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(2,2',2''-TERPYRIDINE)PALLADIUM(II) COMPLEXES OF PHENYLCYANAMIDE
AND 1,4-DICYANAMIDE-2,5-DIMETHYLBENZENE LIGANDS

by

WEIGANG ZHANG, B.Sc., M.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, Ontario

April, 1993

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(2,2',2''-TERPYRIDINE)PALLADIUM(II) COMPLEXES OF PHENYLCYANAMIDE
AND 2,5-DIMETHYL-DICYANAMIDOBENZENE LIGANDS

submitted by

WEIGANG ZHANG, B.Sc., M.Sc.

in partial fulfilment of the requirements
for the degree of Master of Science

Thesis Supervisor

Chair, Department of Chemistry

Carleton University

April, 1993

ABSTRACT

A series of square planar terpyridinepalladium(II) complexes of phenylcyanamide anion ligands (i.e. $[(\text{trpy})\text{Pd}(\text{pcyd})](\text{PF}_6)$) have been synthesized and characterized by IR, ^1H NMR, UV-vis spectroscopies and X-ray crystallography. The crystal structure of $[(\text{trpy})\text{Pd}(\text{pcyd})](\text{PF}_6)$ shows that the complex molecule is almost planar and the Pd-NCN bond is bent having a bond angle of 146.4° . The planarity of the complex is important since it allows for the formation of π stacks in the crystal lattice. The formation of π -stacks in organic charge transfer (CT) salts has been shown to result in highly conductive materials. A mononuclear terpyridinepalladium(II) complex of 1,4-dicyanamide-2,5-dimethylbenzene radical anion ligand and a dinuclear terpyridinepalladium(II) complex of 1,4-dicyanamide-2,5-dimethylbenzene dianion ligand have also been prepared and characterized by IR, ^1H NMR, UV-vis spectroscopies and cyclic voltammetry. Almost all of the above complexes show an unusual ligand to metal charge-transfer (LMCT) absorption in the range 360-700 nm. It is suggested that the bending of cyanamide group makes the mixing of metal's σ^* and ligand's π_{nb} orbitals possible and results in the LMCT absorption.

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This work is dedicated to my wife, Songyan Wu, and my parents.

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CHAPTER 1

INTRODUCTION

1.1 Background

1.1.1 Molecular Metals: Some Concepts and Developments

The past two decades have witnessed unabated interest in the synthesis and characterization of new materials that display unusual solid-state properties such as metallic conductivity and superconductivity. Among them, molecular metals (most are charge-transfer CT salts) have become important because they not only display high conductivity, but also display novel magnetic and optical properties.¹⁻¹⁴ The motivations behind research on these exotic materials are: (a) there is a wealth of fundamental solid-state chemistry and physics to be uncovered and (b) there are potentially many far-reaching technological applications within the arena of molecular electronic devices.

Generally speaking, molecular metals are organic compounds which possess metallic properties in certain circumstances. They can be classified into two types: (1) well formed organic stacking systems that can display conductivity by oxidation or reduction; (2) conducting CT salts that consist of highly ordered arrays of donor and acceptor species, one or both of which must be a radical ion which is thermodynamically stable. The latter can be either single-chain conductors, e.g. $(\text{TMTSF})_2^+ \text{X}^-$ salts where the anion is a closed shell species, or two-chain

conductors, such as $\text{TTF}^+ \cdot \text{TCNQ}^-$ CT complexes in which both components are open shell molecules.

The most important feature of these materials is that their conductivity is different along different directions in the solid. In most cases there is one axis along which the conductivity is high, sometimes close to that of elemental metals. The conductivity in perpendicular direction can be 100,000 times smaller. This anisotropy reflects the molecular structure of chains or stacks along which the high conductivity is found. They are often called quasi-one-dimensional solids or linear-chain materials.¹⁵

The conductivity of a solid is determined by its electronic structure. The distribution of the electrons in the vicinity of an atom is described by a set of orbitals, each of which has a characteristic shape and size. In a highly conductive solid, orbitals of adjacent atoms or molecules overlap, so that electrons can move readily from site to site through the lattice. Linear-chain conductors are materials in which there is extensive overlapping of orbitals only along one axis.

In order to explain the mechanism of electrical conduction it is necessary to discuss the state of the electrons in a solid. A three-dimensional crystalline solid has the order of 10^{23} atomic or molecular orbital overlaps. Each energy level of the original atoms is split into a corresponding number of finely spaced levels. The separation between adjacent energy levels is so small that each set of levels can be considered as a continuous band where an electron can take on any energy between the lower and the upper boundaries of the band. Since each of the levels that make

up the band can hold no more than two electrons, in a solid made up of n atoms, each band can be filled with no more than $2n$ electrons. If any more electrons are added, they must go into the lowest unoccupied band, sometimes at a substantial cost in energy.

Figure 1.1 Formation of energy bands in a solid resulted from the overlapping of the orbitals of adjacent atoms.¹⁵

Most electrical properties of a solid are determined by the extent of occupation of the energy bands and the magnitude of the gaps between them. In

order to form an electric current, there must be a net movement of electrons in one direction. If the energy levels in a band are filled continuously from the lowest available level to the highest allowed one, there can be no net motion of the electrons. Whether this kind of material is an insulator or a semiconductor depends on the band gap between the completely filled band and the completely empty band.

Figure 1.2 Band structure of a solid.¹¹

In semiconductor conduction, it is possible when an electron is excited by heat or light to move from a filled band to one of the vacant levels of an empty

band. Such a change in the energy of an electron effectively creates two charge carriers: the electron itself and the "hole" left behind in the previously filled band. The minimum energy needed to create these charge carriers is equal to the width of the band gap. Charge carriers can also be supplied by defects or by impurities such as dopants.

If the band gap between filled band and empty band is so large that almost no charge carriers can be created by thermal excitation, this material is an insulator. The bulk conductivity that is observed in such materials results mainly from defects and impurities in the structure.

In metal, there is a partially filled electron-energy band where electrons can readily move to unoccupied levels that are only infinitesimally higher in energy. Thus electrons are always freely available for conduction. A partially filled band is created whenever the orbitals that combine to form the band are not fully occupied. For example, if each orbital is occupied by only one electron (instead of the maximum of two electrons), the corresponding energy band in the solid will have only n electrons rather than the maximum of $2n$. The remaining levels in the band are available for conduction.

In a charge-transfer (CT) salt, the highest occupied energy band is derived from the HOMOs of the donor species or the acceptor species. A supermolecular orbital provides a mechanism for metallic delocalization of electrons, with the width of the conduction band dependent upon interaction between molecular orbitals on neighbouring molecules.

Another important factor that affects the conductivity of a CT salt is the stacking pattern. Normally, there are two types of stacking:¹³

- (a) mixed stacks, in which the donors (D) and acceptors (A) stack alternately face-to-face such as [D-A-D-A.....], and
- (b) segregated stacks, in which the donors and acceptors form separate donor stacks [D-D-D.....] and acceptor stacks [A-A-A.....].

Compounds with mixed stacks are not highly conductive because of electron localization on the acceptors. However, most of the charge-transfer compounds that form segregated stacks are highly conductive. The π -overlap and charge-transfer interaction between adjacent molecules in the stacking direction are strong, causing the unpaired electrons to partially delocalize along these one-dimensional molecular stacks thereby enhancing conduction in that direction.

The temperature dependence of conductivity in organic metals is dominated by the interaction (scattering) of electrons with vibrations of the atomic lattice (phonons); as the temperature is lowered there are fewer lattice vibrations which, in effect, increases the intermolecular orbital overlap, so the conductivity increases. The conductivity of a semiconductor, in contrast to metals, decreases as the temperature is lowered, because there is less energy available to excite charge carriers across the band gap.

Superconductivity as described by the Bardeen, Cooper, and Schrieffer (BCS) theory for inorganic materials, is caused by the highly coordinated motion of electron

pairs (Cooper pairs).¹⁶ This mechanism is clearly distinct from metallic conduction for which individual electrons are the charge carrier. Electron pairing can be driven by phonons below a critical temperature, T_c , if a strict set of structural and electronic energy condition is fulfilled; at higher temperatures the thermal agitation of the electrons dissociates the pairs and superconduction is lost. Currently it is not clear yet whether or not BCS theory can adequately explain organic superconduction.¹⁴

The first report of perylene bromide, a molecular compound, exhibiting low resistivity of $\rho \approx 10 \text{ ohm cm}$ was made by Akamatu et al. in 1954.¹⁷ (perylene itself is an insulator with a resistivity $\rho = 10^{14} - 10^{16} \text{ ohm cm}$.) This observation was a verification of earlier predictions by McCoy and Moore in 1911¹⁸ (the same year superconductivity was discovered in mercury), that certain organic solid might exhibit electrical conductivity comparable with that of metals. This is the first time that metallic properties were observed in materials which did not contain metal atoms!

In 1962, the first stable, highly conducting organic molecule, TCNQ (7,7,8,8-tetracyano-p-quinodimethane), was synthesized by Melby *et al.*¹⁹ Thereafter, interest in the syntheses and characterizations of conducting organic solids developed rapidly when it was discovered that many TCNQ salts were electrically conductive.^{20,21}

The TCNQ anions in the metallic salt are packed in pancake-like molecular stacks with extended π -electronic system above and below the molecular planes, utilizing p_z orbitals of the acceptor. Electrons are delocalized in this system and move from plane to plane along the TCNQ stacks. The conductivities are highly

anisotropic, being 500 times greater in the direction parallel to the stacks than in the perpendicular direction. This conduction anisotropy is an indication of the lack of interstack interactions in these systems. The room-temperature conductivities of TCNQ salts ranged from insulator values to $\sim 10^3 \text{ Scm}^{-1}$. They demonstrated a wide range of novel magnetic, electrical and structural properties. Simple salts often have the stoichiometry of 1:1 (cation donor-TCNQ acceptor), but can reach values of 1:2 or 1:4 in more complex salts. The reaction between donor (D) and acceptor (A) molecules in these salts is illustrated as follows in which charge-transfer salts are formed:

Charge-transfer compound

In 1970, an organic electron-donor TTF (tetrathiafulvalene) was synthesized by Wudl *et al.*²² and high conductivity was found in its halogen salts. TTF contains four sulfur atoms and is a good electron donor, readily giving up an electron to form a stable cation. The 1:1 salt of TCNQ which was synthesized by Ferraris *et al.*²³ in 1973 was the first molecular crystal exhibiting genuine metallic behaviour. Between 54 and 298 K, the electrical conductivity of TTF-TCNQ increased with decreasing temperature. Superconductivity was never observed in TTF-TCNQ due to low temperature metal-insulator transitions (38 and 54 K).

TTF and TCNQ are found to form independent molecular stacks in the TTF-

TCNQ compound. Extensive π -interaction and electron delocalization occurs along the stacks but not between them and this leads to structural transition in each separate stack (TTF and TCNQ) and concomitant changes in electrical properties. Below 54 K the material exhibits a semiconducting state similar to some of the alkali metal salts of TCNQ.

Figure 1.3 Structure of TTF-TCNQ.¹³

To improve the electron-donating properties of TTF and the electron-accepting properties of TCNQ, many TTF and TCNQ variants were synthesized and studied. The earliest modification was the synthesis of TSF, the selenium analogue of TTF. The corresponding TSF-TCNQ salt was found to be isomorphous with TTF-TCNQ but had double electrical conductivity. Table 1 shows some typical compounds and their conductivities.

Table 1.1 Conductivities of Several TCNQ Salts¹³ (Segregated Stacks)

Salt	σ_a (Scm ⁻¹)
TTF-TCNQ	~500
TSF-TCNQ	~700-800
TMTTF-TCNQ	350
TMTSF-TCNQ	800
HMTTF-TCNQ	500
HMTSF-TCNQ	2000
TMTSF-DMTCNQ	400-600/2x10 ⁵ (p=10 kbar at -1 K)

Donor:

Acceptor:

Figure 1.4 Some typical donors and acceptors that form CT salts.

A landmark in the development of highly electrically conductive molecular metals was reached in 1986 with the discovery of a series of highly conducting copper (II) DCNQI (N,N'-dicyanoquinonediimine) salts by Hünig *et al.*²⁴ The crystal structure data^{24,25} of copper(II) DCNQIs show that the DCNQI molecules are arranged in stacks linked together by tetrahedrally coordinated copper ions (see Figure 1.5).

Figure 1.5 Perspective view of the crystal structure along the c axis: the chain of copper atoms is surrounded by four stacks of 2,5-DM-DCNQI molecules (H atoms not shown)

The highest conductivity occurs via π stacks of DCNQI molecules (metallic behaviour between 295-1.3 K with extremely high conductivity of $\sigma=500,000 \text{ S cm}^{-1}$

at 3.5 K and 1000 S cm^{-1} at room temperature for $\text{Cu}(\text{DM-DCNQI})_2$ (DM-DCNQI is 2,5-dimethyldicyanoquinonediimine, radical anion).²⁴ This salt is also a three-dimensional conductor with transverse conductivity occurring via NCN-Cu-NCN bridges between the individual stacks of 100 S cm^{-1} at room temperature.²⁶ In these salts, high conductivity along π acceptor stacks occurs when each π acceptor molecule has a partial negative charge, because electrons can move within a π stack freely without a Coulombic barrier.

For $\text{Cu}(\text{DCNQI})_2$ molecular metals, low-temperature X-ray diffraction and XPS studies indicate that copper exists in a mixed-valence state with an average oxidation state of 1.3.^{27,28} The mixed-valence state of copper arises from the direct coupling of copper's d orbitals with radical anion DCNQI $p\pi$ orbitals.

In order to obtain efficient intermolecular interactions in a CT salt, the structural and redox properties of the constituent molecules are clearly of crucial importance. (There are, of course, other important design constraints.²⁹) The donor and/or acceptor moieties are typically planar (or nearly planar) molecules that form either segregated stacks or planar sheets. Thus the resultant electrical properties of the salt are highly anisotropic, *i.e.* associated with a unique direction within the crystal.

It is very likely that high conductivity can be obtained in other conjugated, planar organic molecules which can form effective π stacks. Some metal complexes of DCNQIs dianion ligands and of phenylcyanamide anion ligands may be suitable candidates. Conductivity can be achieved by properly oxidizing the complexes to form partially charged

π stacking system.

1.1.2 Metal-Phenylcyanamide Anion and Metal-DCNQI Dianion Complexes

The phenylcyanamide anion (pcyd-) ligands are pseudo-halides³⁰ and resonance-stabilized three-atom π systems. Two pairs of nonbonding electrons can be delocalized in these systems (see Figure 1.6).³¹

Figure 1.6 (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 atomic orbitals approximate their contribution to the molecular orbital.³⁰

These ligands are strong π -donor ligands and prefer to coordinate to π -acid metal ions. Moreover, not only π_{nb} non-bonding electron pairs can interact with cations, but also the σ lone electron pair. So the phenylcyanamide anions are both π and σ donating ligands and have greater donor number than their nitrile analogues.^{31,32} In the two resonance forms, π_{nb1} is more stable than π_{nb2} because only π_{nb1} has the correct symmetry to delocalize into both the phenyl ring and the nitrile group. Because the strong coupling of the cyanamide group with the phenyl π system, free anionic phenylcyanamide ligands are expected to be planar in the absence of steric effects.³³

The coordination chemistry of pentaammineruthenium(III)phenylcyanamide complexes,^{31,33,34} 2,2'-bipyridinecopper(II)phenylcyanamide complexes,³⁵ 1,3-bis(2'-pyridylimino)isoindolinateonickel(II)phenylcyanamide complexes,³⁶ bis(2,2'-bipyridine)ruthenium(III)bis(phenylcyanamide) complexes³⁷ and pentaammineruthenium(III)dicyanamidobenzene dinuclear complexes³⁸⁻⁴⁰ have been studied by Crutchley *et al.* in order to explore the coordination chemistry of the cyanamide group, the dependence of LMCT band energies and oscillator strength on the nature of the phenylcyanamide ligands and the dependence of electronic coupling and magnetic coupling on the nature of the dicyanamidobenzene dianion bridging ligands.

For pentaammineruthenium(III)phenylcyanamide complexes, X-ray crystal structure showed that the anionic cyanamide and phenyl groups in the 2,3-dichlorophenylcyanamide ligand are nearly coplanar, indicating that a strong π interaction exists between $-\text{NCN}^-$ group and Ru(III).³³ This is also demonstrated by observing changes in the ligand to metal charge transfer (LMCT) absorptions and redox properties of the

Ru(III) metal ion corresponding to the changes in pcyd⁻ ligands. A linear correlation was found between the $b_1^* \leftarrow b_1$ LMCT energy and the difference between ligand, L(0/-), and metal, Ru(III/II), reduction couples, indicating the complexes have similar properties with the only variable being the nature of the cyanamide-ruthenium interaction. The oscillator strength of the $b_1^* \leftarrow b_1$ transition was found to decrease with increasing energy of the transition for those complexes. Therefore, changing the substituent on the phenyl ring can effectively "tune" the extent of electronic interaction between the pcyd⁻ ligands and the metal.

The coordination sphere of Ru(III) (or so called "co-ligand") can also affect the interaction between the metal ion and -NCN⁻ group by means of changing the energies of the metal's π orbitals. Rezvani *et al.*³⁷ compared [(bpy)₂Ru(pcyd)₂](PF₆) complexes with [(NH₃)₅Ru(pcyd)]²⁺ complexes. When a strong π -acid co-ligand bipyridine was used instead of a σ donating co-ligand amine, the LMCT band shifted to lower energies without any change in oscillator strength. From previous studies,^{33,34} this implies that the extent of overlap between Ru(III) $d\pi$ and cyanamide π_{nb} orbitals is also unchanged.

In order to explore the nature of the interaction between copper(II) and anionic cyanamide group and further understand the conduction mechanism of Cu(DCNQI)₂ molecular metals, Crutchley *et al.* synthesized and characterized a series of four- and five-coordinate copper(II) complexes of 2,2'-bipyridine and phenylcyanamide anion ligands.³⁴ It was found that for the five-coordinate complex, [(bpy)₂Cu(2,3-Cl₂pcyd)][PF₆], the coordination geometry around Cu(II) is a distorted square pyramid made of nitrogen donor atoms in which the phenylcyanamide ligand occupies a basal coordination site. For the four-

coordination complex, $[(bpy)Cu(2,3-Cl_2pcyd)_2]$, the coordination geometry is a distorted square planar. In both complexes, the anionic cyanamide group of $2,3-Cl_2pcyd^-$ ligand is nearly coplanar with the phenyl ring due to a strong π coupling and coordination to copper(II) via the cyano nitrogen. In the distorted square planar four-coordinate complex, Cu(II)-cyanamide bond angles are between $141.4(7)$ and $165.3(9)^\circ$ which are much smaller than that of Ru(III) complex of $2,3-Cl_2pcyd^-$, because Cu(II) is a far weaker π -acceptor than Ru(III). Crystal data, LMCT band intensity and electrochemical potentials are consistent with a mostly σ bonding interaction between Cu(II) and the cyanamide anion group. However, there is also a partially allowed $p\pi \rightarrow d_{x^2-y^2}$ transition which supports an electronic interaction between Cu(II) and $DCNQI^-$ necessary to form a mixed-valence state in $Cu(DCNQI)_2$ molecular metals.

Letcher *et al.* synthesized and studied a series of [1,3-bis(2'-pyridylimino)isoindolinato]nickel(II)phenylcyanamide [(PVP)Ni(pcyd)] complexes with an attempt to construct a planar molecule which may form a potential conductive molecular system.³⁶ X-ray crystal structure of the complex with $2-Clpcyd$ ligand showed that Ni(II) was in a distorted square planar coordination sphere of nitrogen donor atoms and was coordinated by cyanamide ligand via the terminal nitrogen. The UV-vis spectra of those complexes showed a cyanamide to Ni(II) $\pi \rightarrow \sigma^*$ LMCT transition ranging from 23,000 to $25,000\text{ cm}^{-1}$. Coordination of solvent molecules to Ni(II) causes this absorption to disappear, which is suggested that the allowedness of the $\pi \rightarrow \sigma^*$ LMCT transition is strongly dependent on Ni(II) coordination geometry. In the crystal form of $(PVP)Ni(2-Clpcyd)$, although the interplanar separations range from 3.699 to $4.083\text{ \AA}$ which are considerably greater than the

normal separations for efficient π - π interactions (for macrocyclic N4 square planar Ni(II) complexes range from 3.255 to 3.350 Å), the difference of π - π^* transition energies between solid state and solution electronic absorption was indeed observed for this complex. This suggests that an interplanar π interaction may exist in the solid state.

Aquino *et al.* synthesized and investigated a series of bis(pentaammineruthenium(III)) dinuclear complexes bridged by a 1,4-dicyanamidebenzene dianion (dicyd²⁻) derivative ligand.³⁸⁻⁴⁰ The X-ray crystal structures of tetraphenylarsonium salts of the bridging ligands showed that all of the ligands except TM-Dicyd²⁻ were planar and in the anti configuration. TM-Dicyd²⁻ showed significant out-of-plane distortion. X-ray crystal structure of one complex, $[(\text{NH}_3)_5\text{Ru}]_2\text{-Dicyd}(\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3)_4$, showed that a linear and a bent form of the dimer existed in the unit cell. Magnetic susceptibility studies of these complexes showed the Ru(III) ions to be antiferromagnetically coupled. The magnitude of exchange integral, $-2J$ (100 to ≥ 800 cm⁻¹), is unprecedented at a separation between Ru(III) ions of 13 Å.

To further understand and explore the properties of dinuclear complexes bridged by DCNQI dianion ligands, extensive studies on the complexes of other metals (such as Cu(II), Cr(III) and Pd(II)) and coordination sphere ligands (such as bipyridine, bis-bipyridine, PVP, dien and terpyridine) are undergoing in the laboratory of Dr. R. J. Crutchley at the Department of Chemistry of Carleton University.

1.2 Research Goals and Design Strategy

The initial goal of this research was to design a planar mononuclear complex which

contains a phenylcyanamide anion ligand and a planar dinuclear complex having a DCNQI dianion ligand. These molecules may potentially form proper π stacking systems which, upon oxidation, may become new electrical conductors. In addition, the metal-ligand interaction between a cyanamide group ($-\text{NCN}^-$) and a metal ion is also of interest because it affects the molecular conformation and the electronic properties of complexes. Complexes $[(\text{trpyPd})^{2+}]$ ($\text{trpy}=2,2',2''$ -terpyridine) with the above ligands were chosen for study. To the author's knowledge, reports concerning such research have not been seen yet.

From previous studies, it is known that in most cases, phenylcyanamide anion ligands and DCNQI dianion ligands were planar in their complexes because the π -electrons of cyanamide groups delocalize into the phenyl ring. To form planar complexes containing the above ligands, the coordination sphere (or co-ligand) of the metal ion has to be planar itself and coplanar with the rest, *i.e.* either phenylcyanamide anion in mononuclear complex or DCNQI dianion in dinuclear complex. Palladium(II) was chosen to build such complexes because normally it forms stable four coordination square planar complexes with nitrogen-donor ligands. A neutral tridentate ligand, terpyridine, was used to secure the planarity of the coordination sphere of Pd(II).

Some square-planar complexes of Pd(II) have been known for a long time, such as $[\text{Pd}(\text{NH}_3)_4][\text{PdCl}_4]$ and $\text{Pd}(\text{CN})_4^{2+}$.⁴¹ In the former, the square planar molecular units are stacked vertically with short axial metal-metal distances (3.25 Å), leading to anomalous visible spectra, semiconductivity and photoconductivity.⁴² These properties are not due to metal-metal bonding but are thought to arise from the overlap of the p_z and d_{z^2} metal orbitals creating a filled and empty band structure.⁴³

Many palladium(II) amine complexes have been synthesized. Among them, the largest class is $[\text{PdX}_2\text{L}_2]$ (X =halide or pseudohalide; L =amine) complex that is readily prepared by addition of amine to $[\text{PdCl}_4]^{2-}$ in aqueous solution or by reaction of amine with $[\text{PdCl}_2]$ or $[\text{PdCl}_2(\text{PhCN})_2]$ in organic solvent.⁴¹ Complexes of the majority of simple amines have been prepared, including those of hydroxylamine,⁴⁴ aziridine⁴⁵ and tertiary amine NMe_3 .⁴⁶ Normally the *trans* isomer (or a mixture of isomers) is isolated, though by control of the conditions the pure *cis* isomer may be obtained.

Multidentate amine ligands react readily with palladium(II) halides to yield chelated products. Crystal structure of bis(ethylenediamine)palladium(II) chloride $[\text{Pd}(\text{en})_2]\text{Cl}_2$ showed that the palladium ion was four-coordinated by the nitrogen atoms of the en ligands in a planar configuration with an average Pd-N distance of 2.036 Å.⁴⁷ N-(2-Aminoethyl)-1,2-diaminoethane (dien) forms complexes $[\text{PdX}(\text{dien})]\text{X}$ ($\text{X}=\text{Cl}$ or I)^{48,49} which are suggested square planar complexes. N,N'-Di(2-aminoethyl)-1,2-diaminoethane (trien) acts as a tetradentate ligand in complexes $[\text{Pd}(\text{trien})]\text{X}_2$ ($\text{X}=\text{PF}_6$, ClO_4). A crystal structure determination for $[\text{Pd}(\text{trien})](\text{PF}_6)_2\text{KPF}_6$ confirmed that the palladium ion retains planar coordination with the four nitrogen atoms in a trapezoidal arrangement (Pd-N varying from 1.95 to 2.08 Å).⁵⁰

Some polypyridine ligands can also coordinate to palladium(II) and yield stable complexes in which π -bonding with the metal centre may exist. A typical complex is (2,2',2''-terpyridine)palladium(II)chloride. The crystal structure determination (Figure 1.7) showed that the complex consists of a basically planar 4-coordinate $[\text{Pd}(\text{trpy})\text{Cl}]^+$ cation and a Cl^- anion.⁵¹ The molecules are packed in a layer structure in which the average separation

Some other palladium(II)-nitrogen complexes also exhibit π -bonding between metal centre and nitrogen. A number of salicylaldimine complexes were synthesized where the ligand chelates through the N and O atoms in a trans isomeric form (see figure below). While the Pd atom retains square planar coordination in these complexes, the ligands bend away from the planar form, which gives the maximum delocalized π bonding. The extent of this folding increases with the increasing bulk of the R substituent.⁵²⁻⁵⁷

2,2',2''-terpyridine was chosen as the "co-ligand" because it retains planarity upon coordination to metal ions. There are also other advantages using terpyridine ligand:

- (a) the π -acid nature of terpyridine can stabilize the π -basic metal ion Pd(II);
- (b) the polydentate nature of terpyridine enhances the thermodynamic stability of a coordination complex relative to complexes of similar coordination number but with ligands of less denticity;
- (c) terpyridinepalladium(II) complexes are cations and by careful choice of the counter anion, the solubility and other properties of the complex can be modified and controlled;
- (d) the formed molecules may form stacking system and therefore may produce π - π interaction in crystal lattice.

1.3 Aims of the Thesis

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

2. To synthesize and characterize a mononuclear terpyridinepalladium(II)-dicyanamidobenzene (radical) chloride complex:

3. To synthesize and characterize a dinuclear terpyridinepalladium(II)-dicyanamidobenzene triflate complex:

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

CHAPTER 2

EXPERIMENTAL

2.1 Starting Materials

2.1.1 Reagents for Ligand Syntheses

Ammonium thiocyanate (99.6%, reagent grade, Fisher Scientific Co.), benzoyl chloride (99%, reagent grade, Aldrich), lead acetate trihydrate (reagent grade, Anachemia), sodium hydroxide (lab grade, Anachemia), glacial acetic acid (99.7%, reagent grade, Anachemia), aniline (99%, Aldrich), thallium acetate (99.99%, Aldrich), triethylamine (TEA, 99+%, Aldrich), 1,4-phenylenediamine (97%, Aldrich), 2,5-dimethyl-1,4-phenylenediamine (97%, Aldrich), 2,5-dichloro-1,4-phenylenediamine (97%, Aldrich), 2,3,5,6-tetramethyl-1,4-phenylenediamine (97%, Aldrich) were all used as received.

2.1.2 Reagents for Metal Complex Syntheses

Palladium(II) chloride (99.9%, Johnson Matthey Co.), 2,2',2''-terpyridine (98%, Aldrich), ammonium hexafluorophosphate (99.99%, Aldrich), hydrochloric acid (36.5-38.0%, reagent grade, Anachemia) were used without further purification.

2.1.3 Solvents

Acetonitrile (HPLC grade, Caledon Labs Ltd.), chloroform (spectro grade, Caledon

Labs Ltd.), 2-methoxyethanol (MET, 99+%, A.C.S. reagent, Aldrich), N,N'-dimethylformamide (DMF, glass distilled, Anachemia), methanol (spectro grade, Caledon Labs Ltd.), anhydrous diethyl ether (Caledon Labs Ltd.), absolute ethanol (Consolidated Alcohols Ltd.), 1-methyl-2-pyrrolidinone (NMP, HPLC grade, Aldrich), acetone (spectro grade, Caledon Labs Ltd.), deuterated dimethyl sulphoxide (99.9 atom % D, MSD Isotopes) were used as received. Acetonitrile for electrochemistry was purified by distilling under nitrogen and stored under Ar. DMF for electrochemistry was deoxygenated and stored under Ar.

2.1.4 Electrolyte

Tetrabutylammonium hexafluorophosphate (98%, Aldrich) was recrystallized from ethanol twice and dried under vacuum at 118 °C for at least 16 h.

2.2 Syntheses of the Ligands

2.2.1 Thallium Salts of Phenylcyanamide Anion Ligand, Tl(pcvd)

2.2.1.1 General Description

The preparation of protonated phenylcyanamide starts with the formation of benzoyl thiocyanate **A**.³¹ Then aniline reacts with **A** to form **B** which upon heating in base gave the thiourea derivative **C**. **C** is desulphurised with a heavy metal salt, lead(II)

acetate, and upon gentle heating the phenylcyanamide anion **D** is formed *in situ*. The anion is then protonated with acetic acid and precipitated from solution as **E** or **F** (dimer).

The thallium salts of the phenylcyanamide anions are prepared from their protonated monomer or dimer analogues. The anion ligands are sensitive to dimerization, so careful control of reaction condition is necessary to ensure product purity. The amine proton of Hpcyd is acidic due to the resonance stabilization of the pcyd anion. The greater chloro substitution on the phenyl ring, the more sensitive to dimerization. Addition of a weak base to a dimer ligand creates an equilibrium between the dimer and its anion monomer. Introduction of thallium acetate shifts the equilibrium to the monomer anion by precipitate of Tl(pcyd). The following is the preparation scheme:

Scheme 2.1

2.2.1.2 Ligand Synthesis

Caution: thallium is extremely toxic so care should be taken when it is handled.

Thallium salt of phenylcyanamide anion Tl(pcyd)

Ammonium thiocyanate (1.5 g, 0.02 mol) and 20 mL acetone were brought to boiling. A solution of benzyl chloride (2.8 g, 0.02 mol) in 20 mL acetone was added

dropwise. Ammonium chloride immediately precipitated. After addition was complete, the reaction mixture was allowed to reflux for an additional 10 min. Then, aniline (1.9 g, 0.02 mol) in 20 mL acetone was added dropwise and the reaction mixture was allowed to reflux for 1h. The milky yellow solution was then slowly poured into 300 mL of distilled water with vigorous stirring. The yellowish benzoylthiourea derivative was collected on a Büchner funnel and washed with copious amounts of water. The wet benzoylthiourea derivative was dissolved in 50 mL of hot 2M aqueous NaOH solution, and the resulting solution was then boiled for 5 min. To the magnetically stirred solution, cooled to 60 °C, was added lead acetate (6.5 g, 0.02 mol in 20 mL water). While the reaction mixture was maintained between 50 and 60 °C for 5 min, a deep black precipitate of PbS formed. PbS was filtered off. To the filtrate cooled in an ice bath, was added approximately 5 mL of glacial acetic acid. A white product immediately precipitated from solution. This was filtered, washed with water and dried in air. The product was pure enough for use in the synthesis of the thallium salt of the anion ligand. Yield: 1.8 g (77%).

The above phenylcyanamide (1.8 g, 15 mmol) was dissolved into 70 mL of a boiling mixture of acetone/water (1:1). Thallium acetate (6.9 g, 25 mmol) in 70 mL of acetone/water (1:1) was slowly added to the first solution. Immediately after, triethylamine (2.0 g, 20 mmol) was added. Boiling was maintained for one more min. The solution was then set aside to cool. The resulting white needle crystals from the cooled solution were collected by filtration, washed with water followed by acetone, and then dried in air. Yield: 2.3 g (73%).

Thallium salt of 2-chlorophenylcyanamide anion $\text{Tl}(2\text{-Clpcyd})$, thallium salt of 2,3-dichlorophenylcyanamide anion $\text{Tl}(2,3\text{-Cl}_2\text{-pcyd})$, thallium salt of 2,4,6-trichlorophenylcyanamide anion $\text{Tl}(2,4,6\text{-Cl}_3\text{pcyd})$ and thallium salt of 2,3,4,5-tetrachlorophenylcyanamide anion $\text{Tl}(2,3,4,5\text{-Cl}_4\text{pcyd})$ were prepared in the similar manner to $\text{Tl}(\text{pcyd})$ in the laboratory. The thallium salt of 2,3,4,5,6-pentachlorophenylcyanamide anion $\text{Tl}(\text{Cl}_5\text{pcyd})$ was prepared by A. Razvani in a similar fashion.

2.2.2 Neutral 1,4-Dicyanamidebenzene Derivative Ligands, H,Dicyd

2.2.2.1 General Description

The preparation of dicyanamidebenzene derivative ligands has been reported previously.³⁶ 1,4-Phenylenediamine was reacted with benzoyl thiocyanate (formed from the reaction of benzoyl chloride with ammonium thiocyanate) to form **G** which upon heating in base gave the thiourea derivative **H**. Then **H** was desulphurised with lead(II) acetate with gentle heating to produce the dicyanamide dianion **I** *in situ*. The dianion **I** was then precipitated with acetic acid and precipitated out as **J**. During the reaction, the temperature must be maintained below 80 °C to avoid dimerization. The dimer formation can be detected by IR. A strong band at about 1680 cm^{-1} is present due to $\nu(\text{C}=\text{N})$ of the dimer **K**.

Scheme 2.2

K

2.2.2.2 Ligand Synthesis

1,4-Dicyanamidebenzene (H₂Dicyd)

Benzoyl chloride (14.0 g, 0.1 mol) in 100 mL acetone was added to a boiling solution of ammonium thiocyanate (7.6 g, 0.1 mol) in 100 mL of acetone. A white precipitate formed immediately. The mixture was kept boiling and stirring until a yellow colour appeared. Then 1,4-phenylenediamine (5.4 g, 0.05 mol) in 100 mL acetone was added dropwise. The mixture was boiled for a further 15 min.. The mixture was then slowly added to 1500 mL of distilled water with vigorous stirring. After that, the precipitate was filtered and washed with 150 mL of acetone followed by 150 mL of water and then 150 mL acetone again. The pale yellow solid (**G**) was then allowed to air dry.

G (18.6 g, 0.04 mol) was dissolved in NaOH (21.5 g, 0.5 mol) in 250 mL of water solution and boiled for 10 min to form **H** which was then cooled to 80 °C. To **H**, a

solution of lead(II) acetate trihydrate (37.9 g, 0.1 mol) in 100 mL of water was added with stirring. The temperature was maintained between 60 °C and 80 °C during which time black PbS formed. The completely black mixture was filtered through a Büchner funnel. The clear filtrate containing **I** was cooled in an ice bath and acidified with glacial acetic acid. A white precipitate **J** was formed, filtered off and washed with water until the smell of acetic acid was minimal (if the precipitate was green in colour, more acid should be added). The crude product was then vacuum dried overnight.

The recrystallization was done by dissolving the crude in hot acetone to produce a blue solution. The solution was filtered and an equal amount of distilled water was added to it. Then the solution was cooled in the fridge at 5 °C. The resulting pale-purple plate crystals were collected and washed with cold acetone/water (1:1) and vacuum dried for 18h. Yield: 5.5 g (70%).

2,5-Dichloro-1,4-dicyanamidebenzene (DC-H₂Dicyd)

This was prepared in an analogous manner to H₂Dicyd except that 2,5-dichloro-1,4-phenylenediamine (8.85 g, 0.05 mol) was used instead of 1,4-phenylenediamine and the temperature was controlled below 70 °C during the addition of lead(II) acetate. The crude product (8.5 g, 75%) was recrystallized from acetone.

2,5-Dimethyl-1,4-dicyanamidebenzene (DM-H₂Dicyd)

This was prepared in a similar manner to DC-H₂Dicyd except that 2,5-dimethyl-1,4-phenylenediamine (4.0 g, 0.03 mol) was used instead of 2,5-dichloro-1,4-phenylenediamine. The crude product (3.2 g, 59%) was recrystallized from acetone.

2,3,5,6-Tetramethyl-1,4-dicyanamidebenzene (TM-H₂Dicyd)

This was prepared in a similar fashion to DC-H₂Dicyd except that 2,3,5,6-tetramethyl-1,4-phenylenediamine (8.2 g, 0.05 mol) was used instead of the 2,5-dichloro-1,4-phenylenediamine. The crude product (5.8 g, 54%) was recrystallized from acetone.

2.3 Syntheses of the Metal Complexes

2.3.1 Syntheses of Precursor and Mononuclear Complexes

2.3.1.1 General Description

The precursor complex was originally prepared as [(trpy)PdCl]Cl (Scheme 2.3, **L**). Because the chloride salt is not soluble in most non-aqueous solvents, it is necessary to convert it to a more soluble salt, such as PF₆ salt **M**, in mononuclear complex preparations. Even so, because it is a good donating ligand, Cl⁻ is not easily substituted

by a ligand like dicyd². Therefore, impurities may be introduced in the preparation of dinuclear complexes. To overcome this problem, triflic anion (CF_3SO_3^-) was chosen as both the coordinate ligand and the counter anion of the precursor complex N, because it is a good leaving group and its salt is soluble in many non-aqueous solvents.

Scheme 2.3

The syntheses of these mononuclear complexes were quite straightforward. Because the by-product was TiCl which is not soluble in non-aqueous solvents, the reaction was driven to completion and the products were easily purified. Further purifications were done by recrystallization in CH_3CN .

Scheme 2.4

2.3.1.2 Complex Synthesis**(Chloro)(terpyridinepalladium(II)) Chloride Dihydrate, $[(\text{trpy})\text{PdCl}]\text{Cl}\cdot 2\text{H}_2\text{O}$**

This complex was made using a modified literature method.⁵⁸ A mixture of terpyridine (2.0 g, 8.6 mmol) and palladium(II)chloride (1.5 g, 8.6 mmol) in 110 mL of water was maintained refluxing for 18 h. The resulting red solution was filtered while it was warm. The cooled solution was acidified with HCl (6 M) to ~ pH 4. A light yellow precipitate was formed which was filtered, washed with diluted aqueous HCl followed by acetone and ether, and dried in air.

Recrystallization was done by dissolving the crude in 80 mL of hot ethanol/water (1:1). The solution was filtered and cooled to room temperature. The yellow needle crystals were collected and vacuum dried at r.t. overnight. Yield: 3.0 g (77%).

(Triflic)(terpyridinepalladium(II)) Triflate, $[(\text{trpy})\text{Pd}(\text{CF}_3\text{SO}_3)](\text{CF}_3\text{SO}_3)$

Triflic acid (10 mL) was slowly added to 2.9 g of $[(\text{Trpy})\text{PdCl}]\text{Cl}\cdot 2\text{H}_2\text{O}$ in a three-neck flask. The temperature was maintained at about 100 °C while N₂ was flowed through the flask. More triflic acid (8 mL) was added before the reaction continued overnight. The reaction mixture was cooled to r.t. and ether was added to precipitate the

product. The product was filtered, and washed with ether and air dried.

Recrystallization was done by dissolving the crude product in 300 mL of hot acetone. The solution was filtered and cooled to r.t.. Ether (300 mL) was added to precipitate the product. A yellow crystalline precipitate was collected, washed with ether and vacuum dried at r.t. overnight. Yield: 3.8 g (85%).

(Chloro)(terpyridinepalladium(II)) Hexafluorophosphate, [(trpy)PdCl]PF₆

[(trpy)PdCl]Cl.2H₂O (2.0 g, 4.9 mmol) in 80 mL of distilled water was heated to 40 °C. To this orange solution, NH₄PF₆ (1.5 g, 9.2 mmol) was added with vigorous stirring. A pale yellow precipitate formed immediately. After 30 min, the precipitate was filtered off, washed with copious amounts of water followed by 30 mL of acetone, and air dried overnight.

Recrystallization was done by dissolving the crude product in 300 mL of boiling acetonitrile followed by a filtration. The filtrate was slowly cooled to r.t. to produce yellow needle crystals which were collected and washed with ether. The product was vacuum dried at r.t. for 18 h. Yield: 1.6 g (61%). Anal. Calcd.(%) for C₁₅H₁₁N₃ClPdPF₆: C, 34.63; H, 2.14; N, 8.08. Found(%): C, 34.69; H, 2.15; N, 8.11.

(trpy)Pd(pcyd)](PF₆)

A solution of [(trpy)PdCl]PF₆ (0.52 g, 1.0 mmol) in 150 mL of acetonitrile was

heated to 50 °C. To this stirring yellow solution, 0.32 g (1.0 mmol) Tlpcyd was added. The solution immediately changed to an orange-red colour and a white precipitate was formed. Heating and stirring was maintained for a further 40 min before a filtration. The filtrate's volume was reduced to about 10 mL at which point a red-orange precipitate could be seen. Then it was cooled to room temperature. A red-orange solid was collected and washed with ether followed by drying in air. Yield: 0.45 g (75%).

Purification was performed by dissolving 0.20 g of the crude product in 60 mL acetonitrile. The solution was filtered through a pipet filled with glass wool to a 150 mL pre-rinsed beaker. This was placed into a diffusion jar along with 100 mL anhydrous ether for two weeks. Large red crystals were collected, washed with ether, and vacuum dried overnight. Yield: 0.13 g (65% based on the crude). Anal. Calcd.(%) for $C_{22}H_{16}N_5PdPF_6$: C, 43.91; H, 2.66; N, 11.63. Found(%): C, 43.82; H, 2.67; N, 11.76.

Crystals suitable for X-ray structure determination were obtained by dissolving 0.03 g purified complex in 7 mL acetonitrile then diffused by ether for 1 week. About 20 small cubic crystals were obtained.

$[(trpy)Pd(2-Clpcyd)](PF_6)$

A solution of $[(trpy)PdCl](PF_6)$ (0.26 g, 0.5 mmol) in 60 mL of acetonitrile was brought to boiling. To this yellow solution, $Tl(2-Clpcyd)$ (0.18 g, 0.5 mmol) was added. An orange solution formed immediately. After boiling for 40 min, the reaction mixture was filtered and the filtrate was cooled to r.t. to yield the orange crystalline product. The

product was isolated and washed with ether, followed by vacuum drying. Yield: 0.27 g (85%).

Recrystallization was done by allowing ether to diffuse into a solution of 0.10 g of the crude product in 45 mL of acetonitrile. Red-orange needle-like products were obtained and washed with ether. Then vacuum dried overnight. Yield: 0.083 g (83%). Anal. Calcd.(%) for $C_{22}H_{15}N_3PdClPF_6$: C, 41.53; H, 2.38; N, 11.01. Found(%): C, 41.18; H, 2.36; N, 10.95.

$[(trpy)Pd(2,3-Cl_2pcyd)](PF_6)$

This complex was prepared in a similar way to $[(trpy)Pd(2-Clpcyd)](PF_6)$ with the following starting reagents: $[(trpy)PdCl](PF_6)$ (0.26 g, 0.5 mmol), $Tl(2,3-Cl_2pcyd)$ (0.20 g, 0.5 mmol) and acetonitrile (60 mL). The crude complex was obtained by concentrating the solution (to 15 mL). Yield: 0.26 g (78%).

Recrystallization was done in a similar manner to $[(trpy)Pd(2-Clpcyd)](PF_6)$ except that only 40 ml of acetonitrile was used. The product crystallized as red-orange needles. Yield: 0.08 g (81% based on the crude). Anal. Calcd.(%) for $C_{22}H_{14}N_3Cl_2PdPF_6$: C, 39.39; H, 2.11; N, 10.44. Found(%): C, 38.92; H, 2.15; N, 10.34.

$[(trpy)Pd(2,4,6-Cl_3pcyd)](PF_6)$

This complex was prepared in a similar manner to $[(trpy)Pd(2-Clpcyd)](PF_6)$ with

the following reagents: $[(\text{trpy})\text{PdCl}](\text{PF}_6)$ (0.26 g, 0.5 mmol), $\text{Ti}(2,4,6\text{-Cl}_3\text{pcyd})$ (0.21 g, 0.5 mmol) and 80 mL of acetonitrile. The crude product was obtained by evaporating the solvent. Yield: 0.31 g (88%).

Recrystallization was carried out in a similar fashion to $[(\text{trpy})\text{Pd}(2\text{-Clpcyd})](\text{PF}_6)$ except that 50 mL of acetonitrile was used. The purified complex had a yellow hair-like crystalline form. Yield: 0.073 g (73% based on the crude). Anal. Calcd.(%) for $\text{C}_{22}\text{H}_{13}\text{N}_5\text{Cl}_3\text{PdPF}_6$: C, 37.47; H, 1.86; N, 9.93. Found(%): C, 36.69; H, 2.00; N, 9.74.

$[(\text{trpy})\text{Pd}(2,3,4,5\text{-Cl}_4\text{pcyd})](\text{PF}_6)$

This complex was prepared in a similar way to $[(\text{trpy})\text{Pd}(2\text{-Clpcyd})](\text{PF}_6)$ with the following starting reagents: $[(\text{trpy})\text{PdCl}](\text{PF}_6)$ (0.26 g, 0.5 mmol), $\text{Ti}(2,3,4,5\text{-Cl}_4\text{pcyd})$ (0.23 g, 0.5 mmol) and 60 mL of acetonitrile. Yield: 0.29 g (78%).

Recrystallization was done in a similar manner to $[(\text{trpy})\text{Pd}(2\text{-Clpcyd})](\text{PF}_6)$, and gave small orange needles. Yield: 0.076 g (76% based on the crude). Anal. Calcd.(%) for $\text{C}_{22}\text{H}_{12}\text{N}_5\text{Cl}_4\text{PdPF}_6$: C, 35.72; H, 1.64; N, 9.47. Found(%): C, 35.75; H, 1.65; N, 9.49.

$[(\text{trpy})\text{Pd}(\text{Cl}_5\text{pcyd})](\text{PF}_6)$

This complex was again prepared in a similar manner to $[(\text{trpy})\text{Pd}(2\text{-Clpcyd})](\text{PF}_6)$ with the following reagents: $[(\text{trpy})\text{PdCl}](\text{PF}_6)$ (0.26 g, 0.5 mmol), $\text{Ti}(\text{Cl}_5\text{pcyd})$ (0.25 g, 0.5 mmol) and 100 mL of acetonitrile. Yield: 0.32 g (83%).

Recrystallization was accomplished in a similar fashion to $[(\text{trpy})\text{Pd}(2\text{-Clpcyd})](\text{PF}_6)$

Clpcyd)](PF₆) except that 50 mL acetonitrile was used, and gave orange plates. Yield: 0.058 g (58% based on the crude). Anal. Calcd.(%) for C₂₂H₁₁N₅Cl₄PdPF₆: C, 34.13; H, 1.43; N, 9.05. Found(%): C, 34.37; H, 1.55; N, 9.08.

2.3.2 Synthesis of Terpyridinepalladium(II)(1,4-dicyanamide-2,5-dimethylbenzene) Mononuclear Radical Anion Complex, [(trpy)Pd(DM-Dicyd)](PF₆)

2.3.2.1 General Description

The radical complex could be formed either by carrying out the reaction under Ar first then exposing the reaction mixture to air or by doing the reaction in air. Both ways generated the same complex as the chloride salt **P** in low yields (about 20%). When the complex was isolated, a significant amount of unreacted precursor complex [(trpy)PdCl](PF₆) was found.

Scheme 2.5

The isolated product was in the form of dark blue needle or powder. IR showed that both forms were identical. An attempt was also made to synthesize other complexes of Dicyd[•], DC-Dicyd[•] and TM-Dicyd[•] radical ligands, but it wasn't successful. It is

suggested that the corresponding dianion ligands could not be oxidized to their radical forms by the air in DMF solution.

2.3.3.2 Complex Synthesis

To a stirred solution of $[(\text{trpy})\text{PdCl}](\text{PF}_6)$ (0.15 g, 0.3 mmol) and $\text{H}_2\text{-DMDicyd}$ (0.05 g, 0.3 mmol) in DMF (30 mL), 0.09 mL of TEA (0.6 mmol) was added. The solution changed colour from orange to green immediately, then changed to dark blue eventually. The reaction was maintained for 5 h. Then half of the reaction solution was diffused by ether. Two days later, some small blue and large brown needle crystals (unreacted $[(\text{trpy})\text{PdCl}](\text{PF}_6)$) were obtained. The blue needle crystals were isolated, washed with ether and dried under vacuum. Yield: 0.019 g (23%). Anal. Calcd.(%) for $\text{C}_{25}\text{H}_{19}\text{N}_7\text{-PdCl}$: C, 53.68; H, 3.40; N, 17.53. Found(%): C, 53.43; H, 3.55; N, 17.58.

2.3.4 Synthesis of Bis(terpyridinepalladium(II))(1,4-dicyanamide-2,5-dimethylbenzene) Dianion Dinuclear Complex $[(\text{trpy})\text{Pd}]_2(\text{DM-Dicvd})(\text{CF}_3\text{SO}_3)_2$

2.3.4.1 General Description

The synthesis of dinuclear terpyridinepalladium(II) complex bridged by 1,4-dicyanamide-2,5-dimethylbenzene dianion proved difficult when using either

$[(\text{trpy})\text{PdCl}]\text{Cl}$ or $[(\text{trpy})\text{PdCl}](\text{PF}_6)$ as starting material. Some impurities were always found in the product and hard to separate. Probably because Cl^- bonded to $\text{Pd}(\text{II})$ ion quite strongly and was hardly substituted by the DM-Dicyd^{2-} ligand. To solve this problem, $[(\text{trpy})\text{Pd}(\text{CF}_3\text{SO}_3)](\text{CF}_3\text{SO}_3)$ was used as the starting material (Scheme 2.6) because CF_3SO_3^- is a relatively weak ligand and a good leaving group. In addition, this salt is soluble in many solvents. It is therefore an ideal candidate for the synthesis and the purification.

Scheme 2.6

Recrystallizations of this dinuclear complex were carried out in DMF, CH_3CN and NMP respectively, diffused by ether or acetone, but none gave crystals. The best result we have obtained so far is a crystalline form powder.

2.3.4.2 Complex Synthesis

$[(\text{trpy})\text{Pd}(\text{CF}_3\text{SO}_3)](\text{CF}_3\text{SO}_3)$ (0.35 g, 0.55 mmol, slightly excess) was dissolved in 100 mL of acetone (spectro-grade) and 10 mL of H_2O . The resulting solution was purged with argon. Then 0.38 mL (5x0.55 mmol, excess) of TEA was added. To a

separate round-bottom flask. DM-H₂Dicyd (0.047g, 0.25 mmol) was placed and deoxygenated. The solution was transferred into the flask containing the Pd complex under argon with stirring. The solution turned to deep purple/black immediately and a deeply coloured solid was formed. The reaction was kept for 3 h before filtration. The collected solid was washed with 30 mL of acetone followed by 30 mL of ether, and then vacuum dried overnight. Yield: 0.26 g (90%).

To recrystallize, 0.10 g of the crude product was dissolved in 30 mL of DMF. The solution was filtered through a pipet filled with glass wool and ether allowed to diffuse into the filtrate for 1 week. A black powder was isolated and washed with acetone and ether, and finally vacuum dried overnight. Yield: 0.054 g (54% based on the crude). Anal. Calcd.(%) for C₄₂H₃₀N₁₀Pd₂F₆S₂O₆: C, 43.42; H, 2.61; N, 12.06. Found(%): C, 42.91; H, 2.72; N, 11.83.

2.4 Physical Measurements

2.4.1 Infrared Spectra

Infrared spectra were recorded on a Perkin-Elmer 1600 Series FTIR spectrophotometer which was online to a Hewlett-Packard Colorpro Plotter. All samples were prepared as KBr (oven dried at 120 °C) disks. Reference spectra of air were run prior to all sample spectra.

2.4.2 NMR Spectra

All the ^1H spectra were recorded on a Bruker AMX-400 NMR spectrometer at ambient temperature. Samples (vacuum dried) were dissolved in d_6 -dimethyl sulphoxide and analyzed in a Norell XR-55 NMR tube. Normally, 1.5-3 mg of sample was dissolved in 0.5-0.75 mL of d_6 -DMSO depending on the sample's solubility. The solution was filtered through a pasteur pipette filled with glass wool directly into a NMR tube. Chemical shifts were derived from an internal TMS reference or from residual solvent peak positions.

2.4.3 Electronic Absorption Spectra

Electronic spectra were recorded on a Cary 5 UV-vis/NIR spectrophotometer interfaced with a Raven 386/16 PC online to a HP laser IID Printer. Solution samples were run using matching quartz cells and a background correction was performed prior to each run. Solid state spectra were performed on the same spectrophotometer. Samples were prepared as KBr disks and a KBr background correction was carried out before each run.

2.4.4 Cyclic Voltammetry

Cyclic voltammetry was recorded on a BAS cv-27 electrochemistry system online

to a BAS X-Y Recorder. The electrochemical cell consisted of a double-jacketed glass container with an inner volume of approximately 15 mL. Cell temperature was controlled by means of a Haake D8-G refrigerated bath and circulator (accuracy ± 0.02 °C). The cell was fitted with a Teflon plug through which holes had been drilled to permit insertion of electrodes and an argon gas inlet frit. Non-aqueous cyclic voltammetry was performed in dry N,N-dimethylformamide (DMF) (0.1 M tetrabutylammoniumhexafluorophosphate, TBAH) at 25 °C with a three-electrode system consisting of a platinum-disk working (BAS 1.6 mm diameter) and wire counter electrodes and a silver-wire quasi-reference electrode. Ferrocene ($E^0 = 0.400$ V vs NHE) was used as an internal reference.⁵⁹

2.4.5 X-ray Structure Determination

Crystal structure determination was performed at the University of Ottawa. For single crystal of $[(\text{trpy})\text{Pd}(\text{pcyd})](\text{PF}_6)$ complex with dimensions of 0.2mm x 0.2mm x 0.2mm, all the measurements were made on a Rigaku diffractometer with Mo K α radiation. Data were collected at -130 °C using the omega 2 θ scan technique to a maximum 2 θ value of 45 °. The structure was solved by direct methods including a final cycle full matrix least-squares refinement. All the atoms were refined anisotropically except for the hydrogen atom which was calculated. Calculations were performed using the NRCVAX crystallographic software package.

2.4.6 Elemental Analyses

Elemental analyses of all samples were performed by Canadian Microanalytical Services Ltd..

CHAPTER 3

Terpyridinepalladium(II) Complexes of Phenylcyanamide Ligands: Physical Characterization and Result Discussion

3.1 Infrared Spectroscopy

IR spectra of the six $[(\text{trpy})\text{Pd}(\text{pcyd})](\text{PF}_6)$ complexes are shown in Figures 3.1-3.7. They all show the characteristic strong $\nu(\text{NCN})$ stretch in the range 2142-2191 cm^{-1} . The $\nu(\text{NCN})$ of complexes is shifted to a higher frequency compared to that of the corresponding free ligands by 44 to 113 cm^{-1} (see Table 3.1). A similar shift was also observed in $\nu(\text{C}\equiv\text{N})$ when hard cations bind to nitrile ligands.^{60, 62} Phenylcyanamide anion has two resonance forms and there are two filled orthogonal π_{nb} molecular orbitals in resonance form B (Fig. 1.5).³¹ For a strong π acid such as $[(\text{NH}_3)_5\text{Ru(III)}]^{3+}$ moiety, polarization of electron density by Ru(III) would favour resonance form B. The $[(\text{trpy})\text{Pd(II)}]^{2+}$ moiety is a much poorer π acid because Pd(II) (d8) has filled $d\pi$ orbitals. It more likely favours resonance form A of phenylcyanamide anion upon coordination. This results in the $\nu(\text{NCN})$ of $[(\text{trpy})\text{Pd}(\text{pcyd})]^{2+}$ complexes shifted positive compared to those of $[(\text{NH}_3)_5\text{Ru}(\text{pcyd})]^{3+}$ complexes (see Table 3.1).

The $\nu(\text{NCN})$ of $[(\text{trpy})\text{Pd}(\text{pcyd})](\text{PF}_6)$, unlike other five chloro-substituted complexes, splits into two sharp peaks (see Fig. 3.1) in both KBr disk and DMF solution (see Fig. 3.1 and Fig. 3.2). It is suggested that there are two types of Pd-N bonding in this complex. Coordination of phenylcyanamide ligands (both neutral and anionic) to metal cations can occur via amine or nitrile nitrogen. Due to the π -back-bonding and donor properties of the nitrile group and the steric factor, transition metal complexes

Table 3.1 IR Data for the $\nu(\text{NCN})$ of Some Phenylcyanamide Complexes^a

pcyd anion(L)	Complexes		
	$[(\text{trpy})\text{PdL}](\text{PF}_6)$	TiL	$[(\text{NH}_3)_5\text{RuL}](\text{PF}_6)_2$
pcyd	2191(m), 2145	2078, 2056	2112
2-Clpcyd	2142	2098	2115
2,3-Cl ₂ pcyd	2178	2102	2111
2,4,6-Cl ₃ pcyd	2184	2135	2149
2,3,4,5-Cl ₄ pcyd	2169	2136	2132
Cl ₅ pcyd	2180	2078	2113

^a In cm^{-1} , absorptions are strong unless stated. m=medium. All spectra were obtained in KBr.

prefer coordination to the nitrile nitrogen.³¹ For the unsubstituted $[(\text{trpy})\text{Pd}(\text{pcyd})](\text{PF}_6)$ complex, it is possible that Pd(II) can coordinate to the amine nitrogen of the unsubstituted ligand, because of a smaller steric hindrance compared to other chloro-substituted phenylcyanamide ligands. Two linkage isomers of $[(\text{trpy})\text{Pd}(\text{pcyd})](\text{PF}_6)$ might explain the observation of two $\nu(\text{NCN})$ bands in the IR spectrum. A similar split was also seen in the thallium salt of unsubstituted phenylcyanamide anion (Table 3.1).

The characteristic pyridyl skeletal vibrations are observed in the range 1390-1607 cm^{-1} in the six complexes. The characteristic vibrations of PF_6^- counter anion are shown in the range 834-845 cm^{-1} .

Figure 3.1 Infrared spectrum of $[(\text{trpy})\text{Pd}(\text{pcyd})](\text{PF}_6)$ (KBr disk).

Figure 3.2 infrared spectrum of $[(\text{trpy})\text{Pd}(\text{pcyd})](\text{PF}_6)$ (part, in DMF solution).

Figure 3.3 Infrared spectrum of $[(\text{trpy})\text{Pd}(2\text{-Clpcyd})](\text{PF}_6)$ (KBr disk).

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

Figure 3.5 Infrared spectrum of $[(\text{trpy})\text{Pd}(2,4,6\text{-Cl}_3\text{pcyd})](\text{PF}_6)$ (KBr disk).

Figure 3.6 Infrared spectrum of $[(\text{trpy})\text{Pd}(2,3,4,5\text{-Cl}_4\text{pcyd})](\text{PF}_6)$ (KBr disk).

Figure 3.7 Infrared spectrum of $[(\text{trpy})\text{Pd}(\text{Cl}_2\text{pcyd})](\text{PF}_6)$ (KBr disk).

Figure 3.8 Infrared spectrum of $[(\text{trpy})\text{PdCl}](\text{PF}_6)$ (KBr).

3.2 Proton NMR Spectroscopy

As another characterization method, the ^1H NMR of six complexes and a precursor complex $[(\text{trpy})\text{PdCl}]\text{Cl}$ were performed in d_6 -DMSO. Assignments of the ^1H spectra are summarized in Table 3.2 along with the proton numbering scheme in Figure 3.9.

Figure 3.9 Proton numbering schemes:

(a) $[(\text{trpy})\text{Pd}]^{2+}$ moiety; (b) phenylecyanamide anion (pcyd⁻) ligands.

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

L	Pd(trpy)						pcyd			
	H3	H3'	H4	H4'	H5	H6	H8	H9	H10	H11
Cl	8.71	8.59	8.44	8.59	7.87	8.61				
pcyd	8.68	8.62	8.47	8.62 ^b	7.88	8.19	7.57	7.24	6.88	
2-Clpcyd	8.66	8.61	8.50	8.61 ^b	7.97	8.56	7.18	7.19 ^c	6.83	7.28
2,3-Cl ₂ pcyd	8.66	8.61	8.50	8.61 ^b	7.96	8.54	7.17	7.03	7.17 ^c	
2,4,6-Cl ₃ pcyd	8.66	8.61	8.50	8.61 ^b	7.95	8.56		7.59 ^d		7.29 ^d
2,3,4,5-Cl ₄ pcyd	8.66	8.61	8.50	8.61	7.95	8.55	7.31			
Cl ₅ pcyd	8.64	8.59	8.49	8.59	7.95	8.52				

^a Chemical shifts are in ppm (median calculated if proton coupled). Values were recorded vs TMS at 0.00 ppm with residual solvent or TMS as an internal reference. Solutions were made by dissolving ca. 1.5-3 mg of sample in ca. 0.8 mL of d_6 -DMSO at room temperature.

^b overlaps with H3'. ^c overlaps with H8. ^d approximate assignment due to the unusual peaks broadening and shifting.

The conformation of the free terpyridine molecule is *trans-trans* due to the repulsion of nitrogen non-bonding orbitals.⁶³ Its ^1H NMR spectrum in d_6 -DMSO contains 6 chemical shifts with the order of $\text{H5} > \text{H4} \geq \text{H4}' > \text{H3} \geq \text{H3}' > \text{H6}$ (see scheme in Figure 3.9).⁶³ The slight downfield shift of H3' and H4' is due to the centre ring possessing increased aromatic character as a result of the pyridine rings at the 2 and 6 positions. When terpyridine is coordinated to Pd(II) ion, the nitrogen of the centre ring forms the strongest bond with Pd(II) (the bond length is 1.931 Å, the other two are 2.005 and 2.018

Δ , respectively. see Table 3.5) and has the highest effective charge. Because of the resonance forms pyridine can adopt, H4' is shifted downfield to the point that is almost equivalent chemically with H3'. One singlet peak which counts for 3 protons was observed in ^1H NMR spectra of $[(\text{trpy})\text{Pd}(\text{2,4,6-Cl}_3\text{pcyd})](\text{PF}_6)$, $[(\text{trpy})\text{Pd}(\text{2,3,4,5-Cl}_4\text{pcyd})](\text{PF}_6)$ and $[(\text{trpy})\text{Pd}(\text{Cl}_3\text{pcyd})](\text{PF}_6)$ as a result of the equivalency of H3' and H4'. In the other complexes, H3' and H4' gave a singlet peak with slight split. The chemical shift of H3 is shifted downfield upon coordination because H3 doesn't experience the shielding effect of the lone pair electron of the centre ring's nitrogen as it did before coordination (terpyridine changed to *cis-cis* conformation when binded to metal ion). The H6 protons showed a dramatic upfield shift upon coordination due to the diamagnetic anisotropic effect of the aromatic ring of the adjacent ligand.⁶⁵

The ^1H NMR spectrum of $[(\text{trpy})\text{Pd}(\text{pcyd})](\text{PF}_6)$ shows some significant impurity peaks (see Figure 3.11). It is reasonable to assign them to the isomer complex in which the pcyd anion ligand binds to Pd(II) via the amide nitrogen instead of nitrile nitrogen.

The proton peak broadening observed in the ^1H spectra of $[(\text{trpy})\text{Pd}(\text{2,4,6-Cl}_3\text{pcyd})](\text{PF}_6)$ and $[(\text{trpy})\text{Pd}(\text{2,3,4,5-Cl}_4\text{pcyd})](\text{PF}_6)$ is probably due to the rotation of the phenyl ring about the carbon-cyanamide amide nitrogen bond in the solution. The steric hindrance of the Cl substituents on the phenyl ring is suggested to result in a lower rate of rotation, broadening the proton peaks. This could be verified by low temperature ^1H NMR spectroscopy.⁶⁶ Unfortunately, due to the solubility limits of the complexes and technical reason, this experiment was not conducted.

Figure 3.10 400 MHz ^1H NMR of $[(\text{trpy})\text{PdCl}](\text{PF}_6)$ in d_6 -DMSO.

Figure 3.11 400 MHz ^1H NMR spectrum of $[(\text{trpy})\text{Pd}(\text{pcyd})](\text{PF}_6)$ in d_6 -DMSO.

Figure 3.12 400 MHz ^1H NMR of $[(\text{trpy})\text{Pd}(2\text{-Clpcyd})](\text{PF}_6)$ in $\text{d}_6\text{-DMSO}$.

Figure 3.13 400 MHz ^1H NMR of $[(\text{trpy})\text{Pd}(2,3\text{-Cl}_2\text{pcyd})](\text{PF}_6)$ in $\text{d}_6\text{-DMSO}$.

Figure 3.14 400 MHz ^1H NMR of $[(\text{trpy})\text{Pd}(\text{2,4,6-Cl}_3\text{pcyd})](\text{PF}_6)$ in d_6 -DMSO.

Figure 3.15 400 MHz ^1H NMR of $[(\text{trpy})\text{Pd}(\text{2,3,4,5-Cl}_4\text{pcyd})](\text{PF}_6)$ in d_6 -DMSO.

Figure 3.16 400 MHz ^1H NMR of $[(\text{trpy})\text{Pd}(\text{Cl},\text{pcyd})](\text{PF}_6)$ in d_6 -DMSO.

3.3 Electronic Absorption Spectroscopy

The UV-vis spectra for one precursor complex and six complexes in acetonitrile solution are shown in Figure 3.18-3.24. The spectral assignments are listed in Table 3.3. All the spectra showed $\pi \rightarrow \pi^*$ transitions of the aromatic trpy ligand in the range 200-300 nm and metal-to-ligand charge-transfer (MLCT, Pd(II) $\rightarrow$ trpy) transitions in the range 300-370 nm. The assignment of the MLCT bands are similar to that of Pt(trpy)L²⁺ (L=Cl⁻, Im, His etc.) complexes^{67,68} and is based on the band intensity, dependence on the second ligand, and the spectrum of free trpy ligand (see Figure 3.25). The phenylcyanamide ligands used in this research have $\pi \rightarrow \pi^*$ absorptions in the range 200-300 nm³³ that overlap with the absorptions of the trpy ligand. In square planar Pd(II) (d⁸) systems, d-orbitals split and give three possible d-d transitions (see Figure 3.17). For PdN₄ systems, d-d transitions normally occur in the range below 400 nm with rather low intensity.⁶⁹ In our complexes, d-d transitions were obscured by their overlap with other more intense bands in that region.

Figure 3.17 d-orbital splitting in a square planar environment for Pd(II) (d⁸).

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

Figure 3.19 UV-vis absorption spectrum of $[(\text{trpy})\text{Pd}(\text{pcyd})](\text{PF}_6)$ in CH_3CN ($3.00 \times 10^{-5} \text{ M}$).

Figure 3.20 UV-vis absorption spectrum of $[(\text{trpy})\text{Pd}(2\text{-Clpcyd})](\text{PF}_6)$ in CH_3CN (3.00×10^{-5} M).

Figure 3.21 UV-vis absorption spectrum of $[(\text{trpy})\text{Pd}(2,3\text{-Cl}_2\text{pcyd})](\text{PF}_6)$ in CH_3CN (3.00×10^{-5} M).

Figure 3.22 UV-vis absorption spectrum of $[(\text{trpy})\text{Pd}(2,4,6\text{-Cl}_3\text{pcyd})](\text{PF}_6)$ in CH_3CN (3.00×10^{-5} M).

Figure 3.23 UV-vis absorption spectrum of $[(\text{trpy})\text{Pd}(2,3,4,5\text{-Cl}_4\text{pcyd})](\text{PF}_6)$ in CH_3CN (3.00×10^{-5} M).

Figure 3.24 UV-vis absorption spectrum of $[(\text{trpy})\text{Pd}(\text{Cl}_5\text{pcyd})](\text{PF}_6)$ in CH_3CN (3.00×10^{-5} M).

Figure 3.25 UV-vis absorption spectrum of free terpyridine in CH_3CN (5.00×10^{-5} M).

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

L	$\pi \rightarrow \pi^*$ (trpy)	$\pi \rightarrow \pi^*$ (pcyd)	MLCT	LMCT ^b
Cl	205 (57520) 246 (25810) 279 (23903) 297 (11880)(sh.)		328 (8670) 345 (9050) 362 (8180)	
pcyd ^c	243 (43310)		331 (7170) 345 (9640) 361 (9210)	417 (1820)
2-Cl	206 (59230) 243 (36580)	268 (30610)	330 (8740) 345 (10650) 362 (9850)	403 (3770)
2,3-Cl ₂	206 (59050) 243 (34990)	271 (36470)	331 (9100) 345 (11210) 362 (10420)	400 (4130)
2,4,6-Cl ₃	242 (35060)	275 (42580)	346 (11980) 362 (11120)	401 (4210)
2,3,4,5-Cl ₄	232 (40260) 242 (38280)(sh.)	278 (43400)	329 (11220) 346 (12350) 362 (11700)	392 (4370)
Cl ₅	205 (62580) 230 (46530) 239 (41580)(sh.)	279 (36150)	330 (11550) 345 (12240) 362 (11050)	390 (4040)
trpy	236 (19030) 251 (16630) 278 (22010)			

^a All data were recorded in 3.00×10^{-5} M CH₃CN solution except for trpy free ligand which was collected in 5.00×10^{-5} M CH₃CN solution. Extinction coefficient ϵ in (). sh=shoulder.

^b All of them are broad bands.

^c pcyd $\pi \rightarrow \pi^*$ absorptions are obscured by the trpy absorptions.

The most characteristic feature of the electronic spectra of the six $[(\text{trpy})\text{Pd}(\text{pcyd})](\text{PF}_6)$ complexes is that a broad ligand-to-metal charge-transfer (LMCT, $\text{pcyd} \rightarrow \text{Pd(II)}$) band appears in the range about 370-520 nm. This is unusual for square planar Pd(II) complexes, because in a moderately strong coordination field, the LUMO of Pd(II) is $d_{x^2-y^2}$ (σ^* , see Figure 3.16) and the two orthogonal molecular orbitals of cyanamide group derived from the delocalization of the two pairs of nonbonding electrons are of π symmetry (π_{nb} , see Figure 1.6). The LMCT transition is symmetry forbidden. The reason that this could happen is due to the unique structure of the complex's molecules. The entire molecule is nearly planar (see Figure 3.26 of next section) and the coordination environment around Pd(II) is that of a slightly distorted square plane of nitrogen donor atoms, with the anionic cyanamide group coordinated "end-on" by the nitrile nitrogen. The cyanamide group is almost straight (the bond angle of N4-C16-N5 is 174.6°), but the bond between Pd(II) and cyanamide group (NCN) is bent (the bond angle of Pd-N4-C16 is 146.4°). It is the bending of this bond that allows some mixing of the π_{nb} orbitals of the cyanamide group with the σ^* ($d_{x^2-y^2}$) orbital of Pd(II) (see Figure 3.25) and results in a partially allowed LMCT transition ($\pi \rightarrow \sigma^*$).

Figure 3.26 Schematic diagram of molecular structure and orbital interaction in $[(\text{trpy})\text{Pd}(\text{pcyd})](\text{PF}_6)$.

A trend was observed in increasing LMCT energies as the number of electron-withdrawing substituents (Cl) on the phenyl ring increases. Clearly the addition of Cl substituents stabilizes the π_{nb} orbitals of pcyd⁻ and increases the energy separation between the metal σ^* orbital and ligand π_{nb} orbitals. A similar trend was also found in $[(NH_3)_5Ru(pcyd)]^{2+}$ complexes with greater effect.³³ The importance of this effect is that by introducing electron donor or withdrawing substituents on the phenyl ring, not only the σ and π basicity of the anionic cyanamide ligand can be "tuned", but also the properties of the metal ion can be adjusted.

3.4 X-ray Structure Determination

The X-ray crystallographic data of $[(\text{trpy})\text{Pd}(\text{pcyd})](\text{PF}_6)$ and data collection parameters are given in Table 3.4. An ORTEP diagram is shown in Figure 3.27 including the atomic labelling scheme. A structure drawing including hydrogen atoms and labelling scheme is illustrated in Figure 3.28. A stereoview of the unit cell is displayed in Figure 3.29. Table 3.5 lists selected bond lengths and angles. Table 3.6 gives dihedral angles between ideal planes within the molecule. Finally, Table 3.7 summarized atomic positional parameters.

The residuals of this crystal structure are slightly high with R_f for the significant reflections being 0.084. The absorption correction didn't improve the results much. This may be because the crystal measured was not perfectly formed. Unfortunately, the crystal measured was unexpectedly lost during crystallographic analysis and could not be examined further.

In this crystal structure, only cyanamide anion group "end on" binding to Pd(II) via the nitrile nitrogen was observed but not via the amine nitrogen. It doesn't suggest that this kind of bonding can not exist in other crystals of the complex. IR spectra and $^1\text{H-NMR}$ of this complex show only a small amount of the amine nitrogen bonded to Pd(II) isomer.

The crystal structure of $[(\text{trpy})\text{Pd}(\text{pcyd})](\text{PF}_6)$ (Figure 3.27 and Table 3.5) indicates that the coordination environment around Pd(II) is that of a slightly distorted square plane of nitrogen donor atoms, with the anionic cyanamide group coordinated "end-on" by the nitrile nitrogen.

Table 3.4 Crystallographic Data for [(trpy)Pd(pecy)](PF₆)

Parameter	Value ^a
Empirical Formula	PdPF ₆ N ₅ C ₂₂ H ₁₆
Formula Weight	601.76
Crystal Dimensions (mm)	0.20 × 0.20 × 0.20
Space Group	P2 ₁ /c, Monoclinic
Cell Dimensions	
a, (Å)	8.1733(18)
b, (Å)	21.604(5)
c, (Å)	12.625(3)
Vol., (Å ³)	2169.8(9)
β, (deg.)	103.270(18)
Z, (molecules/cell)	4
F (000), (electrons)	1188.29
d _{calc} , (g/cm ³)	1.842
Lin. Abs. Coeff. (μ, mm ⁻¹)	0.99
Radiation, (Å)	0.70930 (Mo)
2θ(max), (deg.)	44.9
No. of Reflcs. Measd.	2999
No. of Unique Reflcs.	2774
No. of Reflcs with I _{net} > 2.5σ(I _{net})	2302
Transmission Factor Range	0.885316 - 0.999697
Last Least Squares Cycle Calcd.	51 atoms, 317 parameters, 2302 out of 2774 reflections
Rf (sig. refl.) ^b	0.084
Rw (sig.refl.) ^c	0.060
Goodness of Fit ^d	10.09
Rf (all refl.)	0.106
Rw (all refl.)	0.060
Max. Shift/σ	0.106
Last D-map:	
Deepest Hole, (e/Å ³)	-1.490
Highest Peak, (e/Å ³)	1.180

^a ESD's are in parentheses and refer to the last digit printed.

^b $R_f = \sum ||F_o| - |F_c|| / \sum |F_o|$.

^c $R_w = [\sum W(|F_o| - |F_c|)^2 / \sum (W|F_o|)^2]^{1/2}$

^d Goodness of Fit = $[\sum W(|F_o| - |F_c|)^2 / (\text{No. of refl.} - \text{No. of parameters})]^{1/2}$

Figure 3.27 ORTEP drawing for the complex $[(\text{trpy})\text{Pd}(\text{pcyd})](\text{PF}_6)$. The PF_6^- has not been shown for clarity.

Figure 3.28 A whole view of the complex molecule labelling scheme including hydrogens.

Figure 3.29 Stereoview of the unit cell for the complex $[(\text{trpy})\text{Pd}(\text{pcyd})](\text{PF}_6)$.

Table 3.5 Selected Bond Lengths ($\text{\AA}$) and Angles (deg.) for $[(\text{trpy})\text{Pd}(\text{pcyd})](\text{PF}_6)$.^a

Bond Lengths			
Pd - N1	2.018(13)	Pd - N2	1.931(12)
Pd - N3	2.005(14)	Pd - N4	2.010(13)
N4 - C16	1.176(21)	N5 - C16	1.270(21)
N5 - C17	1.388(20)		
Bond Angles			
N1-Pd-N2	82.8(5)	N1-Pd-N3	163.6(6)
N1-Pd-N4	97.1(5)	N2-Pd-N3	80.8(5)
N2-Pd-N4	178.4(5)	N3-Pd-N4	99.3(6)
Pd-N4-C16	146.4(12)	N4-C16-N5	174.6(17)
C16-N5-C17	125.4(14)		

^a Estimated standard deviations are in parentheses and refer to the last digit.

Table 3.6 Dihedral Angles for $[(\text{trpy})\text{Pd}(\text{pcyd})](\text{PF}_6)^+$

Equations of Selected Least-Squares Planes						
plane no.	plane atoms		equation of the plane			
1	Pd-N1-N2-N3-N4		$-6.24(3)x+4.15(10)y+9.79(4)z=0.39(11)$			
2	N1-C1-C2-C3-C4-C5		$-5.82(4)x+5.14(15)y+10.18(6)z=1.13(18)$			
3	N2-C6-C7-C8-C9-C10		$-6.35(4)x+4.02(15)y+9.64(6)z=0.69(16)$			
4	N3-C11-C12-C13-C14-C15		$-5.93(4)x+4.44(16)y+10.17(6)z=0.14(14)$			
5	C17-C18-C19-C20-C21-C22		$-6.68(3)x+4.06(16)y+9.05(6)z=0.88(18)$			
6	N4-N5-C16-C17		$-6.75(5)x+4.6(5)y+8.81(6)z=0.3(5)$			
Distances to the Plane from the Atoms in the Plane						
plane no.	distances (Å)					
1	Pd	0.0003(18)	N1	0.009(17)	N4	-0.027(17)
	N2	-0.026(16)	N3	0.010(17)		
2	N1	-0.009(17)	C1	0.003(21)	C2	0.016(23)
	C3	-0.023(24)	C4	0.005(22)	C5	0.010(20)
3	N2	-0.001(16)	C6	-0.013(20)	C7	0.016(22)
	C8	0.00(3)	C9	-0.019(23)	C10	0.018(20)
4	N3	-0.005(18)	C11	0.012(22)	C12	-0.010(24)
	C13	0.00(3)	C14	0.007(23)	C15	-0.002(21)
5	C17	0.005(20)	C18	-0.010(22)	C19	0.009(22)
	C20	-0.002(23)	C21	-0.003(23)	C22	0.001(22)
6	N4	0.009(19)	N5	0.007(19)		
	C16	-0.023(18)	C17	0.001(23)		
Dihedral Angle Between Plane A and B						
A	B	angle	A	B	angle	
1	2	4.6(5)	2	3	5.8(6)	
1	3	1.2(5)	2	4	2.0(6)	
1	4	3.2(5)	2	5	9.5(6)	
1	5	5.2(5)	2	6	10.4(6)	
1	6	6.6(5)	3	4	4.5(6)	
4	5	8.4(6)	3	5	4.0(6)	
4	6	9.6(6)	3	6	5.5(6)	
5	6	1.9(11)				

* Estimated Standard Deviations are in parentheses and refer to the last digit printed.

Table 3.7 Atomic Parameters x,y,z and B_{iso}^a for $[\text{trpy}]\text{Pd}(\text{pcyd})]^{2+ \cdot b}$

	x	y	z	B_{iso}
Pd	0.83814(15)	0.99602(6)	0.07122(10)	1.84(5)
N1	0.9686(16)	1.0740(6)	0.1222(10)	1.7(5)
N2	1.0025(16)	0.9592(6)	0.1889(10)	1.4(5)
N3	0.7557(17)	0.9083(7)	0.0569(11)	2.3(6)
N4	0.6714(17)	1.0340(6)	-0.05409(11)	2.0(6)
N5	0.4475(17)	1.0114(6)	-0.2140(11)	1.8(6)
C1	0.9422(22)	1.1316(8)	0.0791(14)	2.2(7)
C2	1.0493(23)	1.1809(9)	0.1167(15)	2.7(8)
C3	1.1878(24)	1.1696(9)	0.1979(16)	3.0(8)
C4	1.2181(22)	1.1109(8)	0.2476(14)	2.4(7)
C5	1.1038(20)	1.0644(7)	0.2062(13)	1.8(7)
C6	1.1204(20)	1.0024(7)	0.2472(12)	1.6(7)
C7	1.2394(22)	0.9809(8)	0.3377(14)	2.2(7)
C8	1.2338(25)	0.9159(10)	0.3595(16)	3.3(9)
C9	1.1166(23)	0.8748(8)	0.2974(15)	2.6(8)
C10	0.9954(21)	0.9018(8)	0.2101(13)	1.9(7)
C11	0.8574(22)	0.8700(8)	0.1346(14)	2.3(7)
C12	0.8236(24)	0.8069(9)	0.1403(15)	2.9(9)
C13	0.6840(3)	0.7828(10)	0.0704(17)	3.5(10)
C14	0.5820(22)	0.8197(8)	-0.0045(14)	2.4(8)
C15	0.6235(21)	0.8798(8)	-0.0075(14)	2.1(7)
C16	0.5663(20)	1.0250(7)	-0.1333(13)	1.8(7)
C17	0.3702(20)	1.0523(7)	-0.2951(13)	1.8(7)
C18	0.2429(21)	1.0294(8)	-0.3805(14)	2.2(8)
C19	0.1599(22)	1.0732(8)	-0.4593(14)	2.5(7)
C20	0.2044(23)	1.1325(8)	-0.4543(15)	2.6(8)
C21	0.3314(23)	1.1559(8)	-0.3710(14)	2.4(8)
C22	0.4149(22)	1.1139(8)	-0.2902(14)	2.3(7)

^a B_{iso} is the mean of the principal axes of the thermal ellipsoid.

^b Estimated Standard Deviations are in the parentheses.

The bond lengths of Pd-N range 1.931-2.018 Å in this complex, which is normal for Pd-N of amine and pyridine complexes,⁷⁰⁻⁷⁷ indicating that the Pd(II)-N bond is mainly of σ bonding character. The bond between the anionic cyanamide group and Pd(II) is bent, having an angle of Pd-N4-C16=146.4°. The bond angle between a cyanamide group and a metal ion is mainly determined by the resonance of the anionic phenylcyanamide ligand (see Figure 1.6 a). If only σ bonding interactions between metal ion and cyanamide ligand are taken into account, resonance structure A will coordinate to a metal ion via the nitrile lone pair electrons, resulting in an ideal bond angle of 180° as a result of the sp hybridized nitrile nitrogen. Coordination of resonance structure B to a metal ion should result in an ideal bond angle of 120° as a result of the sp^2 hybridization. But in reality, the bonding description of the cyanamide group will have contributions from both resonance structures A and B and the coordination bond angle between 120 and 180° is expected.³⁵ Furthermore, coordination of the anionic cyanamide group to a strongly polarizing metal ion should increase the contribution of resonance structure B to the molecular orbital description of the cyanamide anionic group, and if the metal ion has significant π acceptor properties, the preferred bond angle will be close to 180° in order to maximize the metal's interaction with the two terminal lone electron pairs of resonance structure B. Because of this, Ru(III), a strong π acceptor, has a bond angle of 171.4(10)° when coordinated to 2,3-Cl₂pcyd⁻. Pd(II) is a much weaker π acceptor compared to Ru(III), and so has Pd(II)-cyanamide bond angle of 146.4° which is close to that of [(bpy)Cu(2,3-Cl₂pcyd)₂].³⁵

Both cyanamide group and phenyl ring are almost perfectly planar (with the

greatest out of plane distances of 0.023(18) Å and 0.010(22) Å respectively, see Figure 3.27 and Table 3.6). The dihedral angle between cyanamide group and phenyl ring is $1.9(11)^\circ$, showing the two planes are coplanar. This, in addition to the short bond lengths of the N4-C16 (1.18 Å) and N5-C16 (1.27 Å) bonds, indicates a strong π interaction between cyanamide and phenyl groups. Similar results were also observed in other phenylcyanamide-metal complexes.^{33,35}

The crystal structure data (see Figure 3.27 and Table 3.6) also indicate that the Pd(II) coordination sphere is nearly perfectly planar (the greatest out of plane distance is 0.027(17) Å), and this plane is coplanar with the phenylcyanamide anion ligand (the dihedral angle between Pd(II) plane and cyanamide group plane is $5.2(5)^\circ$, and the dihedral angle between Pd(II) plane and phenyl ring plane is $6.6(5)^\circ$. This is the fulfilment of our primary goal of constructing a planar Pd(II) phenylcyanamide complex.

Unfortunately, as seen in the stereoview of the complex's unit cell, the complex molecules didn't form a continuous π stacking system. Instead, they formed an alternate stacking system. This kind of stacking system can't form the correct band structure in the complex solid and so this complex can't be electrically conductive. The reason of forming this kind of alternate stacks is that there is a Pd(II)-N interaction between two complex molecules which form a "pair". The distance between pairs is 6.825 Å which is too far to have interaction. Within the pair, the distance between these two neighbour molecules is 3.255 Å, and the distance between a Pd(II) and the amine nitrogen from the neighbour molecule is 3.265 Å which is close enough to have interaction. The distance between this Pd(II) and the nitrile nitrogen from the neighbour molecule is 4.116 Å which

is greater than the distance between Pd(II) and amine nitrogen and so is unlikely to have an interaction. The similar interaction and stacking pattern were also observed in other Pd(II) and Pt(II) square planar complexes, such as [(trpy)PdCl]Cl⁵¹ and [(trpy)Pt(HET)]NO₃.⁷⁸ To form continuous stacks in [(trpy)Pd(peyd)](PF₆) complex, the Pd(II)-N interaction must be overcome.

CHAPTER 4

Terpyridinepalladium(II) Complexes of 2,5-Dimethyl-Dicyanamidobenzene Ligand: Physical Characterization and Result Discussion

4.1 [(trpy)Pd(DM-Dicyd)]Cl Complex

DM-Dicyd²⁻ is a very unusual ligand that can be readily oxidized by O₂ in air or by other oxidants to a radical anion [DM-Dicyd]^{•-} and form stable complexes with some metal ions.^{79,80} In Figure 4.1, the IR spectrum of [(trpy)Pd(DM-Dicyd)]Cl shows two characteristic $\nu(\text{NCN})$ stretches at 2088 and 2115 cm⁻¹, respectively. This is consistent with only one cyanamide group bound to Pd(II) and the another cyanamide group free.

Figure 4.1 IR spectrum of [(trpy)Pd(DM-Dicyd)]Cl, KBr disk.

The resonance equilibrium for this complex is expected to be $(\text{trpy})\text{Pd}-\text{N}^{\ominus}=\text{C}=\text{N}-\text{ph}-\text{N}^{\ominus}-\text{C}\equiv\text{N} \leftrightarrow (\text{trpy})\text{Pd}-\text{N}^{\ominus}=\text{C}=\text{N}-\text{ph}^{\ominus}=\text{N}-\text{C}\equiv\text{N}$. As one can see, the free cyanamide group has more nitrile character and so it should appear at higher energy (2115 cm^{-1}). Some characteristic trpy skeletal vibrations are shown in the range $1340\text{--}1602\text{ cm}^{-1}$.

Figure 4.2 shows the UV-vis spectrum of the free DM-Dicyd radical anion ligand (AsPh_4 salt) in DMF. There is a split $\pi \rightarrow \pi^*$ absorption band of the phenyl ring in the range $320\text{--}440\text{ nm}$. The characteristic absorptions of DCNQI radical anions are the three bands in the range $440\text{--}740\text{ nm}$ which are assigned to $\pi \rightarrow \pi_{\text{nb}}$ transitions. Both solid state and solution UV-vis spectra of radical complex $[(\text{trpy})\text{Pd}(\text{DM-Dicyd})]\text{Cl}$ show the characteristic DM-Dicyd absorptions (in the range $440\text{--}740\text{ nm}$ for solution, see Figure 4.3 and $500\text{--}900\text{ nm}$ for solid, see Figure 4.4). The MLCT ($\text{Pd}(\text{II})$ to trpy) absorptions overlap with the $\pi \rightarrow \pi^*$ absorption of the DM-Dicyd ligand in the range $320\text{--}440\text{ nm}$.

Figure 4.2 UV-vis spectrum of $(\text{AsPh}_4)(\text{DM-Dicyd})$ in DMF.

Figure 4.3 UV-vis spectrum of $[(\text{trpy})\text{Pd}(\text{DM-Dicyd})]\text{Cl}$ in DMF, 3.00×10^{-5} M.

Figure 4.4 Solid state UV-vis spectrum of $[(\text{trpy})\text{Pd}(\text{DM-Dicyd})]\text{Cl}$ (KBr disk).

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PM-1 3 1/2" x 4" PHOTOGRAPHIC MICROCOPY TARGET
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PRECISIONSM RESOLUTION TARGETS

The cyclic voltammetry of $(\text{AsPh}_4)_2(\text{DM-Dicyd})$ and $[(\text{trpy})\text{Pd}(\text{DM-Dicyd})]\text{Cl}$ was performed in DMF using a platinum working and counter electrode, a silver wire pseudo-reference electrode and the ferrocene/ferrocenium couple (0.400 V vs. NHE) as an internal reference (see Figures 4.5 and 4.6).

Figure 4.5 Cyclic Voltammogram of $(\text{AsPh}_4)_2(\text{DM-Dicyd})$ in DMF.

Figure 4.6 Cyclic Voltammogram of $[(\text{trpy})\text{Pd}(\text{DM-Dicyd})]\text{Cl}$ in DMF.

Both the ligand and the complex show two characteristic one-electron redox processes.

For the free dianion ligand, two redox couples are seen at $E_1^\circ = -0.638$ V vs. NHE and $E_2^\circ = 0.125$ V vs. NHE, with the separation between these two redox couples ($\Delta E^0 = E_2^\circ - E_1^\circ$) of 0.763 V. In the spectrum of the radical complex, E_1° and E_2° appear at -0.563 and -0.325 V vs. NHE respectively. The first redox couple (E_1°) shifted to anodic potential and the second one shifted to cathodic potential, and the separation (ΔE^0) between them is reduced to 0.238 V. This is evidence that the radical anion ligand [DM-Dicyd] $^{\cdot-}$ is coordinated to Pd(II) in the complex.

The radical anion ligand in the above complex behaves quite differently compared to the dianion ligands in the dinuclear $\{[(NH_3)_5Ru]_2Dicyd\}^{4+}$ complexes.⁶⁶ In these Ru(III) complexes, although the separation between the two ligand redox couples also became smaller (0.3-0.4 V) than those in the free ligands (0.5-0.7 V), both couples shifted to more anodic potentials. This is likely due to the π -stabilization afforded the ligands upon complexation to Ru(III).

The half-wave potential of Pd(II) reduction in the complex is -0.988 V vs. NHE, and is irreversible. The suggested reaction scheme is

This potential is higher than that in the precursor complex $[(\text{trpy})\text{PdCl}](\text{PF}_6)$ (-0.800 V vs. NHE, Figure 4.7) and mononuclear complex $[(\text{trpy})\text{Pd}(\text{pcyd})](\text{PF}_6)$ (-0.763 V vs. NHE, Figure 4.8), and indicates that the DM-Dicyd⁻ radical anion ligand significantly stabilizes Pd(II). The half-wave potential of the first one-electron redox couple of trpy ligand is -2.163 V vs. NHE which is similar to that of $[(\text{trpy})\text{PdCl}](\text{PF}_6)$ and $[(\text{trpy})\text{Pd}(\text{pcyd})](\text{PF}_6)$ (both are -2.125 V vs. NHE). However, this potential is much higher than that of $[\text{Fe}(\text{trpy})_2]^{2+}$ complex in DMF (-1.477 V vs NHE).⁸¹

Figure 4.7 Cyclic Voltammogram of $[(\text{trpy})\text{PdCl}](\text{PF}_6)$ in DMF.

Figure 4.8 Cyclic Voltammogram of $[(\text{trpy})\text{Pd}(\text{pcyd})](\text{PF}_6)$ in DMF.

The radical anion ligand in this complex is expected to be a paramagnetic centre and therefore, EPR (Electron Paramagnetic Resonance) studies will be helpful. Some measurements on the acetone solutions of both the free radical anion ligand and the complex have been performed at NRC. But due to the polarity of the solvent, the resolution of the spectra was too poor to tell anything. Several long needle-like crystals were obtained from this complex. But due to imperfections, these crystals were not suitable for X-ray crystallography studies.

4.2 $\{[(\text{trpy})\text{Pd}]_2(\text{DM-Picvd})\}(\text{CF}_3\text{SO}_3)_2$, Dinuclear Complex

In the hope of eliminating the alternate crystal packing effect found in mononuclear complex $[(\text{trpy})\text{Pd}(\text{pcyd})](\text{PF}_6)$, a dinuclear terpyridinepalladium(II) complex bridged by dicyanamidobenzene ligand was synthesized. In this complex, there may be Pd-N interactions between neighbour molecules in solid state. However, if both Pd(II) ions in a molecule interact with the two amide nitrogens (most likely) of the neighbour molecule, there still is a good chance to get some extent of overlap between neighbour phenyl rings (see Figure 4.9). If every molecules overlap with its neighbour molecules and form continuous π stacks, a conductive material might be obtained upon doping with I_2 .

Figure 4.9 The packing pattern of $\{[(\text{trpy})\text{Pd}]_2(\text{Dicyd})\}^{2+}$ complex molecules simulated by Alchemy.

IR spectra of the dinuclear complex and the precursor complex are shown in

Figures 4.10 and 4.11 respectively. In the spectrum of dinuclear complex, two characteristically strong $\nu(\text{NCN})$ stretches are seen at 2070 cm^{-1} and 2123 cm^{-1} . The split may be due to some DM-Dicyd²⁻ binded to Pd(II) via the amide nitrogens (see section 3.1). The $\nu(\text{NCN})$ energy of the complex is slightly lower than that of $\{[(\text{NH}_3)_5\text{Ru}]_2(\text{DM-Dicyd})\}(\text{ClO}_4)_4$ (2088 cm^{-1}). Since $(\text{trpy})\text{Pd}(\text{II})$ moiety is a weaker π -acid compared to $(\text{NH}_3)_5\text{Ru}(\text{III})$, the ability to shift electron density from cyanamide group to Pd(II) is weaker.

The characteristic trpy skeletal vibrations are observed in range $1450\text{--}1604\text{ cm}^{-1}$ in both the dinuclear complex and the precursor complex. The positions of these peaks changed very little upon the coordination of DM-Dicyd²⁻ ligand. The characteristic stretches of CF_3SO_3^- are seen in range $1166\text{--}1266\text{ cm}^{-1}$ in both the dinuclear complex

Figure 4.10 IR spectrum of $\{[(\text{trpy})\text{Pd}]_2(\text{DM-Dicyd})\}(\text{CF}_3\text{SO}_3)_2$, (KBr disk).

Figure 4.11 IR spectrum of $[(\text{trpy})\text{Pd}(\text{CF}_3\text{SO}_3)](\text{CF}_3\text{SO}_3)$, (KBr disk).

Figure 4.12 IR spectrum of $\text{DM-H}_2\text{Dicyd}$, (KBr disk).

Figure 4.10) and the precursor complexes (Figure 4.11). For the dinuclear complex, there are a strong peak at 1263 cm^{-1} and a split peak at 1224 cm^{-1} which are agreed with the two peaks observed in a triflate salt NaCF_3SO_3 (1272 and 1225 cm^{-1}). When CF_3SO_3^- coordinated, the symmetry of the CSO_3 group is lowered and these two peaks split into three peaks in the spectrum of precursor complex (Figure 4.11).^{82,83}

The ^1H NMR spectrum of dinuclear complex in d_6 -DMSO is shown in Figure 4.13. The assignments for the spectrum are similar to those for mononuclear terpyridinepalladium(II) phenylcyanamide complexes (see section 3.2). The methyl protons are obscured by the solvent peaks. The positions of trpy protons didn't change much compared to those of the mononuclear complexes, indicating that their environments are similar. The ^1H NMR spectrum shows some impurity peaks, probably because DMSO is substituting for the DM-Dcyd²⁻ ligand.

Figure 4.13 ^1H NMR spectrum of $\{[(\text{trpy})\text{Pd}]_2(\text{DM-Dicyd})\}(\text{CF}_3\text{SO}_3)_2$ in d_6 -DMSO.

The UV-vis spectra of dinuclear complex and the precursor complex are shown in Figures 4.14 and 4.15, respectively. In the spectrum of $[(\text{trpy})\text{Pd}(\text{CF}_3\text{SO}_3)](\text{CF}_3\text{SO}_3)$, one $\pi \rightarrow \pi^*$ absorption band of DM-Dicyd²⁻ ligand is centred at 270 nm and overlaps with some $\pi \rightarrow \pi^*$ transitions of trpy ligand. One $\pi \rightarrow \pi^*$ transition of trpy is at 244 nm. MLCT transitions (Pd(II) to trpy) are similar to those of $[(\text{trpy})\text{PdCl}](\text{PF}_6)$. A characteristic feature of the UV-vis spectrum of $\{[(\text{trpy})\text{Pd}]_2(\text{DM-Dicyd})\}(\text{CF}_3\text{SO}_3)_2$ is the broad LMCT (DM-Dicyd²⁻ to Pd(II)) band centred at 451 nm with $\epsilon=8820 \text{ M}^{-1}\text{cm}^{-1}$. The intensity of this band is almost twice of the LMCT band observed for the mononuclear $[(\text{trpy})\text{Pd}(\text{pcyd})](\text{PF}_6)$ complexes (see table 3.3), because there are two LMCT chromophores/mole of dinuclear complex. The energy of this band shifts 30-50 nm lower compared to those of mononuclear $[(\text{trpy})\text{Pd}(\text{pcyd})](\text{PF}_6)$ complexes.

Figure 4.14 UV-vis spectrum of $\{[(\text{trpy})\text{Pd}]_2(\text{DM-Dicyd})\}(\text{CF}_3\text{SO}_3)_2$, $2.00 \times 10^{-5} \text{ M}$ CH_3CN solution.

Figure 4.15 UV-vis spectrum of $[(\text{trpy})\text{Pd}(\text{CF}_3\text{SO}_3)](\text{CF}_3\text{SO}_3)$, 5.00×10^{-5} M CH_3CN solution.

The dinuclear complex is stable in solid state but not in CH_3CN solution. Figures 4.16 and 4.17 are UV-vis spectra of the complex in solid state (KBr disk) and CH_3CN solution after they were exposed to air for 20 min. In the solid state spectrum, the LMCT band and two MLCT bands are seen. The LMCT band shifts 50 nm to lower energies and the ratio of intensity of the LMCT band over that of the two MLCT bands reduces about 50-60%, compared to those in the solution. This is very likely due to the intra-molecular Pd(II)-N interactions that were also found in the $[(\text{trpy})\text{Pd}(\text{pcyd})](\text{PF}_6)$ complexes. The solution UV-vis spectrum shows two characteristic absorptions of radical DM-Dicyd²⁻ at 607 nm and 668 nm. The LMCT band has largely disappeared and a new

band forms at around 370-430 nm, that belongs to $\pi \rightarrow \pi^*$ absorption of DM-Dicyd⁻ radical anion.

Figure 4.16 Solid state UV-vis spectrum of $[(trpy)Pd]_2(DM-Dicyd)(CF_3SO_3)_2$ (KBr disk).

Figure 4.17 UV-vis spectrum of $[(trpy)Pd]_2(DM-Dicyd)(CF_3SO_3)_2$ in CH_3CN solution after exposing to the air for 20 min.

The cyclic voltammogram of this dinuclear complex in DMF is shown in Figure 4.18. In the range scanned (1.575 to -2.175 V vs. NHE), three redox couples (peaks) are seen. Among them, two irreversible peaks at -0.713 and -1.375 V vs. NHE are assigned to Pd reduction, since some black powder was seen on the Pt working electrode at the end of the experiment. The third redox couple is quite unusual in that the anodic to cathodic peak separation (ΔE_{pc}) is 0.225 V, which is much larger than a single electron process (ideally 0.059 V). The separation was found to be scan rate independent (50 and 100 mV/s were tested). A controlled-potential electrolysis experiment determined that this process is a two-electron process ($n=2.01$ determined by $Q=nFN$) which can be expressed as $\text{DM-Dicyd}^{2+} \xrightleftharpoons[+2e^-]{-2e^-} \text{DM-DCNQI}$. This kind

Figure 4.18 Cyclic Voltammogram of $[(\text{trpy})\text{Pd}]_2(\text{DM-Dicyd})(\text{CF}_3\text{SO}_3)_2$ in DMF.

of behaviour has not been seen in other dinuclear complexes containing Dicyd^{2-} ligands. It seems that DM-Dicyd^- radical anion ligand is destabilized with respect to DM-Dicyd^0 and DM-Dicyd^{2-} when bridging two Pd(II) ions.

Attempts to grow crystals of this complex suitable for crystallographic studies have not succeeded so far. Diffusion and evaporation methods in several common solvents such as CH_3CN , DMF , NMP and acetone have been tried. The crystal structure will be crucial in order to know how the complex molecules pack together in the solid state and if they form a stacking system or not.

CHAPTER 5

CONCLUSIONS AND FUTURE STUDIES

The recent development in $M(\text{DCNQI})_n$ molecular metals has lighted the hope for new electronic materials in organic charge-transfer complexes. In this research, we used a planar cation ($(\text{trpy})\text{Pd}(\text{II})$) and a planar ligand ($\text{pcyd}^\cdot$ or DM-Dicyd radical anion or dianion) to construct a planar molecule in the hope of forming π stacks in crystal lattice. If an X-ray structure shows π stacking, we can check for conductivity and also vary the electronic properties of the π stack by changing the ligand substituents. This thesis has accomplished the aims that were outlined in Section 1.3. It has covered a series of terpyridinepalladium(II) complexes of phenylcyanamide anion ligands as well as of dimethyl-dicyanamidobenzene anion radical and dianion ligand: their syntheses and characterization. The crystal structure of $[(\text{trpy})\text{Pd}(\text{pcyd})](\text{PF}_6)$ complex shows that the coordination environment around $\text{Pd}(\text{II})$ is that of a slightly distorted square planar of nitrogen atoms and the entire molecule is almost planar. The bending of cyanamide group in the crystal structure results in a mixing of the metal's σ^* and the ligand's π_{nb} orbitals, which results in an unusual ligand to metal charge-transfer (LMCT) transition in these complexes. The distance and orientation of the $[(\text{trpy})\text{Pd}(\text{pcyd})](\text{PF}_6)$ molecules in the unit cell indicate that there is a dimerization.

The mononuclear radical complex $[(\text{trpy})(\text{DM-Dicyd})]\text{Cl}$ showed some unusual stability both in solid state and in DMF solution. Further studies on a crystal structure for this complex are necessary to understand the relationship between the properties and

the crystal structure. Recent studies show that some radical complexes can have novel magnetic properties,⁸⁴ and it is worth while to make some further explorations in this area.

The dinuclear complex $\{[(\text{trpy})\text{Pd}]_2(\text{DM-Dicyd})\}(\text{CF}_3\text{SO}_3)_2$ illustrated some unusual electrochemical properties. When it was initially oxidized in DMF solution, it didn't undergo single electron process to radical complex $\{[(\text{trpy})\text{Pd}]_2\text{Pd}(\text{DM-Dicyd})\}^{3+}$ as Ru(III) dinuclear complexes did, but underwent two electron process to fully oxidized form $\{[(\text{trpy})\text{Pd}]_2(\text{DM-DCNQI})\}^{4+}$. The mechanism for this is unclear yet and requires further study.

From this research and some other previous studies, it is clear that the substituents on the phenyl ring of both pcyd⁻ anion and Dicyd²⁻ dianion ligands affect the ligand's π donating properties. By changing the substituents, we can "tune" the donor properties of the ligands and so "tune" the properties of complexes. It is necessary to study other dinuclear terpyridinepalladium(II) complexes of Dicyd²⁻, DC-Dicyd²⁻, TC-Dicyd²⁻ and TM-dicyd²⁻ ligands to explore their properties. Since the crystal structure is crucial to verify the molecule's packing pattern as well as to understand the complex's properties, more efforts should be made to grow crystals that are suitable for crystallographic studies. Some strategies may be used such as changing counteranions and crystallization solvents and so on.

One modification would be the synthesis of a Pd analogue to the Cu(DCNQI)₂ molecular metals (see Figure 1.5). This could be done by electrochemical synthesis using either DCNQIs or Dicyd²⁻ and Pd(II) salts. It is very likely that in this material, every

Pd(II) will be coordinated by four cyanamide groups in square planar geometry. Since X-ray structures of Pd(II) complexes show that Pd(II) ions have the tendency to line up and keep close distance between each other, the chance to get a well formed π stack system seems very high. It may form partially charged π stacks during the synthesis as $\text{Cu}(\text{DCNQI})_2$ does. If not, we can oxidize or reduce it chemically to form partially charged π stacking systems. This may result a highly conducting material.

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