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**(2,2',2''-TERPYRIDINE)PLATINUM(II) COMPLEXES OF
PHENYLCYANAMIDE AND 1,4-DICYANAMIDO-2,5-
DIMETHYLBENZENE LIGANDS**

by

Fahad A.I. AL-mutlaq, B.Sc.

A thesis submitted to
the Faculty of Graduate Studies and Research
in partial fulfilment of
the requirements for the degree of
Master of Science

Department of Chemistry

Carleton University

Ottawa, ON

December, 1999

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Abstract

A series of square planar terpyridineplatinum(II) complexes of the phenylcyanamide ligand and its derivatives has been synthesized and characterized by IR, ^1H NMR, UV-Visible spectroscopy, cyclic voltammetry and X-ray crystallography. The crystal structures of $[(\text{trpy})\text{Pt}(\text{pcyd})](\text{PF}_6)$ and $[(\text{trpy})\text{Pt}(2,4\text{-Me}_2\text{-pcyd})](\text{CF}_3\text{SO}_3)$ show that the complexes are planar and the Pt-NCN bond is bent with angles in the range of 159 to 175°. Since the formation of π -stacks in the crystal lattice requires planarity, the fact that the molecule is planar leads to the comparison with organic charge transfer salts that show π -stacking and are highly conductive. It is suggested that the bending of the cyanamide group allows for mixing between the σ^* orbital of the metal and the π_{nb} orbital of the ligand and causes the appearance of the ligand-to-metal charge transfer (LMCT) in the visible spectrum.

Two dinuclear terpyridineplatinum (II) complexes of derivatives of the 1,4-dicyanamidobenzene dianion (dicyd^{2-}) were also synthesized and characterized by IR, ^1H NMR, UV-Visible spectroscopy, and cyclic voltammetry.

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Finally, I would like to thank my colleagues: Dr. Chris White, Maria DeRosa, Peter Mosher and any other people who have assisted me during my time at Carleton.

Dedication

*This work is dedicated to my
parents, my wife, Hissah
Alabdulkarim, and my children,
Afnan, Yasser, and Mohammad.*

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List of Abbreviations

Me	methyl
DC	dichloro
MeO	methoxy
TBAH	tetrabutylammonium Hexafluorophosphate
trpy	terpyridine
TMS	tetramethylsilane
Pcyd ⁻	phenylcyanamide
Dicyd ²⁻	1,4-dicyanamidobenzene
Dip	1,3-bis(2-pyridylimino) isoindolinato

Chapter 1

Introduction

1.1 Background Information

1.1.1 Introduction to Molecular Metals

In recent years, many materials with remarkable electronic properties have been synthesized. Among these are the molecular metals, which are generally composed of radical ions derived from donors (π -bases) and acceptors (π -acids).¹ High conductivity in these types of complexes is associated with crystal structures in which planar molecules are packed face to face.² π overlap and charge transfer interaction between molecules cause the unpaired π -electrons to be partially delocalized along these one-dimensional stacks. This means that these complexes can conduct electricity in that direction. Two important molecules involved in this branch of chemistry are tetracyano *p*-quinodimethane (TCNQ) and tetrathiafulvalene (TTF) (see figure 1.1).

Figure 1.1: Diagrams of TCNQ and TTF

The single crystals of these molecular metals have certain properties³:

1. The crystal lattices consist of planar stacks of donors and acceptors.
2. The stacks themselves must be partially charged, i.e. consist of neutral and charged molecules.
3. The conductivity in these stacks is one dimensional, i.e. the conductivity is highest along the stacking axis.

The stacking pattern is also important in the conductivity of charge transfer salts.

There are two main types of stacking ⁴:

1. Mixed stacks, where donors (D) and acceptors (A) stack alternatively (i.e. D-A-D-A-D-A)
2. Segregated stacks, where donors and acceptors stack separately (i.e. D-D-D-D-D..., and A-A-A-A-A....)

Compounds that are segregated stacks conduct much more efficiently than mixed stacks. This is because in segregated stacks, the electrons are less localized due to efficient π -orbital overlap. Short interplanar distances (3.17 Å for TCNQ and 3.4 Å for TTF) are crucial to the design of molecular metals, because it allows for π -molecular orbital interaction and leads to the formation of a band,⁵ as illustrated by figure 1.2.

Figure 1.2: Formation of energy bands in a solid based on the overlap of atomic orbitals⁶

Each band is made up of electronic states and the energy of these states form a continuous range.⁴ When the energy gap between the valence band and conduction band (see figure 1.3) is large, the material is considered to be an insulator. In materials with smaller band gaps, promotion of an electron from the valence band to the conduction band is possible. These materials are known as semiconductors. In metals, the valence band is partially filled, where electrons can move easily into unlimited higher unoccupied levels, allowing for conduction. The highest occupied level is known as the Fermi level. Its electrons, and those close to this level have a major influence on the physical properties of the material.⁵

In charge transfer complexes, the bands are derived from the HOMO from the donor species and the LUMO for the acceptor species. Conductivity increases in these complexes as the temperature decreases due to the reduction in the vibration of the atomic lattice, thus increasing orbital overlap. This is the opposite of the temperature

dependence of semiconductors. At lower temperatures, less energy is available to promote electron across the band gap.

Figure 1.3: Band structure of solids.⁷

Organic molecules such as TCNQ and TTF are not the only molecules that act as molecular metals. If a planar molecule within a π -stack is bound to a transition metal, variations in its molecular properties can be introduced by changing the nature of the π interactions with the metal.⁸ This can cause variations in the conductivity of the molecular metal, as long as these perturbations do not affect the π stack. In the 1960's, inorganic complexes such as $K_2[Pt(CN)_4]Br_{0.3} \cdot 3H_2O$ showed one dimensional metal-like characteristics due to the overlap of the metal d_z^2 orbitals.⁹ Much effort has been put into incorporating the structural features of the organic metals into the ligands for metal complexes. In 1986, a series of highly conducting copper(II) DCNQI (N,N'-dicyanoquinonediimine) salts were discovered (see figure 1.4).¹⁰ The crystal structure

showed that the DCNQI molecules are arranged in stacks linked with tetrahedrally coordinated copper ions (see figure 1.5).

Figure 1.4: Diagram of DCNQI

Figure 1.5: Perspective view of the crystal structure of $\text{Cu}(\text{DCNQI})_2$ (H-atoms not shown)

The DCNQI molecule is almost planar and the copper compound consists of uniform face-to-face stacks of DCNQI molecules. By looking at the crystal structure, the conduction path seems to be formed mainly by overlapping π -orbitals of DCNQI.¹¹

Conduction through the copper atoms is unlikely, due to the large Cu-Cu distance (388 pm vs. the Cu-Cu distance in copper metal, which is 256 pm). In 2,5-dimethyl-DCNQI, the metallic conductivity was found to be caused by the mixture of carbon 2p, nitrogen 2p and copper 3d molecular orbitals in the valence band.¹²

With the discovery of the properties of this DCNQI complex, interest has grown in other conjugated, planar organic molecules which can π -stack as ligands. Other metal complexes of DCNQI and of phenyl cyanamide anion ligands may show high conductivity.¹³ Platinum(II) terpyridine complexes of phenylcyanamide or dicyanamidobenzene ligands may also be incorporated as building blocks in molecular wires and switches.

1.1.2 Introduction to the Chemistry of the Starting Materials

The study of transition metal complexes may be important in the understanding of electron transfer processes, mixed valence complexes, and magnetic coupling interactions, etc.¹⁴ Platinum(II) terpyridine complexes have been well studied, and this section will describe some of the chemistry of this system.

The inflexibility of terpyridine (trpy) as a ligand can cause steric effects to be severe in some metal complexes. Trpy is an interesting ligand because it does not allow for the regular octahedral geometries $[M(\text{trpy})_2]^{\text{m}+}$.¹⁵ Backbonding from filled metal d-orbitals to empty antibonding orbitals of planar ligands such as bipyridine, phenanthroline and terpyridine increases the stability of the metal complexes with these ligands.¹⁶ Platinum (II) complexes of terpyridine are known to be planar molecules similar to other 4-covalent palladium and platinum salts.¹⁷ The crystal structure of

palladium analogues confirms the square planar coordination. Figure 1.6 is the crystal structure of $[\text{PdCl}(\text{trpy})]^+$.

Figure 1.6: Crystal structure of $[\text{PdCl}(\text{trpy})]^+$ showing bond angles.

The structure is square planar with the coordinated terpyridine acting as a tridentate ligand. The empty coordination site is filled with a covalently bonded chlorine atom.¹⁸ The crystal structure consists of essentially planar molecules packed in layers as shown in figure 1.7.

Figure 1.7: View of the crystal structure of $[\text{PdCl}(\text{trpy})]^+$ showing intermolecular contact.

The distortion in the planarity of these complexes is likely due to the steric limitations of the terpyridine molecule. This means that there is some decrease in the stabilization energy afforded by the delocalized π bonding.¹⁹ The distance between palladium is about 3.4 Å which is close to the normal Vander Waal's radius. The closest distance between the palladium and the nitrogen of neighbouring molecules is 3.13 Å, 0.6 Å less than the Vander Waal's radius, showing that there is some interaction between the two groups.

The crystal structure of a $[(\text{trpy})\text{PtCl}]^+$ has also been determined.²⁰ Figure 1.8 is the ORTEP drawing of the structure which is similar to many diimine and tris-chelate complexes of platinum. The platinum-platinum bond in diimines arises from the overlap of the $5d_z^2$ and $6p_z$ orbitals of the neighbouring metal centres. The central trpy nitrogen and the platinum are relatively close with a short bond length of 1.952(15) Å. The other

Pt-N bond distances are near to 2 Å. The nitrogen-platinum-nitrogen bond angles are all less than 90°.

Figure 1.8: ORTEP crystal structure of $[\text{PtCl}(\text{trpy})]^-$

Figure 1.9 shows the two independent cations in the crystal lattice. The cations form a continuous stack along the x-direction, and show repeating short and long platinum-platinum interactions. Figure 1.9 A shows the short Pt-Pt bond, whose vector is nearly perpendicular to the two square planes. Figure 1.9B displays the long Pt-Pt distance. One of the platinum trpy units is shifted laterally. The Pt-Pt distance is longer, but the trpy-trpy interaction is essentially the same as in figure 1.9A.

The ligand field strength strongly influences the Pt-Pt interaction and stacking. Strong field ligands destabilize $5d_{22}$ and allow for more interaction with stacking. Also, π -acceptor and donor ligands affect stacking. Acceptors decrease the electron density on the metal centre, lessening the repulsion and shortening the Pt-Pt distance.²¹

Figure 1.9: ORTEP drawings of the two types of cation-cation interactions along the $[\text{Pt}(\text{trpy})\text{Cl}]^+$ chains. Structure A has a shorter Pt-Pt distances, while B has longer Pt-Pt distances.

Different colours of the platinum terpyridine starting material can be explained by variations in the stacking arrangements of the planar cations.

The UV-vis spectrum of platinum(II) terpyridine complexes has been extensively studied. An intense visible absorption in these complexes has been assigned to a spin-allowed metal-to-ligand charge transfer (MLCT) involving $d\pi$ -orbital of platinum as the donor orbital and the π^* -orbitals of trpy as acceptors. As the σ -electron donating ability of the fourth coordinated ligand increases, the removal of an electron from the $d\pi$ -orbital becomes easier and corresponding bands move to lower energies.²² The apparent extinction coefficient in the UV decreases with increases $[(\text{trpy})\text{PtCl}]^+$ concentration due to the fact that the UV absorption bands of the oligomers are broader than those of the monomers.¹⁹

1.1.3 Introduction to Metal Complexes of the Phenylcyanamide Anion and the Dicyanamidobenzene Dianion

The study of the transition metal coordination chemistry of phenylcyanamide systems is important as its information may lead to the construction of molecular materials.

The cyanamide functional group is a resonance stabilized three-atom π -system. There are two pairs of non-bonding electrons that can be delocalized in these systems (See figure 1.10).²³ Resonance structure A will coordinate to the metal via the nitrile lone pair, if only σ -bonding interactions to the terminal cyanamide nitrogen are considered. This results in an ideal bond angle of 180° . Resonance structure B will lead to the ideal bond angle of 120° . However, a mixture of the two resonance of A and B results in a bond angle between the two extremes.²⁴ Resonance structure B will be favoured in cases of strongly electropositive metal ions and metal ions with strong π -acceptor character. The bond angle in these cases will be close to 180° , to maximize interaction with the electron pairs on the nitrogens.

Free anionic cyanamide ligands are anticipated to be planar, if there are no steric effects. This is easily explained by the strong interaction of the cyanamide group with the phenyl ring.²² An interesting property of the phenyl cyanamide ligands is that the σ and π -donor properties can be adjusted by changing the substituents on the phenyl ring.²¹

In $[(\text{trpy})\text{Pd}(\text{Cl}_2\text{-pcyd})]^+$, the pcyd is in the same plane as the trpy. This is due to the extra space available in the fourth coordination site and the lack of steric hindrance. This is in contrast to the $[\text{Ni}(\text{dip})(2\text{-Clpcyd})]$ complex, where the phenylcyanamide is forced out of the plane by the sterically hindered ligand.⁸ In most transition metal-phenyl

cyanamide complexes planarity of the cyanamide ligand is retained, provided steric hindrance is not a problem.

a)

b)

Figure 1.10: a) Resonance stabilized phenylcyanamide anion ligand. b) Orthogonal π -symmetry molecular orbitals resulting from the delocalization of two non-bonding electron pairs as in resonance form B. The size of the atomic orbitals approximate their contribution to the molecular orbital.

Dinuclear metal systems involving dicyd²⁻ have been well investigated for their possible role in molecular switching devices. The control of metal-metal coupling is very important in the control of signal transfer. Metal-metal coupling in dinuclear ruthenium complexes were shown to be sensitive to the nature of the outer-coordination sphere.²⁵

Palladium dinuclear dicyd complexes, such as $[\{(\text{trpy})\text{Pd}\}_2-\mu-(\text{Me}_2\text{dicyd})]\text{Cl}$ have also been synthesized and characterized by IR, ¹H NMR, UV and cyclic voltammetry.²⁶ These complexes were shown to have unusual electrochemical properties, undergoing 2-

electron processes, unlike similar dinuclear ruthenium complex. It was also found that the substituents on the dicyd phenyl ring affect the ligand's π -donor properties.

1.2 Aims of this Thesis

Referring to the figure 1.5, the crystal structure of $\text{Cu}(\text{DCNQI})_2$ shows planarity of the DCNQI molecules and the high conductivity through the partially empty rings of this molecule is due to the segregated π -stacking. Interactions exist through the 2p of the carbon and nitrogen and the 3d of copper. The proposal of this research depends on the possibility of building similar systems by taking two copper atoms and using dicyd²⁻ instead of DCNQI as a bridging ligand. Also, the other three DCNQI ligands bonded to each copper are replaced by trpy, because trpy is a planar ligand. At the same time, platinum is used instead of copper, due to its square planar geometry. Thus, the dinuclear complex will be planar and this should facilitate π -stacking. The goal of this project is to grow crystals which have conductive properties through π -stacking of dicyd²⁻ molecules when oxidized by doping with I_2 .

1. To synthesize and characterize a series of mononuclear terpyridineplatinum(II) phenylcyanamide complexes:

where $\text{X} = \text{H}, 2,3\text{-Cl}_2, 3,5\text{-Me}_2, 3,5\text{-(MeO)}_2$

2. To synthesize and characterize dinuclear terpyridineplatinum(II) dicyanamidobenzene complexes:

where X = 2,5-Cl₂
2,5-Me₂

3. To investigate the spectroscopic and structural properties of the above complexes.

Chapter 2

Experimental Section

2.1 Starting Materials

2.1.1. Reagents for Ligand Synthesis

Ammonium thiocyanate (97%, ACS Reagent, Aldrich), benzoyl chloride (99%, Reagent Grade, Aldrich), lead (II) acetate trihydrate (>99%, Aldrich), glacial acetic acid (99.7%, Anachemia), triethylamine (TEA, >99%, Alfa Aesar), sodium hydroxide (Lab Grade, Anachemia), thallium (I) acetate (99.99%, Aldrich), ammonium thiocyanate (98%, Aldrich), aniline (99%, Aldrich), 2,5-dimethylaniline (99%, Aldrich), 3,5-dimethoxyaniline (99%, Aldrich), 1,4-phenylenediamine (97%, Aldrich), 3,5-dimethyl-1,4-phenylenediamine (97%, Aldrich), 3,5-dichloro-1,4-phenylenediamine (97%, Aldrich), Ferrocene (J.T. Baker Chemical Co., sublimed) all have been used as received.

2.1.2 Reagents for Complex Synthesis

Potassium tetrachloroplatinate(II) (99.9%, Pressure Chemical Co.), 2,2':6',2''-terpyridine (98%, Aldrich), ammonium hexafluorophosphate (>95%, Aldrich), hydrochloric acid (36.5-38.0%, Reagent Grade, Anachemia) have been used without further purification.

2.1.3 Compressed Gases

Nitrogen (BOC Gases), argon (Ultra high purity, BOC Gases).

2.2 Solvents

2.2.1 Solvents of the Synthesis

Ethanol (anhydrous, Commercial Alcohols, Inc.), methanol (Lab Grade, Anachemia; glass distilled before use), acetone (Lab Grade, Anachemia, glass distilled before use), diethyl ether (99%, anhydrous, Caledon Labs), acetonitrile (99.83%, HPLC Grade, Aldrich), dimethylformamide (99.98%, Anachemia), dimethylsulfoxide (99.9% min., ACS Reagent, Anachemia), water (distilled using an analytical deionizer).

2.2.2 U.V. Solvent

Dimethylformamide (99.8% min., ACS Reagent, Anachemia).

2.2.3 NMR Solvent

Deuterated dimethyl sulphoxide (DMSO isotopes), dimethyl-d₆-sulphoxide (99.9 atom% D, CDN Isotopes), tetramethylsilane (>99.9% NMR Grade, ACS Reagent, Aldrich).

2.2.4 Cyclic Voltammetry Electrolyte and Solvent

Tetrabutylammonium hexafluorophosphate was made by combining aqueous solutions of tetrabutylammonium bromide (99%, Aldrich) and ammonium hexafluorophosphate (>95%, Aldrich). The crude salt was recrystallized from ethanol twice and dried under vacuum at 110°C overnight. Dimethylformamide was purified by Al_2O_3 and distilled under vacuum and argon.

2.3 Syntheses of the Ligands

2.3.1 Thallium salts of phenylcyanamide derivatives

2.3.1.1 General Description

Benzoyl thiocyanate was prepared from the reaction of benzoyl chloride with ammonium thiocyanate, in acetone. To this was added the aniline to form thiourea derivative. This compound was desulphurised by a heavy metal salt such as lead (II) acetate, resulting in the phenylcyanamide anion which is protonated by acetic acid. The general scheme of the reaction is shown on the following page.

Scheme 2.1

where $R = \text{H}, \text{Cl}, \text{CH}_3, \text{or } \text{OCH}_3$

The neutral phenylcyanamide could be converted to its thallium salt. To get pure product, the reaction conditions should be carefully controlled. Also, there is equilibrium between the dimer and its anion monomer. As a result, when thallium acetate is introduced, the equilibrium will shift to the monomer anion to give thallium phenylcyanamide as the precipitate.

Scheme 2.1 (cont.)

2.3.1.2 Ligand Synthesis of phenylcyanamide and its derivatives

Thallium salt of phenylcyanamide anion [$\text{Tl}(\text{pcyd})$]

Benzoylchloride (2.8 g, 20 mmol in 20 ml acetone) was added dropwise to a boiling solution of ammonium thiocyanate (1.5 g, 20 mmol) in 20 ml acetone.

Immediately, ammonium chloride precipitated. The reaction was allowed to reflux for 10 min. After that, aniline (1.9 g, 20 mmol) in 20 ml of acetone was added dropwise to the reaction mixture. Then, the reaction was allowed to reflux for one hour to give milky

yellow solution which was poured slowly into 300 ml of distilled water with vigorous stirring. The yellowish precipitate (benzoylthiourea) was filtered by Buchner funnel and washed copiously with distilled water. The benzoyl thiourea was dissolved in 50 ml of hot aqueous solution of sodium hydroxide and boiled for 5 min. The solution was cooled to 60°C, and then 6.5 g (20 mmol) of lead acetate in 20 ml of distilled water was added. The reaction was maintained between 50-60°C for 5 min to give a deep black precipitation of PbS. Then, PbS was filtered off to get clear solution of phenylcyanamide anion which could be converted to thallium salt of the ligand by two methods:

First method:

The clear solution of phenylcyanamide anion was cooled in an ice bath. Then, 5 ml of glacial acetic acid was added to give immediately a white precipitate which was filtered and washed with distilled water. The yield of neutral of phenylcyanamide was 1.68 g (72%). The neutral phenylcyanamide (1.68 g, 14 mmol) was dissolved in 65 ml of a boiling mixture of water/acetone (1:1). Then, thallium acetate (6.5 g, 23.5 mmol) in 65 ml of water/acetone (1:1) was slowly added to main solution. Immediately, triethylamine (1.9 g, 18.7 mmol) was added. The solution was allowed to maintain boiling for one more minute and then was cooled to RT. White needle crystals were formed from the cooled solution which were filtered, collected and washed with water followed by acetone. The yield was 2.15 g (68.2%).

Second method:

Thallium acetate (5.3 g, 20.12 mmol) in 50 ml of water was added slowly to the clear solution of phenylcyanamide anion described above (2.4 g, 20 mmol). Then, the solution was heated for 5 minutes. It was allowed to cool, and a white precipitate was collected by filtration, washed with acetone and air dried. The yield was 4.60 g (72%).

Thallium salt of phenylcyanamide anion $\text{Tl}(\text{pcyd})$, and thallium salt of 2,3-dichlorophenylcyanamide anion, $\text{Tl}(2,3\text{-Cl}_2\text{pcyd})$, were prepared by both methods. However, thallium salt of 3,5-dimethylphenylcyanamide anion $\text{Tl}(3,5\text{-Me}_2\text{pcyd})$ and thallium salt of 3,5-dimethoxyphenylcyanamide anion $\text{Tl}(3,5\text{-(MeO)}_2\text{pcyd})$ were prepared by the first method.

2.3.2 Thallium salts of 1,4-Dicyanamidobenzene Derivatives

2.3.2.1 General Description

To prepare protonated dicyanamidobenzene, benzoyl thiocyanate was reacted with 1,4-phenylenediamine derivative with heating to form thiourea derivative. This was desulphurised by metal salt such as lead (II) acetate with gentle heating to get the dicyanamide dianion and was protonated by acetic acid to form white precipitation of neutral of 1,4-dicyanamidobenzene ($\text{H}_2\text{-dcyd}$). However, the temperature of the reaction should be maintained under 80°C to prevent dimerization.

2.3.2.2 Ligand Synthesis of 1,4-dicyanamidobenzene and its derivatives

Thallium salt of 2,5-dimethyl-1,4-dicyanamidobenzene $\text{Tl}_2(\text{Me}_2\text{-Dicyd})$

Ammonium thiocyanate (6.4 g, 84.2 mmol) in 85 ml of acetone was heated to boiling. Benzoyl chloride (11.8 g, 84.3 mmol) in 100 ml acetone was added to the boiling solution to give immediately a white precipitate of NH_4Cl . Then, 2,5-dimethyl-1,4-phenylenediamine (4.6 g, 42.6 mmol) in 85 ml of acetone was added slowly. After that, the mixture was allowed to boil for 15 min. Then, the mixture was poured to 1500 ml of distilled water with stirring. The white precipitation was filtered off by Buchner funnel and was washed with 150 ml of acetone, 150 ml of water and once more 150 ml acetone. The pale yellow wet complex was air dried.

The complex (15.9 g, 34 mmol) was dissolved in 200 ml of hot aqueous solution of NaOH (18.4 g, 0.4 mol). The solution was boiled for 10 min. and then was cooled to 70°C . Lead (II) acetate trihydrate (32.5 g, 85 mmol) in 80 ml of water was added to the solution with the temperature of the reaction kept between $60\text{--}70^\circ\text{C}$. A black (PbS) precipitate was filtered off by Buchner funnel. Then, the clear solution of 2,5-dimethyl-1,4-dicyanamidobenzene dianion was cooled by an ice bath and acidified with glacial acetic acid. The white precipitation of $\text{Me}_2\text{-H}_2\text{Dicyd}$ was filtered off and washed with water. Then, the product was allowed to dry overnight

The crude product was recrystallized by dissolving in minimum of hot acetone and then adding distilled water until it started to precipitate. Then, it was put in a fridge (5°C). After some time the crystals were filtered off and washed with very cold water/acetone (1:1). The yield was 3.39 g (54%).

Alternatively, the crude product was dissolved in hot minimum DMF and then was filtered (very deep blue solution in case of DM-H₂Dicyd and pink in case of DC-H₂-Dicyd). An equal volume of water was added to the filtrate, precipitating some product. The mixture was placed in the fridge overnight. The product was filtered and vacuum dried. The yield was high (80-90%). The IR spectra for the product derived by the two recrystallization methods were identical.

To convert 3,5-Me₂Dicyd to its thallium salt, there are two methods:

First method:

The neutral 2,5-dimethyl-1,4-dicyanamidobenzene (2.15 g, 12 mmol) in 150 ml of hot acetonitrile and the solution was filtered. Thallium acetate (6.3 g, 24 mmol) was added slowly. Triethylamine (2.7 g, 26.5 mmol) was added. Then, the solution was allowed to set aside to cool to give yellow precipitate which was filtered off and washed with water followed by acetone and dried. The yield was 5 g (70%).

Second method:

Thallium acetate (26.3 g, 100 mmol) which was dissolved in 25 ml of distilled water which was added to the clear solution of 2,5-dimethyl-1,4-dicyanamidobenzene dianion (2.6 g, 14 mmol). The solution was boiled for 10 min and then cooled to RT. The yellow precipitate was filtered off and washed with acetone and dried in air. The yield was 7.71 g (65%).

Scheme 2.2

2.4 Syntheses of starting materials

2.4.1 Chloro(terpyridine) platinum(II) chloride dihydrate [(trpy)PtCl]Cl•2H₂O

This complex was prepared by using the method for the analogous Pd complexes.²⁶ Potassium tetrachloroplatinate (II) (4.14 g, 10 mmol) was dissolved in 200 ml of deionized water. Terpyridine (2.87 g, 12 mmol) was added to the solution which, after 2 h of reflux, gave a colour change to yellow orange. The reaction was refluxed for four days until a Pt mirror began to form on the round-bottomed flask. The red solution was filtered and the filtrate's volume was reduced to 20% (40 ml). The red precipitate was filtered and washed with very cold water followed by acetone. The yield was 75-95%.

Scheme 2.3

The crude [(trpy)PtCl]Cl• 2H₂O (1.85 g, 3.7 mmol) was dissolved in a minimum of hot acetonitrile, filtered and was cooled to room temperature, yielding red crystals which were filtered and washed with acetone. The yield was 1.7 g (92% from crude).

Chloro(trpy) platinum(II)chloride dihydrate must be converted to the salt which is more soluble in most non-aqueous solvents such as PF₆ and CF₃SO₃.

2.4.2 Chloro(terpyridine) platinum (II) hexafluorophosphate $[(trpy)PtCl]PF_6$

This complex was made by using the method described for the analogous Pd complexes.²⁶ Chloro(terpy) platinum(II)chloride dihydrate (0.85 g, 1.7 mmol) was dissolved in 100 ml of distilled water and was heated to 50°C. Then, ammonium hexafluorophosphate (0.45 g, 2.8 mmol) was dissolved in 50 ml of distilled water. The latter was added slowly to the first solution with vigorous stirring, forming a yellow canary precipitate. The mixture was allowed to stir for 30 min. The precipitate was filtered off and washed with distilled water followed by acetone and dried in air overnight. The yield of the crude was (0.96 g, 1.6 mmol), 93%.

Scheme 2.4

To recrystallize the crude of $[(trpy)PtCl]PF_6$, it was dissolved in minimum of DMF solvent without heating. The solution was filtered and ether was allowed to diffuse into the solution. Yellow needle crystals were formed which were collected by filtration and washed with ether and dried under vacuum.

2.4.3 Triflate(terpyridine) platinum(II) Triflate $[(trpy)Pt(CF_3SO_3)](CF_3SO_3)$

This complex was made by using the method described for the analogous Pd complexes.²⁶ Chloro(trpy) platinum(II) chloride dihydrate (1.38 g, 2.8 mmol) was put in three-necked flask (25 ml) which was put in oil (SiO₂) bath. Nitrogen gas was allowed to

flow through the flask. Then, triflic acid (0.9 g, 5.5 mmol) was added carefully and slowly to the flask with stirring and increasing the temperature to 100°C. Hydrochloride gas evolved and was monitored by passing it through a silver nitrate solution (AgCl ↓). More triflic acid (0.1 g, 0.7 mmol) was added and the reaction continued overnight. After cooling the reaction solution, ether was added to precipitate the complex which was filtered, washed with ether and air dried. The yield of the crude was 1.80 g (88%)

Scheme 2.5

The triflic(trpy) platinum(II) triflate (1.8 g, 2.8 mmol) was dissolved in 150 ml of hot acetone, the solution was filtered and was allowed to cool at RT. 150 ml of ether was added to precipitate the complex which was filtered, was washed with ether and was air dried overnight. The yield was 1.52 g (75%).

An improved method for making the starting material is to use platinum(II) chloride PtCl₂ and 10% dimethylsulfoxide (DMSO) 1:1 water-acetonitrile as the solvent. Using this method, the starting material, [(trpy)PtCl]Cl•2H₂O, can be prepared in a few hours and in nearly quantitative yield.²⁷

2.5 Syntheses of mononuclear complexes of Platinum

2.5.1 [(trpy)Pt pcyd]PF₆

[(trpy)Pt pcyd]PF₆ (0.2 g, 0.33 mmol) was dissolved in 75 ml of acetonitrile, which was heated to 50°C. Tlpcyd (0.11 g, 0.33 mmol) was dissolved in 50 ml of acetonitrile and was added to the first solution. After short time, the colour of the mixture solution changed to red-orange and a white precipitate formed. The reaction was heated and stirred for a further 40 min, and then the solution was filtered. The volume of the filtrate was reduced to about 50%, and then ether was added to crash the complex which was filtered and washed with ether.

Scheme 2.6

To recrystallize the crude of the complex, it was dissolved in minimum hot acetonitrile and was filtered. Ether was allowed to diffuse into the clear solution for a couple of days, slowly crystallizing the complex which was filtered, washed with ether and was vacuum dried overnight. The yield was 0.15 g (66%).

Elemental analysis based upon [(trpy)Pt pcyd][PF₆] (as C₂₂H₁₆N₅F₆PPt, FW=690.5 g/mol)

Calcd (%) C, 38.27; H, 2.34; N, 10.14

Found (%) C, 38.2; H, 2.36; N, 10.33

2.5.2 [(trpy)Pt(3,5-Me₂pcyd)](PF₆)

This complex was prepared in a similar manner to the previous one. The recrystallization of the crude complex was done as before. The yield was 0.14 g (60%).

Elemental analysis based upon [(trpy)Pt(DMpcyd)][PF₆] as (C₂₄H₂₀N₅F₆PPt, FW=718.5 g/mol)

Calcd (%) C, 40.12; H, 2.81; N, 9.75

Found (%) C, 39.08; H, 2.91; N, 9.49

2.5.3 [(trpy)Pt(2,3-Cl₂-pcyd)](PF₆)

This complex was made in similar manner to the previous one. The recrystallization of the crude was done as before. The yield was 0.20 g (80%).

Elemental analysis based upon [(trpy)Pt Cl₂-pcyd][PF₆] (as C₂₂H₁₄N₅Cl₂F₆PPt, FW=759.34 g/mol)

Calcd (%) C, 34.80; H, 1.86; N, 9.22

Found (%) C, 34.89; H, 2.22; N, 9.36

2.5.4 [(trpy)Pt(3,5-(MeO)₂-pcyd)][PF₆]

This complex was made in similar manner to the previous one. The yield was 0.23 g (93%).

Elemental analysis based upon [(trpy)Pt-(MeO)₂-pcyd][PF₆] (as C₂₄H₂₀N₅F₆O₂PPt)

Calcd (%) C, 38.41; H, 2.69; N, 9.33

Found (%) C, 38.54; H, 2.90; N, 9.61

2.6 Syntheses of dinuclear complexes of platinum

2.6.1 [{Pt(trpy)}₂(μ-2,5-Me₂dicyd)](PF₆)₂

(Tl)₂ Me₂dicyd (0.25g, 0.42 mmol) was placed in a flask and was degassed under argon. In another flask, [(trpy)PtCl]PF₆ (0.5 g, 9.82 mmol) was dissolved in DMF and degassed under argon. This solution was then transferred to the ligand flask. Initially, the colour changed from orange to dark green and after one week became dark blue with a white precipitate. The solution was filtered and the product was forced out of the filtrate by the addition of ether.

Scheme 2.7

The crude complex was dissolved in hot DMF and then was filtered. Ether was allowed to diffuse into the clear deep blue filtrate. After a couple days, the solution was filtered to give crystalline deep blue complex which was vacuum dried overnight. The yield was 0.46 g (84%).

Elemental analysis based upon $[\{\text{Pt}(\text{trpy})\}_2(\mu\text{-2,5-Me}_2\text{dicyd})](\text{PF}_6)$ (as

$\text{C}_{40}\text{H}_{30}\text{N}_{10}\text{F}_{12}\text{P}_2\text{Pt}_2$, FW= 1330.83 g/mol)

Calcd (%) C, 36.10; H, 2.27; N, 10.52

Found (%) C, 36.04; H, 2.35; N, 10.71

2.6.2 $[\{\text{Pt}(\text{trpy})\}_2(\mu\text{-2,5-Cl}_2\text{dicyd})](\text{CF}_3\text{SO}_3)_2$

$[\{\text{Pt}(\text{trpy})\}_2(\text{CF}_3\text{SO}_3)](\text{CF}_3\text{SO}_3)$ (0.4 g, 0.55 mmol) was dissolved in 150 ml of DMF and was degassed by argon. This solution was transferred to a flask containing DC-H₂dicyd (0.07 g, 0.31 mmol, excess) (degassed). Then, TEA (0.45 ml) was injected into the solution. After a short time, the colour of the solution changed to light green and then changed to purple. The reaction was allowed to continue under argon atmosphere for couple days.

Scheme 2.8

The recrystallization was done by dissolving the crude of the complex in DMF and filtering. Then, the clear solution was diffused by ether. After a couple of days, the product was filtered, washed with ether and dried in vacuo overnight. The yield was 0.16 g, (42%).

Elemental analysis based upon $[\{\text{Pt}(\text{trpy})\}_2(\mu\text{-2,5-Cl}_2\text{dicyd})](\text{CF}_3\text{SO}_3)_2$ (as $\text{C}_{40}\text{H}_{24}\text{N}_{10}\text{F}_6\text{Cl}_2\text{O}_6\text{S}_2\text{Pt}_2$, FW= 1379.9 g/mol)

Calcd (%) C, 34.82; H, 1.75; N, 10.15

Found (%) C, 34.79; H, 2.03; N, 9.86

2.7 Physical Measurements

2.7.1 Infrared Spectroscopy (IR)

Infrared spectroscopy was executed on Bomem Michelson 120 FT-IR as KBr (oven dried at 120°C) disks. The spectra were corrected for background air. Data were analysed by using Bomem Grams/386 version 3.04.

2.7.2 Spectroscopy of NMR

^1H NMR spectra were obtained on a Bruker AMX-400 spectrometer at 300K by using ultra-imperial grade PP 507 sample tubes (Wilmad) and were referenced TMS. Samples were dissolved in d_6 -dimethyl sulphoxide. Usually, 10 mg of the sample was dissolved in 1.00 ml of d_6 -DMSO

2.7.3 Electronic Absorption Spectroscopy

Electronic spectroscopy was performed on a Cary UV-Vis/NIR spectrophotometer. The samples were dissolved in acetonitrile for mononuclear complexes and DMF for dinuclear complexes. Normally, 10-15 mg of the sample was dissolved in 200 ml of the proper solvent. Matching quartz cells were used and solvent background correction (baseline) was determined.

2.7.4 Cyclic Voltammetry (CV)

Cyclic voltammetry was performed on a BAS CV-27 electrochemistry system online to a BAS X-Y recorder. The electrochemical cell was made up of a double-jacketed glass container. The temperature was governed by means of a Haake D8-G refrigerated bath and circulator (precision $\pm 0.02^\circ\text{C}$). The teflon cap of the cell has four holes for a platinum disk work electrode, wire counter electrode, reference electrode (silver wire) and an argon gas inlet tube. Tetrabutylammonium hexafluorophosphate (TBAH) was dissolved in 15 ml of distilled DMF. Each sample was prepared by

dissolving 10-15 mg in the DMF solution. Ferrocene ($E^0 = 0.665$ V vs NHE) was used as a internal reference.²⁸

2.7.5 X-ray Crystallography

The X-ray structure determination was performed by Dr. G.P.A Yap at Ottawa University. There were two X-ray structures where determined for single crystal of [(try)Pt(pcyd)]PF₆ and [(trpy)Pt DM-(pcyd)]PF₆. Data were collected on a Bruker SMART CCD diffractometer.

2.7.6 Elemental Analyses (EA)

Elemental analyses of all samples were performed by the chemistry department of the University of Ottawa. All of the samples have been recrystallized and dried for overnight.

Chapter 3

Mononuclear Complexes of Phenylcyanamide Ligands: Physical Characterization and Discussion

3.1 Infrared Spectroscopy of Mononuclear Complexes of Platinum

Infrared spectra of the four mononuclear complexes, as well as the starting material, are shown in Figures 3.1-3.5. All complexes show the $\nu(\text{NCN})$ in the range of 2165-2194 cm^{-1} . Compared to the free ligand, the $\nu(\text{NCN})$ is shifted to higher wavelength by 66-116 cm^{-1} (see Table 3.1). Similar shifting is seen in the $\nu(\text{C}\equiv\text{N})$ of hard cations bound to nitriles.²⁸

The $\nu(\text{NCN})$ of $[(\text{trpy})\text{Pt}(\text{pcyd})](\text{PF}_6)$ differs from the other mononuclear platinum complexes, in that two are visible. This may suggest the presence of two types of Pt-N bonding in the complex: through the amine and nitrile nitrogen. It is possible that due to the smaller steric hindrance of the phenylcyanamide ligand, the Pt(II) can coordinate to the amine nitrogen as well as to the preferred nitrile nitrogen. This may also be explained by the crystal packing. Two $\nu(\text{NCN})$ are also seen in the thallium salt of the unsubstituted phenylcyanamide anion.

Figure 3.1: Infrared spectrum of [(trpy)PtCl](PF₆) (KBr disk)

Figure 3.2: Infrared spectrum of [(trpy)Pt(pcyd)](PF₆) (KBr disk)

Figure 3.3: Infrared spectrum of $[(\text{trpy})\text{Pt}(3,5\text{-Me}_2\text{pcyd})](\text{PF}_6)$ (KBr disk)

Figure 3.4: Infrared spectrum of $[(\text{trpy})\text{Pt}(2,3\text{-Cl}_2\text{pcyd})](\text{PF}_6)$ (KBr disk)

Figure 3.5: Infrared spectrum of $[(\text{trpy})\text{Pt}(3,5\text{-(MeO)}_2\text{pcyd})](\text{PF}_6)$ (KBr disk)

Table 3.1 IR Data for the Mononuclear Phenylcyanamide Complexes ^a

pcyd anion (L)	Tl salt of Ligand	$[(\text{trpy})\text{PtL}](\text{PF}_6)$
pcyd	2078, 2056	2194, 2154
3,5-Me ₂ pcyd	2099	2165
3,4-Cl ₂ pcyd	2102	2192
3,5-MeO ₂ pcyd	2084	2177

In cm⁻¹. All spectra were obtained as KBr mulls

3.2 Proton NMR Spectroscopy of Mononuclear Complexes of Platinum

The proton NMR spectra of the four mononuclear complexes were taken as a second method of characterization. The spectra were taken in d_6 -DMSO and all assignments are tabulated in Table 3.2.

Figure 3.6: Proton numbering schemes for mononuclear complexes of platinum

Table 3.2 ^1H NMR Spectroscopy Data for $[(\text{trpy})\text{PtL}]^+$ Complexes ^a

	pcyd			trpy					
L	H2	H3	H4	H5	H6	H7	H8	H9	H10
Cl				8.60	8.60	8.74	8.48	7.90	8.60
pcyd	7.52	7.25	6.90	8.52	8.62	8.67	8.42	7.94	8.02
3,5-dimethylpcyd	7.13		6.54	8.54	8.61	8.67	8.41	7.96	8.01
2,3-dichloropcyd	7.16	7.03	7.10	8.59	8.59	8.65	8.50	7.98	8.54
3,5-dimethoxypcyd	6.66		6.09	8.54	8.62	8.68	8.41	7.98	8.01

^aChemical shifts are in ppm. All NMR spectra were taken in d_6 -DMSO

Figure 3.7: 400 MHz ^1H NMR spectrum of $[(\text{trpy})\text{PtCl}](\text{PF}_6)$ in d_6 -DMSO

Figure 3.8: 400 MHz ^1H NMR spectrum of $[(\text{trpy})\text{Pt}(\text{pcyd})](\text{PF}_6)$ in d_6 -DMSO

Figure 3.9: 400 MHz ^1H NMR spectrum of $[(\text{trpy})\text{Pt}(3,5\text{-Me}_2\text{pcyd})](\text{PF}_6)$ in d_6 -DMSO (terpyridine and pcyd peaks)

Figure 3.10: 400 MHz ^1H NMR spectrum of $[(\text{trpy})\text{Pt}(3,5\text{-Me}_2\text{pcyd})](\text{PF}_6)$ in $\text{d}_6\text{-DMSO}$ (methyl peaks)

Figure 3.11: 400 MHz ^1H NMR spectrum of $[(\text{trpy})\text{Pt}(\text{Cl}_2\text{pcyd})](\text{PF}_6)$ in $\text{d}_6\text{-DMSO}$

Figure 3.12: 400 MHz ^1H NMR spectrum of $[(\text{trpy})\text{Pt}((\text{MeO})_2\text{pcyd})](\text{PF}_6)$ in d_6 -DMSO (terpyridine and pcyd peaks)

Figure 3.13: 400 MHz ^1H NMR spectrum of $[(\text{trpy})\text{Pt}((\text{MeO})_2\text{pcyd})](\text{PF}_6)$ in d_6 -DMSO (methyl peaks)

The ^1H NMR spectra showed many similarities to those of $[\text{trpy}(\text{Pd})]^{2+}$ phenylcyanamide mononuclear complexes taken by Zhang.²⁹ This is reasonable since Zhang's complexes resemble those of this study, with the only major difference being the metal centre.

3.3 Electronic Absorption Spectroscopy of Mononuclear Complexes of Platinum

The electronic spectra of the four mononuclear platinum complexes, as well as the $[(\text{trpy})\text{PtCl}]^+$ starting material were generated in acetonitrile solution and are shown in figures 3.14-3.18. All spectral assignments are listed in Table 3.3.

In the range of 200-300 nm, the spectra show $\pi\text{-}\pi^*$ transitions of the aromatic trpy ligand. Metal-to-Ligand charge transfer (MLCT) bands were seen in the range of 300-350 nm. Another interesting feature of the UV-vis spectra is the broad ligand-to-metal charge transfer (LMCT) bands that appear around 370-490 nm. The transitions are broad and are not very intense, because the LMCT is symmetry forbidden. However, the bond between the Pt and cyanamide group is bent with an angle of $159.1\text{-}175.9^\circ$. This causes some mixing between the π_{ab} orbitals of the cyanamide and the $\sigma^*_{(dx^2-y^2)}$ orbital of platinum and results in a partially allowed LMCT transition. ($\pi\text{-}\sigma^*$).

A difference in the LMCT energies was noted when the ligand loses some of its donating character. All phenylcyanamides are donor ligands. However, the donor properties of the cyanamide group can be reduced by the addition of electron withdrawing substituents on the phenyl ring, e.g. Cl. The chlorinated phenylcyanamide, shows a higher energy LMCT compared to the dimethyl phenylcyanamide, which has more donating character. This can be explained by the fact that the presence of the Cl

substituents on the phenyl ring stabilizes the π_{nb} orbitals of the pcyd. This increases the energy gap between the π_{nb} of the ligand and σ^* of the metal and shows that the LMCT energies can be modified simply by changing the donating nature of the ligand.

Table 3.3 UV-vis Absorption Data for [(trpy)PtL]⁺ Complexes ^a

L	$\pi-\pi^*$ (trpy)	MLCT	LMCT
Cl	209 (38000)	303 (15700)	387 (3500)
	255 (44000)	316 (16950) sh	
	270 (33300) sh	332 (23900)	
	280 (43800)	348 (13900)	
Pcyd	245 (86200)	307 (26500) sh	370 (5000) sh
	277 (59000)	328 (27700)	390 (3000) sh
		342 (38900)	490 (2000) br
3,5-dimethylpcyd	208 (50500)	312 (16400) sh	370 (3500)
	250 (41000)	328 (17800)	390 (2700)
	282 (36500)	343 (18000)	490 (2900) br
2,3-dichloropcyd	208 (49400)	327 (16000)	370 (3700) sh
	220 (42000) sh	340 (19200)	390 (2500) sh
	248 (37500)		462 (3200) br
	276 (42600)		
3,5-dimethoxypcyd	216 (47200)	328 (15550)	370 (3300) sh
	245 (36800) sh	342 (16550)	390 (2300) sh
	280 (32000)		490 (2500) br

^a All data were recorded in 3.00×10^{-5} M CH₃CN solution. Extinction coefficients are in parentheses. sh = shoulder; br = broad

Figure 3.14: UV-vis absorption spectrum of $[(\text{trpy})\text{PtCl}](\text{PF}_6)$ in CH_3CN ($3.00 \times 10^{-5}\text{M}$)

Figure 3.15: UV-vis absorption spectrum of $[(\text{trpy})\text{Pt}(\text{pcyd})](\text{PF}_6)$ in CH_3CN ($3.00 \times 10^{-5}\text{M}$)

Figure 3.16: UV-vis absorption spectrum of $[(\text{trpy})\text{Pt}(3,5\text{-Me}_2\text{pcyd})](\text{PF}_6)$ in CH_3CN ($3.00 \times 10^{-5}\text{M}$)

Figure 3.17: UV-vis absorption spectrum of $[(\text{trpy})\text{Pt}(\text{Cl}_2\text{pcyd})](\text{PF}_6)$ in CH_3CN ($3.00 \times 10^{-5}\text{M}$)

Figure 3.18: UV-vis absorption spectrum of $[(\text{trpy})\text{Pt}((\text{MeO})_2\text{pcyd})](\text{PF}_6)$ in CH_3CN ($3.00 \times 10^{-5} \text{ M}$)

3.4 Cyclic Voltammetry of Mononuclear Complexes of Platinum

Cyclic voltammetry is an important technique that has been used to study electrochemical reactions for many years. The effect of ligands on the redox potential of the metal ion in inorganic complexes is one of the significant applications of cyclic voltammetry.³⁰

The electrochemical data for the five platinum complexes, including the starting material, are shown in Table 3.4 and the cyclic voltammograms are presented in figures 3.19-3.24. The cyclic voltammetry experiments were performed in distilled DMF using platinum working and counter electrodes, a silver wire pseudo-electrode and ferrocene/ferrocenium couple (0.665 V vs. N.H.E.) as an internal reference.

The two major features of the cyclic voltammograms are the platinum (+2/+) couple, with a range of -0.56 to -0.45 V, and the terpyridine (0/-) couple, with a range of -1.14 to -1.05 V. Since the oxidation of ferrocene is a known one-electron event, and the concentration of ferrocene added was the same as that of the complex added, comparison of current heights of this couple with the platinum and terpyridine couples lead to the conclusion that these were also one-electron events. Although, the peak currents of ferrocene and platinum complex couples are very reversible, there is a lack of equivalence between ferrocenium/ferrocene peak currents and those of the one electron redox couples of the platinum complexes. This could be due to error in the addition of the ferrocene and platinum complexes. Also, it could be related to the reversibility of these waves. The ferrocene couples possess a more ideal reversible behaviour compared to the platinum and trpy couples and this will have the effect of narrowing the voltammogram waves. All redox events of the five mononuclear platinum complexes

were reversible. Cyanamide ligand oxidation events should also be visible on the cyclic voltammograms but are not seen for these complexes. By varying the scan rate for the platinum mononuclear complexes, it was found that the voltages of the redox couples were independent of scan rate (see figure 3.21).

Table 3.4: Electrochemical Data for Mononuclear Platinum Complexes ^a

Complex	Platinum couple ($^{2+}/^{+}$)	Terpyridine couple (0/-)
$[(\text{trpy})\text{PtCl}]\text{PF}_6$	-0.56	-1.14
$[(\text{trpy})\text{Pt}(\text{pcyd})]\text{PF}_6$	-0.52	-1.09
$[(\text{trpy})\text{Pt}(3,5\text{-Me}_2\text{pcyd})]\text{PF}_6$	-0.51	-1.05
$[(\text{trpy})\text{Pt}(2,3\text{-Cl}_2\text{pcyd})]\text{PF}_6$	-0.45	-1.05
$[(\text{trpy})\text{Pt}(3,5\text{-(MeO)}_2\text{pcyd})]\text{PF}_6$	-0.51	-1.07

^a All potentials are in volts vs. N.H.E. using ferrocene as the internal reference (665 mV vs. N.H.E.). Measured using 3.6 mM solutions in distilled DMF at 25°C at a scan rate of 100mV/s. Electrolyte used was 0.1M tetrabutylammonium hexafluorophosphate.

Figure 3.19: Cyclic Voltammogram of $[(\text{trpy})\text{PtCl}](\text{PF}_6)$ in distilled DMF

Figure 3.20: Cyclic Voltammogram of $[(\text{trpy})\text{Pt}(\text{pcyd})](\text{PF}_6)$ in distilled DMF

Figure 3.21: Cyclic Voltammogram of $[(\text{trpy})\text{Pt}(3,5\text{-Me}_2\text{pcyd})](\text{PF}_6)$ in distilled DMF

Figure 3.22: Cyclic Voltammogram of $[(\text{trpy})\text{Pt}(2,3\text{-Cl}_2\text{pcyd})](\text{PF}_6)$ in distilled DMF

Figure 3.23: Cyclic Voltammogram of $[(\text{trpy})\text{Pt}((\text{MeO})_2\text{pcyd})](\text{PF}_6)$ in distilled DMF

Figure 3.24: Scan Rate Dependence Cyclic Voltammogram for $[(\text{trpy})\text{Pt}((\text{MeO})_2\text{pcyd})](\text{PF}_6)$ in distilled DMF

3.5 X-Ray Structure Determination

The X-ray crystallographic data for two complexes, $[(\text{trpy})\text{Pt}(\text{pcyd})][\text{PF}_6]$ and $[(\text{trpy})\text{Pt}(2,4\text{-Me}_2\text{-pcyd})][\text{CF}_3\text{SO}_3]$ are given in tables 3.5-3.7 and 3.8-3.10, respectively. The ball-and-stick diagram for $[(\text{trpy})\text{Pt}(\text{pcyd})][\text{PF}_6]$ is shown in figure 3.25 and both the ORTEP diagram for $[(\text{trpy})\text{Pt}(2,4\text{-Me}_2\text{-pcyd})][\text{CF}_3\text{SO}_3]$ are shown in figures 3.26- 3.28. The ball-and-stick unit cell diagram are shown in figures 3.29 and 3.30. The stereoviews of $[(\text{trpy})\text{Pt}(2,4\text{-Me}_2\text{-pcyd})][\text{CF}_3\text{SO}_3]$ are also displayed in figures 3.31 and 3.32.

3.5.1 X-ray Structure for $[(\text{trpy})\text{Pt}(\text{pcyd})][\text{PF}_6]$

The residuals of this crystal structure are very high with the R for the significant reflections being 0.1592. Furthermore, the goodness of fit was very bad at 3.454 resulting in values of low confidence. Here we see that the Metal-Ligand bond occurs via the nitrile nitrogen of the phenylcyanamide ligand as has been seen in similar studies involving palladium complexes of this nature. The crystal structure of $[(\text{trpy})\text{Pt}(\text{pcyd})][\text{PF}_6]$ indicates that the coordination environment about the Pt(II) metal ion is one of a distorted square planar geometry with four nitrogen donor atoms making up the coordination sphere.

Due to the poor data resulting from this crystal analysis, emphasis on bond lengths and angles will not be mentioned, however, this structure does confirm the results obtained from elemental analysis. A more useful structure for elucidating the geometry of this complex is that of $[(\text{trpy})\text{Pt}(2,4\text{-Me}_2\text{-pcyd})][\text{CF}_3\text{SO}_3]$.

3.5.2 X-ray structure for $[(\text{trpy})\text{Pt}(2,4\text{-Me}_2\text{-pcyd})][\text{CF}_3\text{SO}_3]$

The residuals of this crystal structure are acceptable with the R for the significant reflections being 0.0530 and the goodness of fit being 1.034. When compared to the previous structure, we see that the Metal-Ligand bond occurs via the same nitrile nitrogen to platinum bonding mode. Subsequently, the crystal structure of $[(\text{trpy})\text{Pt}(2,4\text{-Me}_2\text{-pcyd})][\text{CF}_3\text{SO}_3]$ indicates that the coordination environment about the Pt(II) metal ion is one of a distorted square planar geometry with four nitrogen donor atoms making up the coordination sphere.

One of the more interesting factors of this structure analysis is the fact that there are 3 unique geometries present in this one crystal. We see from figures 3.26, 3.27 and 3.28 that the structures do not appear very dissimilar however, when closely examining the bond length and angle data, we see some small variations in the coordination sphere about the Pt(II) ion. For example, the Pt-cyanamide bond angle in the three different structures varies from 159-175°. Two things, however, are for certain. First, the geometry of the Pt(II) ion remains distorted square planar in all three structures and second, the phenyl ring of the phenylcyanamide ligand and the Pt-trpy complex are coplanar in all three structures.

Close examination of the ball-and-stick diagram of the unit cell shows how the complexes “stack” with respect to one another. A dotted line suggests some degree of interaction between the Pt(II) ion and the nitrile nitrogen of the phenylcyanamide ligand. However, the distance between these two moieties is of the order of 5.4 Å, indicating very little, if any, interaction between them.

Table 3.5: Crystal data and structure refinement for [(trpy)Pt(pcyd)][PF₆]

Parameter	Value
Empirical Formula	C ₂₂ H ₁₆ F ₆ N ₅ PPt
Formula Weight	690.46
Temperature	203(2) K
Wavelength	0.71073 Å
Space Group	Triclinic, P1
Cell Dimensions:	
a (Å)	9.379(3) Å
b (Å)	10.546(4) Å
c (Å)	12.315(4) Å
α (degrees)	93.672(4)°
β (degrees)	98.991(4)°
γ (degrees)	115.172(5)°
Volume (Å ³)	1077.2(6) Å ³
Z, Calculated density	2, 2.129 mg/m ³
Absorption Coefficient	6.662 mm ⁻¹
F (000) (electrons)	660
Crystal size	0.4 x 0.1 x 0.1 mm
θ range for data collection	1.69 – 20.99 °
Limiting indices	-9 ≤ h ≤ 9, -10 ≤ k ≤ 10, 0 ≤ l ≤ 12
Reflections collected/unique	2306 / 2306 (R(int) = 0.0000)
Completeness to θ = 20.99	99.6%
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	2306 / 0 / 142
Goodness of fit on F ²	3.454
Final R indices	R1=0.1592, wR2=0.4172
R indices (all data)	R1=0.1714, wR2=0.4213
Extinction coefficient	0.014(5)
Largest difference (peak and hole)	12.570 and -4.002 Å ⁻³

Figure 3.25: Ball-and-stick drawing for the complex $[(\text{trpy})\text{Pt}(\text{pcyd})][\text{PF}_6]$

Table 3.6: Atomic coordinates^a and equivalent isotropic displacement parameters^b for [(trpy)Pt(pcyd)][PF₆]

	x	y	z	U (eq)
Pt	-4853 (3)	7611 (2)	5220 (2)	30 (1)
P	-2035 (19)	7870 (17)	913 (13)	45 (4)
F (1)	-970 (60)	9490 (50)	1080 (40)	101 (14)
F (2)	-3170 (50)	6170 (40)	670 (40)	83 (12)
F (3)	-2120 (50)	7850 (40)	2190 (30)	76 (11)
F (4)	-560 (50)	7500 (50)	1120 (40)	85 (12)
F (5)	-1940 (40)	7830 (40)	-400 (30)	68 (10)
F (6)	-3600 (50)	8080 (50)	680 (40)	88 (13)
N (1)	-5760 (60)	6600 (50)	3630 (40)	50 (13)
N (2)	-6620 (60)	8100 (50)	4920 (40)	54 (14)
N (3)	-4440 (60)	8770 (50)	6740 (40)	46 (13)
N (4)	-2970 (60)	7200 (50)	5550 (40)	53 (14)
N (5)	-1070 (70)	6160 (60)	5770 (50)	63 (15)
C (1)	-5250 (80)	5830 (70)	3080 (50)	54 (17)
C (2)	-5990 (80)	5230 (70)	1990 (50)	54 (17)
C (3)	-7330 (80)	5380 (70)	1530 (50)	50 (16)
C (4)	-7920 (70)	6200 (60)	2100 (50)	38 (14)
C (5)	-7160 (60)	6820 (50)	3150 (40)	26 (12)
C (6)	-7530 (70)	7630 (60)	3870 (50)	45 (15)
C (7)	-8910 (70)	7960 (60)	3690 (50)	45 (15)
C (8)	-9090 (80)	8760 (70)	4490 (50)	53 (17)
C (9)	-8150 (60)	9190 (50)	5540 (40)	34 (13)
C (10)	-6940 (60)	8840 (50)	5710 (40)	22 (11)
C (11)	-5590 (80)	9310 (70)	6720 (50)	52 (16)
C (12)	-5500 (80)	10120 (70)	7690 (50)	61 (18)
C (13)	-4360 (70)	10380 (60)	8590 (50)	48 (16)
C (14)	-3190 (70)	9840 (60)	8580 (50)	46 (15)
C (15)	-3370 (70)	9010 (60)	7580 (50)	43 (15)
C (16)	-2180 (50)	6650 (50)	5690 (40)	21 (11)
C (17)	340 (70)	7250 (60)	7720 (50)	50 (16)
C (18)	1460 (70)	7440 (60)	8630 (50)	41 (14)
C (19)	2410 (70)	6740 (60)	8530 (50)	49 (16)
C (20)	2280 (80)	5970 (70)	7560 (50)	59 (18)
C (21)	1120 (60)	5800 (60)	6690 (50)	41 (14)
C (22)	90 (60)	6380 (50)	6680 (40)	36 (14)

^a value x 10⁴; ^b in Å² x 10³

Table 3.7: Bond lengths (Å) and angles (deg) for [(trpy)Pt(pcyd)][PF₆]

Pt-N(2)	1.93(5)
Pt-N(4)	1.98(5)
Pt-N(1)	2.03(5)
Pt-N(3)	2.06(5)
P-F(1)	1.55(5)
P-F(6)	1.56(5)
P-F(4)	1.58(5)
P-F(3)	1.59(4)
P-F(2)	1.62(5)
P-F(5)	1.63(4)
N(1)-C(1)	1.32(8)
N(1)-C(5)	1.47(7)
N(2)-C(10)	1.36(7)
N(2)-C(6)	1.36(7)
N(3)-C(15)	1.25(7)
N(3)-C(11)	1.42(8)
N(4)-C(16)	1.12(6)
N(5)-C(16)	1.34(7)
N(5)-C(22)	1.36(8)
C(1)-C(2)	1.37(8)
C(2)-C(3)	1.37(9)
C(3)-C(4)	1.42(8)
C(4)-C(5)	1.35(7)
C(5)-C(6)	1.37(8)
C(6)-C(7)	1.47(8)
C(7)-C(8)	1.33(8)
C(8)-C(9)	1.37(8)
C(9)-C(10)	1.32(7)
C(10)-C(11)	1.51(8)
C(11)-C(12)	1.40(9)
C(12)-C(13)	1.34(8)
C(13)-C(14)	1.44(8)
C(14)-C(15)	1.41(8)
C(17)-C(18)	1.35(8)
C(17)-C(22)	1.45(8)
C(18)-C(19)	1.40(8)
C(19)-C(20)	1.36(9)
C(20)-C(21)	1.35(8)
C(21)-C(22)	1.35(8)
N(2)-Pt-N(4)	177(2)
N(2)-Pt-N(1)	82(2)
N(4)-Pt-N(1)	99(2)
N(2)-Pt-N(3)	82(2)
N(4)-Pt-N(3)	96(2)
N(1)-Pt-N(3)	164.6(18)
F(1)-P-F(6)	91(3)
F(1)-P-F(4)	94(3)
F(6)-P-F(4)	174(3)
F(1)-P-F(3)	93(2)
F(6)-P-F(3)	90(2)
F(4)-P-F(3)	90(2)
F(1)-P-F(2)	177(3)

C(66)-C(67)-C(68)	117.7(15)
C(66)-C(67)-C(71)	120.5(17)
C(68)-C(67)-C(71)	121.7(16)
C(69)-C(68)-C(67)	122.2(15)
C(70)-C(69)-C(68)	118.2(15)
C(70)-C(69)-C(72)	119.0(15)
C(68)-C(69)-C(72)	122.8(15)
C(69)-C(70)-C(65)	120.2(14)
O(3)-S(1)-O(2)	115.6(6)
O(3)-S(1)-O(1)	114.7(6)
O(2)-S(1)-O(1)	114.6(6)
O(3)-S(1)-C(73)	103.1(5)
O(2)-S(1)-C(73)	103.7(5)
O(1)-S(1)-C(73)	102.7(5)
F(3)-C(73)-F(2)	108.4(11)
F(3)-C(73)-F(1)	107.8(10)
F(2)-C(73)-F(1)	106.6(11)
F(3)-C(73)-S(1)	111.2(8)
F(2)-C(73)-S(1)	111.9(8)
F(1)-C(73)-S(1)	110.8(9)
O(5)-S(2)-O(6)	117.7(7)
O(5)-S(2)-O(4)	114.1(6)
O(6)-S(2)-O(4)	113.5(6)
O(5)-S(2)-C(74)	102.5(7)
O(6)-S(2)-C(74)	103.1(7)
O(4)-S(2)-C(74)	103.4(6)
F(6)-C(74)-F(4)	110.4(13)
F(6)-C(74)-F(5)	110.6(12)
F(4)-C(74)-F(5)	108.5(11)
F(6)-C(74)-S(2)	108.0(10)
F(4)-C(74)-S(2)	109.9(10)
F(5)-C(74)-S(2)	109.5(10)
O(8)-S(3)-O(9)	120.7(7)
O(8)-S(3)-O(7)	100.1(10)
O(9)-S(3)-O(7)	103.5(10)
O(8)-S(3)-C(75)	111.8(9)
O(9)-S(3)-C(75)	111.5(8)
O(7)-S(3)-C(75)	107.3(10)
F(7)-C(75)-F(8)	111.0(17)
F(7)-C(75)-F(9)	114.3(19)
F(8)-C(75)-F(9)	108.6(19)
F(7)-C(75)-S(3)	109.8(14)
F(8)-C(75)-S(3)	109.2(14)
F(9)-C(75)-S(3)	103.6(14)
F(9')-C(75')-F(8')	113(2)
F(9')-C(75')-F(7')	109.3(19)
F(8')-C(75')-F(7')	105.5(17)

Symmetry transformations used to generate equivalent atoms:

F(6)-P-F(2)	88(2)
F(4)-P-F(2)	86(2)
F(3)-P-F(2)	90(2)
F(1)-P-F(5)	88(2)
F(6)-P-F(5)	91(2)
F(4)-P-F(5)	89(2)
F(3)-P-F(5)	179(2)
F(2)-P-F(5)	89(2)
C(1)-N(1)-C(5)	122(5)
C(1)-N(1)-Pt	128(4)
C(5)-N(1)-Pt	110(3)
C(10)-N(2)-C(6)	123(5)
C(10)-N(2)-Pt	122(4)
C(6)-N(2)-Pt	115(4)
C(15)-N(3)-C(11)	123(5)
C(15)-N(3)-Pt	129(5)
C(11)-N(3)-Pt	109(4)
C(16)-N(4)-Pt	164(5)
C(16)-N(5)-C(22)	126(5)
N(1)-C(1)-C(2)	120(6)
C(1)-C(2)-C(3)	119(6)
C(2)-C(3)-C(4)	122(6)
C(5)-C(4)-C(3)	118(5)
C(4)-C(5)-C(6)	129(5)
C(4)-C(5)-N(1)	118(4)
C(6)-C(5)-N(1)	114(5)
N(2)-C(6)-C(5)	118(5)
N(2)-C(6)-C(7)	113(5)
C(5)-C(6)-C(7)	128(5)
C(8)-C(7)-C(6)	120(6)
C(7)-C(8)-C(9)	124(6)
C(10)-C(9)-C(8)	116(5)
C(9)-C(10)-N(2)	124(5)
C(9)-C(10)-C(11)	128(5)
N(2)-C(10)-C(11)	108(5)
C(12)-C(11)-N(3)	117(6)
C(12)-C(11)-C(10)	124(6)
N(3)-C(11)-C(10)	119(5)
C(13)-C(12)-C(11)	121(7)
C(12)-C(13)-C(14)	121(6)
C(15)-C(14)-C(13)	115(6)
N(3)-C(15)-C(14)	124(6)
N(4)-C(16)-N(5)	171(6)
C(18)-C(17)-C(22)	125(6)
C(17)-C(18)-C(19)	115(6)
C(20)-C(19)-C(18)	122(6)
C(21)-C(20)-C(19)	119(7)
C(22)-C(21)-C(20)	125(6)
C(21)-C(22)-N(5)	122(5)
C(21)-C(22)-C(17)	113(5)
N(5)-C(22)-C(17)	125(5)

Symmetry transformations used to generate equivalent atoms:

Table 3.8: Crystal data and structure refinement for [(trpy)Pt(2,4-Me₂-pcyd)][CF₃SO₃]

Parameter	Value
Empirical Formula	C ₂₅ H ₂₀ F ₃ N ₅ O ₃ PPt
Formula Weight	722.61
Temperature	203(2) K
Wavelength	0.71073 Å
Space Group	Triclinic, P1
Cell Dimensions:	
a (Å)	10.345(3) Å
b (Å)	15.524(4) Å
c (Å)	23.506(7) Å
α (degrees)	78.819(5)°
β (degrees)	83.794(5)°
γ (degrees)	81.834(6)°
Volume (Å ³)	3653(2) Å ³
Z, Calculated density	6, 1.971 mg/m ³
Absorption Coefficient	5.910 mm ⁻¹
F (000) (electrons)	2100
Crystal size	0.05 x 0.1 x 0.2 mm
θ range for data collection	1.35 – 22.50 °
Limiting indices	-8 ≤ h ≤ 11, -16 ≤ k ≤ 15, -24 ≤ l ≤ 25
Reflections collected/unique	15237 / 9427 (R(int) = 0.0621)
Completeness to θ = 20.99	98.7%
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	9427 / 224 / 1043
Goodness of fit on F ²	1.034
Final R indices	R1=0.0530, wR2=0.1112
R indices (all data)	R1=0.0751, wR2=0.1149
Largest difference (peak and hole)	2.480 and -2.307 Å ⁻³

Figure 3.26: ORTEP drawing for the complex $[(\text{trpy})\text{Pt}(2,4\text{-Me}_2\text{-pcyd})][\text{CF}_3\text{SO}_3]$. The triflate ion has been removed for clarity

Figure 3.27: ORTEP drawing for the complex $[(\text{trpy})\text{Pt}(2,4\text{-Me}_2\text{-pcyd})][\text{CF}_3\text{SO}_3]$. The triflate ion has been removed for clarity

Figure 3.28: ORTEP drawing for the complex $[(\text{trpy})\text{Pt}(2,4\text{-Me}_2\text{-pcyd})][\text{CF}_3\text{SO}_3]$. The triflate ion has been removed for clarity

Figure 3.29: Unit-cell diagram for the complex $[(\text{trpy})\text{Pt}(2,4\text{-Me}_2\text{-pcyd})][\text{CF}_3\text{SO}_3]$.

Figure 3.30: Unit-cell diagram for the complex $[(\text{trpy})\text{Pt}(2,4\text{-Me}_2\text{-pcyd})][\text{CF}_3\text{SO}_3]$

Figure 3.32: Stereoview for the complex $[(\text{trpy})\text{Pt}(2,4\text{-Me}_2\text{-pcyd})][\text{CF}_3\text{SO}_3]$

Table 3.9: Atomic coordinates^a and equivalent isotropic displacement parameters^b for [(trpy)Pt(2,4-Me₂-pcyd)][CF₃SO₃]

	x	y	z	U (eq)
Pt (1)	12795 (1)	9535 (1)	6266 (1)	34 (1)
Pt (2)	6332 (1)	6331 (1)	9233 (1)	34 (1)
Pt (3)	9550 (1)	7450 (1)	7308 (1)	41 (1)
N (1)	13008 (9)	8343 (7)	6004 (5)	40 (3)
N (2)	12803 (9)	8784 (7)	7011 (5)	35 (3)
N (3)	12588 (9)	10454 (7)	6776 (5)	39 (3)
N (4)	12818 (12)	10305 (8)	5492 (5)	55 (3)
N (5)	13651 (11)	11195 (7)	4592 (5)	45 (3)
N (6)	6355 (10)	5147 (7)	8989 (4)	35 (3)
N (7)	6675 (9)	5549 (6)	9966 (4)	29 (2)
N (8)	6377 (10)	7246 (7)	9726 (5)	39 (3)
N (9)	6034 (13)	7134 (8)	8486 (5)	60 (4)
N (10)	6100 (11)	8156 (7)	7543 (5)	43 (3)
N (11)	9776 (10)	6688 (7)	6689 (5)	41 (3)
N (12)	9444 (9)	8363 (7)	6638 (5)	35 (3)
N (13)	9330 (9)	8486 (7)	7726 (5)	38 (3)
N (14)	9608 (17)	6546 (9)	7998 (6)	94 (6)
N (15)	9608 (11)	5507 (7)	8954 (5)	46 (3)
C (1)	13103 (12)	8227 (11)	5452 (7)	50 (4)
C (2)	13225 (13)	7363 (9)	5334 (6)	41 (3)
C (3)	13204 (13)	6665 (10)	5778 (6)	47 (4)
C (4)	13116 (11)	6799 (9)	6352 (6)	43 (4)
C (5)	12981 (12)	7664 (9)	6451 (6)	34 (3)
C (6)	12936 (11)	7880 (8)	7041 (6)	34 (3)
C (7)	12998 (13)	7319 (9)	7565 (6)	45 (4)
C (8)	12916 (14)	7726 (9)	8049 (6)	52 (4)
C (9)	12836 (14)	8603 (9)	8025 (6)	50 (4)
C (10)	12782 (12)	9119 (9)	7494 (6)	34 (3)
C (11)	12618 (12)	10124 (9)	7349 (6)	40 (3)
C (12)	12562 (13)	10635 (9)	7764 (7)	47 (4)
C (13)	12415 (13)	11553 (10)	7582 (8)	56 (4)
C (14)	12286 (14)	11907 (10)	7008 (8)	57 (4)
C (15)	12381 (12)	11348 (9)	6603 (7)	47 (4)
C (16)	13237 (13)	10775 (9)	5059 (7)	41 (4)
C (17)	13570 (12)	12119 (8)	4476 (6)	36 (3)
C (18)	13415 (12)	12646 (9)	4885 (6)	40 (3)
C (19)	13342 (13)	13558 (9)	4751 (6)	41 (3)
C (20)	13388 (11)	13965 (8)	4165 (6)	36 (3)
C (21)	13546 (12)	13446 (8)	3734 (5)	34 (3)
C (22)	13630 (12)	12554 (8)	3886 (6)	39 (3)
C (23)	13153 (16)	14101 (10)	5226 (7)	68 (5)
C (24)	13595 (13)	13902 (9)	3089 (6)	47 (4)
C (25)	6131 (12)	5041 (9)	8460 (6)	42 (4)
C (26)	6145 (13)	4166 (11)	8362 (6)	55 (4)
C (27)	6351 (13)	3458 (10)	8792 (6)	44 (4)
C (28)	6574 (11)	3600 (8)	9326 (6)	36 (3)

^a value x 10⁴; ^b in Å² x 10³

C(29)	6568(11)	4434(8)	9420(5)	30(3)
C(30)	6781(11)	4671(7)	9982(5)	26(3)
C(31)	7107(12)	4096(9)	10507(6)	42(4)
C(32)	7240(13)	4478(10)	10969(6)	46(4)
C(33)	7100(12)	5383(9)	10939(6)	40(4)
C(34)	6825(11)	5931(8)	10412(5)	29(3)
C(35)	6624(12)	6906(9)	10285(6)	36(3)
C(36)	6732(13)	7411(9)	10699(6)	45(4)
C(37)	6530(15)	8333(10)	10500(7)	56(4)
C(38)	6251(16)	8657(10)	9963(7)	61(4)
C(39)	6166(13)	8124(9)	9577(6)	47(4)
C(40)	6090(13)	7645(10)	9064(7)	45(4)
C(41)	5977(12)	9083(9)	7432(6)	41(4)
C(42)	5916(12)	9578(9)	7882(6)	42(3)
C(43)	5826(13)	10504(9)	7752(6)	42(4)
C(44)	5837(12)	10900(9)	7171(6)	41(3)
C(45)	5930(12)	10429(10)	6720(6)	44(4)
C(46)	6003(11)	9536(8)	6863(5)	32(3)
C(47)	5735(16)	11041(9)	8232(6)	64(5)
C(48)	5914(13)	10898(9)	6096(5)	42(3)
C(49)	9238(15)	8496(9)	8292(6)	52(4)
C(50)	9159(16)	9262(11)	8497(7)	65(5)
C(51)	9139(13)	10055(9)	8132(7)	49(4)
C(52)	9174(13)	10077(10)	7537(7)	54(4)
C(53)	9229(12)	9297(9)	7331(6)	42(4)
C(54)	9272(11)	9221(9)	6712(6)	37(3)
C(55)	9186(12)	9894(9)	6232(6)	45(4)
C(56)	9230(12)	9635(11)	5709(6)	51(4)
C(57)	9364(13)	8809(10)	5613(6)	45(4)
C(58)	9467(11)	8156(8)	6106(5)	32(3)
C(59)	9656(12)	7199(10)	6132(6)	43(4)
C(60)	9780(12)	6762(11)	5659(6)	53(4)
C(61)	10003(14)	5849(11)	5747(7)	57(4)
C(62)	10139(14)	5384(11)	6303(7)	57(4)
C(63)	10028(13)	5812(9)	6769(7)	48(4)
C(64)	9618(12)	6025(11)	8451(8)	53(4)
C(65)	9674(12)	4601(9)	8993(6)	41(3)
C(66)	9605(12)	4189(10)	8526(7)	50(4)
C(67)	9671(15)	3289(11)	8586(8)	63(5)
C(68)	9912(14)	2782(11)	9126(8)	62(5)
C(69)	9991(13)	3169(10)	9620(7)	53(4)
C(70)	9869(13)	4076(9)	9548(6)	46(4)
C(71)	9529(15)	2868(12)	8067(7)	76(5)
C(72)	10200(15)	2637(11)	10203(7)	76(5)
S(1)	6988(4)	5814(2)	2544(2)	43(1)
O(1)	6603(9)	6537(6)	2075(4)	53(3)
O(2)	6870(10)	4958(5)	2440(4)	60(3)
O(3)	8159(8)	5891(7)	2791(4)	61(3)
C(73)	5716(12)	5977(8)	3127(5)	46(4)
F(1)	5878(11)	5344(6)	3581(4)	90(3)
F(2)	4546(8)	5963(7)	2969(4)	90(4)
F(3)	5739(7)	6738(5)	3296(4)	58(2)
S(2)	587(4)	7571(3)	3977(2)	56(1)
O(4)	919(9)	8018(6)	4423(4)	60(3)
O(5)	-505(9)	7097(7)	4146(5)	77(3)
O(6)	674(11)	8091(7)	3401(4)	76(3)
C(74)	1955(13)	6680(9)	3944(6)	71(5)

F(4)	3067(8)	7016(7)	3829(5)	99(4)
F(5)	1815(10)	6252(6)	3525(5)	93(3)
F(6)	1939(11)	6143(7)	4451(5)	107(4)
S(3)	7204(4)	10966(3)	433(2)	76(2)
O(7)	8454(16)	10628(15)	749(9)	91(4)
O(8)	7062(13)	11845(6)	480(5)	96(4)
O(9)	6291(9)	10405(6)	731(4)	61(3)
C(75)	7570(20)	10820(14)	-300(7)	73(4)
F(7)	8020(20)	10004(11)	-314(9)	99(5)
F(8)	8400(20)	11343(13)	-553(9)	129(6)
F(9)	6454(18)	11080(16)	-529(9)	125(5)
S(3')	7204(4)	10966(3)	433(2)	76(2)
O(7')	6890(20)	11119(17)	-232(7)	91(4)
O(8')	7062(13)	11845(6)	480(5)	96(4)
O(9')	6291(9)	10405(6)	731(4)	61(3)
C(75')	8756(17)	10317(13)	311(9)	73(4)
F(7')	8670(20)	9595(13)	94(10)	99(5)
F(8')	9580(20)	10759(14)	-56(10)	129(6)
F(9')	9150(20)	10081(17)	833(9)	125(5)

Table 3.10: Bond lengths (Å) and angles (deg) for [(trpy)Pt(2,4-Me₂-pcyd)][CF₃SO₃]

Pt(1)-N(2)	1.906(10)
Pt(1)-N(4)	1.974(14)
Pt(1)-N(3)	2.011(10)
Pt(1)-N(1)	2.036(10)
Pt(2)-N(7)	1.942(9)
Pt(2)-N(9)	1.971(12)
Pt(2)-N(8)	2.008(10)
Pt(2)-N(6)	2.025(10)
Pt(3)-N(12)	1.906(10)
Pt(3)-N(14)	1.927(14)
Pt(3)-N(11)	2.020(10)
Pt(3)-N(13)	2.016(11)
N(1)-C(1)	1.336(16)
N(1)-C(5)	1.339(16)
N(2)-C(10)	1.335(15)
N(2)-C(6)	1.379(15)
N(3)-C(15)	1.362(16)
N(3)-C(11)	1.347(17)
N(4)-C(16)	1.209(18)
N(5)-C(16)	1.230(17)
N(5)-C(17)	1.399(16)
N(6)-C(25)	1.333(15)
N(6)-C(29)	1.358(15)
N(7)-C(34)	1.332(14)
N(7)-C(30)	1.345(14)
N(8)-C(39)	1.333(16)
N(8)-C(35)	1.355(16)
N(9)-C(40)	1.146(18)
N(10)-C(40)	1.323(19)
N(10)-C(41)	1.403(16)
N(11)-C(63)	1.328(16)
N(11)-C(59)	1.402(17)
N(12)-C(54)	1.361(15)
N(12)-C(58)	1.349(15)
N(13)-C(49)	1.328(16)
N(13)-C(53)	1.410(16)
N(14)-C(64)	1.21(2)
N(15)-C(64)	1.30(2)
N(15)-C(65)	1.383(16)
C(1)-C(2)	1.408(18)
C(2)-C(3)	1.352(18)
C(3)-C(4)	1.395(17)
C(4)-C(5)	1.392(17)
C(5)-C(6)	1.482(17)
C(6)-C(7)	1.367(18)
C(7)-C(8)	1.393(18)
C(8)-C(9)	1.342(18)
C(9)-C(10)	1.348(18)
C(10)-C(11)	1.520(18)
C(11)-C(12)	1.363(18)
C(12)-C(13)	1.398(19)
C(13)-C(14)	1.37(2)
C(14)-C(15)	1.395(19)

C(17)-C(18)	1.363(17)
C(17)-C(22)	1.418(18)
C(18)-C(19)	1.383(17)
C(19)-C(20)	1.398(18)
C(19)-C(23)	1.507(17)
C(20)-C(21)	1.394(16)
C(21)-C(22)	1.354(17)
C(21)-C(24)	1.543(17)
C(25)-C(26)	1.419(18)
C(26)-C(27)	1.351(19)
C(27)-C(28)	1.364(17)
C(28)-C(29)	1.354(16)
C(29)-C(30)	1.485(16)
C(30)-C(31)	1.417(17)
C(31)-C(32)	1.363(17)
C(32)-C(33)	1.380(18)
C(33)-C(34)	1.393(17)
C(34)-C(35)	1.474(17)
C(35)-C(36)	1.386(17)
C(36)-C(37)	1.411(19)
C(37)-C(38)	1.31(2)
C(38)-C(39)	1.359(18)
C(41)-C(46)	1.385(18)
C(41)-C(42)	1.415(17)
C(42)-C(43)	1.403(18)
C(43)-C(44)	1.384(18)
C(43)-C(47)	1.516(17)
C(44)-C(45)	1.387(17)
C(45)-C(46)	1.355(17)
C(45)-C(48)	1.508(18)
C(49)-C(50)	1.355(18)
C(50)-C(51)	1.356(19)
C(51)-C(52)	1.391(19)
C(52)-C(53)	1.380(18)
C(53)-C(54)	1.477(18)
C(54)-C(55)	1.381(17)
C(55)-C(56)	1.361(19)
C(56)-C(57)	1.330(18)
C(57)-C(58)	1.386(18)
C(58)-C(59)	1.460(18)
C(59)-C(60)	1.396(18)
C(60)-C(61)	1.38(2)
C(61)-C(62)	1.38(2)
C(62)-C(63)	1.376(19)
C(65)-C(66)	1.386(18)
C(65)-C(70)	1.415(19)
C(66)-C(67)	1.37(2)
C(67)-C(68)	1.39(2)
C(67)-C(71)	1.52(2)
C(68)-C(69)	1.42(2)
C(69)-C(70)	1.374(19)
C(69)-C(72)	1.48(2)
S(1)-O(3)	1.429(8)
S(1)-O(2)	1.421(8)
S(1)-O(1)	1.457(8)
S(1)-C(73)	1.824(12)
C(73)-F(3)	1.323(12)

C(73)-F(2)	1.307(12)
C(73)-F(1)	1.310(12)
S(2)-O(5)	1.415(9)
S(2)-O(6)	1.436(9)
S(2)-O(4)	1.458(9)
S(2)-C(74)	1.839(13)
C(74)-F(6)	1.315(14)
C(74)-F(4)	1.310(13)
C(74)-F(5)	1.322(13)
S(3)-O(8)	1.377(9)
S(3)-O(9)	1.413(8)
S(3)-O(7)	1.538(14)
S(3)-C(75)	1.774(16)
C(75)-F(7)	1.292(17)
C(75)-F(8)	1.286(17)
C(75)-F(9)	1.303(17)
C(75')-F(9')	1.302(18)
C(75')-F(8')	1.307(17)
C(75')-F(7')	1.336(17)
N(2)-Pt(1)-N(4)	179.0(5)
N(2)-Pt(1)-N(3)	80.3(4)
N(4)-Pt(1)-N(3)	100.0(4)
N(2)-Pt(1)-N(1)	81.2(4)
N(4)-Pt(1)-N(1)	98.4(5)
N(3)-Pt(1)-N(1)	161.5(5)
N(7)-Pt(2)-N(9)	178.4(5)
N(7)-Pt(2)-N(8)	81.0(4)
N(9)-Pt(2)-N(8)	98.4(5)
N(7)-Pt(2)-N(6)	80.4(4)
N(9)-Pt(2)-N(6)	100.2(5)
N(8)-Pt(2)-N(6)	161.3(4)
N(12)-Pt(3)-N(14)	178.1(5)
N(12)-Pt(3)-N(11)	81.2(5)
N(14)-Pt(3)-N(11)	100.2(6)
N(12)-Pt(3)-N(13)	82.6(4)
N(14)-Pt(3)-N(13)	96.1(5)
N(11)-Pt(3)-N(13)	163.7(5)
C(1)-N(1)-C(5)	122.0(12)
C(1)-N(1)-Pt(1)	125.3(10)
C(5)-N(1)-Pt(1)	112.6(9)
C(10)-N(2)-C(6)	120.2(11)
C(10)-N(2)-Pt(1)	120.8(9)
C(6)-N(2)-Pt(1)	118.9(8)
C(15)-N(3)-C(11)	118.4(12)
C(15)-N(3)-Pt(1)	126.9(10)
C(11)-N(3)-Pt(1)	114.6(9)
C(16)-N(4)-Pt(1)	159.1(11)
C(16)-N(5)-C(17)	123.1(12)
C(25)-N(6)-C(29)	120.4(11)
C(25)-N(6)-Pt(2)	124.9(9)
C(29)-N(6)-Pt(2)	114.7(8)
C(34)-N(7)-C(30)	125.1(10)
C(34)-N(7)-Pt(2)	116.8(8)
C(30)-N(7)-Pt(2)	118.1(8)
C(39)-N(8)-C(35)	117.2(11)
C(39)-N(8)-Pt(2)	128.5(10)

C(35)-N(8)-Pt(2)	114.2(9)
C(40)-N(9)-Pt(2)	167.0(13)
C(40)-N(10)-C(41)	125.7(11)
C(63)-N(11)-C(59)	121.3(12)
C(63)-N(11)-Pt(3)	126.9(10)
C(59)-N(11)-Pt(3)	111.8(9)
C(54)-N(12)-C(58)	121.1(11)
C(54)-N(12)-Pt(3)	118.8(9)
C(58)-N(12)-Pt(3)	120.0(8)
C(49)-N(13)-C(53)	119.0(11)
C(49)-N(13)-Pt(3)	129.6(9)
C(53)-N(13)-Pt(3)	111.4(9)
C(64)-N(14)-Pt(3)	175.6(13)
C(64)-N(15)-C(65)	120.3(12)
N(1)-C(1)-C(2)	119.2(14)
C(1)-C(2)-C(3)	119.9(13)
C(4)-C(3)-C(2)	120.0(13)
C(5)-C(4)-C(3)	118.4(13)
N(1)-C(5)-C(4)	120.3(12)
N(1)-C(5)-C(6)	116.5(11)
C(4)-C(5)-C(6)	122.9(12)
N(2)-C(6)-C(7)	120.6(11)
N(2)-C(6)-C(5)	110.5(11)
C(7)-C(6)-C(5)	128.9(12)
C(8)-C(7)-C(6)	115.5(12)
C(9)-C(8)-C(7)	124.6(13)
C(10)-C(9)-C(8)	116.9(12)
N(2)-C(10)-C(9)	122.2(12)
N(2)-C(10)-C(11)	110.2(12)
C(9)-C(10)-C(11)	127.5(12)
C(12)-C(11)-N(3)	123.7(13)
C(12)-C(11)-C(10)	122.4(13)
N(3)-C(11)-C(10)	113.8(12)
C(11)-C(12)-C(13)	117.6(15)
C(12)-C(13)-C(14)	119.9(14)
C(15)-C(14)-C(13)	119.7(15)
N(3)-C(15)-C(14)	120.4(14)
N(4)-C(16)-N(5)	174.4(15)
C(18)-C(17)-N(5)	125.2(12)
C(18)-C(17)-C(22)	116.5(12)
N(5)-C(17)-C(22)	118.2(12)
C(17)-C(18)-C(19)	123.3(12)
C(20)-C(19)-C(18)	118.5(11)
C(20)-C(19)-C(23)	120.9(12)
C(18)-C(19)-C(23)	120.5(13)
C(19)-C(20)-C(21)	119.6(12)
C(22)-C(21)-C(20)	119.8(12)
C(22)-C(21)-C(24)	121.0(11)
C(20)-C(21)-C(24)	119.2(12)
C(21)-C(22)-C(17)	122.1(12)
N(6)-C(25)-C(26)	118.1(13)
C(27)-C(26)-C(25)	121.3(13)
C(26)-C(27)-C(28)	118.5(13)
C(29)-C(28)-C(27)	120.2(13)
N(6)-C(29)-C(28)	121.4(12)
N(6)-C(29)-C(30)	113.4(10)
C(28)-C(29)-C(30)	125.1(11)

N(7)-C(30)-C(31)	118.3(11)
N(7)-C(30)-C(29)	113.4(10)
C(31)-C(30)-C(29)	128.3(11)
C(32)-C(31)-C(30)	117.1(13)
C(31)-C(32)-C(33)	122.9(13)
C(32)-C(33)-C(34)	118.6(11)
N(7)-C(34)-C(33)	117.9(11)
N(7)-C(34)-C(35)	114.5(11)
C(33)-C(34)-C(35)	127.6(11)
N(8)-C(35)-C(36)	124.3(13)
N(8)-C(35)-C(34)	113.5(10)
C(36)-C(35)-C(34)	122.2(13)
C(35)-C(36)-C(37)	114.6(14)
C(38)-C(37)-C(36)	120.8(13)
C(37)-C(38)-C(39)	121.7(15)
N(8)-C(39)-C(38)	121.4(14)
N(9)-C(40)-N(10)	172.5(16)
C(46)-C(41)-N(10)	119.6(12)
C(46)-C(41)-C(42)	118.1(12)
N(10)-C(41)-C(42)	122.1(13)
C(43)-C(42)-C(41)	120.4(13)
C(44)-C(43)-C(42)	117.4(12)
C(44)-C(43)-C(47)	121.9(13)
C(42)-C(43)-C(47)	120.8(13)
C(43)-C(44)-C(45)	123.4(13)
C(46)-C(45)-C(44)	117.6(13)
C(46)-C(45)-C(48)	121.3(12)
C(44)-C(45)-C(48)	121.1(13)
C(45)-C(46)-C(41)	123.1(12)
C(50)-C(49)-N(13)	121.6(13)
C(49)-C(50)-C(51)	121.5(15)
C(50)-C(51)-C(52)	118.7(14)
C(53)-C(52)-C(51)	119.6(14)
C(52)-C(53)-N(13)	119.3(13)
C(52)-C(53)-C(54)	125.5(14)
N(13)-C(53)-C(54)	115.1(11)
N(12)-C(54)-C(55)	119.7(13)
N(12)-C(54)-C(53)	112.1(12)
C(55)-C(54)-C(53)	128.2(13)
C(56)-C(55)-C(54)	115.9(13)
C(57)-C(56)-C(55)	126.9(13)
C(56)-C(57)-C(58)	115.2(13)
N(12)-C(58)-C(57)	121.1(12)
N(12)-C(58)-C(59)	111.5(11)
C(57)-C(58)-C(59)	127.3(13)
C(60)-C(59)-N(11)	118.3(14)
C(60)-C(59)-C(58)	126.3(14)
N(11)-C(59)-C(58)	115.3(11)
C(61)-C(60)-C(59)	120.1(14)
C(60)-C(61)-C(62)	119.0(14)
C(63)-C(62)-C(61)	121.1(15)
N(11)-C(63)-C(62)	120.2(14)
N(14)-C(64)-N(15)	176.4(16)
C(66)-C(65)-C(70)	119.2(13)
C(66)-C(65)-N(15)	124.3(13)
C(70)-C(65)-N(15)	116.5(13)
C(67)-C(66)-C(65)	122.3(15)

Chapter 4

Dinuclear Complexes of Dicyanamidobenzene (dicyd^{2-}) Ligands: Physical Characterization and Discussion

4.1 Infrared Spectroscopy of Dinuclear Complexes of Platinum

Infrared spectra of the two dinuclear complexes are shown in Figures 4.1 and 4.2. All complexes show a single $\nu(\text{NCN})$ in the range of $2114\text{--}2158\text{ cm}^{-1}$. Compared to the free dicyd^{2-} ligand, the $\nu(\text{NCN})$ is shifted to higher wavelength by $21\text{--}58\text{ cm}^{-1}$ (see Table 4.1).

In similar work done by Zhang³¹, a dinuclear palladium complex of Me_2dicyd was synthesized. The infrared spectrum of this complex showed two equally intense $\nu(\text{NCN})$ stretches. $[\{(\text{trpy})\text{Pt}\}_2\text{-}\mu\text{-Me}_2\text{dicyd}](\text{PF}_6)_2$ and $[\{(\text{trpy})\text{Pt}\}_2\text{-}\mu\text{-Cl}_2\text{dicyd}](\text{CF}_3\text{SO}_3)_2$ showed single cyanamide stretches.

Table 4.1 IR Data for the Dinuclear Dicyd^{2-} Complexes ^a

Complex	$\nu(\text{NCN})\text{ cm}^{-1}$	Complex	$\nu(\text{NCN})\text{ cm}^{-1}$
$\text{Me}_2\text{dicyd}^{2-}$	2093	$\text{Cl}_2\text{dicyd}^{2-}$	2100
$[\{(\text{trpy})\text{Pt}\}_2\text{-}\mu\text{-Me}_2\text{dicyd}](\text{PF}_6)_2$	2114	$[\{(\text{trpy})\text{Pt}\}_2\text{-}\mu\text{-Cl}_2\text{dicyd}](\text{CF}_3\text{SO}_3)_2$	2158

^a All spectra were obtained as KBr mulls.

Figure 4.1: Infrared Spectrum of [((trpy)Pt)₂-μ-Me₂dicyd](PF₆)₂ (KBr disc)

Figure 4.2: Infrared Spectrum of [((trpy)Pt)₂-μ-Cl₂dicyd](CF₃SO₃)₂ (KBr disc)

4.2 Proton NMR Spectroscopy of Dinuclear Complexes of Platinum

The proton NMR spectra of the two dinuclear complexes were taken as a second method of characterization. The spectra were taken in d_6 -DMSO using a 400MHz NMR spectrometer. The assignments for the spectra are similar to those for the mononuclear platinum complexes (see table 4.2). Since the position of the trpy resonances changes very little for the dinuclear complexes compared to the mononuclear complexes, it can be concluded that their environments are very similar.

Table 4.2 ^1H NMR Spectroscopy Data for $[(\text{trpy})\text{PtL}]_2^{2+}$ Complexes ^a

	dicyd	trpy					
L		H5	H6	H7	H8	H9	H10
Me_2dicyd	6.74	8.54	8.54	8.64	8.48	7.96	8.54
Cl_2dicyd	6.92	8.47	8.47	8.58	8.36	7.94	8.47

^aChemical shifts are in ppm. All NMR spectra were taken in d_6 -DMSO

Figure 4.3: 400 MHz ^1H NMR spectrum of $[\{(\text{trpy})\text{Pt}\}_2\text{-}\mu\text{-Me}_2\text{dicyd}](\text{PF}_6)_2$ in $\text{d}_6\text{-DMSO}$ (terpyridine peaks)

Figure 4.4: 400 MHz ^1H NMR spectrum of $[\{(\text{trpy})\text{Pt}\}_2\text{-}\mu\text{-Me}_2\text{dicyd}](\text{PF}_6)_2$ in $\text{d}_6\text{-DMSO}$ (methyl peaks)

Figure 4.5: 400 MHz ^1H NMR spectrum of $[\{(\text{trpy})\text{Pt}\}_2\text{-}\mu\text{-Cl}_2\text{dicyd}](\text{CF}_3\text{SO}_3)_2$ in d_6 -DMSO

4.3 Electronic Absorption Spectroscopy of Dinuclear Complexes of Platinum

The electronic spectra of the two dinuclear platinum complexes in distilled DMF solution are shown in figures 4.5-4.6. All spectral assignments are listed in table 4.2. The $\pi\text{-}\pi^*$ transitions of the aromatic trpy ligand are obscured by the solvent cutoff of DMF. Metal-to-Ligand charge transfer (MLCT) bands were seen in the range of 335-400 nm. Also seen on the UV-Vis spectra is the broad Ligand-to-Metal charge transfer (LMCT) bands that appear around 537-580 nm. These LMCT are considerably more intense than those for the mononuclear complexes, because there are two LMCT chromophores per mole of complex.

Table 4.3 UV-vis Absorption Data for $[\{(\text{trpy})\text{Pt}\}_2-\mu\text{-L}]^{2+}$ Complexes ^a

L	$\pi\text{-}\pi^*$ (trpy)	MLCT	LMCT
Me ₂ dicyd	obscured by solvent cut-off	335 (35000)	537 (29500) br
		348 (31800)	
		390 (12000)sh	
Cl ₂ dicyd	obscured by solvent cutoff	333 (94500)	580 (10200) br
		345 (86000) sh	
		400 (24000) sh	

^a All data were recorded in 3.00×10^{-5} M distilled DMF solution. Extinction coefficients are in brackets. sh = shoulder; br = broad

Figure 4.6: UV-vis absorption spectrum of $[\{(\text{trpy})\text{Pt}\}_2-\mu\text{-Me}_2\text{dicyd}](\text{PF}_6)_2$ in distilled DMF (3.00×10^{-5} M)

Figure 4.7: UV-vis absorption spectrum of $[\{(\text{trpy})\text{Pt}\}_2\text{-}\mu\text{-Cl}_2\text{dicyd}](\text{CF}_3\text{SO}_3)_2$ in distilled DMF ($3.00 \times 10^{-5}\text{M}$)

4.4 Cyclic Voltammetry of Dinuclear Complexes of Platinum

The electrochemical data for the two dinuclear platinum complexes are shown in Table 4.3 and the cyclic voltammograms are presented in figures 4.7 and 4.10. The cyclic voltammetry experiments were performed in distilled DMF using platinum working and counter electrodes, a silver wire pseudo-reference electrode and ferrocene/ferrocenium couple (0.665 V vs. N.H.E.) as an internal reference.

The cyclic voltammetry of $[\{(\text{trpy})\text{Pt}\}_2\text{-}\mu\text{-Me}_2\text{dicyd}](\text{PF}_6)_2$ and $[\{(\text{trpy})\text{Pt}\}_2\text{-}\mu\text{-Cl}_2\text{dicyd}](\text{CF}_3\text{SO}_3)_2$ was very difficult. In order to complete a cyclic voltammogram without decomposition of the dinuclear complex, it was necessary to use scan rates of 400 mV/s or more. The first cyclic voltammograms obtained for these complexes were very messy (see figures 4.7 and 4.9). When Pt(II) is reduced to Pt(I) there is a possibility

of disproportionation. If these two species [Pt(0) and Pt(II)] exist, the cyclic voltammogram will be very messy. Nevertheless, the cyclic voltammograms in figure 4.8 resemble that of mononuclear complexes (see figure 3.19), even though they are not very clean. It can be suggested that the first wave is the Pt(II)/Pt(I) reduction couple and the second wave is the trpy reduction couple. In fact, if this is true, then the poor reversibility that is seen may be due to the disproportionation reaction in which two Pt(I) are formed from the same complex and react to make Pt(0) and Pt(II). These products may deposit on the surface of the work electrode. After many scans and frequent cleaning of the electrodes, reproducible cyclic voltammograms were obtained (see figures 4.8 and 4.10).

The two major features of the cyclic voltammograms are the platinum (+2/+) couple, with a range of -0.62 to -0.71 V, and the terpyridine (0/-) couple, with a range of -1.1 to -1.3 V. All redox events of the dinuclear platinum complexes appeared to be somewhat reversible. In dinuclear complexes, it is sometimes possible to see two metal-centred redox events. In the two dinuclear platinum complexes presented, these events are superimposed, so only one peak is visible.

Table 4.4: Electrochemical Data for Dinuclear Platinum Complexes ^a

Complex	Platinum couple (^{+2/+})	Terpyridine couple (0/-)	Ligand couples
[{(trpy)Pt} ₂ -μ-Me ₂ dicyd](PF ₆) ₂	-0.62	-1.1	+0.58, +0.26
[{(trpy)Pt} ₂ -μ-Cl ₂ dicyd] (CF ₃ SO ₃) ₂	-0.71	-1.3	+0.87, +0.59

^a All potentials are in volts vs. N.H.E. using ferrocene as the internal reference (665 mV vs. N.H.E.).

Measured using 3.6 mM solutions in distilled DMF at 25°C at a scan rate of 400mV/s. Electrolyte used was 0.1M tetrabutylammonium hexafluorophosphate

Figure 4.8: Cyclic voltammogram of $[\{(\text{trpy})\text{Pt}\}_2-\mu\text{-Me}_2\text{dicyd}](\text{PF}_6)_2$ in distilled DMF

Figure 4.9 : Cyclic voltammogram of $[\{(\text{trpy})\text{Pt}\}_2-\mu\text{-Me}_2\text{dicyd}](\text{PF}_6)_2$ in distilled DMF

Figure 4.10 : Cyclic voltammogram of $[\{(\text{trpy})\text{Pt}\}_2-\mu\text{-Cl}_2\text{dicyd}](\text{CF}_3\text{SO}_3)_2$ in distilled DMF

Figure 4.11 : Cyclic voltammogram of $[\{(\text{trpy})\text{Pt}\}_2-\mu\text{-Cl}_2\text{dicyd}](\text{CF}_3\text{SO}_3)_2$ in distilled DMF

Attempts to grow X-ray quality crystals of these two dinuclear platinum complexes have been unsuccessful. Many attempts were made using different solvents such as dichloromethane, dimethylsulfoxide, benzonitrile and methoxyethanol. Also, many different kinds of diffused solvents such as water, acetone, ethanol, ether, and ethyl acetate at RT and 5°C were used. However, none of these methods succeeded to give proper crystals for X-ray structure.

Chapter 5

Summary and Future Work

The following mononuclear complexes have been made: $[(trpy)PtPCyD]PF_6$, $[(trpy)PtDM-PCyD]PF_6$, $[(trpy)PtDC-PCyD]PF_6$, $[(trpy)PtDMO-PCyD]PF_6$ which are characterized by IR, NMR, UV, CV and X-ray. Importantly, the crystal structure of these complexes is shown to be planar and this suggests that perhaps the dinuclear complexes are planar as well. Unfortunately, we could not grow crystals of the dinuclear complexes to prove planar geometry. Unfortunately, there was not sufficient time to measure the conductivity of dinuclear complexes, however, this will be done by Dr. Crutchley in the near future.

Moreover, the steps are involved in making the dinuclear complexes conducting assume that there is π -stacking in the crystal lattice through dicyd²⁻ ligands. The dicyd²⁻ ligands are a filled π system and overlapping filled π system are not going to be conducting. They have to be partially oxidized in the same way as the copper DCNQI system and this can be done by doping the powder with I_2 . The progress of oxidation can be monitored spectroscopically by watching the growth of the radical anion bands in the visible spectrum.³¹

The electrochemistry of the dinuclear complexes, $[{(trpy)Pt}_2-\mu-Me_2dicyd](PF_6)_2$ and $[{(trpy)Pt}_2-\mu-Cl_2dicyd](CF_3SO_3)_2$, gave ambiguous cyclic voltammograms, as seen in figures 4.7 and 4.9. This phenomenon requires further study before definite conclusions can be made.

This study also gave the results that the substitution on the phenyl ring on both the pcyd anion and dicyd dianion ligands affected the ligand's π -donating properties. By changing the substituents, one can adjust the donor properties of the ligand and so adjust the properties of the complex. Future studies could involve the synthesis of other dinuclear (trpy)Pt(II) complexes of other dicyd derivatives to study their properties. Also, the effect of the steric bulk of the counter ion on stacking crystal lattice could be investigated.

The purity of the complex plays a crucial role in the chemical and physical properties. For this reason, more effort and different techniques should be employed to ensure the purification of the complexes.

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