)₂), 1.33 (m, 18H, NCH(CH₃)₂), 1.32 (d, 6H, NCH(CH₃)₂), 1.20 (d, 6H, NCH(CH₃)₂), 1.15 (d, 6H, NCH(CH₃)₂).

7.5 Structural Determination for Compound 22

A suitable crystal was mounted with viscous oil on a plastic mesh and cooled to the data collection temperature. Unit cell parameters were determined using data frames from four different sections of the Ewald sphere. SADABS multi-scan absorption corrections were applied. No symmetry higher than orthorhombic was observed. Solution in the centrosymmetric space group option, Ccca, yielded chemically reasonable and computationally stable results of refinement. The structure was solved using direct methods and refined with full matrix least squares procedures of F2 data. All hydrogen atoms were treated as idealized contributions and all non-hydrogen atoms were refined with anisotropic displacement coefficients. Atomic scattering factors are contained in the SHELXTL program library.

7.6 References

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Chapter 8: Future Work

This thesis presented the synthesis, characterization, and thermolysis of twenty one heteroleptic organometallic compounds, two homoleptic titanium (III) complexes, and one new ligand. A large portion of the work focused on the synthesis of novel ancillary ligands for potential use in ALD and CVD processes (Chapter 2). The “ip” ligands were engineered to prevent CDI deinsertion (Scheme 2-1 and Figure 2-1) and the melting point could be tuned by simply altering the R-group of the exocyclic nitrogen (Table 2-2). It was found that the longer and the less branched the alkyl group, the lower the melting point.

Three heteroleptic aluminum species were synthesized (Chapter 2), out of which, only one was not fully purified. Repeating this reaction in a more controlled manner (perhaps at lower temperatures) may allow the isolation of pure diethyl aluminum “npip”. Alkyl elimination was the sole synthetic method that was attempted throughout this work. One may attempt the salt metathesis synthetic route to see if this would produce purer results. Once isolated in good yields, further studies, such as sealed NMR tube boil-ups as well as TG and DSC analysis should be conducted and the results compared to the analogous diethyl aluminum amidinate species (Figure 2-7). If suitable, ALD should be attempted with this species as well.

DFT calculations should be conducted to help discover the isomerization of these dimers in solution (Scheme 2-5). This would help to discern the decomposition pathway of the organometallic species and the thermolysis of the “ip” ligands could then be compared more thoroughly to the thermolysis of amidinates and guanidates. This will

help to design and engineer optimal precursors for both ALD and CVD processes. Since the melting points of these ligands can be tuned by simply changing the R-group of the exocyclic nitrogen, and the melting point trend can be carried through when reacted to a metal centre (Table 2-5), these ligands should be used with many different metals and analyzed for ALD purposes. This presents the opportunity for a great deal of future work in synthetic inorganic chemistry, resulting in many novel compounds.

Five heteroleptic titanium (III) guanidinate species were synthesized in this work (Figure 3-1 and Table 3-1). Only one species was studied for the surface reactivity with high surface area silica. It would be very interesting to see if changing the R groups of the exocyclic position of the guanidinate ligand would change the absorption of the titanium species onto the oxide substrate. Perhaps compound **5** (which has a proton on the exocyclic nitrogen) would have a different bonding arrangement than compounds **6**, **7**, or **8**, as they each have a bulkier exocyclic nitrogen (Figure 3-1). Hydrogen bonding might be suppressed by the bulkier species; thus the guanidinate ligand may not be stabilized upon exposure to high surface area silica – no matter the surface hydroxyl concentration (Figure 3-8 and Figure 3-11). Further exposure experiments can be conducted to fully understand the chemisorption of this family of heteroleptic titanium species.

An extremely stable monomer was produced during the exposure experiments of compound **5** (Chapter 3), as indicated by the lengthy oxidation that took place when exposed to air. ALD was attempted with NH_3 , however, no film was produced. It would be beneficial to either attempt ALD with a stronger reductant or use plasma or radical enhanced ALD to make the desired TiN films.

Four heteroleptic titanium (III) amidinate complexes were synthesized throughout this work (Figure 4-1). Their thermolysis was also studied with promising results (Table 4-3). Conducting exposure experiments is the next step for this family of heteroleptic titanium species. It would be interesting to see if the adsorption of these species would be similar to their guanidinate analogues. Without the exocyclic nitrogen for H-bonding stabilization with surface hydroxyl species, would the amidinate ligands be able to withstand the elevated temperatures of the exposure experiment?

ALD was attempted with H_2O as the reducing precursor and the acetamidinate titanium species as the metallic precursor; however, no film was produced (Figure 4-6). TiO_2 film deposition could be repeated with a stronger reductant such as ozone or hydrogen peroxide. A TiN film deposition could also be attempted with compound **11** and NH_3 , as the reactivity of this compound might be higher than the guanidinate analogue.

Three heteroleptic titanium (IV) species were synthesized within this work (Scheme 6-1 and Table 6-1). Their synthesis was successful; however, their thermolysis was not. The poor stability of these compounds may be due to the monodentate amido ligands. Perhaps the stability of these compounds could be increased if a bulkier ligand, such as cyclopentadienyl, was used in place of the small monodentate amido ligand. The synthesis of a bisguanidinate or bisamidinate with two “ip” ligands, $[(\text{guan})_2\text{Ti}(\text{ip})_2]$ or $[(\text{amid})_2\text{Ti}(\text{ip})_2]$, would also be interesting to study. The bidentate nature of the amidinate and guanidinate ligand could help increase the thermal stability.

Another interesting branch of chemistry that could be explored concerning this family of titanium (III) and titanium (IV) heteroleptic species is catalysis. Previously,

$[\text{Cp}_2\text{TiCl}]_2$ has been employed as a catalyst for the intermolecular addition of epoxides to activated olefins.¹ The titanium (III) species was used as a transition-metal-centred radical that instigates homolysis of an epoxide C-O bond.² A second equivalent of Ti(III) scavenged the resulting radical from solution preventing further additions from occurring.¹

Many metallocene transition-metal complexes have been used in polymerization of 1-alkenes.³ Metallocene titanium species were found to undergo reduction when used as soluble Ziegler – Natta catalysts.⁴ Catalysts based on metal complexes with multidentate ligands, such as guanidines and amidines, have also been studied.⁵ The fluxional behaviour of these bidentate ligands allows a vacant site at the metal centre to be exposed where insertion of a C=C can occur.⁶ It would be interesting to see if this combination of ligands (cyclopentadienyl with guanidine or amidine) and the +3 oxidation state can be used as a catalyst for olefin polymerization.

Iminopyrrolidinate ligands have been used as spectator ligands for titanium complexes as pre-catalysts for inter- and intramolecular hydroamination of alkynes.⁷ The “ip” ligands that were synthesized and studied in this work, which are less bulky than previous “ip” ligands, have not been used in such catalysis and so this may be an area to explore in future work of such compounds.

8.1 References

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Appendix A: Crystallographic Data for Compounds 2, 5, 6, 8, 9, 10, 11, 15, 16, 18, 19, 22.

A.1 Compound 2

data_seab051

```

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;
?
;
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_atom_type_description
_atom_type_scatter_dispersion_real
_atom_type_scatter_dispersion_imag
_atom_type_scatter_source
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'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
'H' 'H' 0.0000 0.0000
'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
'N' 'N' 0.0061 0.0033
'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
'Al' 'Al' 0.0645 0.0514
'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'

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_symmetry_space_group_name_H-M P-1

loop_
_symmetry_equiv_pos_as_xyz
'x, y, z'
'-x, -y, -z'

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_cell_length_b              8.424(3)
_cell_length_c              8.511(3)
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_cell_angle_beta            92.335(5)
_cell_angle_gamma           108.428(5)
_cell_volume                 557.8(4)
_cell_formula_units_Z        1
_cell_measurement_temperature 200(2)

```



```

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_exptl_crystal_size_min         0.21
_exptl_crystal_density_meas     ?
_exptl_crystal_density_diffn    1.085
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_exptl_crystal_F_000            200
_exptl_absorpt_coefficient_mu    0.138
_exptl_absorpt_correction_type   multi-scan
_exptl_absorpt_correction_T_min  0.9478
_exptl_absorpt_correction_T_max  0.9717
_exptl_absorpt_process_details   'SADABS (Sheldrick, 2003)'

_exptl_special_details
;
Data collection is performed with four batch runs at
\l = 0.00 \% (600 frames), at \l = 90.00 \%
(600 frames), at \l = 180 \% (600 frames) and
at \l = 270 \% (600 frames).
Frame width = 0.30 \& in \w. Data is
merged, corrected for decay, and treated with
multi-scan absorption corrections.
;

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_diffn_radiation_source         'fine-focus sealed tube'
_diffn_radiation_monochromator   graphite
_diffn_measurement_device_type   'Bruker AXS APEX diffractometer'
_diffn_measurement_method       \w
_diffn_detector_area_resol_mean  836.6
_diffn_standards_number         0
_diffn_standards_interval_count  0
_diffn_standards_interval_time  0
_diffn_standards_decay_%        1
_diffn_reflns_number            6725
_diffn_reflns_av_R_equivalents  0.0183
_diffn_reflns_av_sigmaI/netI    0.0226
_diffn_reflns_limit_h_min       -10
_diffn_reflns_limit_h_max       10
_diffn_reflns_limit_k_min       -11
_diffn_reflns_limit_k_max       11
_diffn_reflns_limit_l_min       -11
_diffn_reflns_limit_l_max       11
_diffn_reflns_theta_min         2.41
_diffn_reflns_theta_max         28.29
_reflns_number_total            2751
_reflns_number_gt               2443
_reflns_threshold_expression     >2sigma(I)

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_computing_cell_refinement      'SAINT (Bruker, 2002)'
_computing_data_reduction       SAINT
_computing_structure_solution   'SHELXS-97 (Sheldrick, 1990)'
_computing_structure_refinement 'SHELXL-97 (Sheldrick, 1997)'
_computing_molecular_graphics   'SHELXTL (Sheldrick, 2001)'
_computing_publication_material 'SHELXTL (Sheldrick, 2001)'

_refine_special_details
;
Refinement of F2 against ALL reflections. The weighted R-factor wR and
goodness of fit S are based on F2, conventional R-factors R are based
on F, with F set to zero for negative F2. The threshold expression of
F2 > 2sigma(F2) is used only for calculating R-factors(gt) etc. and is
not relevant to the choice of reflections for refinement. R-factors based
on F2 are statistically about twice as large as those based on F, and R-
factors based on ALL data will be even larger.
;

_refine_ls_structure_factor_coef Fsqd
_refine_ls_matrix_type          full
_refine_ls_weighting_scheme     calc
_refine_ls_weighting_details
'calc w=1/[sigma^2(Fo^2)+(0.1011P)^2+0.2531P] where P=(Fo^2+2Fc^2)/3'
_atom_sites_solution_primary    direct
_atom_sites_solution_secondary  difmap
_atom_sites_solution_hydrogens  geom
_refine_ls_hydrogen_treatment   constr
_refine_ls_extinction_method     none
_refine_ls_extinction_coef      ?
_refine_ls_number_reflns        2751
_refine_ls_number_parameters    112
_refine_ls_number_restraints    0
_refine_ls_R_factor_all         0.0600
_refine_ls_R_factor_gt          0.0548
_refine_ls_wR_factor_ref        0.1665
_refine_ls_wR_factor_gt         0.1602
_refine_ls_goodness_of_fit_ref  1.000
_refine_ls_restrained_S_all     1.000
_refine_ls_shift/su_max         0.001
_refine_ls_shift/su_mean        0.000

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_atom_site_refinement_flags
_atom_site_disorder_assembly

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_atom_site_disorder_group

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 N1 N 0.42026(19) 0.28615(18) 0.37441(18) 0.0367(3) Uani 1 1 d . . .
 N2 N 0.68207(18) 0.49081(18) 0.34675(18) 0.0362(3) Uani 1 1 d . . .
 C1 C 0.3159(3) 0.6044(3) 0.3010(2) 0.0450(4) Uani 1 1 d . . .
 H1A H 0.4393 0.6638 0.3021 0.068 Uiso 1 1 calc R . .
 H1B H 0.2575 0.6823 0.3415 0.068 Uiso 1 1 calc R . .
 H1C H 0.2709 0.5603 0.1926 0.068 Uiso 1 1 calc R . .
 C2 C 0.0394(2) 0.2580(3) 0.4150(3) 0.0469(5) Uani 1 1 d . . .
 H2A H 0.0286 0.1735 0.4905 0.070 Uiso 1 1 calc R . .
 H2B H 0.0139 0.2023 0.3074 0.070 Uiso 1 1 calc R . .
 H2C H -0.0414 0.3194 0.4372 0.070 Uiso 1 1 calc R . .
 C3 C 0.5673(2) 0.3413(2) 0.3053(2) 0.0357(4) Uani 1 1 d . . .
 C4 C 0.5897(3) 0.2094(3) 0.1838(2) 0.0463(5) Uani 1 1 d . . .
 H4A H 0.6925 0.1782 0.2124 0.056 Uiso 1 1 calc R . .
 H4B H 0.5995 0.2499 0.0773 0.056 Uiso 1 1 calc R . .
 C5 C 0.4266(4) 0.0620(3) 0.1904(4) 0.0714(8) Uani 1 1 d . . .
 H5A H 0.3481 0.0507 0.0960 0.086 Uiso 1 1 calc R . .
 H5B H 0.4534 -0.0440 0.1957 0.086 Uiso 1 1 calc R . .
 C6 C 0.3472(3) 0.1016(2) 0.3368(3) 0.0482(5) Uani 1 1 d . . .
 H6A H 0.2210 0.0674 0.3185 0.058 Uiso 1 1 calc R . .
 H6B H 0.3754 0.0421 0.4246 0.058 Uiso 1 1 calc R . .
 C7 C 0.8166(2) 0.5562(3) 0.2369(2) 0.0437(4) Uani 1 1 d . . .
 H7A H 0.8239 0.4618 0.1640 0.052 Uiso 1 1 calc R . .
 H7B H 0.9285 0.6053 0.2981 0.052 Uiso 1 1 calc R . .
 C8 C 0.7834(3) 0.6865(4) 0.1427(3) 0.0693(7) Uani 1 1 d . . .
 H8B H 0.7630 0.7752 0.2147 0.083 Uiso 1 1 calc R . .
 H8C H 0.6791 0.6346 0.0711 0.083 Uiso 1 1 calc R . .
 C9 C 0.9345(4) 0.7645(5) 0.0463(4) 0.0891(10) Uani 1 1 d . . .
 H9C H 0.9172 0.8599 -0.0031 0.134 Uiso 1 1 calc R . .
 H9D H 0.9438 0.6804 -0.0359 0.134 Uiso 1 1 calc R . .
 H9A H 1.0400 0.8036 0.1155 0.134 Uiso 1 1 calc R . .

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_atom_site_aniso_U_22
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_atom_site_aniso_U_23
_atom_site_aniso_U_13
_atom_site_aniso_U_12

Al 0.0282(3) 0.0327(3) 0.0414(3) 0.0025(2) 0.0038(2) 0.0091(2)
 N1 0.0343(7) 0.0295(7) 0.0448(8) -0.0013(6) 0.0035(6) 0.0091(6)
 N2 0.0319(7) 0.0352(7) 0.0425(8) 0.0022(6) 0.0076(6) 0.0119(6)
 C1 0.0397(9) 0.0445(10) 0.0538(11) 0.0121(8) 0.0047(8) 0.0157(8)
 C2 0.0320(9) 0.0475(11) 0.0566(11) 0.0033(9) 0.0019(8) 0.0066(8)
 C3 0.0357(8) 0.0366(8) 0.0378(8) 0.0003(7) 0.0014(6) 0.0168(7)
 C4 0.0460(10) 0.0457(10) 0.0484(10) -0.0078(8) 0.0055(8) 0.0187(8)
 C5 0.0805(18) 0.0446(12) 0.0806(18) -0.0144(11) 0.0273(14) 0.0102(12)
 C6 0.0475(11) 0.0309(9) 0.0623(12) -0.0033(8) 0.0062(9) 0.0088(8)
 C7 0.0368(9) 0.0463(10) 0.0472(10) 0.0023(8) 0.0111(7) 0.0116(8)
 C8 0.0545(13) 0.0847(18) 0.0753(17) 0.0371(14) 0.0184(12) 0.0232(13)
 C9 0.081(2) 0.103(3) 0.080(2) 0.0428(18) 0.0242(16) 0.0150(18)

_geom_special_details

;

All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

;

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Al N2 1.9285(17) 2_666 ?
Al C1 1.970(2) . ?
Al C2 1.978(2) . ?
N1 C3 1.332(2) . ?
N1 C6 1.483(2) . ?
N2 C3 1.326(2) . ?
N2 C7 1.477(2) . ?
N2 Al 1.9286(17) 2_666 ?
C3 C4 1.520(2) . ?
C4 C5 1.521(3) . ?
C5 C6 1.495(3) . ?
C7 C8 1.493(3) . ?
C8 C9 1.518(4) . ?
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  _geom_angle_atom_site_label_3
  _geom_angle
  _geom_angle_site_symmetry_1
  _geom_angle_site_symmetry_3
  _geom_angle_publ_flag
N1 Al N2 113.46(7) . 2_666 ?
N1 Al C1 108.53(8) . . ?
N2 Al C1 108.38(9) 2_666 . ?
N1 Al C2 105.67(8) . . ?
N2 Al C2 106.20(8) 2_666 . ?
C1 Al C2 114.73(9) . . ?
C3 N1 C6 108.80(15) . . ?
C3 N1 Al 126.04(12) . . ?
C6 N1 Al 120.66(12) . . ?
C3 N2 C7 117.41(15) . . ?
C3 N2 Al 120.95(12) . 2_666 ?
C7 N2 Al 118.20(12) . 2_666 ?
N2 C3 N1 122.62(16) . . ?
N2 C3 C4 125.32(16) . . ?
N1 C3 C4 111.96(16) . . ?
C3 C4 C5 103.07(16) . . ?
C6 C5 C4 105.48(18) . . ?
N1 C6 C5 105.83(17) . . ?
N2 C7 C8 112.67(17) . . ?
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C7 C8 C9 110.7(2) . . ?

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_geom_torsion_atom_site_label_3

_geom_torsion_atom_site_label_4

_geom_torsion

_geom_torsion_site_symmetry_1

_geom_torsion_site_symmetry_2

_geom_torsion_site_symmetry_3

_geom_torsion_site_symmetry_4

_geom_torsion_publ_flag

N2 Al N1 C3 -95.13(16) 2_666 . . . ?

C1 Al N1 C3 25.40(17) ?

C2 Al N1 C3 148.92(15) ?

N2 Al N1 C6 111.39(15) 2_666 . . . ?

C1 Al N1 C6 -128.08(16) ?

C2 Al N1 C6 -4.56(17) ?

C7 N2 C3 N1 -164.43(17) ?

Al N2 C3 N1 36.9(2) 2_666 . . . ?

C7 N2 C3 C4 19.5(3) ?

Al N2 C3 C4 -139.15(16) 2_666 . . . ?

C6 N1 C3 N2 -163.28(17) ?

Al N1 C3 N2 40.7(2) ?

C6 N1 C3 C4 13.2(2) ?

Al N1 C3 C4 -142.83(14) ?

N2 C3 C4 C5 176.8(2) ?

N1 C3 C4 C5 0.4(2) ?

C3 C4 C5 C6 -13.6(3) ?

C3 N1 C6 C5 -21.8(2) ?

Al N1 C6 C5 135.81(19) ?

C4 C5 C6 N1 21.3(3) ?

C3 N2 C7 C8 102.5(2) ?

Al N2 C7 C8 -98.2(2) 2_666 . . . ?

N2 C7 C8 C9 173.3(2) ?

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_refine_diff_density_min -0.363

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A.2 Compound 5

data_seab007

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;
_chemical_name_common      ?
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'C20 H31 N3 Ti'
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'C' 'C' 0.0033 0.0016
'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
'H' 'H' 0.0000 0.0000
'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
'N' 'N' 0.0061 0.0033
'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
'Ti' 'Ti' 0.2776 0.4457
'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
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_symmetry_space_group_name_H-M P2(1)/n
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_symmetry_equiv_pos_as_xyz
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'-x+1/2, y+1/2, -z+1/2'
'-x, -y, -z'
'x-1/2, -y-1/2, z-1/2'
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_cell_length_b              8.449(2)
_cell_length_c              16.922(5)
_cell_angle_alpha           90.00
_cell_angle_beta            111.68(4)
_cell_angle_gamma           90.00
_cell_volume                1975.8(13)
_cell_formula_units_Z        4
_cell_measurement_temperature 120(2)
_cell_measurement_reflns_used 689
_cell_measurement_theta_min  2.59
_cell_measurement_theta_max  27.25
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_exptl_crystal_size_mid      0.24
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_exptl_crystal_density_meas   ?
_exptl_crystal_density_diffn  1.215
_exptl_crystal_density_method 'not measured'
_exptl_crystal_F_000          776
_exptl_absorpt_coefficient_mu 0.439
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_exptl_absorpt_correction_T_min 0.8870
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_exptl_special_details
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Data collection is performed with four batch runs at
\l = 0.00 \% (600 frames), at \l = 90.00 \%
(600 frames), at \l = 180 \% (600 frames) and
at \l = 270 \% (600 frames).
Frame width = 0.30 \& in \w. Data is
merged, corrected for decay, and treated with
multi-scan absorption corrections.
;

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_diffn_measurement_method      \w
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_diffn_standards_number        ?
_diffn_standards_interval_count ?
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_diffn_reflns_limit_h_max       19
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_diffn_reflns_limit_l_max       21
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_reflns_number_total            4394
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_reflns_threshold_expression     >2sigma(I)

_computing_data_collection      'SMART, Bruker (2002)'
_computing_cell_refinement      'SHELXTL, Sheldrick (2001)'

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_computing_data_reduction      'SHELXTL, Sheldrick (2001)'
_computing_structure_solution  'SHELXS-97 (Sheldrick, 1990)'
_computing_structure_refinement 'SHELXL-97 (Sheldrick, 1997)'
_computing_molecular_graphics  'SHELXTL, Sheldrick (2001)'
_computing_publication_material 'SHELXTL, Sheldrick (2001)'

_refine_special_details
;
Refinement of F2 against ALL reflections. The weighted R-factor wR and
goodness of fit S are based on F2, conventional R-factors R are based
on F, with F set to zero for negative F2. The threshold expression of
F2 > 2sigma(F2) is used only for calculating R-factors(gt) etc. and is
not relevant to the choice of reflections for refinement. R-factors based
on F2 are statistically about twice as large as those based on F, and R-
factors based on ALL data will be even larger.
;

_refine_ls_structure_factor_coef Fsqd
_refine_ls_matrix_type          full
_refine_ls_weighting_scheme     calc
_refine_ls_weighting_details
'calc w=1/[sigma2(Fo2)+(0.0665P)2+0.8038P] where P=(Fo2+2Fc2)/3'
_atom_sites_solution_primary    direct
_atom_sites_solution_secondary  difmap
_atom_sites_solution_hydrogens  geom
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_refine_ls_extinction_method     none
_refine_ls_extinction_coef       ?
_refine_ls_number_reflns        4394
_refine_ls_number_parameters     223
_refine_ls_number_restraints     0
_refine_ls_R_factor_all         0.0666
_refine_ls_R_factor_gt          0.0505
_refine_ls_wR_factor_ref        0.1379
_refine_ls_wR_factor_gt         0.1256
_refine_ls_goodness_of_fit_ref  1.015
_refine_ls_restrained_S_all     1.015
_refine_ls_shift/su_max         0.001
_refine_ls_shift/su_mean        0.000

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  _atom_site_fract_y
  _atom_site_fract_z
  _atom_site_U_iso_or_equiv
  _atom_site_adp_type
  _atom_site_occupancy
  _atom_site_symmetry_multiplicity
  _atom_site_calc_flag
  _atom_site_refinement_flags
  _atom_site_disorder_assembly
  _atom_site_disorder_group
Ti Ti -0.05957(3) 0.93433(5) 0.23392(2) 0.01588(14) Uani 1 1 d . . .
N1 N 0.04935(12) 0.8675(2) 0.35398(11) 0.0164(4) Uani 1 1 d . . .

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N2 N 0.08344(12) 1.0296(2) 0.26650(11) 0.0170(4) Uani 1 1 d . . .
 N3 N 0.21500(12) 0.9526(2) 0.39855(12) 0.0182(4) Uani 1 1 d . . .
 C1 C 0.06682(15) 0.7737(3) 0.43089(14) 0.0194(5) Uani 1 1 d . . .
 H1A H 0.1127 0.8335 0.4804 0.023 Uiso 1 1 calc R . .
 C2 C -0.02759(17) 0.7496(3) 0.44553(16) 0.0272(6) Uani 1 1 d . . .
 H2A H -0.0517 0.8521 0.4563 0.041 Uiso 1 1 calc R . .
 H2B H -0.0160 0.6802 0.4947 0.041 Uiso 1 1 calc R . .
 H2C H -0.0757 0.7010 0.3950 0.041 Uiso 1 1 calc R . .
 C3 C 0.11217(18) 0.6128(3) 0.42626(16) 0.0271(5) Uani 1 1 d . . .
 H3A H 0.1726 0.6289 0.4166 0.041 Uiso 1 1 calc R . .
 H3B H 0.0671 0.5509 0.3793 0.041 Uiso 1 1 calc R . .
 H3C H 0.1258 0.5558 0.4799 0.041 Uiso 1 1 calc R . .
 C4 C 0.14194(15) 1.1202(3) 0.22935(14) 0.0193(5) Uani 1 1 d . . .
 H4A H 0.1798 1.2005 0.2722 0.023 Uiso 1 1 calc R . .
 C5 C 0.07515(18) 1.2092(3) 0.15059(16) 0.0307(6) Uani 1 1 d . . .
 H5A H 0.0367 1.2867 0.1676 0.046 Uiso 1 1 calc R . .
 H5B H 0.0318 1.1337 0.1104 0.046 Uiso 1 1 calc R . .
 H5C H 0.1142 1.2639 0.1234 0.046 Uiso 1 1 calc R . .
 C6 C 0.21348(17) 1.0167(3) 0.20760(17) 0.0304(6) Uani 1 1 d . . .
 H6A H 0.2535 0.9577 0.2583 0.046 Uiso 1 1 calc R . .
 H6B H 0.2550 1.0836 0.1881 0.046 Uiso 1 1 calc R . .
 H6C H 0.1779 0.9422 0.1625 0.046 Uiso 1 1 calc R . .
 C7 C 0.11854(14) 0.9526(3) 0.34095(14) 0.0154(4) Uani 1 1 d . . .
 C8 C 0.27399(16) 1.0981(3) 0.42402(15) 0.0224(5) Uani 1 1 d . . .
 H8A H 0.2890 1.1346 0.3740 0.027 Uiso 1 1 calc R . .
 C9 C 0.22065(18) 1.2317(3) 0.44863(17) 0.0336(6) Uani 1 1 d . . .
 H9A H 0.1602 1.2546 0.4010 0.050 Uiso 1 1 calc R . .
 H9B H 0.2614 1.3266 0.4625 0.050 Uiso 1 1 calc R . .
 H9C H 0.2060 1.1997 0.4982 0.050 Uiso 1 1 calc R . .
 C10 C 0.36903(16) 1.0577(3) 0.49481(15) 0.0242(5) Uani 1 1 d . . .
 H10A H 0.4012 0.9725 0.4760 0.036 Uiso 1 1 calc R . .
 H10B H 0.3566 1.0229 0.5451 0.036 Uiso 1 1 calc R . .
 H10C H 0.4108 1.1514 0.5091 0.036 Uiso 1 1 calc R . .
 C11 C -0.00570(17) 0.6971(3) 0.18609(16) 0.0272(6) Uani 1 1 d . . .
 H11A H 0.0587 0.6453 0.2145 0.033 Uiso 1 1 calc R . .
 C12 C -0.02940(17) 0.8045(3) 0.11765(16) 0.0277(6) Uani 1 1 d . . .
 H12A H 0.0155 0.8429 0.0900 0.033 Uiso 1 1 calc R . .
 C13 C -0.12961(17) 0.8343(3) 0.08917(15) 0.0267(5) Uani 1 1 d . . .
 H13A H -0.1681 0.8973 0.0378 0.032 Uiso 1 1 calc R . .
 C14 C -0.16774(16) 0.7432(3) 0.13933(15) 0.0251(5) Uani 1 1 d . . .
 H14A H -0.2380 0.7308 0.1292 0.030 Uiso 1 1 calc R . .
 C15 C -0.09161(17) 0.6585(3) 0.19959(16) 0.0252(5) Uani 1 1 d . . .
 H15A H -0.0985 0.5744 0.2386 0.030 Uiso 1 1 calc R . .
 C16 C -0.14879(17) 1.1771(3) 0.18990(17) 0.0304(6) Uani 1 1 d . . .
 H16A H -0.1540 1.2413 0.1387 0.037 Uiso 1 1 calc R . .
 C17 C -0.21428(17) 1.0594(3) 0.19371(19) 0.0336(7) Uani 1 1 d . . .
 H17A H -0.2741 1.0263 0.1454 0.040 Uiso 1 1 calc R . .
 C18 C -0.18760(17) 1.0093(3) 0.27927(19) 0.0332(6) Uani 1 1 d . . .
 H18A H -0.2255 0.9367 0.3019 0.040 Uiso 1 1 calc R . .
 C19 C -0.10689(18) 1.1023(3) 0.32835(17) 0.0287(6) Uani 1 1 d . . .
 H19A H -0.0763 1.1027 0.3918 0.034 Uiso 1 1 calc R . .
 C20 C -0.08357(17) 1.2043(3) 0.27400(17) 0.0277(6) Uani 1 1 d . . .
 H20A H -0.0330 1.2890 0.2921 0.033 Uiso 1 1 calc R . .

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_geom_special_details

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All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

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A.3 Compound 6

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'H' 'H' 0.0000 0.0000
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'N' 'N' 0.0061 0.0033
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'y, -x+1/2, z+1/2'
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\l = 0.00 \% (600 frames), at \l = 90.00 \%
(600 frames), at \l = 180 \% (600 frames) and
at \l = 270 \% (600 frames).
Frame width = 0.30 \& in \w. Data is
merged, corrected for decay, and treated with
multi-scan absorption corrections.
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Refinement of F2 against ALL reflections. The weighted R-factor wR and
goodness of fit S are based on F2, conventional R-factors R are based
on F, with F set to zero for negative F2. The threshold expression of
F2 > 2sigma(F2) is used only for calculating R-factors(gt) etc. and is
not relevant to the choice of reflections for refinement. R-factors based
on F2 are statistically about twice as large as those based on F, and R-
factors based on ALL data will be even larger.
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_refine_ls_solution_secondary   difmap
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N2 N 0.2500 0.2500 0.46793(15) 0.0319(10) Uani 1 4 d S . .
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C2 C 0.5193(4) 0.1745(5) 0.30471(17) 0.0705(13) Uani 1 1 d . A .
H2A H 0.6208 0.2378 0.3120 0.085 Uiso 1 1 calc R . .
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C5 C 0.0736(5) 0.0103(6) 0.41166(18) 0.0333(14) Uani 0.50 1 d PD A -1
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H6B H -0.1152 -0.1411 0.3923 0.051 Uiso 0.50 1 calc PR A -1
H6C H 0.0247 -0.1293 0.3527 0.051 Uiso 0.50 1 calc PR A -1
C7 C 0.1918(10) -0.1256(8) 0.4273(2) 0.0615(19) Uani 0.50 1 d PD A -1
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H7B H 0.1330 -0.2055 0.4468 0.092 Uiso 0.50 1 calc PR A -1
H7C H 0.2811 -0.0778 0.4459 0.092 Uiso 0.50 1 calc PR A -1
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N2 0.0398(16) 0.0398(16) 0.016(2) 0.000 0.000 -0.0018(17)
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C2 0.0215(15) 0.084(3) 0.106(3) -0.052(3) 0.0086(18) 0.0040(16)
C3 0.077(2) 0.066(2) 0.0514(18) 0.0045(16) 0.0382(19) 0.0205(18)
C4 0.0258(16) 0.0258(16) 0.020(2) 0.000 0.000 0.0012(18)
C5 0.040(3) 0.028(3) 0.033(2) 0.0007(18) 0.0041(19) -0.009(2)
C6 0.019(5) 0.029(7) 0.053(2) -0.003(3) 0.002(2) -0.003(6)
C7 0.087(5) 0.037(4) 0.061(4) 0.020(3) -0.022(4) -0.018(4)
C8 0.047(3) 0.057(4) 0.029(3) 0.014(3) -0.001(2) -0.007(3)

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All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

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Ti C2 2.360(3) 16 ?

Ti C2 2.360(3) . ?

Ti C3 2.388(3) 15_665 ?

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Ti C3 2.388(3) 16 ?

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 C2 Ti C3 32.52(14) 2 2 ?
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 C2 Ti C3 119.38(17) 2 . ?
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 C1 Ti C3 55.45(13) 2 16 ?
 C2 Ti C3 119.38(17) 15_665 16 ?

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 C2 Ti C3 32.52(14) 16 16 ?
 C2 Ti C3 103.19(17) . 16 ?
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A.4 Compound 8

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_chemical_name_common ?

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'C23 H38 N3 Ti'

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'C' 'C' 0.0033 0.0016

'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'

'H' 'H' 0.0000 0.0000

'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'

'N' 'N' 0.0061 0.0033

'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'

'Ti' 'Ti' 0.2776 0.4457

'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'

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_symmetry_space_group_name_H-M P2(1)/n

loop_

_symmetry_equiv_pos_as_xyz

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'-x+1/2, y+1/2, -z+1/2'

'-x, -y, -z'

'x-1/2, -y-1/2, z-1/2'

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_cell_length_b 29.036(4)

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_cell_angle_gamma 90.00

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_exptl_special_details
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Data collection is performed with four batch runs at
\l = 0.00 \% (600 frames), at \l = 90.00 \%
(600 frames), at \l = 180 \% (600 frames) and
at \l = 270 \% (600 frames).
Frame width = 0.30 \& in \w. Data is
merged, corrected for decay, and treated with
multi-scan absorption corrections.
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_diffn_radiation_monochromator graphite
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_diffn_measurement_method      \w
_diffn_detector_area_resol_mean 836.6
_diffn_standards_number        0
_diffn_standards_interval_count 0
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_diffn_reflns_number           13137
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_diffn_reflns_av_sigma/netI     0.0410
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_computing_cell_refinement      'SAINT (Bruker, 2002)'

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_computing_data_reduction      SAINT
_computing_structure_solution  'SHELXS-97 (Sheldrick, 1990)'
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_computing_molecular_graphics  'SHELXTL (Sheldrick, 2001)'
_computing_publication_material 'SHELXTL (Sheldrick, 2001)'

_refine_special_details
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Refinement of F2 against ALL reflections. The weighted R-factor wR and
goodness of fit S are based on F2, conventional R-factors R are based
on F, with F set to zero for negative F2. The threshold expression of
F2 > 2sigma(F2) is used only for calculating R-factors(gt) etc. and is
not relevant to the choice of reflections for refinement. R-factors based
on F2 are statistically about twice as large as those based on F, and R-
factors based on ALL data will be even larger.
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_refine_ls_matrix_type          full
_refine_ls_weighting_scheme     calc
_refine_ls_weighting_details
'calc w=1/[sigma^2(Fo^2)+(0.0655P)^2+0.2947P] where P=(Fo^2+2Fc^2)/3'
_atom_sites_solution_primary    direct
_atom_sites_solution_secondary  difmap
_atom_sites_solution_hydrogens  geom
_refine_ls_hydrogen_treatment  constr
_refine_ls_extinction_method     none
_refine_ls_extinction_coef      ?
_refine_ls_number_reflns        3842
_refine_ls_number_parameters    252
_refine_ls_number_restraints    0
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_refine_ls_wR_factor_ref        0.1159
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N1 N 0.1141(2) 0.14794(6) 0.24844(19) 0.0184(4) Uani 1 1 d . . .

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N2 N 0.2567(2) 0.10017(5) 0.16147(19) 0.0183(4) Uani 1 1 d . . .
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 C2 C 0.1954(3) 0.22434(8) -0.0994(3) 0.0370(6) Uani 1 1 d . . .
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 C4 C 0.3195(3) 0.21457(8) 0.1605(3) 0.0314(6) Uani 1 1 d . . .
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 C6 C -0.1515(3) 0.16766(8) -0.1342(3) 0.0307(6) Uani 1 1 d . . .
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 C10 C -0.1417(3) 0.12521(8) -0.0567(3) 0.0297(6) Uani 1 1 d . . .
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 C11 C 0.2072(2) 0.11076(7) 0.2792(2) 0.0172(4) Uani 1 1 d . . .
 C12 C 0.0473(3) 0.16793(7) 0.3603(2) 0.0232(5) Uani 1 1 d . . .
 H12A H 0.0712 0.1465 0.4519 0.028 Uiso 1 1 calc R . .
 C13 C -0.1356(3) 0.17395(9) 0.2867(3) 0.0326(6) Uani 1 1 d . . .
 H13A H -0.1866 0.1439 0.2537 0.049 Uiso 1 1 calc R . .
 H13B H -0.1615 0.1942 0.1948 0.049 Uiso 1 1 calc R . .
 H13C H -0.1762 0.1876 0.3641 0.049 Uiso 1 1 calc R . .
 C14 C 0.1226(3) 0.21490(8) 0.4218(3) 0.0340(6) Uani 1 1 d . . .
 H14A H 0.2401 0.2116 0.4721 0.051 Uiso 1 1 calc R . .
 H14B H 0.0775 0.2266 0.4987 0.051 Uiso 1 1 calc R . .
 H14C H 0.0982 0.2366 0.3338 0.051 Uiso 1 1 calc R . .
 C15 C 0.3599(3) 0.06023(7) 0.1660(2) 0.0207(5) Uani 1 1 d . . .
 H15A H 0.3781 0.0435 0.2670 0.025 Uiso 1 1 calc R . .
 C16 C 0.5249(3) 0.07455(8) 0.1629(3) 0.0292(5) Uani 1 1 d . . .
 H16A H 0.5793 0.0945 0.2533 0.044 Uiso 1 1 calc R . .
 H16B H 0.5104 0.0913 0.0653 0.044 Uiso 1 1 calc R . .
 H16C H 0.5909 0.0470 0.1683 0.044 Uiso 1 1 calc R . .
 C17 C 0.2788(3) 0.02696(7) 0.0313(3) 0.0288(5) Uani 1 1 d . . .
 H17A H 0.1780 0.0155 0.0399 0.043 Uiso 1 1 calc R . .
 H17B H 0.3515 0.0010 0.0369 0.043 Uiso 1 1 calc R . .
 H17C H 0.2547 0.0430 -0.0693 0.043 Uiso 1 1 calc R . .
 C18 C 0.1508(3) 0.04533(7) 0.4325(2) 0.0212(5) Uani 1 1 d . . .
 H18A H 0.1374 0.0461 0.5372 0.025 Uiso 1 1 calc R . .
 C19 C -0.0180(3) 0.04758(8) 0.3081(3) 0.0317(6) Uani 1 1 d . . .
 H19A H -0.0748 0.0747 0.3269 0.048 Uiso 1 1 calc R . .
 H19B H -0.0781 0.0197 0.3136 0.048 Uiso 1 1 calc R . .
 H19C H -0.0099 0.0499 0.2035 0.048 Uiso 1 1 calc R . .
 C20 C 0.2282(3) -0.00125(7) 0.4213(3) 0.0302(5) Uani 1 1 d . . .
 H20A H 0.3415 -0.0013 0.4922 0.045 Uiso 1 1 calc R . .
 H20B H 0.2229 -0.0062 0.3129 0.045 Uiso 1 1 calc R . .
 H20C H 0.1695 -0.0260 0.4515 0.045 Uiso 1 1 calc R . .
 C21 C 0.4171(3) 0.08803(8) 0.5326(2) 0.0263(5) Uani 1 1 d . . .
 H21A H 0.4795 0.0645 0.4973 0.032 Uiso 1 1 calc R . .
 C22 C 0.4913(3) 0.13486(8) 0.5294(3) 0.0313(6) Uani 1 1 d . . .

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H22B H 0.6068 0.1340 0.5935 0.047 Uiso 1 1 calc R . .
H22C H 0.4374 0.1580 0.5719 0.047 Uiso 1 1 calc R . .
C23 C 0.4316(3) 0.07672(8) 0.7006(3) 0.0312(6) Uani 1 1 d . . .
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N2 0.0173(10) 0.0170(9) 0.0197(9) 0.0001(7) 0.0055(7) 0.0002(8)
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C3 0.0346(16) 0.0175(12) 0.0502(15) -0.0026(10) 0.0112(12) -0.0058(11)
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C5 0.0175(13) 0.0233(12) 0.0607(17) 0.0082(11) 0.0084(12) -0.0090(11)
C6 0.0172(13) 0.0284(12) 0.0356(13) -0.0034(10) -0.0040(11) -0.0002(10)
C7 0.0284(15) 0.0327(13) 0.0225(11) 0.0065(9) -0.0011(10) -0.0064(11)
C8 0.0255(14) 0.0346(13) 0.0248(12) -0.0101(10) 0.0019(10) -0.0067(11)
C9 0.0235(14) 0.0232(12) 0.0298(12) -0.0005(10) -0.0068(10) -0.0060(10)
C10 0.0164(13) 0.0416(14) 0.0258(11) -0.0026(10) 0.0008(10) -0.0118(11)
C11 0.0132(11) 0.0166(10) 0.0186(10) -0.0035(8) 0.0017(8) -0.0051(9)
C12 0.0235(13) 0.0230(11) 0.0234(11) -0.0020(9) 0.0087(10) 0.0048(10)
C13 0.0281(15) 0.0313(13) 0.0416(14) -0.0040(11) 0.0163(12) 0.0073(11)
C14 0.0372(16) 0.0310(13) 0.0357(13) -0.0109(10) 0.0151(12) 0.0031(11)
C15 0.0223(13) 0.0201(11) 0.0217(11) 0.0007(8) 0.0100(9) 0.0026(9)
C16 0.0236(14) 0.0303(12) 0.0356(13) -0.0013(10) 0.0130(11) 0.0055(11)
C17 0.0339(15) 0.0245(12) 0.0298(12) -0.0058(9) 0.0133(11) 0.0021(11)
C18 0.0235(13) 0.0199(11) 0.0223(11) 0.0016(8) 0.0106(10) -0.0011(9)
C19 0.0276(14) 0.0289(12) 0.0364(13) 0.0065(10) 0.0088(11) -0.0077(11)
C20 0.0378(16) 0.0201(11) 0.0362(13) -0.0003(9) 0.0174(11) -0.0029(11)
C21 0.0205(13) 0.0311(12) 0.0226(11) 0.0006(9) 0.0017(9) 0.0016(10)
C22 0.0215(13) 0.0380(14) 0.0263(12) 0.0022(10) -0.0014(10) -0.0074(11)
C23 0.0286(14) 0.0352(13) 0.0244(12) 0.0030(10) 0.0027(10) -0.0009(11)

_geom_special_details

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All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

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Ti C7 2.391(2) . ?
Ti C1 2.397(2) . ?
Ti C4 2.403(2) . ?
Ti C8 2.405(2) . ?
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C15 C17 1.523(3) . ?
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N2 Ti C3 128.33(8) . . ?
C6 Ti C3 95.97(9) . . ?

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C5 Ti C10 C9 -7(3) ?
 N1 Ti C10 C6 124.33(14) ?
 N2 Ti C10 C6 -176.95(14) ?
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 Ti N1 C11 N3 179.99(16) ?
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 C18 N3 C11 N2 -84.0(3) ?
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A.5 Compound 9

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(600 frames), at \l = 180 \% (600 frames) and
at \l = 270 \% (600 frames).
Frame width = 0.30 \& in \w. Data is
merged, corrected for decay, and treated with
multi-scan absorption corrections.
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Refinement of  $F^2$  against ALL reflections. The weighted R-factor  $wR$  and
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on  $F$ , with  $F$  set to zero for negative  $F^2$ . The threshold expression of
 $F^2 > 2\sigma(F^2)$  is used only for calculating R-factors(gt) etc. and is
not relevant to the choice of reflections for refinement. R-factors based
on  $F^2$  are statistically about twice as large as those based on  $F$ , and R-
factors based on ALL data will be even larger.
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 N2 N 0.4825(2) 0.03242(14) 0.64622(7) 0.0255(5) Uani 1 1 d D A .
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 C2 C 0.4771(3) 0.2619(2) 0.67256(12) 0.0446(8) Uani 1 1 d . . .
 H2A H 0.4008 0.2835 0.6539 0.054 Uiso 1 1 calc R . .
 C3 C 0.5971(3) 0.2981(2) 0.66814(12) 0.0462(8) Uani 1 1 d . . .
 H3B H 0.6213 0.3509 0.6462 0.055 Uiso 1 1 calc R . .
 C4 C 0.6722(3) 0.2572(2) 0.70516(12) 0.0487(8) Uani 1 1 d . . .
 H4A H 0.7597 0.2757 0.7141 0.058 Uiso 1 1 calc R . .
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 C9 C 0.7999(3) 0.0489(2) 0.65345(11) 0.0393(7) Uani 1 1 d . . .
 H9A H 0.8200 0.0096 0.6836 0.047 Uiso 1 1 calc R . .
 C10 C 0.7424(3) 0.0199(2) 0.60875(11) 0.0386(7) Uani 1 1 d . . .
 H10A H 0.7131 -0.0432 0.6015 0.046 Uiso 1 1 calc R . .
 C11 C 0.4210(2) 0.06286(16) 0.60535(9) 0.0241(5) Uani 1 1 d D . .
 C12 C 0.4403(3) 0.18213(18) 0.53852(10) 0.0348(6) Uani 1 1 d . . .
 H12A H 0.3521 0.2041 0.5423 0.042 Uiso 1 1 calc R A .
 C13 C 0.5259(4) 0.2646(2) 0.53057(13) 0.0548(9) Uani 1 1 d . A .
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 H13B H 0.4962 0.2998 0.5011 0.082 Uiso 1 1 calc R . .
 H13C H 0.6118 0.2439 0.5242 0.082 Uiso 1 1 calc R . .
 C14 C 0.4473(4) 0.1216(2) 0.49142(11) 0.0495(8) Uani 1 1 d . A .
 H14A H 0.3952 0.0677 0.4968 0.074 Uiso 1 1 calc R . .
 H14B H 0.5344 0.1030 0.4857 0.074 Uiso 1 1 calc R . .
 H14C H 0.4169 0.1550 0.4614 0.074 Uiso 1 1 calc R . .
 C15 C 0.4453(3) -0.04584(17) 0.67815(10) 0.0317(6) Uani 1 1 d . . .
 C16 C 0.3131(4) -0.0382(3) 0.70128(14) 0.0617(10) Uani 1 1 d . A .
 H16A H 0.3025 0.0219 0.7168 0.093 Uiso 1 1 calc R . .
 H16B H 0.3020 -0.0849 0.7277 0.093 Uiso 1 1 calc R . .
 H16C H 0.2505 -0.0466 0.6742 0.093 Uiso 1 1 calc R . .
 C17 C 0.4577(4) -0.1357(2) 0.64922(12) 0.0519(9) Uani 1 1 d . A .
 H17A H 0.5444 -0.1432 0.6374 0.078 Uiso 1 1 calc R . .
 H17B H 0.4012 -0.1356 0.6195 0.078 Uiso 1 1 calc R . .
 H17C H 0.4355 -0.1859 0.6721 0.078 Uiso 1 1 calc R . .
 C18 C 0.5331(3) -0.0491(2) 0.72431(12) 0.0521(9) Uani 1 1 d . A .
 H18A H 0.6201 -0.0521 0.7124 0.078 Uiso 1 1 calc R . .
 H18B H 0.5141 -0.1029 0.7450 0.078 Uiso 1 1 calc R . .
 H18C H 0.5214 0.0055 0.7452 0.078 Uiso 1 1 calc R . .
 N3 N 0.3132(3) 0.0246(2) 0.58347(11) 0.0240(7) Uani 0.824(4) 1 d PD A 1
 H3A H 0.3163 -0.0334 0.5759 0.029 Uiso 0.824(4) 1 calc PR A 1
 C19 C 0.1971(3) 0.0715(3) 0.57217(15) 0.0406(9) Uani 0.824(4) 1 d PD A 1
 H19A H 0.2086 0.1032 0.5386 0.049 Uiso 0.824(4) 1 calc PR A 1
 C20 C 0.1659(4) 0.1434(3) 0.61187(16) 0.0449(10) Uani 0.824(4) 1 d PD A 1
 H20A H 0.2393 0.1822 0.6174 0.067 Uiso 0.824(4) 1 calc PR A 1
 H20B H 0.1426 0.1141 0.6442 0.067 Uiso 0.824(4) 1 calc PR A 1

H20C H 0.0958 0.1804 0.5996 0.067 Uiso 0.824(4) 1 calc PR A 1
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 H21C H 0.0792 -0.0298 0.5975 0.083 Uiso 0.824(4) 1 calc PR A 1
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 H3A H 0.3402 -0.0480 0.5798 0.029 Uiso 0.176(4) 1 calc PR A 2
 C19' C 0.1926(13) 0.0196(12) 0.6044(5) 0.0406(9) Uani 0.176(4) 1 d PD A 2
 H19B H 0.1581 -0.0381 0.6189 0.049 Uiso 0.176(4) 1 calc PR A 2
 C20' C 0.1733(16) 0.0924(12) 0.6451(6) 0.0449(10) Uani 0.176(4) 1 d PD A 2
 H20D H 0.1106 0.0717 0.6700 0.067 Uiso 0.176(4) 1 calc PR A 2
 H20E H 0.1441 0.1483 0.6288 0.067 Uiso 0.176(4) 1 calc PR A 2
 H20F H 0.2527 0.1039 0.6628 0.067 Uiso 0.176(4) 1 calc PR A 2
 C21' C 0.1209(18) 0.0382(16) 0.5550(7) 0.0555(13) Uani 0.176(4) 1 d PD A 2
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 N2 0.0286(11) 0.0258(11) 0.0222(10) 0.0049(8) 0.0016(8) -0.0004(9)
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 C2 0.0457(18) 0.0393(16) 0.0488(18) -0.0231(14) -0.0017(14) 0.0092(14)
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 C4 0.0448(18) 0.0531(19) 0.0481(18) -0.0282(15) -0.0007(15) -0.0029(16)
 C5 0.076(3) 0.052(2) 0.0269(15) -0.0141(13) 0.0024(15) 0.0082(18)
 C6 0.0340(16) 0.067(2) 0.0307(15) -0.0067(14) 0.0072(12) 0.0125(15)
 C7 0.0403(18) 0.0441(17) 0.066(2) 0.0096(16) 0.0305(16) 0.0008(14)
 C8 0.0255(15) 0.0520(19) 0.053(2) -0.0146(15) 0.0015(13) -0.0044(13)
 C9 0.0283(15) 0.0468(17) 0.0429(16) 0.0040(13) 0.0021(12) 0.0101(13)
 C10 0.0284(15) 0.0390(16) 0.0483(17) -0.0092(13) 0.0079(13) 0.0024(12)
 C11 0.0265(13) 0.0244(12) 0.0216(12) -0.0050(9) 0.0025(10) 0.0031(10)
 C12 0.0456(17) 0.0330(15) 0.0259(13) 0.0061(11) -0.0015(12) 0.0113(13)
 C13 0.082(3) 0.0396(17) 0.0424(17) 0.0168(14) -0.0004(17) 0.0011(17)
 C14 0.078(2) 0.0476(18) 0.0228(14) 0.0024(12) -0.0023(15) 0.0149(17)
 C15 0.0401(16) 0.0280(13) 0.0271(13) 0.0069(11) 0.0067(12) -0.0015(12)
 C16 0.068(2) 0.062(2) 0.055(2) 0.0060(17) 0.0107(19) -0.0053(19)
 C17 0.084(3) 0.0287(16) 0.0431(18) 0.0071(12) 0.0173(17) 0.0044(16)
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 C19 0.0286(18) 0.048(2) 0.045(2) -0.0140(16) -0.0084(16) 0.0044(16)
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 C21 0.030(2) 0.060(3) 0.077(3) -0.018(2) -0.009(2) -0.0098(19)
 N3' 0.0278(13) 0.0193(17) 0.0250(17) -0.0002(12) -0.0060(11) 0.0045(11)
 C19' 0.0286(18) 0.048(2) 0.045(2) -0.0140(16) -0.0084(16) 0.0044(16)
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All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

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Ti C7 2.388(3) . ?

Ti C8 2.391(3) . ?

Ti C9 2.399(3) . ?

Ti C5 2.400(3) . ?

Ti C4 2.401(3) . ?

Ti C3 2.402(3) . ?

Ti C6 2.423(3) . ?

Ti C1 2.424(3) . ?

Ti C2 2.426(3) . ?

Ti C10 2.429(3) . ?

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N1 C12 1.461(3) . ?

N2 C11 1.328(3) . ?

N2 C15 1.477(3) . ?

C1 C2 1.389(5) . ?

C1 C5 1.401(5) . ?

C2 C3 1.392(5) . ?

C3 C4 1.391(5) . ?

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 C11 N1 C12 C13 178.7(2) ?
 Ti N1 C12 C13 -5.4(4) ?
 C11 N2 C15 C18 -173.1(2) ?
 Ti N2 C15 C18 -1.0(4) ?
 C11 N2 C15 C17 68.3(3) ?
 Ti N2 C15 C17 -119.6(3) ?
 C11 N2 C15 C16 -57.1(3) ?
 Ti N2 C15 C16 115.0(3) ?
 N2 C11 N3 C19 127.5(3) ?
 N1 C11 N3 C19 -53.7(4) ?
 N3' C11 N3 C19 135(2) ?
 Ti C11 N3 C19 -16(4) ?
 C11 N3 C19 C21 -161.8(3) ?
 C11 N3 C19 C20 -35.8(5) ?
 N2 C11 N3' C19' 104.5(15) ?
 N1 C11 N3' C19' -80.3(18) ?
 N3 C11 N3' C19' -69(2) ?
 Ti C11 N3' C19' 105(2) ?
 C11 N3' C19' C21' 107.6(18) ?

C11 N3' C19' C20' -20(2) ?

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_diffn_reflns_theta_full 25.00
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A.6 Compound 10

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_audit_creation_method SHELXL-97

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'C' 'C' 0.0033 0.0016

'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'

'H' 'H' 0.0000 0.0000

'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'

'Zn' 'Zn' 0.2839 1.4301

'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'

'N' 'N' 0.0061 0.0033

'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'

'Cl' 'Cl' 0.1484 0.1585

'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'

_symmetry_cell_setting Monoclinic

_symmetry_space_group_name_H-M P2(1)/c

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_symmetry_equiv_pos_as_xyz

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'-x, y+1/2, -z+1/2'

'-x, -y, -z'

'x, -y-1/2, z-1/2'

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_cell_length_b 34.697(10)

_cell_length_c 10.581(3)

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_cell_angle_beta 104.206(4)

_cell_angle_gamma 90.00

_cell_volume 3816.8(18)

_cell_formula_units_Z 4

_cell_measurement_temperature 120(2)

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_exptl_crystal_density_meas      ?
_exptl_crystal_density_diffn     1.251
_exptl_crystal_density_method    'not measured'
_exptl_crystal_F_000             1544
_exptl_absorpt_coefficient_mu     1.358
_exptl_absorpt_correction_type    multi-scan
_exptl_absorpt_correction_T_min  0.7729
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_exptl_absorpt_process_details    'SADABS (Sheldrick, 2003)'

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Data collection is performed with four batch runs at
\l = 0.00 \% (600 frames), at \l = 90.00 \%
(600 frames), at \l = 180 \% (600 frames) and
at \l = 270 \% (600 frames).
Frame width = 0.30 \& in \w. Data is
merged, corrected for decay, and treated with
multi-scan absorption corrections.
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_computing_cell_refinement    'SAINT (Bruker, 2002)'
_computing_data_reduction     SAINT
_computing_structure_solution 'SHELXS-97 (Sheldrick, 1990)'
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_computing_molecular_graphics 'SHELXTL (Sheldrick, 2001)'
_computing_publication_material SHELXTL

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_refine_special_details
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Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2 , conventional R-factors R are based on F, with F set to zero for negative F^2 . The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

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_atom_sites_solution_secondary difmap
_atom_sites_solution_hydrogens geom
_refine_ls_hydrogen_treatment  constr
_refine_ls_extinction_method    none
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_refine_ls_number_reflns       8930
_refine_ls_number_parameters    379
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_refine_ls_R_factor_all         0.0614
_refine_ls_R_factor_gt          0.0432
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 Zn2 Zn 0.18693(3) 0.135638(8) 0.72014(3) 0.01754(9) Uani 1 1 d ...
 Cl1 Cl 0.06074(6) 0.156300(19) 0.85239(6) 0.02667(15) Uani 1 1 d ...
 N1 N 0.09965(19) 0.15140(6) 0.53366(19) 0.0182(4) Uani 1 1 d ...
 N2 N 0.17971(18) 0.10327(5) 0.42560(19) 0.0172(4) Uani 1 1 d ...
 N3 N -0.01690(19) 0.13270(6) 0.32254(19) 0.0202(4) Uani 1 1 d ...
 H3A H -0.0939 0.1310 0.3374 0.024 Uiso 1 1 calc R ...
 N4 N 0.41927(19) 0.15983(6) 0.58221(19) 0.0183(4) Uani 1 1 d ...
 N5 N 0.36186(19) 0.16172(6) 0.77892(19) 0.0180(4) Uani 1 1 d ...
 N6 N 0.50770(19) 0.20820(6) 0.7351(2) 0.0198(4) Uani 1 1 d ...
 H6B H 0.4737 0.2286 0.7630 0.024 Uiso 1 1 calc R ...
 N7 N 0.19854(18) 0.07665(6) 0.73547(19) 0.0179(4) Uani 1 1 d ...
 N8 N 0.39520(19) 0.06961(6) 0.68636(19) 0.0187(4) Uani 1 1 d ...
 N9 N 0.3214(2) 0.02032(6) 0.8042(2) 0.0232(5) Uani 1 1 d ...
 H9D H 0.3081 0.0191 0.8830 0.028 Uiso 1 1 calc R ...
 C1 C -0.0374(2) 0.07384(8) 0.6605(3) 0.0289(6) Uani 1 1 d ...
 H1A H -0.0276 0.0746 0.5709 0.043 Uiso 1 1 calc R ...
 H1B H -0.0481 0.1001 0.6900 0.043 Uiso 1 1 calc R ...
 H1C H -0.1133 0.0585 0.6637 0.043 Uiso 1 1 calc R ...
 C2 C 0.0337(3) 0.18950(7) 0.5146(3) 0.0246(6) Uani 1 1 d ...
 H2A H 0.0244 0.1973 0.4217 0.029 Uiso 1 1 calc R ...
 C3 C 0.3050(2) 0.05594(7) 0.7414(2) 0.0192(5) Uani 1 1 d ...
 C4 C 0.4301(2) 0.17624(7) 0.6987(2) 0.0177(5) Uani 1 1 d ...
 C5 C 0.6752(3) 0.25109(8) 0.6969(3) 0.0345(7) Uani 1 1 d ...
 H5A H 0.6170 0.2589 0.6142 0.052 Uiso 1 1 calc R ...
 H5B H 0.7643 0.2521 0.6888 0.052 Uiso 1 1 calc R ...
 H5C H 0.6650 0.2686 0.7662 0.052 Uiso 1 1 calc R ...
 C6 C 0.1551(2) 0.06990(7) 0.3377(2) 0.0218(5) Uani 1 1 d ...
 H6A H 0.0707 0.0736 0.2729 0.026 Uiso 1 1 calc R ...
 C7 C 0.5304(2) 0.05766(7) 0.7281(3) 0.0236(5) Uani 1 1 d ...
 H7A H 0.5371 0.0350 0.7877 0.028 Uiso 1 1 calc R ...
 C8 C 0.0692(3) 0.05453(8) 0.8907(3) 0.0352(7) Uani 1 1 d ...
 H8A H 0.1467 0.0429 0.9464 0.053 Uiso 1 1 calc R ...
 H8B H -0.0061 0.0391 0.8953 0.053 Uiso 1 1 calc R ...
 H8C H 0.0591 0.0808 0.9208 0.053 Uiso 1 1 calc R ...
 C9 C 0.2426(3) -0.03877(8) 0.6797(3) 0.0330(7) Uani 1 1 d ...
 H9A H 0.1879 -0.0231 0.6108 0.050 Uiso 1 1 calc R ...
 H9B H 0.1937 -0.0464 0.7427 0.050 Uiso 1 1 calc R ...
 H9C H 0.2708 -0.0619 0.6412 0.050 Uiso 1 1 calc R ...
 C10 C 0.0886(2) 0.12928(7) 0.4279(2) 0.0184(5) Uani 1 1 d ...
 C11 C 0.6433(2) 0.21021(7) 0.7302(2) 0.0222(5) Uani 1 1 d ...
 H11A H 0.6557 0.1927 0.6592 0.027 Uiso 1 1 calc R ...
 C12 C 0.3305(3) 0.18889(8) 0.3653(2) 0.0275(6) Uani 1 1 d ...
 H12A H 0.2722 0.2049 0.4012 0.041 Uiso 1 1 calc R ...
 H12B H 0.2876 0.1647 0.3326 0.041 Uiso 1 1 calc R ...
 H12C H 0.3540 0.2027 0.2936 0.041 Uiso 1 1 calc R ...
 C13 C 0.2607(3) 0.06662(8) 0.2654(3) 0.0314(6) Uani 1 1 d ...
 H13A H 0.2629 0.0902 0.2148 0.047 Uiso 1 1 calc R ...
 H13B H 0.2436 0.0444 0.2064 0.047 Uiso 1 1 calc R ...
 H13C H 0.3438 0.0632 0.3283 0.047 Uiso 1 1 calc R ...
 C14 C 0.6145(2) 0.09005(8) 0.7997(3) 0.0288(6) Uani 1 1 d ...
 H14A H 0.5845 0.0975 0.8765 0.043 Uiso 1 1 calc R ...
 H14B H 0.6094 0.1123 0.7415 0.043 Uiso 1 1 calc R ...
 H14C H 0.7039 0.0812 0.8272 0.043 Uiso 1 1 calc R ...
 C15 C 0.5784(3) 0.04612(9) 0.6100(3) 0.0356(7) Uani 1 1 d ...

H15A H 0.5250 0.0251 0.5637 0.053 Uiso 1 1 calc R..
 H15B H 0.6679 0.0375 0.6383 0.053 Uiso 1 1 calc R..
 H15C H 0.5732 0.0683 0.5517 0.053 Uiso 1 1 calc R..
 C16 C 0.3593(3) -0.01540(7) 0.7486(3) 0.0250(6) Uani 1 1 d...
 H16A H 0.4089 -0.0083 0.6834 0.030 Uiso 1 1 calc R..
 C17 C 0.4512(2) 0.18031(7) 0.4715(2) 0.0218(5) Uani 1 1 d...
 H17A H 0.4946 0.2052 0.5037 0.026 Uiso 1 1 calc R..
 C19 C 0.3878(3) 0.13413(7) 0.9993(2) 0.0272(6) Uani 1 1 d...
 H19A H 0.4263 0.1112 0.9699 0.041 Uiso 1 1 calc R..
 H19B H 0.2951 0.1302 0.9863 0.041 Uiso 1 1 calc R..
 H19C H 0.4270 0.1385 1.0920 0.041 Uiso 1 1 calc R..
 C20 C -0.0109(3) 0.18185(7) 0.1558(2) 0.0270(6) Uani 1 1 d...
 H20A H 0.0608 0.1947 0.2164 0.040 Uiso 1 1 calc R..
 H20B H -0.0924 0.1930 0.1644 0.040 Uiso 1 1 calc R..
 H20C H -0.0028 0.1854 0.0663 0.040 Uiso 1 1 calc R..
 C21 C -0.1003(3) 0.18834(9) 0.5389(3) 0.0368(7) Uani 1 1 d...
 H21A H -0.1523 0.1690 0.4821 0.055 Uiso 1 1 calc R..
 H21B H -0.1409 0.2137 0.5200 0.055 Uiso 1 1 calc R..
 H21C H -0.0940 0.1816 0.6302 0.055 Uiso 1 1 calc R..
 C22 C 0.5438(3) 0.15553(8) 0.4176(3) 0.0302(6) Uani 1 1 d...
 H22A H 0.6211 0.1503 0.4869 0.045 Uiso 1 1 calc R..
 H22B H 0.5678 0.1692 0.3461 0.045 Uiso 1 1 calc R..
 H22C H 0.5019 0.1311 0.3851 0.045 Uiso 1 1 calc R..
 C23 C 0.4116(2) 0.16924(7) 0.9205(2) 0.0209(5) Uani 1 1 d...
 H23A H 0.5066 0.1732 0.9379 0.025 Uiso 1 1 calc R..
 C24 C 0.1496(3) 0.03287(7) 0.4148(3) 0.0270(6) Uani 1 1 d...
 H24A H 0.0804 0.0349 0.4601 0.040 Uiso 1 1 calc R..
 H24B H 0.2319 0.0292 0.4788 0.040 Uiso 1 1 calc R..
 H24C H 0.1331 0.0109 0.3549 0.040 Uiso 1 1 calc R..
 C25 C 0.4462(3) -0.03907(8) 0.8560(3) 0.0374(7) Uani 1 1 d...
 H25A H 0.5216 -0.0237 0.8982 0.056 Uiso 1 1 calc R..
 H25B H 0.4740 -0.0624 0.8183 0.056 Uiso 1 1 calc R..
 H25C H 0.3988 -0.0463 0.9207 0.056 Uiso 1 1 calc R..
 C26 C 0.1161(3) 0.21983(7) 0.6006(3) 0.0312(6) Uani 1 1 d...
 H26A H 0.2014 0.2205 0.5824 0.047 Uiso 1 1 calc R..
 H26B H 0.1249 0.2133 0.6924 0.047 Uiso 1 1 calc R..
 H26C H 0.0752 0.2451 0.5821 0.047 Uiso 1 1 calc R..
 C27 C -0.0086(2) 0.13900(7) 0.1873(2) 0.0209(5) Uani 1 1 d...
 H27A H 0.0746 0.1280 0.1771 0.025 Uiso 1 1 calc R..
 C28 C 0.0817(2) 0.05578(7) 0.7492(3) 0.0250(6) Uani 1 1 d...
 H28A H 0.0880 0.0286 0.7197 0.030 Uiso 1 1 calc R..
 C29 C 0.7329(2) 0.19725(8) 0.8571(3) 0.0302(6) Uani 1 1 d...
 H29A H 0.7110 0.1709 0.8769 0.045 Uiso 1 1 calc R..
 H29B H 0.7238 0.2145 0.9276 0.045 Uiso 1 1 calc R..
 H29C H 0.8219 0.1980 0.8489 0.045 Uiso 1 1 calc R..
 C50 C 0.3528(3) 0.20538(7) 0.9662(3) 0.0280(6) Uani 1 1 d...
 H50A H 0.3688 0.2277 0.9156 0.042 Uiso 1 1 calc R..
 H50B H 0.3923 0.2098 1.0589 0.042 Uiso 1 1 calc R..
 H50C H 0.2599 0.2018 0.9534 0.042 Uiso 1 1 calc R..
 C51 C -0.1184(3) 0.11802(8) 0.0937(2) 0.0284(6) Uani 1 1 d...
 H51A H -0.1152 0.0906 0.1159 0.043 Uiso 1 1 calc R..
 H51B H -0.1097 0.1212 0.0042 0.043 Uiso 1 1 calc R..
 H51C H -0.2007 0.1289 0.1009 0.043 Uiso 1 1 calc R..

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Zn2 0.01792(16) 0.01650(15) 0.01927(16) -0.00108(11) 0.00665(11) -0.00054(10)
Cl1 0.0262(3) 0.0294(3) 0.0283(3) -0.0042(3) 0.0143(3) -0.0003(3)
N1 0.0182(10) 0.0161(10) 0.0210(11) 0.0004(8) 0.0064(8) 0.0026(8)
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N3 0.0159(10) 0.0234(11) 0.0213(11) 0.0026(9) 0.0043(8) -0.0017(8)
N4 0.0210(11) 0.0161(10) 0.0191(10) -0.0004(8) 0.0076(8) -0.0038(8)
N5 0.0183(10) 0.0169(10) 0.0197(10) -0.0029(8) 0.0061(8) -0.0008(8)
N6 0.0188(11) 0.0139(10) 0.0277(11) -0.0026(8) 0.0075(9) -0.0013(8)
N7 0.0153(10) 0.0175(10) 0.0214(11) -0.0020(8) 0.0053(8) -0.0027(8)
N8 0.0170(10) 0.0160(10) 0.0226(11) 0.0009(8) 0.0039(8) 0.0003(8)
N9 0.0298(12) 0.0183(11) 0.0223(11) 0.0032(9) 0.0081(9) 0.0027(9)
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C2 0.0294(14) 0.0197(13) 0.0251(13) 0.0028(10) 0.0075(11) 0.0096(11)
C3 0.0223(13) 0.0175(12) 0.0169(12) -0.0021(9) 0.0033(10) -0.0030(9)
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C7 0.0196(13) 0.0187(13) 0.0308(14) 0.0007(11) 0.0032(11) 0.0013(10)
C8 0.0411(18) 0.0310(16) 0.0400(17) 0.0057(13) 0.0221(14) -0.0027(13)
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C10 0.0178(12) 0.0176(12) 0.0201(12) 0.0023(10) 0.0053(10) -0.0021(9)
C11 0.0199(13) 0.0224(13) 0.0262(13) -0.0036(10) 0.0093(10) -0.0036(10)
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C13 0.0376(17) 0.0289(15) 0.0302(15) -0.0075(12) 0.0130(13) 0.0000(12)
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C15 0.0222(14) 0.0356(16) 0.0501(19) -0.0145(14) 0.0108(13) -0.0006(12)
C16 0.0305(15) 0.0177(13) 0.0265(14) 0.0011(10) 0.0066(11) 0.0008(10)
C17 0.0260(13) 0.0210(13) 0.0201(13) -0.0014(10) 0.0088(10) -0.0066(10)
C19 0.0331(15) 0.0284(15) 0.0190(13) 0.0020(11) 0.0045(11) -0.0010(11)
C20 0.0369(16) 0.0222(13) 0.0221(13) 0.0018(11) 0.0076(12) 0.0023(11)
C21 0.0316(16) 0.0436(18) 0.0353(16) -0.0035(13) 0.0086(13) 0.0160(13)
C22 0.0321(16) 0.0328(16) 0.0302(15) -0.0027(12) 0.0165(12) -0.0046(12)
C23 0.0230(13) 0.0213(13) 0.0188(12) -0.0014(10) 0.0060(10) -0.0031(10)
C24 0.0285(15) 0.0185(13) 0.0321(15) -0.0040(11) 0.0041(12) -0.0011(10)
C25 0.0439(18) 0.0230(14) 0.0406(17) 0.0034(13) 0.0010(14) 0.0078(13)
C26 0.0443(17) 0.0160(13) 0.0336(15) -0.0006(11) 0.0106(13) 0.0056(12)
C27 0.0222(13) 0.0203(13) 0.0195(13) 0.0012(10) 0.0036(10) 0.0013(10)
C28 0.0250(14) 0.0194(13) 0.0329(15) 0.0001(11) 0.0114(11) -0.0053(10)
C29 0.0209(14) 0.0366(16) 0.0323(15) -0.0015(13) 0.0047(11) 0.0010(12)
C50 0.0341(16) 0.0255(14) 0.0274(14) -0.0075(11) 0.0133(12) -0.0063(11)
C51 0.0302(15) 0.0306(15) 0.0216(13) 0.0019(11) 0.0011(11) -0.0066(12)

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;

All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic)

treatment of cell esds is used for estimating esds involving l.s. planes.

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Zn2 N1 2.040(2) . ?
Zn2 N7 2.054(2) . ?
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 N8 Zn1 Zn2 88.29(6) . . ?
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 N1 Zn2 N7 110.36(8) . . ?
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A.7 Compound 11

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'H' 'H' 0.0000 0.0000
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'x+1/2, -y+1/2, z+1/2'
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\l = 0.00 \% (600 frames), at \l = 90.00 \%
(600 frames), at \l = 180 \% (600 frames) and
at \l = 270 \% (600 frames).
Frame width = 0.30 \& in \w. Data is
merged, corrected for decay, and treated with
multi-scan absorption corrections.
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_diffn_measurement_method       \w
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_refine_special_details
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Refinement of F2 against ALL reflections. The weighted R-factor wR and
goodness of fit S are based on F2, conventional R-factors R are based
on F, with F set to zero for negative F2. The threshold expression of
F2 > 2sigma(F2) is used only for calculating R-factors(gt) etc. and is
not relevant to the choice of reflections for refinement. R-factors based
on F2 are statistically about twice as large as those based on F, and R-
factors based on ALL data will be even larger. H12a, H12b, and H12c were
located from the diff. map and refined riding thermal parameters.
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_atom_sites_solution_hydrogens  geom
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C2 C 0.8682(3) 0.12904(19) 0.9179(2) 0.0269(6) Uani 1 1 d ...
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C11 C 1.1104(2) 0.20702(15) 0.73368(19) 0.0229(5) Uani 1 1 d ...
C12 C 1.2663(3) 0.21759(19) 0.7425(2) 0.0320(6) Uani 1 1 d D ..
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H12B H 1.307(3) 0.1652(13) 0.759(2) 0.048 Uiso 1 1 d D ..
H12C H 1.304(3) 0.2577(15) 0.7899(19) 0.048 Uiso 1 1 d D ..
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H15B H 1.0777 -0.0818 0.7202 0.057 Uiso 1 1 calc R ..
H15C H 0.9439 -0.0272 0.6768 0.057 Uiso 1 1 calc R ..
C16 C 1.0649(3) 0.36334(16) 0.7571(2) 0.0261(5) Uani 1 1 d ...
H16A H 1.1467 0.3646 0.8121 0.031 Uiso 1 1 calc R ..
C17 C 0.9480(3) 0.41673(16) 0.8075(2) 0.0319(6) Uani 1 1 d ...
H17A H 0.9281 0.3947 0.8840 0.048 Uiso 1 1 calc R ..
H17B H 0.8638 0.4118 0.7583 0.048 Uiso 1 1 calc R ..
H17C H 0.9766 0.4781 0.8127 0.048 Uiso 1 1 calc R ..
C18 C 1.1102(3) 0.40300(17) 0.6445(2) 0.0374(6) Uani 1 1 d ...
H18A H 1.1845 0.3672 0.6126 0.056 Uiso 1 1 calc R ..
H18B H 1.1450 0.4624 0.6580 0.056 Uiso 1 1 calc R ..
H18C H 1.0301 0.4048 0.5905 0.056 Uiso 1 1 calc R ..

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C9 0.0421(15) 0.0281(15) 0.0340(15) 0.0116(12) -0.0184(12) -0.0047(12)
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All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

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 C6 Ti C9 C10 -37.86(17) ?
 C8 Ti C9 C10 -116.3(2) ?
 C1 Ti C9 C10 159.62(17) ?
 C2 Ti C9 C10 -179.1(3) ?
 C7 Ti C9 C10 -78.84(18) ?
 C8 C9 C10 C6 1.1(3) ?
 Ti C9 C10 C6 66.5(2) ?
 C8 C9 C10 Ti -65.44(19) ?
 C7 C6 C10 C9 -0.4(3) ?
 Ti C6 C10 C9 -66.7(2) ?
 C7 C6 C10 Ti 66.30(18) ?
 N1 Ti C10 C9 -149.07(18) ?
 N2 Ti C10 C9 -87.35(17) ?
 C4 Ti C10 C9 65.0(2) ?
 C3 Ti C10 C9 115.60(19) ?
 C5 Ti C10 C9 12.9(3) ?
 C6 Ti C10 C9 115.0(3) ?
 C8 Ti C10 C9 36.52(16) ?
 C1 Ti C10 C9 -55.2(4) ?
 C2 Ti C10 C9 179.4(2) ?
 C7 Ti C10 C9 77.46(17) ?
 N1 Ti C10 C6 95.96(17) ?
 N2 Ti C10 C6 157.68(17) ?
 C4 Ti C10 C6 -50.0(2) ?
 C3 Ti C10 C6 0.6(3) ?
 C5 Ti C10 C6 -102.0(2) ?
 C9 Ti C10 C6 -115.0(3) ?
 C8 Ti C10 C6 -78.44(18) ?
 C1 Ti C10 C6 -170.2(3) ?
 C2 Ti C10 C6 64.4(3) ?
 C7 Ti C10 C6 -37.51(16) ?
 C13 N1 C11 N2 177.0(2) ?
 Ti N1 C11 N2 -1.11(19) ?
 C13 N1 C11 C12 -4.5(4) ?
 Ti N1 C11 C12 177.4(2) ?
 C13 N1 C11 Ti 178.1(2) ?
 C16 N2 C11 N1 -178.45(19) ?
 Ti N2 C11 N1 1.11(19) ?
 C16 N2 C11 C12 3.1(3) ?
 Ti N2 C11 C12 -177.4(2) ?
 C16 N2 C11 Ti -179.6(2) ?
 N2 Ti C11 N1 -178.8(2) ?
 C10 Ti C11 N1 -86.82(15) ?
 C4 Ti C11 N1 89.59(18) ?
 C3 Ti C11 N1 58.97(15) ?
 C5 Ti C11 N1 123.97(14) ?
 C6 Ti C11 N1 -58.85(16) ?
 C9 Ti C11 N1 -117.05(15) ?
 C8 Ti C11 N1 -116.72(15) ?
 C1 Ti C11 N1 109.07(15) ?
 C2 Ti C11 N1 75.52(15) ?
 C7 Ti C11 N1 -67.13(18) ?
 N1 Ti C11 N2 178.8(2) ?

C10 Ti C11 N2 91.93(15) ?
 C4 Ti C11 N2 -91.65(18) ?
 C3 Ti C11 N2 -122.28(14) ?
 C5 Ti C11 N2 -57.27(16) ?
 C6 Ti C11 N2 119.91(14) ?
 C9 Ti C11 N2 61.71(15) ?
 C8 Ti C11 N2 62.03(17) ?
 C1 Ti C11 N2 -72.17(14) ?
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 C7 Ti C11 N2 111.62(16) ?
 N1 Ti C11 C12 -95(5) ?
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 C10 Ti C11 C12 178(100) ?
 C4 Ti C11 C12 -5(5) ?
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 C5 Ti C11 C12 29(5) ?
 C6 Ti C11 C12 -154(5) ?
 C9 Ti C11 C12 148(5) ?
 C8 Ti C11 C12 148(5) ?
 C1 Ti C11 C12 14(5) ?
 C2 Ti C11 C12 -19(5) ?
 C7 Ti C11 C12 -162(5) ?
 C11 N1 C13 C15 159.7(2) ?
 Ti N1 C13 C15 -23.5(4) ?
 C11 N1 C13 C14 -77.7(3) ?
 Ti N1 C13 C14 99.1(3) ?
 C11 N2 C16 C17 -159.3(2) ?
 Ti N2 C16 C17 21.4(4) ?
 C11 N2 C16 C18 77.6(3) ?
 Ti N2 C16 C18 -101.7(3) ?

 _diffn_measured_fraction_theta_max 0.997
 _diffn_reflns_theta_full 25.00
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 _refine_diff_density_max 0.540
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 _refine_diff_density_rms 0.055

A.8 Compound 15

data_seab037

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?
;
_chemical_name_common       ?
_chemical_melting_point     ?
_chemical_formula_moiety    ?
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'C24 H51 Cl N6 Zn2'
_chemical_formula_weight    589.90
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_atom_type_symbol
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'C' 'C' 0.0033 0.0016
'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
'H' 'H' 0.0000 0.0000
'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
'Cl' 'Cl' 0.1484 0.1585
'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
'N' 'N' 0.0061 0.0033
'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
'Zn' 'Zn' 0.2839 1.4301
'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
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_symmetry_cell_setting      Monoclinic
_symmetry_space_group_name_H-M P2(1)
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_symmetry_equiv_pos_as_xyz
'x, y, z'
'-x, y+1/2, -z'
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_cell_length_a              10.028(4)
_cell_length_b              10.595(4)
_cell_length_c              29.245(11)
_cell_angle_alpha           90.00
_cell_angle_beta            96.308(6)
_cell_angle_gamma           90.00
_cell_volume                3088(2)
_cell_formula_units_Z       4
_cell_measurement_temperature 170(2)
_cell_measurement_reflns_used 984
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_cell_measurement_theta_max 28.25
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_exptl_crystal_colour        colourless
_exptl_crystal_size_max      0.26
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_exptl_crystal_density_diffn  1.269
_exptl_crystal_density_method 'not measured'
_exptl_crystal_F_000         1256
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_exptl_absorpt_correction_T_min 0.6748
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_exptl_absorpt_process_details 'SADABS (Sheldrick, 2003)'

_exptl_special_details
;
Data collection is performed with four batch runs at
\<math>\omega</math> = 0.00 \% (600 frames), at \<math>\omega</math> = 90.00 \%
(600 frames), at \<math>\omega</math> = 180 \% (600 frames) and
at \<math>\omega</math> = 270 \% (600 frames).
Frame width = 0.30 \& in \<math>\omega</math>. Data is
merged, corrected for decay, and treated with
multi-scan absorption corrections.
;

_diffn_ambient_temperature    170(2)
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_diffn_radiation_type          MoK\alpha
_diffn_radiation_source        'fine-focus sealed tube'
_diffn_radiation_monochromator graphite
_diffn_measurement_device_type 'Bruker AXS APEX diffractometer'
_diffn_measurement_method      \<math>\omega</math>
_diffn_detector_area_resol_mean 836.6
_diffn_standards_number        0
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_diffn_reflns_number           42572
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_diffn_reflns_limit_l_max      38
_diffn_reflns_theta_min        1.40
_diffn_reflns_theta_max        28.31
_reflns_number_total           15329
_reflns_number_gt              13854
_reflns_threshold_expression    >2sigma(I)

_computing_data_collection      'SMART (Bruker, 2002)'
_computing_cell_refinement      'SAINT (Bruker, 2002)'

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_computing_structure_solution  'SHELXS-97 (Sheldrick, 1990)'
_computing_structure_refinement 'SHELXL-97 (Sheldrick, 1997)'
_computing_molecular_graphics  'SHELXTL (Sheldrick, 2001)'
_computing_publication_material 'SHELXTL (Sheldrick, 2001)'

_refine_special_details
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Refinement of  $F^2$  against ALL reflections. The weighted R-factor wR and
goodness of fit S are based on  $F^2$ , conventional R-factors R are based
on F, with F set to zero for negative  $F^2$ . The threshold expression of
 $F^2 > 2\sigma(F^2)$  is used only for calculating R-factors(gt) etc. and is
not relevant to the choice of reflections for refinement. R-factors based
on  $F^2$  are statistically about twice as large as those based on F, and R-
factors based on ALL data will be even larger.
;

_refine_ls_structure_factor_coef Fsqd
_refine_ls_matrix_type      full
_refine_ls_weighting_scheme  calc
_refine_ls_weighting_details
'calc w=1/[ $\sigma^2(F_o^2) + (0.0403P)^2$ ] where  $P=(F_o^2+2F_c^2)/3$ '
_atom_sites_solution_primary direct
_atom_sites_solution_secondary difmap
_atom_sites_solution_hydrogens geom
_refine_ls_hydrogen_treatment constr
_refine_ls_extinction_method none
_refine_ls_extinction_coef ?
_refine_ls_abs_structure_details
'Flack H D (1983), Acta Cryst. A39, 876-881'
_refine_ls_abs_structure_Flack -0.02(5)
_refine_ls_number_reflns      15329
_refine_ls_number_parameters  625
_refine_ls_number_restraints  1
_refine_ls_R_factor_all       0.0319
_refine_ls_R_factor_gt        0.0274
_refine_ls_wR_factor_ref       0.0685
_refine_ls_wR_factor_gt       0.0661
_refine_ls_goodness_of_fit_ref 1.037
_refine_ls_restrained_S_all    1.037
_refine_ls_shift/su_max        0.002
_refine_ls_shift/su_mean       0.000

loop_
_atom_site_label
_atom_site_type_symbol
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
_atom_site_U_iso_or_equiv
_atom_site_adp_type
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_atom_site_refinement_flags
_atom_site_disorder_assembly

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_atom_site_disorder_group

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 Zn2 Zn 0.29597(2) 0.57083(2) 0.106773(7) 0.02827(5) Uani 1 1 d ...
 Zn3 Zn 0.90800(2) 0.191517(19) 0.323075(7) 0.02709(5) Uani 1 1 d ...
 Zn4 Zn 0.75263(2) 0.07252(2) 0.394870(7) 0.02838(5) Uani 1 1 d ...
 Cl1 Cl -0.07246(5) 0.72410(5) 0.19497(2) 0.04036(12) Uani 1 1 d ...
 Cl2 Cl 1.11265(5) 0.21949(5) 0.30271(2) 0.04202(12) Uani 1 1 d ...
 N1 N 0.22898(16) 0.83345(16) 0.14590(6) 0.0310(4) Uani 1 1 d ...
 N2 N 0.41096(15) 0.70427(17) 0.13957(5) 0.0313(3) Uani 1 1 d ...
 N3 N 0.25418(15) 0.59083(15) 0.21992(5) 0.0264(3) Uani 1 1 d ...
 N4 N 0.16967(16) 0.50857(14) 0.15211(5) 0.0260(3) Uani 1 1 d ...
 N5 N 0.35941(19) 0.43842(17) 0.06097(6) 0.0371(4) Uani 1 1 d ...
 N6 N 0.24493(19) 0.60992(18) 0.03908(6) 0.0383(4) Uani 1 1 d ...
 N7 N 0.80301(18) 0.32876(15) 0.34723(5) 0.0308(3) Uani 1 1 d ...
 N8 N 0.62922(15) 0.19609(18) 0.35975(6) 0.0339(3) Uani 1 1 d ...
 N9 N 0.78621(15) 0.07422(17) 0.28082(5) 0.0300(3) Uani 1 1 d ...
 N10 N 0.87793(15) 0.00690(14) 0.34953(5) 0.0256(3) Uani 1 1 d ...
 N11 N 0.79963(18) 0.12431(17) 0.46196(6) 0.0349(4) Uani 1 1 d ...
 N12 N 0.69943(19) -0.05661(18) 0.44361(6) 0.0384(4) Uani 1 1 d ...
 C1 C 0.1710(2) 0.9629(2) 0.14590(8) 0.0430(5) Uani 1 1 d ...
 H1A H 0.2318 1.0209 0.1309 0.052 Uiso 1 1 calc R ...
 C2 C 0.0335(3) 0.9654(2) 0.11742(9) 0.0515(6) Uani 1 1 d ...
 H2A H 0.0432 0.9400 0.0857 0.077 Uiso 1 1 calc R ...
 H2B H -0.0035 1.0510 0.1175 0.077 Uiso 1 1 calc R ...
 H2C H -0.0271 0.9069 0.1308 0.077 Uiso 1 1 calc R ...
 C3 C 0.1622(3) 1.0102(2) 0.19445(9) 0.0536(7) Uani 1 1 d ...
 H3A H 0.2518 1.0091 0.2117 0.080 Uiso 1 1 calc R ...
 H3B H 0.1020 0.9555 0.2097 0.080 Uiso 1 1 calc R ...
 H3C H 0.1273 1.0967 0.1933 0.080 Uiso 1 1 calc R ...
 C4 C 0.55756(19) 0.6820(2) 0.14562(8) 0.0403(5) Uani 1 1 d ...
 H4A H 0.6019 0.7536 0.1636 0.048 Uiso 1 1 calc R ...
 C5 C 0.5855(2) 0.5604(3) 0.17291(8) 0.0473(6) Uani 1 1 d ...
 H5A H 0.5546 0.5697 0.2034 0.071 Uiso 1 1 calc R ...
 H5B H 0.6820 0.5431 0.1763 0.071 Uiso 1 1 calc R ...
 H5C H 0.5376 0.4903 0.1566 0.071 Uiso 1 1 calc R ...
 C6 C 0.6132(2) 0.6751(3) 0.09920(9) 0.0580(7) Uani 1 1 d ...
 H6A H 0.5988 0.7561 0.0832 0.087 Uiso 1 1 calc R ...
 H6B H 0.5670 0.6081 0.0805 0.087 Uiso 1 1 calc R ...
 H6C H 0.7095 0.6567 0.1040 0.087 Uiso 1 1 calc R ...
 C7 C 0.3613(2) 0.8183(2) 0.14358(7) 0.0334(4) Uani 1 1 d ...
 C8 C 0.4517(3) 0.9340(2) 0.14455(9) 0.0507(6) Uani 1 1 d ...
 H8A H 0.5458 0.9074 0.1491 0.076 Uiso 1 1 calc R ...
 H8B H 0.4328 0.9895 0.1698 0.076 Uiso 1 1 calc R ...
 H8C H 0.4347 0.9795 0.1153 0.076 Uiso 1 1 calc R ...
 C9 C 0.3355(2) 0.6006(2) 0.26463(7) 0.0338(4) Uani 1 1 d ...
 H9A H 0.4144 0.5426 0.2652 0.041 Uiso 1 1 calc R ...
 C10 C 0.3847(3) 0.7357(2) 0.27053(8) 0.0507(6) Uani 1 1 d ...
 H10A H 0.4407 0.7565 0.2461 0.076 Uiso 1 1 calc R ...
 H10B H 0.4376 0.7450 0.3006 0.076 Uiso 1 1 calc R ...
 H10C H 0.3076 0.7930 0.2687 0.076 Uiso 1 1 calc R ...
 C11 C 0.2518(2) 0.5638(2) 0.30261(6) 0.0376(4) Uani 1 1 d ...
 H11A H 0.2294 0.4739 0.3000 0.056 Uiso 1 1 calc R ...
 H11B H 0.1690 0.6137 0.2998 0.056 Uiso 1 1 calc R ...
 H11C H 0.3028 0.5800 0.3326 0.056 Uiso 1 1 calc R ...
 C12 C 0.0731(2) 0.40869(19) 0.13593(7) 0.0323(4) Uani 1 1 d ...
 H12A H 0.1237 0.3307 0.1293 0.039 Uiso 1 1 calc R ...

C13 C -0.0076(2) 0.4535(3) 0.09163(7) 0.0489(6) Uani 1 1 d . . .
 H13A H 0.0529 0.4667 0.0679 0.073 Uiso 1 1 calc R . .
 H13B H -0.0527 0.5330 0.0974 0.073 Uiso 1 1 calc R . .
 H13C H -0.0747 0.3896 0.0811 0.073 Uiso 1 1 calc R . .
 C14 C -0.0230(2) 0.3778(2) 0.17180(8) 0.0377(5) Uani 1 1 d . . .
 H14A H 0.0287 0.3483 0.2002 0.057 Uiso 1 1 calc R . .
 H14B H -0.0855 0.3115 0.1598 0.057 Uiso 1 1 calc R . .
 H14C H -0.0734 0.4537 0.1783 0.057 Uiso 1 1 calc R . .
 C15 C 0.24166(18) 0.48935(18) 0.19538(6) 0.0262(4) Uani 1 1 d . . .
 C16 C 0.3018(2) 0.36301(19) 0.20951(8) 0.0367(5) Uani 1 1 d . . .
 H16A H 0.2901 0.3049 0.1833 0.055 Uiso 1 1 calc R . .
 H16B H 0.2569 0.3287 0.2349 0.055 Uiso 1 1 calc R . .
 H16C H 0.3977 0.3733 0.2195 0.055 Uiso 1 1 calc R . .
 C17 C 0.4188(2) 0.3142(2) 0.05422(8) 0.0447(5) Uani 1 1 d . . .
 H17A H 0.4608 0.3162 0.0248 0.054 Uiso 1 1 calc R . .
 C18 C 0.5271(3) 0.2860(3) 0.09291(11) 0.0720(9) Uani 1 1 d . . .
 H18A H 0.5998 0.3477 0.0925 0.108 Uiso 1 1 calc R . .
 H18B H 0.5624 0.2009 0.0890 0.108 Uiso 1 1 calc R . .
 H18C H 0.4895 0.2912 0.1224 0.108 Uiso 1 1 calc R . .
 C19 C 0.3135(3) 0.2113(3) 0.05070(12) 0.0753(9) Uani 1 1 d . . .
 H19A H 0.2491 0.2260 0.0235 0.113 Uiso 1 1 calc R . .
 H19B H 0.2664 0.2121 0.0783 0.113 Uiso 1 1 calc R . .
 H19C H 0.3569 0.1292 0.0480 0.113 Uiso 1 1 calc R . .
 C20 C 0.1864(2) 0.7102(2) 0.00850(7) 0.0456(5) Uani 1 1 d . . .
 H20A H 0.2002 0.6884 -0.0239 0.055 Uiso 1 1 calc R . .
 C21 C 0.2545(3) 0.8352(2) 0.02080(8) 0.0484(6) Uani 1 1 d . . .
 H21A H 0.3508 0.8277 0.0182 0.073 Uiso 1 1 calc R . .
 H21B H 0.2410 0.8579 0.0525 0.073 Uiso 1 1 calc R . .
 H21C H 0.2158 0.9008 -0.0003 0.073 Uiso 1 1 calc R . .
 C22 C 0.0367(3) 0.7180(3) 0.01224(13) 0.0788(10) Uani 1 1 d . . .
 H22A H -0.0071 0.6407 -0.0002 0.118 Uiso 1 1 calc R . .
 H22B H -0.0011 0.7910 -0.0052 0.118 Uiso 1 1 calc R . .
 H22C H 0.0216 0.7272 0.0446 0.118 Uiso 1 1 calc R . .
 C23 C 0.3050(2) 0.5082(2) 0.02599(7) 0.0394(5) Uani 1 1 d . . .
 C24 C 0.3100(3) 0.4732(3) -0.02411(8) 0.0578(7) Uani 1 1 d . . .
 H24A H 0.2316 0.5085 -0.0427 0.087 Uiso 1 1 calc R . .
 H24B H 0.3096 0.3811 -0.0272 0.087 Uiso 1 1 calc R . .
 H24C H 0.3921 0.5073 -0.0347 0.087 Uiso 1 1 calc R . .
 C25 C 0.4843(2) 0.1676(2) 0.35728(9) 0.0467(6) Uani 1 1 d . . .
 H25A H 0.4348 0.2270 0.3349 0.056 Uiso 1 1 calc R . .
 C26 C 0.4330(2) 0.1854(3) 0.40428(10) 0.0614(7) Uani 1 1 d . . .
 H26A H 0.4474 0.2731 0.4143 0.092 Uiso 1 1 calc R . .
 H26B H 0.4818 0.1288 0.4267 0.092 Uiso 1 1 calc R . .
 H26C H 0.3370 0.1659 0.4018 0.092 Uiso 1 1 calc R . .
 C27 C 0.4603(2) 0.0336(2) 0.33969(10) 0.0615(8) Uani 1 1 d . . .
 H27A H 0.4944 0.0248 0.3097 0.092 Uiso 1 1 calc R . .
 H27B H 0.3639 0.0154 0.3365 0.092 Uiso 1 1 calc R . .
 H27C H 0.5073 -0.0259 0.3615 0.092 Uiso 1 1 calc R . .
 C28 C 0.8545(3) 0.4590(2) 0.34349(7) 0.0412(5) Uani 1 1 d . . .
 H28A H 0.7899 0.5180 0.3561 0.049 Uiso 1 1 calc R . .
 C29 C 0.9899(3) 0.4724(2) 0.37233(8) 0.0494(6) Uani 1 1 d . . .
 H29A H 0.9805 0.4502 0.4043 0.074 Uiso 1 1 calc R . .
 H29B H 1.0210 0.5599 0.3709 0.074 Uiso 1 1 calc R . .
 H29C H 1.0551 0.4159 0.3603 0.074 Uiso 1 1 calc R . .
 C30 C 0.8641(3) 0.4950(2) 0.29337(8) 0.0556(7) Uani 1 1 d . . .
 H30A H 0.7752 0.4888 0.2759 0.083 Uiso 1 1 calc R . .

H30B H 0.9262 0.4375 0.2801 0.083 Uiso 1 1 calc R . .
 H30C H 0.8972 0.5818 0.2919 0.083 Uiso 1 1 calc R . .
 C31 C 0.6724(2) 0.3094(2) 0.35036(7) 0.0332(4) Uani 1 1 d . . .
 C32 C 0.5750(3) 0.4196(2) 0.34387(10) 0.0542(7) Uani 1 1 d . . .
 H32A H 0.4839 0.3875 0.3354 0.081 Uiso 1 1 calc R . .
 H32B H 0.6005 0.4748 0.3194 0.081 Uiso 1 1 calc R . .
 H32C H 0.5777 0.4674 0.3726 0.081 Uiso 1 1 calc R . .
 C33 C 0.7003(2) 0.0733(2) 0.23658(6) 0.0377(4) Uani 1 1 d . . .
 H33A H 0.6357 0.0013 0.2362 0.045 Uiso 1 1 calc R . .
 C34 C 0.6226(3) 0.1970(3) 0.23227(9) 0.0737(10) Uani 1 1 d . . .
 H34A H 0.5682 0.2050 0.2580 0.110 Uiso 1 1 calc R . .
 H34B H 0.5638 0.1979 0.2032 0.110 Uiso 1 1 calc R . .
 H34C H 0.6857 0.2678 0.2328 0.110 Uiso 1 1 calc R . .
 C35 C 0.7866(2) 0.0578(2) 0.19768(7) 0.0398(5) Uani 1 1 d . . .
 H35A H 0.8229 -0.0281 0.1981 0.060 Uiso 1 1 calc R . .
 H35B H 0.8607 0.1186 0.2014 0.060 Uiso 1 1 calc R . .
 H35C H 0.7322 0.0728 0.1683 0.060 Uiso 1 1 calc R . .
 C36 C 0.9815(2) -0.08519(18) 0.36814(7) 0.0304(4) Uani 1 1 d . . .
 H36A H 0.9362 -0.1624 0.3786 0.036 Uiso 1 1 calc R . .
 C37 C 1.0636(2) -0.0247(2) 0.40937(7) 0.0402(5) Uani 1 1 d . . .
 H37A H 1.0048 -0.0051 0.4331 0.060 Uiso 1 1 calc R . .
 H37B H 1.1050 0.0532 0.3996 0.060 Uiso 1 1 calc R . .
 H37C H 1.1339 -0.0834 0.4219 0.060 Uiso 1 1 calc R . .
 C38 C 1.0738(2) -0.1229(2) 0.33188(8) 0.0376(5) Uani 1 1 d . . .
 H38A H 1.0207 -0.1643 0.3060 0.056 Uiso 1 1 calc R . .
 H38B H 1.1428 -0.1811 0.3456 0.056 Uiso 1 1 calc R . .
 H38C H 1.1166 -0.0472 0.3209 0.056 Uiso 1 1 calc R . .
 C39 C 0.80532(18) -0.02206(18) 0.30712(7) 0.0285(4) Uani 1 1 d . . .
 C40 C 0.7534(2) -0.1530(2) 0.29625(8) 0.0388(5) Uani 1 1 d . . .
 H40A H 0.6552 -0.1527 0.2941 0.058 Uiso 1 1 calc R . .
 H40B H 0.7892 -0.2109 0.3207 0.058 Uiso 1 1 calc R . .
 H40C H 0.7821 -0.1806 0.2669 0.058 Uiso 1 1 calc R . .
 C41 C 0.8494(2) 0.2301(2) 0.49066(7) 0.0392(5) Uani 1 1 d . . .
 H41A H 0.8201 0.2193 0.5220 0.047 Uiso 1 1 calc R . .
 C42 C 0.7911(3) 0.3522(2) 0.47003(8) 0.0460(6) Uani 1 1 d . . .
 H42A H 0.6929 0.3489 0.4681 0.069 Uiso 1 1 calc R . .
 H42B H 0.8185 0.3633 0.4391 0.069 Uiso 1 1 calc R . .
 H42C H 0.8240 0.4233 0.4895 0.069 Uiso 1 1 calc R . .
 C43 C 1.0025(3) 0.2335(3) 0.49491(13) 0.0719(9) Uani 1 1 d . . .
 H43A H 1.0384 0.1557 0.5096 0.108 Uiso 1 1 calc R . .
 H43B H 1.0350 0.3062 0.5136 0.108 Uiso 1 1 calc R . .
 H43C H 1.0324 0.2406 0.4642 0.108 Uiso 1 1 calc R . .
 C44 C 0.6395(3) -0.1792(2) 0.45282(9) 0.0506(6) Uani 1 1 d . . .
 H44A H 0.6842 -0.2116 0.4828 0.061 Uiso 1 1 calc R . .
 C45 C 0.6649(3) -0.2720(2) 0.41571(10) 0.0618(7) Uani 1 1 d . . .
 H45A H 0.7617 -0.2839 0.4155 0.093 Uiso 1 1 calc R . .
 H45B H 0.6265 -0.2394 0.3858 0.093 Uiso 1 1 calc R . .
 H45C H 0.6229 -0.3530 0.4217 0.093 Uiso 1 1 calc R . .
 C46 C 0.4910(3) -0.1674(3) 0.45681(14) 0.0904(12) Uani 1 1 d . . .
 H46A H 0.4759 -0.0989 0.4782 0.136 Uiso 1 1 calc R . .
 H46B H 0.4575 -0.2469 0.4683 0.136 Uiso 1 1 calc R . .
 H46C H 0.4434 -0.1487 0.4265 0.136 Uiso 1 1 calc R . .
 C47 C 0.7448(2) 0.0220(2) 0.47730(7) 0.0362(5) Uani 1 1 d . . .
 C48 C 0.7355(3) -0.0046(2) 0.52773(8) 0.0505(6) Uani 1 1 d . . .
 H48A H 0.8108 0.0357 0.5463 0.076 Uiso 1 1 calc R . .
 H48B H 0.7386 -0.0960 0.5330 0.076 Uiso 1 1 calc R . .

H48C H 0.6508 0.0291 0.5364 0.076 Uiso 1 1 calc R . .

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Zn1 0.02453(10) 0.02333(10) 0.02918(10) 0.00184(10) 0.00299(8) 0.00005(12)
 Zn2 0.02737(11) 0.03061(11) 0.02762(10) 0.00192(10) 0.00661(8) 0.00057(12)
 Zn3 0.02767(11) 0.02391(10) 0.02943(10) -0.00054(10) 0.00201(8) 0.00069(12)
 Zn4 0.02370(10) 0.02895(11) 0.03307(11) -0.00309(11) 0.00570(8) -0.00090(12)
 Cl1 0.0306(2) 0.0356(3) 0.0568(3) 0.0014(2) 0.0135(2) 0.0033(2)
 Cl2 0.0362(3) 0.0368(3) 0.0552(3) 0.0043(2) 0.0147(2) -0.0038(2)
 N1 0.0325(9) 0.0252(8) 0.0358(9) 0.0031(7) 0.0056(7) -0.0024(7)
 N2 0.0232(7) 0.0347(9) 0.0362(8) 0.0038(8) 0.0036(6) -0.0047(7)
 N3 0.0229(7) 0.0290(8) 0.0272(7) 0.0022(6) 0.0026(6) -0.0020(6)
 N4 0.0263(8) 0.0247(8) 0.0273(8) 0.0015(6) 0.0051(6) -0.0023(6)
 N5 0.0403(10) 0.0370(10) 0.0359(9) 0.0000(8) 0.0131(8) 0.0053(8)
 N6 0.0460(11) 0.0400(10) 0.0292(9) 0.0040(7) 0.0060(8) 0.0047(8)
 N7 0.0392(9) 0.0256(8) 0.0275(8) -0.0015(6) 0.0036(7) 0.0035(7)
 N8 0.0217(7) 0.0369(9) 0.0419(9) -0.0084(9) -0.0013(6) 0.0051(8)
 N9 0.0247(8) 0.0334(8) 0.0313(8) -0.0074(8) -0.0002(6) 0.0040(7)
 N10 0.0221(8) 0.0247(8) 0.0300(8) -0.0008(6) 0.0038(6) 0.0018(6)
 N11 0.0372(10) 0.0349(9) 0.0327(9) -0.0044(7) 0.0050(7) -0.0044(8)
 N12 0.0379(10) 0.0354(9) 0.0447(10) -0.0017(8) 0.0164(8) -0.0074(8)
 C1 0.0481(14) 0.0252(10) 0.0577(14) 0.0079(10) 0.0154(11) 0.0009(9)
 C2 0.0551(16) 0.0471(14) 0.0535(14) 0.0163(12) 0.0117(12) 0.0216(12)
 C3 0.0569(16) 0.0347(13) 0.0697(17) -0.0175(12) 0.0092(13) -0.0037(11)
 C4 0.0231(9) 0.0488(13) 0.0492(12) 0.0077(11) 0.0049(8) -0.0032(9)
 C5 0.0275(11) 0.0608(15) 0.0533(13) 0.0170(13) 0.0033(9) 0.0066(11)
 C6 0.0348(12) 0.080(2) 0.0622(15) 0.0208(15) 0.0207(11) 0.0006(13)
 C7 0.0340(11) 0.0349(10) 0.0305(10) 0.0050(8) -0.0002(8) -0.0067(9)
 C8 0.0429(13) 0.0388(13) 0.0697(17) 0.0017(12) 0.0040(12) -0.0162(11)
 C9 0.0256(9) 0.0448(12) 0.0302(9) 0.0024(8) -0.0008(7) -0.0003(8)
 C10 0.0522(14) 0.0622(16) 0.0357(12) 0.0002(11) -0.0043(10) -0.0278(12)
 C11 0.0422(11) 0.0394(11) 0.0317(9) 0.0009(9) 0.0061(8) 0.0013(10)
 C12 0.0320(11) 0.0287(10) 0.0367(11) -0.0071(8) 0.0062(8) -0.0060(8)
 C13 0.0441(13) 0.0647(16) 0.0363(12) -0.0019(11) -0.0033(10) -0.0215(12)
 C14 0.0332(11) 0.0369(11) 0.0439(12) 0.0000(9) 0.0079(9) -0.0108(9)
 C15 0.0208(8) 0.0270(9) 0.0319(9) 0.0068(7) 0.0069(7) 0.0025(7)
 C16 0.0393(12) 0.0314(10) 0.0397(11) 0.0057(9) 0.0059(9) 0.0081(9)
 C17 0.0475(14) 0.0428(12) 0.0464(13) -0.0032(11) 0.0163(11) 0.0071(11)
 C18 0.070(2) 0.0563(18) 0.087(2) -0.0107(16) -0.0044(17) 0.0304(15)
 C19 0.0622(18) 0.0422(16) 0.121(3) -0.0032(17) 0.0096(18) 0.0032(14)
 C20 0.0581(14) 0.0474(14) 0.0304(10) 0.0079(10) 0.0002(9) 0.0054(12)
 C21 0.0565(16) 0.0433(13) 0.0462(13) 0.0144(11) 0.0093(11) 0.0024(11)
 C22 0.0483(16) 0.074(2) 0.107(3) 0.040(2) -0.0198(16) -0.0008(15)
 C23 0.0452(13) 0.0430(12) 0.0320(11) -0.0010(9) 0.0135(9) -0.0019(10)
 C24 0.080(2) 0.0615(17) 0.0338(12) -0.0034(12) 0.0164(12) 0.0085(15)
 C25 0.0234(10) 0.0522(15) 0.0639(15) -0.0186(12) 0.0018(10) 0.0038(9)
 C26 0.0280(11) 0.0746(18) 0.0847(19) -0.0278(17) 0.0194(11) -0.0050(13)
 C27 0.0267(12) 0.0623(17) 0.095(2) -0.0317(15) 0.0036(12) -0.0085(11)
 C28 0.0591(15) 0.0259(10) 0.0408(12) -0.0009(9) 0.0161(10) 0.0029(10)

C29 0.0664(17) 0.0385(13) 0.0452(13) -0.0060(10) 0.0152(12) -0.0222(12)
 C30 0.082(2) 0.0363(13) 0.0490(14) 0.0123(11) 0.0116(13) 0.0080(13)
 C31 0.0343(11) 0.0356(11) 0.0281(9) -0.0071(8) -0.0031(8) 0.0107(9)
 C32 0.0511(15) 0.0433(14) 0.0661(16) -0.0004(12) -0.0030(12) 0.0235(12)
 C33 0.0300(10) 0.0476(12) 0.0336(10) -0.0104(10) -0.0057(8) 0.0059(10)
 C34 0.0764(19) 0.087(2) 0.0501(14) -0.0227(16) -0.0266(13) 0.0533(19)
 C35 0.0447(12) 0.0403(12) 0.0342(10) -0.0012(10) 0.0040(8) 0.0015(10)
 C36 0.0265(10) 0.0264(9) 0.0390(11) 0.0049(8) 0.0064(8) 0.0034(8)
 C37 0.0345(11) 0.0476(13) 0.0373(11) 0.0063(10) -0.0018(9) 0.0102(10)
 C38 0.0303(11) 0.0365(11) 0.0469(12) -0.0016(9) 0.0085(9) 0.0092(8)
 C39 0.0217(9) 0.0296(10) 0.0349(10) -0.0073(8) 0.0059(7) 0.0003(7)
 C40 0.0328(11) 0.0330(11) 0.0510(13) -0.0101(9) 0.0059(9) -0.0073(9)
 C41 0.0426(12) 0.0402(12) 0.0345(11) -0.0069(9) 0.0036(9) -0.0026(9)
 C42 0.0636(16) 0.0419(13) 0.0338(11) -0.0066(9) 0.0105(11) -0.0036(11)
 C43 0.0455(15) 0.0649(19) 0.101(2) -0.0346(17) -0.0093(15) -0.0036(13)
 C44 0.0560(16) 0.0410(13) 0.0590(15) 0.0005(11) 0.0249(12) -0.0120(11)
 C45 0.0730(19) 0.0428(14) 0.0729(18) -0.0092(13) 0.0225(15) -0.0198(13)
 C46 0.058(2) 0.074(2) 0.148(3) -0.009(2) 0.054(2) -0.0266(17)
 C47 0.0349(11) 0.0389(11) 0.0367(11) 0.0015(9) 0.0117(9) 0.0036(9)
 C48 0.0680(17) 0.0479(14) 0.0380(12) 0.0016(10) 0.0159(11) -0.0018(12)

_geom_special_details

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All esds (except the esd in the dihedral angle between two l.s. planes)
 are estimated using the full covariance matrix. The cell esds are taken
 into account individually in the estimation of esds in distances, angles
 and torsion angles; correlations between esds in cell parameters are only
 used when they are defined by crystal symmetry. An approximate (isotropic)
 treatment of cell esds is used for estimating esds involving l.s. planes.

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Zn1 N1 1.9754(17) . ?

Zn1 N3 2.0556(16) . ?

Zn1 N4 2.1485(17) . ?

Zn1 Cl1 2.2125(9) . ?

Zn1 C15 2.513(2) . ?

Zn1 Zn2 3.0201(7) . ?

Zn2 N2 2.0014(18) . ?

Zn2 N6 2.0323(19) . ?

Zn2 N4 2.0412(16) . ?

Zn2 N5 2.0866(18) . ?

Zn2 C23 2.465(2) . ?

Zn3 N7 1.9711(17) . ?

Zn3 N9 2.0570(17) . ?

Zn3 N10 2.1370(17) . ?

Zn3 Cl2 2.2187(9) . ?

Zn3 C39 2.509(2) . ?

Zn3 Zn4 3.0240(8) . ?

Zn4 N8 2.0053(18) . ?

Zn4 N11 2.0419(19) . ?

Zn4 N10 2.0461(16) . ?
Zn4 N12 2.0870(19) . ?
Zn4 C47 2.479(2) . ?
N1 C7 1.346(3) . ?
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N2 C7 1.317(3) . ?
N2 C4 1.480(3) . ?
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N3 C9 1.467(2) . ?
N4 C15 1.401(2) . ?
N4 C12 1.477(2) . ?
N5 C23 1.329(3) . ?
N5 C17 1.467(3) . ?
N6 C23 1.312(3) . ?
N6 C20 1.469(3) . ?
N7 C31 1.339(3) . ?
N7 C28 1.481(3) . ?
N8 C31 1.315(3) . ?
N8 C25 1.478(3) . ?
N9 C39 1.279(3) . ?
N9 C33 1.474(2) . ?
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N10 C36 1.484(2) . ?
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N11 C41 1.456(3) . ?
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N12 C44 1.468(3) . ?
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C4 C6 1.525(3) . ?
C7 C8 1.523(3) . ?
C9 C11 1.515(3) . ?
C9 C10 1.518(3) . ?
C12 C13 1.526(3) . ?
C12 C14 1.536(3) . ?
C15 C16 1.507(3) . ?
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C17 C19 1.513(4) . ?
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C25 C26 1.532(3) . ?
C28 C29 1.524(4) . ?
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C33 C34 1.523(3) . ?
C36 C37 1.525(3) . ?
C36 C38 1.535(3) . ?
C39 C40 1.503(3) . ?
C41 C42 1.517(3) . ?
C41 C43 1.527(4) . ?
C44 C45 1.507(4) . ?
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C47 C48 1.514(3) . ?

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N1 Zn1 N3 112.51(7) . . ?

N1 Zn1 N4 116.15(7) . . ?

N3 Zn1 N4 64.51(6) . . ?

N1 Zn1 Cl1 122.49(5) . . ?

N3 Zn1 Cl1 113.38(5) . . ?

N4 Zn1 Cl1 113.81(4) . . ?

N1 Zn1 C15 121.18(7) . . ?

N3 Zn1 C15 30.80(6) . . ?

N4 Zn1 C15 33.84(6) . . ?

Cl1 Zn1 C15 116.07(4) . . ?

N1 Zn1 Zn2 73.69(6) . . ?

N3 Zn1 Zn2 81.32(5) . . ?

N4 Zn1 Zn2 42.48(4) . . ?

Cl1 Zn1 Zn2 145.531(18) . . ?

C15 Zn1 Zn2 60.95(4) . . ?

N2 Zn2 N6 113.15(7) . . ?

N2 Zn2 N4 106.43(7) . . ?

N6 Zn2 N4 126.21(7) . . ?

N2 Zn2 N5 125.61(7) . . ?

N6 Zn2 N5 64.76(8) . . ?

N4 Zn2 N5 117.03(7) . . ?

N2 Zn2 C23 124.71(7) . . ?

N6 Zn2 C23 32.13(8) . . ?

N4 Zn2 C23 128.78(7) . . ?

N5 Zn2 C23 32.64(7) . . ?

N2 Zn2 Zn1 72.65(5) . . ?

N6 Zn2 Zn1 116.58(6) . . ?

N4 Zn2 Zn1 45.31(5) . . ?

N5 Zn2 Zn1 160.76(5) . . ?

C23 Zn2 Zn1 145.57(6) . . ?

N7 Zn3 N9 110.84(7) . . ?

N7 Zn3 N10 116.31(7) . . ?

N9 Zn3 N10 64.30(7) . . ?

N7 Zn3 Cl2 122.95(6) . . ?

N9 Zn3 Cl2 115.16(5) . . ?

N10 Zn3 Cl2 113.01(4) . . ?

N7 Zn3 C39 120.50(7) . . ?

N9 Zn3 C39 30.55(6) . . ?

N10 Zn3 C39 33.93(6) . . ?

Cl2 Zn3 C39 116.32(4) . . ?

N7 Zn3 Zn4 73.89(5) . . ?

N9 Zn3 Zn4 81.26(5) . . ?

N10 Zn3 Zn4 42.53(4) . . ?

Cl2 Zn3 Zn4 143.553(18) . . ?

C39 Zn3 Zn4 61.37(5) . . ?

N8 Zn4 N11 112.40(7) . . ?

N8 Zn4 N10 106.16(7) . . ?
 N11 Zn4 N10 128.36(7) . . ?
 N8 Zn4 N12 126.03(8) . . ?
 N11 Zn4 N12 64.48(8) . . ?
 N10 Zn4 N12 116.17(7) . . ?
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 N12 Zn4 C47 32.48(7) . . ?
 N8 Zn4 Zn3 73.04(5) . . ?
 N11 Zn4 Zn3 118.23(5) . . ?
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 N12 Zn4 Zn3 159.62(5) . . ?
 C47 Zn4 Zn3 147.04(5) . . ?
 C7 N1 C1 119.82(18) . . ?
 C7 N1 Zn1 118.13(14) . . ?
 C1 N1 Zn1 117.42(13) . . ?
 C7 N2 C4 121.08(18) . . ?
 C7 N2 Zn2 119.14(13) . . ?
 C4 N2 Zn2 117.19(15) . . ?
 C15 N3 C9 124.38(17) . . ?
 C15 N3 Zn1 94.59(11) . . ?
 C9 N3 Zn1 141.03(13) . . ?
 C15 N4 C12 116.10(15) . . ?
 C15 N4 Zn2 109.80(12) . . ?
 C12 N4 Zn2 117.08(12) . . ?
 C15 N4 Zn1 87.51(11) . . ?
 C12 N4 Zn1 129.02(13) . . ?
 Zn2 N4 Zn1 92.21(6) . . ?
 C23 N5 C17 122.25(19) . . ?
 C23 N5 Zn2 89.54(13) . . ?
 C17 N5 Zn2 147.83(15) . . ?
 C23 N6 C20 125.61(19) . . ?
 C23 N6 Zn2 92.41(14) . . ?
 C20 N6 Zn2 141.38(15) . . ?
 C31 N7 C28 119.97(18) . . ?
 C31 N7 Zn3 118.44(14) . . ?
 C28 N7 Zn3 117.16(14) . . ?
 C31 N8 C25 121.38(18) . . ?
 C31 N8 Zn4 120.26(13) . . ?
 C25 N8 Zn4 116.08(16) . . ?
 C39 N9 C33 123.87(19) . . ?
 C39 N9 Zn3 94.63(12) . . ?
 C33 N9 Zn3 141.50(16) . . ?
 C39 N10 C36 117.08(15) . . ?
 C39 N10 Zn4 110.58(12) . . ?
 C36 N10 Zn4 116.14(12) . . ?
 C39 N10 Zn3 87.72(11) . . ?
 C36 N10 Zn3 127.85(12) . . ?
 Zn4 N10 Zn3 92.56(6) . . ?
 C47 N11 C41 124.58(19) . . ?
 C47 N11 Zn4 92.58(14) . . ?
 C41 N11 Zn4 142.13(14) . . ?
 C47 N12 C44 122.07(19) . . ?
 C47 N12 Zn4 90.19(13) . . ?
 C44 N12 Zn4 147.74(16) . . ?

N1 C1 C3 111.51(19) . . ?
 N1 C1 C2 110.13(19) . . ?
 C3 C1 C2 111.3(2) . . ?
 N2 C4 C5 108.67(17) . . ?
 N2 C4 C6 110.89(18) . . ?
 C5 C4 C6 111.2(2) . . ?
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 N2 C7 C8 120.6(2) . . ?
 N1 C7 C8 119.4(2) . . ?
 N3 C9 C11 109.67(16) . . ?
 N3 C9 C10 108.03(17) . . ?
 C11 C9 C10 111.02(19) . . ?
 N4 C12 C13 108.48(17) . . ?
 N4 C12 C14 111.87(16) . . ?
 C13 C12 C14 109.44(18) . . ?
 N3 C15 N4 112.95(16) . . ?
 N3 C15 C16 125.14(17) . . ?
 N4 C15 C16 121.86(17) . . ?
 N3 C15 Zn1 54.61(10) . . ?
 N4 C15 Zn1 58.65(9) . . ?
 C16 C15 Zn1 177.00(14) . . ?
 N5 C17 C18 110.2(2) . . ?
 N5 C17 C19 111.4(2) . . ?
 C18 C17 C19 110.3(2) . . ?
 N6 C20 C21 110.36(19) . . ?
 N6 C20 C22 109.1(2) . . ?
 C21 C20 C22 111.1(2) . . ?
 N6 C23 N5 113.27(19) . . ?
 N6 C23 C24 123.2(2) . . ?
 N5 C23 C24 123.5(2) . . ?
 N6 C23 Zn2 55.46(11) . . ?
 N5 C23 Zn2 57.83(11) . . ?
 C24-C23 Zn2 178.52(18) . . ?
 N8 C25 C27 109.00(19) . . ?
 N8 C25 C26 110.89(19) . . ?
 C27 C25 C26 111.3(2) . . ?
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A.9 Compound 16

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 'y+5/4, -x+3/4, -z+5/4'
 '-y+5/4, x+5/4, -z+3/4'
 'x+3/4, z+3/4, y+3/4'
 '-x+5/4, z+5/4, -y+3/4'
 '-x+3/4, -z+5/4, y+5/4'
 'x+5/4, -z+3/4, -y+5/4'
 'z+3/4, y+3/4, x+3/4'
 'z+5/4, -y+3/4, -x+5/4'
 '-z+5/4, y+5/4, -x+3/4'
 '-z+3/4, -y+5/4, x+5/4'

_cell_length_a	23.739(4)
_cell_length_b	23.739(4)
_cell_length_c	23.739(4)
_cell_angle_alpha	90.00
_cell_angle_beta	90.00
_cell_angle_gamma	90.00
_cell_volume	13378(4)
_cell_formula_units_Z	16
_cell_measurement_temperature	120(2)
_cell_measurement_reflns_used	1006
_cell_measurement_theta_min	2.71
_cell_measurement_theta_max	27.73
_exptl_crystal_description	block
_exptl_crystal_colour	green
_exptl_crystal_size_max	0.33
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_exptl_crystal_size_min	0.16
_exptl_crystal_density_meas	?
_exptl_crystal_density_diffn	1.110
_exptl_crystal_density_method	'not measured'
_exptl_crystal_F_000	4912
_exptl_absorpt_coefficient_mu	0.285
_exptl_absorpt_correction_type	multi-scan

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_exptl_absorpt_correction_T_max 0.9550
_exptl_absorpt_process_details 'SADABS (Sheldrick, 2003)'

_exptl_special_details
;
Data collection is performed with four batch runs at
\l = 0.00 \% (600 frames), at \l = 90.00 \%
(600 frames), at \l = 180 \% (600 frames) and
at \l = 270 \% (600 frames).
Frame width = 0.30 \& in \w. Data is
merged, corrected for decay, and treated with
multi-scan absorption corrections.
;

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_diffn_measurement_device_type 'Bruker AXS APEX diffractometer'
_diffn_measurement_method \w
_diffn_detector_area_resol_mean 836.6
_diffn_standards_number 0
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_diffn_reflns_number 56449
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_diffn_reflns_av_sigmaI/netI 0.0161
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_diffn_reflns_limit_l_min -30
_diffn_reflns_limit_l_max 31
_diffn_reflns_theta_min 2.10
_diffn_reflns_theta_max 28.25
_reflns_number_total 2715
_reflns_number_gt 2598
_reflns_threshold_expression >2sigma(I)

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_computing_cell_refinement 'SAINT (Bruker, 2002)'
_computing_data_reduction SAINT
_computing_structure_solution 'SHELXS-97 (Sheldrick, 1990)'
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_computing_molecular_graphics 'SHELXTL (Sheldrick, 2001)'
_computing_publication_material 'SHELXTL (Sheldrick, 2001)'

_refine_special_details
;
Refinement of  $F^2$  against ALL reflections. The weighted R-factor wR and
goodness of fit S are based on  $F^2$ , conventional R-factors R are based
on F, with F set to zero for negative  $F^2$ . The threshold expression of
 $F^2 > 2\text{sigma}(F^2)$  is used only for calculating R-factors(gt) etc. and is

```

not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F , and R-factors based on ALL data will be even larger.

;

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_refine_ls_matrix_type full
_refine_ls_weighting_scheme calc
_refine_ls_weighting_details
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_atom_sites_solution_primary direct
_atom_sites_solution_secondary difmap
_atom_sites_solution_hydrogens geom
_refine_ls_hydrogen_treatment constr
_refine_ls_extinction_method none
_refine_ls_extinction_coef ?
_refine_ls_abs_structure_details
'Flack H D (1983), Acta Cryst. A39, 876-881; 1250 Friedel pairs'
_refine_ls_abs_structure_Flack -0.03(2)
_refine_ls_number_reflns 2715
_refine_ls_number_parameters 118
_refine_ls_number_restraints 0
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_refine_ls_R_factor_gt 0.0291
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_refine_ls_wR_factor_gt 0.0758
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_atom_site_fract_y
_atom_site_fract_z
_atom_site_U_iso_or_equiv
_atom_site_adp_type
_atom_site_occupancy
_atom_site_symmetry_multiplicity
_atom_site_calc_flag
_atom_site_refinement_flags
_atom_site_disorder_assembly
_atom_site_disorder_group
Ti Ti -0.009939(11) 0.490061(11) 0.009939(11) 0.01731(10) Uani 1 3 d S . .
N1 N -0.03900(5) 0.52530(5) 0.08778(5) 0.0196(2) Uani 1 1 d . . .
N2 N 0.04305(5) 0.55062(5) 0.05088(5) 0.0199(2) Uani 1 1 d . . .
N3 N 0.01421(6) 0.59443(5) 0.13873(5) 0.0255(3) Uani 1 1 d . . .
C1 C -0.09049(6) 0.53530(6) 0.12039(6) 0.0225(3) Uani 1 1 d . . .
H1A H -0.0847 0.5691 0.1448 0.027 Uiso 1 1 calc R . .
C2 C -0.13992(6) 0.54651(7) 0.08069(7) 0.0269(3) Uani 1 1 d . . .
H2A H -0.1328 0.5811 0.0593 0.040 Uiso 1 1 calc R . .
H2B H -0.1746 0.5508 0.1027 0.040 Uiso 1 1 calc R . .
H2C H -0.1441 0.5148 0.0546 0.040 Uiso 1 1 calc R . .
C3 C -0.10473(7) 0.48494(7) 0.15780(7) 0.0320(3) Uani 1 1 d . . .
```

H3A H -0.0735 0.4779 0.1838 0.048 Uiso 1 1 calc R . .
 H3B H -0.1108 0.4516 0.1342 0.048 Uiso 1 1 calc R . .
 H3C H -0.1390 0.4930 0.1793 0.048 Uiso 1 1 calc R . .
 C4 C 0.10190(6) 0.56924(6) 0.05395(6) 0.0217(3) Uani 1 1 d . . .
 H4A H 0.1086 0.5865 0.0918 0.026 Uiso 1 1 calc R . .
 C5 C 0.11464(7) 0.61318(7) 0.00863(7) 0.0294(3) Uani 1 1 d . . .
 H5A H 0.0899 0.6458 0.0138 0.044 Uiso 1 1 calc R . .
 H5B H 0.1082 0.5967 -0.0287 0.044 Uiso 1 1 calc R . .
 H5C H 0.1540 0.6251 0.0117 0.044 Uiso 1 1 calc R . .
 C6 C 0.14182(6) 0.51925(7) 0.04669(7) 0.0277(3) Uani 1 1 d . . .
 H6A H 0.1358 0.4922 0.0773 0.042 Uiso 1 1 calc R . .
 H6B H 0.1809 0.5326 0.0476 0.042 Uiso 1 1 calc R . .
 H6C H 0.1344 0.5009 0.0105 0.042 Uiso 1 1 calc R . .
 C7 C 0.00692(6) 0.55729(6) 0.09320(6) 0.0193(3) Uani 1 1 d . . .
 C8 C 0.03591(7) 0.65086(7) 0.13072(7) 0.0280(3) Uani 1 1 d . . .
 H8A H 0.0318 0.6617 0.0911 0.042 Uiso 1 1 calc R . .
 H8B H 0.0758 0.6519 0.1412 0.042 Uiso 1 1 calc R . .
 H8C H 0.0148 0.6772 0.1544 0.042 Uiso 1 1 calc R . .
 C9 C 0.01576(8) 0.57334(8) 0.19567(7) 0.0328(4) Uani 1 1 d . . .
 H9A H -0.0061 0.5983 0.2202 0.049 Uiso 1 1 calc R . .
 H9B H 0.0549 0.5720 0.2088 0.049 Uiso 1 1 calc R . .
 H9C H -0.0004 0.5354 0.1967 0.049 Uiso 1 1 calc R . .

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 _atom_site_aniso_U_22
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 _atom_site_aniso_U_23
 _atom_site_aniso_U_13
 _atom_site_aniso_U_12
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 N1 0.0189(6) 0.0201(6) 0.0199(6) -0.0025(4) 0.0021(4) 0.0004(4)
 N2 0.0167(6) 0.0230(6) 0.0201(6) -0.0013(5) -0.0015(4) -0.0016(5)
 N3 0.0314(7) 0.0247(6) 0.0203(6) -0.0054(5) -0.0011(5) -0.0030(5)
 C1 0.0215(7) 0.0228(7) 0.0231(7) -0.0029(6) 0.0050(5) 0.0003(5)
 C2 0.0205(7) 0.0299(8) 0.0302(8) -0.0068(6) 0.0026(6) 0.0009(6)
 C3 0.0301(8) 0.0328(8) 0.0329(8) 0.0047(7) 0.0100(6) 0.0014(6)
 C4 0.0169(6) 0.0254(7) 0.0228(7) -0.0037(5) -0.0018(5) -0.0031(5)
 C5 0.0240(7) 0.0310(8) 0.0334(8) 0.0018(7) 0.0000(6) -0.0068(6)
 C6 0.0181(6) 0.0299(8) 0.0352(8) -0.0053(6) -0.0005(6) 0.0009(6)
 C7 0.0215(6) 0.0179(6) 0.0184(6) -0.0007(5) -0.0020(5) 0.0026(5)
 C8 0.0287(8) 0.0242(7) 0.0310(8) -0.0087(6) -0.0027(6) -0.0017(6)
 C9 0.0369(9) 0.0393(9) 0.0221(7) -0.0042(6) -0.0039(7) -0.0026(7)

_geom_special_details

;

All esds (except the esd in the dihedral angle between two l.s. planes)
 are estimated using the full covariance matrix. The cell esds are taken
 into account individually in the estimation of esds in distances, angles
 and torsion angles; correlations between esds in cell parameters are only
 used when they are defined by crystal symmetry. An approximate (isotropic)
 treatment of cell esds is used for estimating esds involving l.s. planes.

;

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 _geom_bond_site_symmetry_2
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 Ti N1 2.1425(12) 8 ?
 Ti N1 2.1425(12) 11_455 ?
 Ti N2 2.1431(13) 8 ?
 Ti N2 2.1432(13) 11_455 ?
 Ti N2 2.1432(13) . ?
 Ti C7 2.5717(14) 8 ?
 Ti C7 2.5717(14) . ?
 Ti C7 2.5717(14) 11_455 ?
 N1 C7 1.335(2) . ?
 N1 C1 1.4661(18) . ?
 N2 C7 1.3303(19) . ?
 N2 C4 1.4672(18) . ?
 N3 C7 1.4055(18) . ?
 N3 C9 1.442(2) . ?
 N3 C8 1.448(2) . ?
 C1 C3 1.527(2) . ?
 C1 C2 1.528(2) . ?
 C4 C6 1.528(2) . ?
 C4 C5 1.529(2) . ?

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 N1 Ti N1 100.65(4) . 11_455 ?
 N1 Ti N1 100.65(4) 8 11_455 ?
 N1 Ti N2 101.73(5) . 8 ?
 N1 Ti N2 62.35(5) 8 8 ?
 N1 Ti N2 154.06(5) 11_455 8 ?
 N1 Ti N2 154.06(5) . 11_455 ?
 N1 Ti N2 101.73(5) 8 11_455 ?
 N1 Ti N2 62.35(5) 11_455 11_455 ?
 N2 Ti N2 100.18(4) 8 11_455 ?
 N1 Ti N2 62.36(5) . . ?
 N1 Ti N2 154.06(5) 8 . ?
 N1 Ti N2 101.73(5) 11_455 . ?
 N2 Ti N2 100.18(4) 8 . ?
 N2 Ti N2 100.18(4) 11_455 . ?
 N1 Ti C7 103.12(5) . 8 ?
 N1 Ti C7 31.24(5) 8 8 ?
 N1 Ti C7 129.35(5) 11_455 8 ?
 N2 Ti C7 31.12(5) 8 8 ?
 N2 Ti C7 102.81(4) 11_455 8 ?
 N2 Ti C7 128.92(5) . 8 ?
 N1 Ti C7 31.24(5) . . ?

N1 Ti C7 129.35(5) 8 . ?
 N1 Ti C7 103.12(5) 11_455 . ?
 N2 Ti C7 102.81(4) 8 . ?
 N2 Ti C7 128.91(5) 11_455 . ?
 N2 Ti C7 31.12(5) . . ?
 C7 Ti C7 119.999(1) 8 . ?
 N1 Ti C7 129.35(5) . 11_455 ?
 N1 Ti C7 103.12(5) 8 11_455 ?
 N1 Ti C7 31.23(5) 11_455 11_455 ?
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 N2 Ti C7 31.12(5) 11_455 11_455 ?
 N2 Ti C7 102.81(4) . 11_455 ?
 C7 Ti C7 120.0 8 11_455 ?
 C7 Ti C7 120.0 . 11_455 ?
 C7 N1 C1 122.53(12) . . ?
 C7 N1 Ti 92.42(8) . . ?
 C1 N1 Ti 141.92(10) . . ?
 C7 N2 C4 122.72(12) . . ?
 C7 N2 Ti 92.52(9) . . ?
 C4 N2 Ti 141.58(10) . . ?
 C7 N3 C9 120.41(13) . . ?
 C7 N3 C8 121.55(13) . . ?
 C9 N3 C8 115.81(13) . . ?
 N1 C1 C3 111.40(12) . . ?
 N1 C1 C2 110.04(12) . . ?
 C3 C1 C2 108.95(13) . . ?
 N2 C4 C6 110.53(12) . . ?
 N2 C4 C5 111.05(12) . . ?
 C6 C4 C5 109.13(13) . . ?
 N2 C7 N1 112.70(12) . . ?
 N2 C7 N3 125.17(13) . . ?
 N1 C7 N3 122.12(13) . . ?
 N2 C7 Ti 56.36(7) . . ?
 N1 C7 Ti 56.34(7) . . ?
 N3 C7 Ti 178.10(11) . . ?

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 N1 Ti N1 C7 97.79(11) 11_455 . . . ?
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 N2 Ti N1 C7 51.65(15) 11_455 . . . ?
 N2 Ti N1 C7 0.03(8) ?
 C7 Ti N1 C7 -127.28(8) 8 . . . ?
 C7 Ti N1 C7 83.95(7) 11_455 . . . ?
 N1 Ti N1 C1 -1.19(17) 8 . . . ?
 N1 Ti N1 C1 -104.29(13) 11_455 . . . ?

N2 Ti N1 C1 62.50(17) 8 ... ?
 N2 Ti N1 C1 -150.43(15) 11_455 ... ?
 N2 Ti N1 C1 157.95(18) ... ?
 C7 Ti N1 C1 30.65(17) 8 ... ?
 C7 Ti N1 C1 157.9(2) ... ?
 C7 Ti N1 C1 -118.12(16) 11_455 ... ?
 N1 Ti N2 C7 -0.03(8) ... ?
 N1 Ti N2 C7 53.10(15) 8 ... ?
 N1 Ti N2 C7 -96.01(9) 11_455 ... ?
 N2 Ti N2 C7 97.97(11) 8 ... ?
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 N1 Ti N2 C4 157.83(18) ... ?
 N1 Ti N2 C4 -149.05(15) 8 ... ?
 N1 Ti N2 C4 61.84(16) 11_455 ... ?
 N2 Ti N2 C4 -104.18(13) 8 ... ?
 N2 Ti N2 C4 -1.78(17) 11_455 ... ?
 C7 Ti N2 C4 -117.54(15) 8 ... ?
 C7 Ti N2 C4 157.9(2) ... ?
 C7 Ti N2 C4 29.88(17) 11_455 ... ?
 C7 N1 C1 C3 -118.45(16) ... ?
 Ti N1 C1 C3 88.00(19) ... ?
 C7 N1 C1 C2 120.60(14) ... ?
 Ti N1 C1 C2 -33.0(2) ... ?
 C7 N2 C4 C6 119.49(15) ... ?
 Ti N2 C4 C6 -33.9(2) ... ?
 C7 N2 C4 C5 -119.24(15) ... ?
 Ti N2 C4 C5 87.35(18) ... ?
 C4 N2 C7 N1 -163.79(13) ... ?
 Ti N2 C7 N1 0.04(12) ... ?
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 Ti N2 C7 N3 -178.64(12) ... ?
 C4 N2 C7 Ti -163.83(15) ... ?
 C1 N1 C7 N2 -164.08(13) ... ?
 Ti N1 C7 N2 -0.04(12) ... ?
 C1 N1 C7 N3 14.6(2) ... ?
 Ti N1 C7 N3 178.69(11) ... ?
 C1 N1 C7 Ti -164.04(16) ... ?
 C9 N3 C7 N2 -120.55(16) ... ?
 C8 N3 C7 N2 41.8(2) ... ?
 C9 N3 C7 N1 60.9(2) ... ?
 C8 N3 C7 N1 -136.81(15) ... ?
 C9 N3 C7 Ti 96(3) ... ?
 C8 N3 C7 Ti -102(3) ... ?
 N1 Ti C7 N2 179.96(13) ... ?
 N1 Ti C7 N2 -153.10(8) 8 ... ?
 N1 Ti C7 N2 91.01(9) 11_455 ... ?
 N2 Ti C7 N2 -88.50(10) 8 ... ?
 N2 Ti C7 N2 26.11(10) 11_455 ... ?
 C7 Ti C7 N2 -116.56(9) 8 ... ?
 C7 Ti C7 N2 62.56(11) 11_455 ... ?
 N1 Ti C7 N1 26.94(10) 8 ... ?
 N1 Ti C7 N1 -88.94(10) 11_455 ... ?
 N2 Ti C7 N1 91.54(9) 8 ... ?
 N2 Ti C7 N1 -153.84(9) 11_455 ... ?

N2 Ti C7 N1 -179.96(13) . . . ?
C7 Ti C7 N1 63.48(11) 8 . . . ?
C7 Ti C7 N1 -117.39(9) 11_455 . . . ?
N1 Ti C7 N3 -36(3) . . . ?
N1 Ti C7 N3 -9(3) 8 . . . ?
N1 Ti C7 N3 -125(3) 11_455 . . . ?
N2 Ti C7 N3 56(3) 8 . . . ?
N2 Ti C7 N3 170(3) 11_455 . . . ?
N2 Ti C7 N3 144(3) . . . ?
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_diffn_measured_fraction_theta_full 1.000
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_refine_diff_density_rms 0.036

A.10 Compound 18

data_seab027

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;
_chemical_name_common      ?
_chemical_melting_point    ?
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_atom_type_symbol
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_atom_type_scatter_dispersion_real
_atom_type_scatter_dispersion_imag
_atom_type_scatter_source
'C' 'C' 0.0033 0.0016
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'H' 'H' 0.0000 0.0000
'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
'N' 'N' 0.0061 0.0033
'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
'Cl' 'Cl' 0.1484 0.1585
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'Ti' 'Ti' 0.2776 0.4457
'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'

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_symmetry_space_group_name_H-M P2(1)/c

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'-x, y+1/2, -z+1/2'
'-x, -y, -z'
'x, -y-1/2, z-1/2'

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_cell_length_b              14.1909(17)
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_cell_angle_gamma           90.00
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_exptl_absorpt_process_details 'SADABS (Sheldrick, 2003)'

_exptl_special_details
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Data collection is performed with four batch runs at
\l = 0.00 \% (600 frames), at \l = 90.00 \%
(600 frames), at \l = 180 \% (600 frames) and
at \l = 270 \% (600 frames).
Frame width = 0.30 \& in \w. Data is
merged, corrected for decay, and treated with
multi-scan absorption corrections.
;

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_diffn_radiation_monochromator   graphite
_diffn_measurement_device_type  'Bruker AXS APEX diffractometer'
_diffn_measurement_method       \w
_diffn_detector_area_resol_mean 836.6
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_diffn_reflns_number            19583
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_diffn_reflns_av_sigmaI/netI    0.0823
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_diffn_reflns_theta_min         1.79
_diffn_reflns_theta_max         28.38
_reflns_number_total            6391
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_reflns_threshold_expression     >2sigma(I)

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_computing_cell_refinement      'SAINT (Bruker, 2002)'
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Refinement of  $F^2$  against ALL reflections. The weighted R-factor wR and
goodness of fit S are based on  $F^2$ , conventional R-factors R are based
on F, with F set to zero for negative  $F^2$ . The threshold expression of
 $F^2 > 2\sigma(F^2)$  is used only for calculating R-factors(gt) etc. and is
not relevant to the choice of reflections for refinement. R-factors based
on  $F^2$  are statistically about twice as large as those based on F, and R-
factors based on ALL data will be even larger.
;

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_refine_ls_matrix_type          full
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'calc w=1/[ $s^2(F_o^2)+(0.0500P)^2$ ] where  $P=(F_o^2+2F_c^2)/3$ '
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_atom_sites_solution_hydrogens  geom
_refine_ls_hydrogen_treatment   constr
_refine_ls_extinction_method     none
_refine_ls_extinction_coef      ?
_refine_ls_number_reflns        6391
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 N2 N 0.3229(2) 0.36131(14) 0.23960(11) 0.0213(5) Uani 1 1 d ...
 N3 N 0.4157(2) 0.30747(15) 0.13909(11) 0.0256(5) Uani 1 1 d ...
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 N5 N 0.1169(2) 0.47661(14) 0.32927(11) 0.0209(5) Uani 1 1 d ...
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 C2 C 0.3731(3) 0.50874(18) 0.09340(13) 0.0225(6) Uani 1 1 d ...
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 H3C H 0.5607 0.5486 0.1542 0.046 Uiso 1 1 calc R ..
 H3D H 0.5701 0.5436 0.0720 0.046 Uiso 1 1 calc R ..
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 H4B H 0.3506 0.6394 0.0449 0.044 Uiso 1 1 calc R ..
 H4C H 0.3393 0.6443 0.1269 0.044 Uiso 1 1 calc R ..
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 C6 C 0.1873(4) 0.2134(2) 0.23485(16) 0.0488(9) Uani 1 1 d ...
 H6B H 0.1846 0.2101 0.1838 0.073 Uiso 1 1 calc R ..
 H6C H 0.1039 0.2470 0.2449 0.073 Uiso 1 1 calc R ..
 H6D H 0.1884 0.1495 0.2542 0.073 Uiso 1 1 calc R ..
 C7 C 0.3250(3) 0.2710(2) 0.34735(13) 0.0316(7) Uani 1 1 d ...
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 H7B H 0.3259 0.2071 0.3668 0.047 Uiso 1 1 calc R ..
 H7C H 0.2426 0.3050 0.3580 0.047 Uiso 1 1 calc R ..
 C8 C 0.3972(3) 0.29232(19) 0.06273(13) 0.0257(6) Uani 1 1 d ...
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 C9 C 0.2429(3) 0.2787(2) 0.03199(15) 0.0370(7) Uani 1 1 d ...
 H9A H 0.1895 0.3346 0.0418 0.055 Uiso 1 1 calc R ..
 H9B H 0.2064 0.2233 0.0534 0.055 Uiso 1 1 calc R ..
 H9C H 0.2333 0.2695 -0.0191 0.055 Uiso 1 1 calc R ..
 C10 C 0.4853(3) 0.2079(2) 0.04924(14) 0.0339(7) Uani 1 1 d ...
 H10A H 0.5839 0.2197 0.0692 0.051 Uiso 1 1 calc R ..
 H10B H 0.4770 0.1975 -0.0016 0.051 Uiso 1 1 calc R ..
 H10C H 0.4520 0.1519 0.0714 0.051 Uiso 1 1 calc R ..
 C11 C -0.0032(3) 0.47050(17) 0.28378(14) 0.0224(6) Uani 1 1 d ...
 C12 C -0.0911(3) 0.46757(19) 0.15627(13) 0.0260(6) Uani 1 1 d ...
 H12A H -0.1801 0.4952 0.1676 0.031 Uiso 1 1 calc R ..
 C13 C -0.1162(3) 0.3635(2) 0.13934(15) 0.0384(7) Uani 1 1 d ...
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 H13B H -0.0305 0.3355 0.1271 0.058 Uiso 1 1 calc R ..
 H13C H -0.1931 0.3569 0.0995 0.058 Uiso 1 1 calc R ..
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 H14C H 0.0329 0.4918 0.0801 0.054 Uiso 1 1 calc R ..
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H16B H 0.2904 0.5097 0.4884 0.045 Uiso 1 1 calc R . .
 H16C H 0.3320 0.5463 0.4159 0.045 Uiso 1 1 calc R . .
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 H17B H 0.1112 0.6429 0.3941 0.060 Uiso 1 1 calc R . .
 H17C H 0.0702 0.6059 0.4667 0.060 Uiso 1 1 calc R . .
 C18 C -0.1734(3) 0.4085(2) 0.36116(16) 0.0415(8) Uani 1 1 d . . .
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 C19 C -0.1121(4) 0.3102(2) 0.37096(18) 0.0587(10) Uani 1 1 d . . .
 H19A H -0.0094 0.3137 0.3768 0.088 Uiso 1 1 calc R . .
 H19B H -0.1475 0.2718 0.3295 0.088 Uiso 1 1 calc R . .
 H19C H -0.1398 0.2814 0.4129 0.088 Uiso 1 1 calc R . .
 C20 C -0.3333(3) 0.4082(3) 0.35238(19) 0.0744(14) Uani 1 1 d . . .
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 H20B H -0.3627 0.3810 0.3945 0.112 Uiso 1 1 calc R . .
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 N3 0.0281(12) 0.0275(12) 0.0207(12) 0.0022(10) 0.0023(10) 0.0099(10)
 N4 0.0192(11) 0.0276(12) 0.0193(11) -0.0003(9) 0.0016(9) -0.0010(9)
 N5 0.0212(11) 0.0235(11) 0.0179(11) -0.0012(9) 0.0032(9) -0.0024(9)
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All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

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Ti C11 2.514(2) . ?
Ti C1 2.534(2) . ?
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N1 C2 1.473(3) . ?
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N4 C12 1.463(3) . ?
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C2 C4 1.527(4) . ?
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C5 C6 1.518(4) . ?
C8 C10 1.516(3) . ?
C8 C9 1.521(4) . ?
C12 C14 1.520(4) . ?
C12 C13 1.524(4) . ?
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 Cl Ti C11 116.32(6) . . ?
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 Cl Ti C1 116.22(6) . . ?
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 C1 N1 Ti 90.59(15) . . ?
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 C1 N3 C8 126.5(2) . . ?
 C11 N4 C12 121.7(2) . . ?
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 C12 N4 Ti 142.66(17) . . ?
 C11 N5 C15 125.1(2) . . ?
 C11 N5 Ti 90.53(15) . . ?
 C15 N5 Ti 141.03(16) . . ?
 C11 N6 C18 127.8(2) . . ?
 N1 C1 N3 127.4(2) . . ?
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 N3 C1 N2 121.4(2) . . ?
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 N3 C1 Ti 174.59(19) . . ?
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 N1 C2 C4 109.6(2) . . ?
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 N5 C15 C16 108.8(2) . . ?
 N5 C15 C17 110.9(2) . . ?
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 Ti N1 C2 C3 92.9(3) ?
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 Ti N1 C2 C4 -28.7(3) ?
 C1 N2 C5 C7 164.0(2) ?
 Ti N2 C5 C7 -47.6(4) ?
 C1 N2 C5 C6 -73.9(3) ?
 Ti N2 C5 C6 74.5(3) ?
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 C1 N3 C8 C9 -55.9(3) ?
 C15 N5 C11 N4 159.2(2) ?
 Ti N5 C11 N4 -4.0(2) ?
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 C15 N5 C11 Ti 163.1(3) ?
 C12 N4 C11 N5 172.4(2) ?
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C18 N6 C11 N5 -24.4(4) ?
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 Cl Ti C11 N5 -64.98(15) ?
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 N1 Ti C11 N4 -26.97(19) ?
 Cl Ti C11 N4 110.39(14) ?
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 N1 Ti C11 N6 8(2) ?
 Cl Ti C11 N6 145.0(19) ?
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 Ti N5 C15 C16 -28.0(3) ?
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A.11 Compound 19

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'C' 'C' 0.0033 0.0016

'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'

'H' 'H' 0.0000 0.0000

'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'

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'x, y, z'

'-x, -y, -z'

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_exptl_special_details
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\l = 0.00 \% (600 frames), at \l = 90.00 \%
(600 frames), at \l = 180 \% (600 frames) and
at \l = 270 \% (600 frames).
Frame width = 0.30 \& in \w. Data is
merged, corrected for decay, and treated with
multi-scan absorption corrections.
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_computing_molecular_graphics 'SHELXTL (Sheldrick, 2001)'
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_refine_special_details
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Refinement of F2 against ALL reflections. The weighted R-factor wR and
goodness of fit S are based on F2, conventional R-factors R are based
on F, with F set to zero for negative F2. The threshold expression of
F2 > 2sigma(F2) is used only for calculating R-factors(gt) etc. and is
not relevant to the choice of reflections for refinement. R-factors based
on F2 are statistically about twice as large as those based on F, and R-
factors based on ALL data will be even larger.
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_atom_sites_solution_secondary difmap
_atom_sites_solution_hydrogens geom
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_refine_ls_number_reflns 10735
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N1 N 0.19602(18) 0.16623(12) 1.00304(11) 0.0322(4) Uani 1 1 d . . .

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 N4 N 0.08780(19) 0.37769(11) 0.94021(10) 0.0307(3) Uani 1 1 d ...
 N5 N -0.10957(19) 0.14682(12) 1.12208(11) 0.0336(4) Uani 1 1 d ...
 N6 N 0.1424(2) 0.24019(12) 1.13245(10) 0.0346(4) Uani 1 1 d ...
 N7 N 0.3239(2) 0.15490(12) 0.48071(11) 0.0353(4) Uani 1 1 d ...
 N8 N 0.51412(19) 0.12523(12) 0.56739(10) 0.0327(4) Uani 1 1 d ...
 N9 N 0.56916(19) 0.33737(12) 0.50660(11) 0.0347(4) Uani 1 1 d ...
 N10 N 0.33395(18) 0.29474(11) 0.56752(10) 0.0302(3) Uani 1 1 d ...
 N11 N 0.3204(2) 0.35969(12) 0.37668(11) 0.0368(4) Uani 1 1 d ...
 N12 N 0.6135(2) 0.26147(13) 0.37802(11) 0.0396(4) Uani 1 1 d ...
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 H1B H 0.4279 0.1467 1.0119 0.048 Uiso 1 1 calc R ...
 C2 C 0.3644(3) 0.10557(19) 0.92110(16) 0.0492(6) Uani 1 1 d ...
 H2A H 0.4266 0.1556 0.8771 0.059 Uiso 1 1 calc R ...
 H2B H 0.4159 0.0445 0.9296 0.059 Uiso 1 1 calc R ...
 C3 C 0.2004(3) 0.11549(16) 0.89400(14) 0.0409(5) Uani 1 1 d ...
 H3A H 0.1956 0.1516 0.8307 0.049 Uiso 1 1 calc R ...
 H3B H 0.1592 0.0540 0.9128 0.049 Uiso 1 1 calc R ...
 C4 C 0.1142(2) 0.16751(13) 0.94117(12) 0.0286(4) Uani 1 1 d ...
 C5 C -0.1194(2) 0.21938(15) 0.86702(13) 0.0351(4) Uani 1 1 d ...
 H5A H -0.0531 0.2338 0.8124 0.042 Uiso 1 1 calc R ...
 C6 C -0.2406(3) 0.29985(17) 0.85090(17) 0.0511(6) Uani 1 1 d ...
 H6A H -0.1893 0.3577 0.8321 0.077 Uiso 1 1 calc R ...
 H6B H -0.3046 0.2877 0.9043 0.077 Uiso 1 1 calc R ...
 H6C H -0.3059 0.3059 0.8059 0.077 Uiso 1 1 calc R ...
 C7 C -0.1970(3) 0.12941(18) 0.89149(18) 0.0517(6) Uani 1 1 d ...
 H7A H -0.1178 0.0785 0.9010 0.078 Uiso 1 1 calc R ...
 H7B H -0.2593 0.1374 0.8446 0.078 Uiso 1 1 calc R ...
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 C8 C -0.2826(3) 0.39774(16) 1.03181(15) 0.0427(5) Uani 1 1 d ...
 H8A H -0.2855 0.4075 1.0843 0.051 Uiso 1 1 calc R ...
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 C9 C -0.2935(3) 0.49053(18) 0.95146(17) 0.0572(7) Uani 1 1 d ...
 H9A H -0.3624 0.4878 0.9110 0.069 Uiso 1 1 calc R ...
 H9B H -0.3346 0.5410 0.9672 0.069 Uiso 1 1 calc R ...
 C10 C -0.1300(3) 0.50744(14) 0.91042(14) 0.0396(5) Uani 1 1 d ...
 H10A H -0.1275 0.5296 0.8471 0.047 Uiso 1 1 calc R ...
 H10B H -0.0833 0.5532 0.9228 0.047 Uiso 1 1 calc R ...
 C11 C -0.0489(2) 0.41183(13) 0.95398(12) 0.0299(4) Uani 1 1 d ...
 C12 C 0.1895(2) 0.43124(15) 0.86506(13) 0.0370(5) Uani 1 1 d ...
 H12A H 0.1792 0.4977 0.8550 0.044 Uiso 1 1 calc R ...
 C13 C 0.3557(3) 0.39394(19) 0.88378(16) 0.0541(6) Uani 1 1 d ...
 H13A H 0.3832 0.4000 0.9342 0.081 Uiso 1 1 calc R ...
 H13B H 0.4244 0.4296 0.8336 0.081 Uiso 1 1 calc R ...
 H13C H 0.3667 0.3282 0.8956 0.081 Uiso 1 1 calc R ...
 C14 C 0.1482(3) 0.42694(19) 0.78370(14) 0.0525(6) Uani 1 1 d ...
 H14A H 0.0396 0.4484 0.7735 0.079 Uiso 1 1 calc R ...
 H14B H 0.1646 0.3627 0.7913 0.079 Uiso 1 1 calc R ...
 H14C H 0.2138 0.4670 0.7341 0.079 Uiso 1 1 calc R ...
 C15 C -0.0539(3) 0.06260(16) 1.19358(15) 0.0487(6) Uani 1 1 d ...
 H15A H -0.1084 0.0579 1.2476 0.073 Uiso 1 1 calc R ...
 H15B H 0.0571 0.0644 1.1965 0.073 Uiso 1 1 calc R ...
 H15C H -0.0727 0.0085 1.1850 0.073 Uiso 1 1 calc R ...
 C16 C -0.2723(2) 0.14581(17) 1.11389(15) 0.0446(5) Uani 1 1 d ...

H16A H -0.2908 0.0901 1.1080 0.067 Uiso 1 1 calc R..
 H16B H -0.3050 0.2014 1.0627 0.067 Uiso 1 1 calc R..
 H16C H -0.3312 0.1453 1.1654 0.067 Uiso 1 1 calc R..
 C17 C 0.0712(3) 0.23340(19) 1.21447(15) 0.0535(6) Uani 1 1 d...
 H17A H 0.0973 0.2864 1.2228 0.080 Uiso 1 1 calc R..
 H17B H 0.1095 0.1753 1.2615 0.080 Uiso 1 1 calc R..
 H17C H -0.0411 0.2340 1.2144 0.080 Uiso 1 1 calc R..
 C18 C 0.3092(3) 0.24034(18) 1.13036(16) 0.0478(6) Uani 1 1 d...
 H18A H 0.3353 0.2882 1.1461 0.072 Uiso 1 1 calc R..
 H18B H 0.3539 0.2537 1.0721 0.072 Uiso 1 1 calc R..
 H18C H 0.3508 0.1792 1.1716 0.072 Uiso 1 1 calc R..
 C19 C 0.2052(3) 0.11000(17) 0.46283(16) 0.0472(6) Uani 1 1 d...
 H19A H 0.2363 0.1010 0.4104 0.057 Uiso 1 1 calc R..
 H19B H 0.1060 0.1481 0.4541 0.057 Uiso 1 1 calc R..
 C20 C 0.1901(4) 0.0162(2) 0.54244(19) 0.0647(8) Uani 1 1 d...
 H20A H 0.1008 0.0193 0.5815 0.078 Uiso 1 1 calc R..
 H20B H 0.1762 -0.0333 0.5253 0.078 Uiso 1 1 calc R..
 C21 C 0.3402(3) -0.00293(15) 0.58641(15) 0.0428(5) Uani 1 1 d...
 H21A H 0.3213 -0.0284 0.6499 0.051 Uiso 1 1 calc R..
 H21B H 0.4124 -0.0468 0.5724 0.051 Uiso 1 1 calc R..
 C22 C 0.4017(2) 0.09277(14) 0.54825(12) 0.0320(4) Uani 1 1 d...
 C23 C 0.5994(3) 0.06745(15) 0.64380(13) 0.0402(5) Uani 1 1 d...
 H23A H 0.6037 0.0012 0.6536 0.048 Uiso 1 1 calc R..
 C24 C 0.7634(3) 0.0983(2) 0.62786(18) 0.0644(8) Uani 1 1 d...
 H24A H 0.8116 0.0954 0.5754 0.097 Uiso 1 1 calc R..
 H24B H 0.8233 0.0570 0.6772 0.097 Uiso 1 1 calc R..
 H24C H 0.7609 0.1623 0.6207 0.097 Uiso 1 1 calc R..
 C25 C 0.5214(3) 0.0742(2) 0.72404(15) 0.0576(7) Uani 1 1 d...
 H25A H 0.4162 0.0538 0.7341 0.086 Uiso 1 1 calc R..
 H25B H 0.5174 0.1388 0.7154 0.086 Uiso 1 1 calc R..
 H25C H 0.5804 0.0343 0.7742 0.086 Uiso 1 1 calc R..
 C26 C 0.7044(3) 0.37632(19) 0.51595(18) 0.0515(6) Uani 1 1 d...
 H26A H 0.7351 0.4295 0.4608 0.062 Uiso 1 1 calc R..
 H26B H 0.7920 0.3287 0.5328 0.062 Uiso 1 1 calc R..
 C27 C 0.6599(3) 0.4083(2) 0.5860(2) 0.0604(7) Uani 1 1 d...
 H27A H 0.7386 0.3846 0.6293 0.072 Uiso 1 1 calc R..
 H27B H 0.6510 0.4771 0.5606 0.072 Uiso 1 1 calc R..
 C28 C 0.5054(3) 0.36925(19) 0.62767(17) 0.0496(6) Uani 1 1 d...
 H28A H 0.5162 0.3188 0.6869 0.059 Uiso 1 1 calc R..
 H28B H 0.4295 0.4184 0.6301 0.059 Uiso 1 1 calc R..
 C29 C 0.4584(2) 0.33228(14) 0.56789(13) 0.0315(4) Uani 1 1 d...
 C30 C 0.2044(2) 0.28551(14) 0.63070(13) 0.0333(4) Uani 1 1 d...
 H30A H 0.2462 0.2726 0.6867 0.040 Uiso 1 1 calc R..
 C31 C 0.0988(3) 0.37467(16) 0.60215(16) 0.0443(5) Uani 1 1 d...
 H31A H 0.1581 0.4265 0.5945 0.066 Uiso 1 1 calc R..
 H31B H 0.0141 0.3665 0.6463 0.066 Uiso 1 1 calc R..
 H31C H 0.0565 0.3882 0.5474 0.066 Uiso 1 1 calc R..
 C32 C 0.1139(3) 0.20351(16) 0.64483(15) 0.0423(5) Uani 1 1 d...
 H32A H 0.1811 0.1462 0.6673 0.063 Uiso 1 1 calc R..
 H32B H 0.0766 0.2136 0.5898 0.063 Uiso 1 1 calc R..
 H32C H 0.0258 0.1981 0.6865 0.063 Uiso 1 1 calc R..
 C33 C 0.3785(3) 0.43779(16) 0.29973(15) 0.0516(6) Uani 1 1 d...
 H33A H 0.3338 0.4962 0.2999 0.077 Uiso 1 1 calc R..
 H33B H 0.3497 0.4343 0.2483 0.077 Uiso 1 1 calc R..
 H33C H 0.4912 0.4357 0.2991 0.077 Uiso 1 1 calc R..
 C34 C 0.1530(3) 0.36470(19) 0.38340(16) 0.0526(6) Uani 1 1 d...

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 H34B H 0.1166 0.3127 0.4369 0.079 Uiso 1 1 calc R . .
 H34C H 0.1157 0.3611 0.3338 0.079 Uiso 1 1 calc R . .
 C35 C 0.5845(3) 0.26158(19) 0.29702(15) 0.0550(6) Uani 1 1 d . . .
 H35A H 0.6401 0.2073 0.2931 0.083 Uiso 1 1 calc R . .
 H35B H 0.6204 0.3186 0.2486 0.083 Uiso 1 1 calc R . .
 H35C H 0.4736 0.2590 0.2948 0.083 Uiso 1 1 calc R . .
 C36 C 0.7781(3) 0.2610(2) 0.38452(18) 0.0572(7) Uani 1 1 d . . .
 H36A H 0.8316 0.2084 0.3766 0.086 Uiso 1 1 calc R . .
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 N9 0.0258(8) 0.0393(9) 0.0397(9) -0.0178(8) 0.0000(7) -0.0063(7)
 N10 0.0266(8) 0.0355(9) 0.0294(8) -0.0150(7) -0.0016(6) -0.0036(7)
 N11 0.0389(10) 0.0376(9) 0.0295(8) -0.0102(7) -0.0072(7) -0.0012(7)
 N12 0.0398(10) 0.0438(10) 0.0316(9) -0.0147(8) 0.0042(7) -0.0032(8)
 C1 0.0302(10) 0.0460(12) 0.0461(12) -0.0226(10) -0.0092(9) 0.0094(9)
 C2 0.0351(12) 0.0644(16) 0.0566(15) -0.0377(13) -0.0044(10) 0.0136(11)
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 C6 0.0477(14) 0.0518(14) 0.0535(14) -0.0212(12) -0.0253(11) 0.0110(11)
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 C9 0.0529(15) 0.0526(15) 0.0504(14) -0.0146(12) -0.0020(12) 0.0216(12)
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 C11 0.0335(10) 0.0296(9) 0.0297(9) -0.0149(8) -0.0073(8) -0.0005(8)
 C12 0.0393(11) 0.0365(11) 0.0303(10) -0.0097(9) 0.0008(8) -0.0088(9)
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 C17 0.0682(17) 0.0636(16) 0.0352(12) -0.0269(12) -0.0003(11) -0.0115(13)
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 C36 0.0386(13) 0.0726(18) 0.0578(16) -0.0299(14) 0.0101(11) -0.0011(12)

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All esds (except the esd in the dihedral angle between two l.s. planes)
 are estimated using the full covariance matrix. The cell esds are taken
 into account individually in the estimation of esds in distances, angles
 and torsion angles; correlations between esds in cell parameters are only
 used when they are defined by crystal symmetry. An approximate (isotropic)
 treatment of cell esds is used for estimating esds involving l.s. planes.

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 Ti1 N1 C4 C3 -178.29(14) ?
 C1 N1 C4 Ti1 177.48(19) ?
 C2 C3 C4 N2 166.3(2) ?
 C2 C3 C4 N1 -14.9(2) ?
 C2 C3 C4 Ti1 -20.5(7) ?
 N5 Ti1 C4 N2 77.38(12) ?
 N6 Ti1 C4 N2 -178.37(11) ?
 N1 Ti1 C4 N2 -179.30(19) ?
 N3 Ti1 C4 N2 -25.61(14) ?
 N4 Ti1 C4 N2 -79.80(12) ?
 C11 Ti1 C4 N2 -55.22(12) ?
 N5 Ti1 C4 N1 -103.31(13) ?
 N6 Ti1 C4 N1 0.93(15) ?
 N3 Ti1 C4 N1 153.70(12) ?
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 N2 Ti1 C4 N1 179.30(19) ?
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 N1 Ti1 C4 C3 6.4(5) ?
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 N4 Ti1 C4 C3 105.9(6) ?
 N2 Ti1 C4 C3 -174.3(6) ?
 C11 Ti1 C4 C3 130.5(6) ?

C4 N2 C5 C6 -159.48(19) ?
 Ti1 N2 C5 C6 17.6(4) ?
 C4 N2 C5 C7 78.0(2) ?
 Ti1 N2 C5 C7 -105.0(3) ?
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 Ti1 N3 C8 C9 -164.3(3) ?
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 C8 C9 C10 C11 16.5(3) ?
 C12 N4 C11 N3 173.16(17) ?
 Ti1 N4 C11 N3 3.41(17) ?
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 C12 N4 C11 Ti1 169.7(2) ?
 C8 N3 C11 N4 177.67(18) ?
 Ti1 N3 C11 N4 -3.66(18) ?
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 Ti1 N3 C11 C10 176.88(14) ?
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 C9 C10 C11 N3 -9.7(2) ?
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 N6 Ti1 C11 N4 82.03(12) ?
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 N1 Ti1 C11 N3 160.25(12) ?
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 Ti2 N7 C19 C20 -167.3(3) ?
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 C19 C20 C21 C22 19.0(3) ?
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 Ti2 N8 C22 N7 1.70(17) ?
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 Ti2 N8 C22 C21 -179.3(2) ?
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 Ti2 N7 C22 N8 -1.86(19) ?
 C19 N7 C22 C21 -1.7(2) ?

Ti2 N7 C22 C21 178.90(14) ?
 C19 N7 C22 Ti2 179.42(19) ?
 C20 C21 C22 N8 169.5(2) ?
 C20 C21 C22 N7 -11.4(2) ?
 C20 C21 C22 Ti2 -7.8(7) ?
 N11 Ti2 C22 N8 -170.35(12) ?
 N12 Ti2 C22 N8 82.17(13) ?
 N7 Ti2 C22 N8 178.08(19) ?
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 N10 Ti2 C22 N8 -77.76(12) ?
 C29 Ti2 C22 N8 -51.91(13) ?
 N11 Ti2 C22 N7 11.56(15) ?
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 N9 Ti2 C22 N7 160.25(12) ?
 N10 Ti2 C22 N7 104.15(12) ?
 N8 Ti2 C22 N7 -178.08(19) ?
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 C22 N8 C23 C24 151.3(2) ?
 Ti2 N8 C23 C24 -43.2(4) ?
 C22 N8 C23 C25 -87.1(3) ?
 Ti2 N8 C23 C25 78.4(3) ?
 C29 N9 C26 C27 -7.2(3) ?
 Ti2 N9 C26 C27 -171.1(3) ?
 N9 C26 C27 C28 10.7(3) ?
 C26 C27 C28 C29 -9.9(3) ?
 C30 N10 C29 N9 -179.70(17) ?
 Ti2 N10 C29 N9 3.90(18) ?
 C30 N10 C29 C28 2.8(3) ?
 Ti2 N10 C29 C28 -173.6(2) ?
 C30 N10 C29 Ti2 176.40(19) ?
 C26 N9 C29 N10 -177.33(19) ?
 Ti2 N9 C29 N10 -4.19(19) ?
 C26 N9 C29 C28 0.7(3) ?
 Ti2 N9 C29 C28 173.80(16) ?
 C26 N9 C29 Ti2 -173.1(2) ?
 C27 C28 C29 N10 -176.4(2) ?
 C27 C28 C29 N9 6.1(3) ?
 C27 C28 C29 Ti2 27.5(8) ?
 N11 Ti2 C29 N10 75.36(13) ?
 N12 Ti2 C29 N10 -178.24(12) ?
 N7 Ti2 C29 N10 -30.10(14) ?
 N9 Ti2 C29 N10 175.69(19) ?
 N8 Ti2 C29 N10 -82.74(12) ?
 C22 Ti2 C29 N10 -59.21(13) ?
 N11 Ti2 C29 N9 -100.33(13) ?
 N12 Ti2 C29 N9 6.07(15) ?
 N7 Ti2 C29 N9 154.21(12) ?
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 N8 Ti2 C29 N9 101.57(13) ?

C22 Ti2 C29 N9 125.09(12) ?
N11 Ti2 C29 C28 -124.8(7) ?
N12 Ti2 C29 C28 -18.4(7) ?
N7 Ti2 C29 C28 129.7(7) ?
N9 Ti2 C29 C28 -24.5(6) ?
N10 Ti2 C29 C28 159.8(7) ?
N8 Ti2 C29 C28 77.1(7) ?
C22 Ti2 C29 C28 100.6(7) ?
C29 N10 C30 C32 -153.21(19) ?
Ti2 N10 C30 C32 19.5(3) ?
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Ti2 N10 C30 C31 -103.1(3) ?

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_diffn_reflns_theta_full 25.00
_diffn_measured_fraction_theta_full 1.000
_refine_diff_density_max 0.409
_refine_diff_density_min -0.251
_refine_diff_density_rms 0.055

A.12 Compound 22

data_seab003a

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;
_chemical_name_common      ?
_chemical_melting_point    ?
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_chemical_formula_weight    643.13
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'C' 'C' 0.0033 0.0016
'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
'H' 'H' 0.0000 0.0000
'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
'N' 'N' 0.0061 0.0033
'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
'Zr' 'Zr' -2.9673 0.5597
'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
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_symmetry_space_group_name_H-M Ccca
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_symmetry_equiv_pos_as_xyz
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'-x+1/2, -y, z'
'-x, y, -z+1/2'
'x+1/2, -y, -z+1/2'
'x+1/2, y+1/2, z'
'-x+1, -y+1/2, z'
'-x+1/2, y+1/2, -z+1/2'
'x+1, -y+1/2, -z+1/2'
'-x, -y, -z'
'x-1/2, y, -z'
'x, -y, z-1/2'
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'-x+1/2, -y+1/2, -z'
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'x+1/2, -y+1/2, z-1/2'
'-x, y+1/2, z-1/2'
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_cell_length_b      35.647(5)
_cell_length_c      15.144(2)
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_cell_angle_beta     90.00
_cell_angle_gamma    90.00
_cell_volume         14508(3)
_cell_formula_units_Z 16
_cell_measurement_temperature 120(2)
_cell_measurement_reflns_used 1013
_cell_measurement_theta_min 2.33
_cell_measurement_theta_max 28.13

_exptl_crystal_description block
_exptl_crystal_colour colorless
_exptl_crystal_size_max 0.40
_exptl_crystal_size_mid 0.30
_exptl_crystal_size_min 0.20
_exptl_crystal_density_meas ?
_exptl_crystal_density_diffn 1.178
_exptl_crystal_density_method 'not measured'
_exptl_crystal_F_000 5568
_exptl_absorpt_coefficient_mu 0.334
_exptl_absorpt_correction_type multi-scan
_exptl_absorpt_correction_T_min 0.8779
_exptl_absorpt_correction_T_max 0.9361
_exptl_absorpt_process_details 'SADABS, Sheldrick (2003)'

_exptl_special_details
;
Data collection is performed with four batch runs at
\l = 0.00 \% (600 frames), at \l = 90.00 \%
(600 frames), at \l = 180 \% (600 frames) and
at \l = 270 \% (600 frames).
Frame width = 0.30 \& in \w. Data is
merged, corrected for decay, and treated with
multi-scan absorption corrections.
;

_diffn_ambient_temperature 120(2)
_diffn_radiation_wavelength 0.71073
_diffn_radiation_type MoK\alpha
_diffn_radiation_source 'fine-focus sealed tube'
_diffn_radiation_monochromator graphite
_diffn_measurement_device_type 'Bruker AXS APEX diffractometer'
_diffn_measurement_method \w
_diffn_detector_area_resol_mean 836.6
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_diffn_standards_interval_count ?
_diffn_standards_interval_time ?
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_diffn_reflns_number 77808
_diffn_reflns_av_R_equivalents 0.0458
_diffn_reflns_av_sigma/netI 0.0256
_diffn_reflns_limit_h_min -34
_diffn_reflns_limit_h_max 34

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_diffrn_reflms_limit_k_max    46
_diffrn_reflms_limit_l_min    -19
_diffrn_reflms_limit_l_max    19
_diffrn_reflms_theta_min      1.65
_diffrn_reflms_theta_max      28.26
_reflms_number_total          8630
_reflms_number_gt             7822
_reflms_threshold_expression   >2sigma(I)

_computing_data_collection    'SMART, Bruker (2002)'
_computing_cell_refinement     'SHELXTL, Sheldrick (2001)'
_computing_data_reduction      'SHELXTL, Sheldrick (2001)'
_computing_structure_solution  'SHELXS-97 (Sheldrick, 1990)'
_computing_structure_refinement 'SHELXL-97 (Sheldrick, 1997)'
_computing_molecular_graphics  'SHELXTL, Sheldrick (2001)'
_computing_publication_material 'SHELXTL, Sheldrick (2001)'

_refine_special_details
;
Refinement of F2 against ALL reflections. The weighted R-factor wR and
goodness of fit S are based on F2, conventional R-factors R are based
on F, with F set to zero for negative F2. The threshold expression of
F2 > 2sigma(F2) is used only for calculating R-factors(gt) etc. and is
not relevant to the choice of reflections for refinement. R-factors based
on F2 are statistically about twice as large as those based on F, and R-
factors based on ALL data will be even larger.
;

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_refine_ls_matrix_type          full
_refine_ls_weighting_scheme      calc
_refine_ls_weighting_details
'calc w=1/[s2(Fo2)+(0.0572P)2+21.5329P] where P=(Fo2+2Fc2)/3'
_atom_sites_solution_primary     direct
_atom_sites_solution_secondary   difmap
_atom_sites_solution_hydrogens   geom
_refine_ls_hydrogen_treatment    constr
_refine_ls_extinction_method      none
_refine_ls_extinction_coef        ?
_refine_ls_number_reflms         8630
_refine_ls_number_parameters     388
_refine_ls_number_restraints     0
_refine_ls_R_factor_all          0.0473
_refine_ls_R_factor_gt           0.0425
_refine_ls_wR_factor_ref         0.1135
_refine_ls_wR_factor_gt          0.1094
_refine_ls_goodness_of_fit_ref   1.063
_refine_ls_restrained_S_all      1.063
_refine_ls_shift/su_max          0.003
_refine_ls_shift/su_mean         0.000

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_atom_site_type_symbol
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_atom_site_fract_z
_atom_site_U_iso_or_equiv
_atom_site_adp_type
_atom_site_occupancy
_atom_site_symmetry_multiplicity
_atom_site_calc_flag
_atom_site_refinement_flags
_atom_site_disorder_assembly
_atom_site_disorder_group
Zr Zr 0.623618(6) 0.376683(5) 0.491472(11) 0.01760(7) Uani 1 1 d ...
N1 N 0.61787(5) 0.43306(4) 0.55186(9) 0.0176(3) Uani 1 1 d ...
N2 N 0.66947(5) 0.42339(4) 0.43764(9) 0.0163(3) Uani 1 1 d ...
N3 N 0.65698(6) 0.48638(4) 0.48286(11) 0.0238(3) Uani 1 1 d ...
H3D H 0.6768(13) 0.4928(10) 0.449(2) 0.029 Uiso 0.67 1 d P ...
N4 N 0.56345(5) 0.38263(4) 0.39683(9) 0.0177(3) Uani 1 1 d ...
N5 N 0.61938(5) 0.33698(4) 0.38163(10) 0.0183(3) Uani 1 1 d ...
N6 N 0.55814(6) 0.34757(5) 0.26462(10) 0.0291(4) Uani 1 1 d ...
H6D H 0.5305(14) 0.3525(10) 0.261(2) 0.035 Uiso 0.67 1 d P ...
N7 N 0.59714(6) 0.34515(4) 0.60654(10) 0.0244(3) Uani 1 1 d ...
N8 N 0.67837(5) 0.34708(4) 0.57680(10) 0.0214(3) Uani 1 1 d ...
N9 N 0.65718(8) 0.31879(5) 0.71184(11) 0.0358(4) Uani 1 1 d ...
H9D H 0.6922(15) 0.3130(11) 0.723(3) 0.043 Uiso 0.67 1 d P ...
C1 C 0.61309(7) 0.44906(5) 0.64108(11) 0.0235(4) Uani 1 1 d ...
H1 H 0.6093 0.4769 0.6354 0.028 Uiso 1 1 calc R ...
C2 C 0.56698(7) 0.43365(7) 0.68603(13) 0.0326(4) Uani 1 1 d ...
H2A H 0.5374 0.4406 0.6518 0.049 Uiso 1 1 calc R ...
H2B H 0.5644 0.4442 0.7456 0.049 Uiso 1 1 calc R ...
H2C H 0.5693 0.4063 0.6897 0.049 Uiso 1 1 calc R ...
C3 C 0.66043(8) 0.44106(8) 0.69319(13) 0.0408(5) Uani 1 1 d ...
H3A H 0.6653 0.4139 0.6978 0.061 Uiso 1 1 calc R ...
H3B H 0.6575 0.4518 0.7525 0.061 Uiso 1 1 calc R ...
H3C H 0.6890 0.4523 0.6628 0.061 Uiso 1 1 calc R ...
C4 C 0.64852(6) 0.44935(5) 0.49176(11) 0.0174(3) Uani 1 1 d ...
C5 C 0.62243(7) 0.51641(6) 0.50825(13) 0.0259(4) Uani 1 1 d ...
H5 H 0.5916 0.5048 0.5330 0.031 Uiso 1 1 calc R ...
C6 C 0.60844(9) 0.53883(7) 0.42665(16) 0.0422(6) Uani 1 1 d ...
H6A H 0.6383 0.5507 0.4020 0.063 Uiso 1 1 calc R ...
H6B H 0.5843 0.5582 0.4427 0.063 Uiso 1 1 calc R ...
H6C H 0.5937 0.5221 0.3825 0.063 Uiso 1 1 calc R ...
C7 C 0.64528(10) 0.54155(6) 0.57812(16) 0.0446(6) Uani 1 1 d ...
H7A H 0.6549 0.5264 0.6293 0.067 Uiso 1 1 calc R ...
H7B H 0.6209 0.5605 0.5964 0.067 Uiso 1 1 calc R ...
H7C H 0.6748 0.5540 0.5538 0.067 Uiso 1 1 calc R ...
C8 C 0.69648(6) 0.43597(5) 0.35891(11) 0.0201(3) Uani 1 1 d ...
H8 H 0.6786 0.4580 0.3333 0.024 Uiso 1 1 calc R ...
C9 C 0.74979(7) 0.44804(5) 0.38202(13) 0.0268(4) Uani 1 1 d ...
H9A H 0.7491 0.4649 0.4330 0.040 Uiso 1 1 calc R ...
H9B H 0.7646 0.4611 0.3314 0.040 Uiso 1 1 calc R ...
H9C H 0.7697 0.4258 0.3963 0.040 Uiso 1 1 calc R ...
C10 C 0.69769(8) 0.40473(5) 0.28998(12) 0.0297(4) Uani 1 1 d ...
H10A H 0.7139 0.3825 0.3151 0.044 Uiso 1 1 calc R ...
H10B H 0.7163 0.4132 0.2381 0.044 Uiso 1 1 calc R ...
H10C H 0.6636 0.3984 0.2725 0.044 Uiso 1 1 calc R ...
C11 C 0.53199(6) 0.41268(5) 0.36041(11) 0.0200(3) Uani 1 1 d ...
H11 H 0.5055 0.4010 0.3231 0.024 Uiso 1 1 calc R ...

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C12 C 0.50694(7) 0.43406(6) 0.43525(13) 0.0291(4) Uani 1 1 d . . .
 H12A H 0.4877 0.4166 0.4716 0.044 Uiso 1 1 calc R . .
 H12B H 0.4847 0.4531 0.4106 0.044 Uiso 1 1 calc R . .
 H12C H 0.5324 0.4462 0.4717 0.044 Uiso 1 1 calc R . .
 C13 C 0.56244(7) 0.43944(5) 0.30249(13) 0.0268(4) Uani 1 1 d . . .
 H13A H 0.5886 0.4511 0.3381 0.040 Uiso 1 1 calc R . .
 H13B H 0.5406 0.4589 0.2785 0.040 Uiso 1 1 calc R . .
 H13C H 0.5776 0.4254 0.2538 0.040 Uiso 1 1 calc R . .
 C14 C 0.57978(6) 0.35426(5) 0.34171(11) 0.0175(3) Uani 1 1 d . . .
 C15 C 0.58045(7) 0.32789(5) 0.18970(11) 0.0228(4) Uani 1 1 d . . .
 H15 H 0.6131 0.3170 0.2085 0.027 Uiso 1 1 calc R . .
 C16 C 0.58933(10) 0.35530(7) 0.11482(15) 0.0450(6) Uani 1 1 d . . .
 H16A H 0.5575 0.3660 0.0957 0.067 Uiso 1 1 calc R . .
 H16B H 0.6050 0.3422 0.0652 0.067 Uiso 1 1 calc R . .
 H16C H 0.6113 0.3755 0.1351 0.067 Uiso 1 1 calc R . .
 C17 C 0.54663(10) 0.29656(7) 0.15981(19) 0.0525(7) Uani 1 1 d . . .
 H17A H 0.5435 0.2780 0.2071 0.079 Uiso 1 1 calc R . .
 H17B H 0.5607 0.2846 0.1072 0.079 Uiso 1 1 calc R . .
 H17C H 0.5137 0.3068 0.1457 0.079 Uiso 1 1 calc R . .
 C18 C 0.63602(7) 0.29867(5) 0.36071(12) 0.0214(3) Uani 1 1 d . . .
 H18 H 0.6135 0.2880 0.3145 0.026 Uiso 1 1 calc R . .
 C19 C 0.68896(8) 0.29927(6) 0.32472(15) 0.0322(4) Uani 1 1 d . . .
 H19A H 0.6898 0.3138 0.2698 0.048 Uiso 1 1 calc R . .
 H19B H 0.6999 0.2735 0.3129 0.048 Uiso 1 1 calc R . .
 H19C H 0.7111 0.3108 0.3683 0.048 Uiso 1 1 calc R . .
 C20 C 0.63316(8) 0.27392(5) 0.44265(13) 0.0301(4) Uani 1 1 d . . .
 H20A H 0.6547 0.2843 0.4888 0.045 Uiso 1 1 calc R . .
 H20B H 0.6442 0.2485 0.4278 0.045 Uiso 1 1 calc R . .
 H20C H 0.5987 0.2731 0.4640 0.045 Uiso 1 1 calc R . .
 C21 C 0.55085(7) 0.33069(6) 0.64501(13) 0.0304(4) Uani 1 1 d . . .
 H21 H 0.5489 0.3392 0.7079 0.036 Uiso 1 1 calc R . .
 C22 C 0.50696(8) 0.34735(8) 0.59477(15) 0.0433(6) Uani 1 1 d . . .
 H22A H 0.5078 0.3748 0.5996 0.065 Uiso 1 1 calc R . .
 H22B H 0.4758 0.3379 0.6199 0.065 Uiso 1 1 calc R . .
 H22C H 0.5091 0.3401 0.5325 0.065 Uiso 1 1 calc R . .
 C23 C 0.54848(10) 0.28788(7) 0.64320(16) 0.0461(6) Uani 1 1 d . . .
 H23A H 0.5461 0.2793 0.5819 0.069 Uiso 1 1 calc R . .
 H23B H 0.5192 0.2794 0.6762 0.069 Uiso 1 1 calc R . .
 H23C H 0.5786 0.2776 0.6704 0.069 Uiso 1 1 calc R . .
 C24 C 0.64329(7) 0.33619(5) 0.63636(12) 0.0237(4) Uani 1 1 d . . .
 C25 C 0.73129(7) 0.34379(5) 0.59798(13) 0.0256(4) Uani 1 1 d . . .
 H25 H 0.7360 0.3505 0.6616 0.031 Uiso 1 1 calc R . .
 C26 C 0.76047(8) 0.37149(6) 0.54205(16) 0.0363(5) Uani 1 1 d . . .
 H26A H 0.7562 0.3653 0.4794 0.054 Uiso 1 1 calc R . .
 H26B H 0.7958 0.3701 0.5576 0.054 Uiso 1 1 calc R . .
 H26C H 0.7482 0.3969 0.5530 0.054 Uiso 1 1 calc R . .
 C27 C 0.75125(8) 0.30403(6) 0.58326(15) 0.0351(5) Uani 1 1 d . . .
 H27A H 0.7317 0.2862 0.6183 0.053 Uiso 1 1 calc R . .
 H27B H 0.7862 0.3029 0.6015 0.053 Uiso 1 1 calc R . .
 H27C H 0.7486 0.2976 0.5205 0.053 Uiso 1 1 calc R . .
 C28 C 0.63215(8) 0.31844(6) 0.79704(13) 0.0335(4) Uani 1 1 d . . .
 H28 H 0.5969 0.3103 0.7880 0.040 Uiso 1 1 calc R . .
 C29 C 0.63199(10) 0.35697(7) 0.84028(15) 0.0436(6) Uani 1 1 d . . .
 H29A H 0.6663 0.3658 0.8471 0.065 Uiso 1 1 calc R . .
 H29B H 0.6161 0.3553 0.8984 0.065 Uiso 1 1 calc R . .
 H29C H 0.6134 0.3746 0.8031 0.065 Uiso 1 1 calc R . .

C30 C 0.65827(9) 0.28969(7) 0.85521(14) 0.0415(5) Uani 1 1 d . . .
H30A H 0.6575 0.2651 0.8263 0.062 Uiso 1 1 calc R . .
H30B H 0.6412 0.2881 0.9123 0.062 Uiso 1 1 calc R . .
H30C H 0.6929 0.2974 0.8645 0.062 Uiso 1 1 calc R . .

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_geom_special_details

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All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

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N6 C15 1.462(2) . ?
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