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(1,3-bis(2'-pyridylimino)isoindolato)Ni(II)
Complexes of Phenylcyanamido Ligands:
Crystal Structure, Solution and Spectroscopic Properties

by

ROBERT J. LETCHER, B.Sc.

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

Master of Science

Department of Chemistry

Carleton University

Ottawa, Ontario

June, 1991

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Complexes of Phenylcyanamido Ligands:
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Dr. Robert Crutchley, Thesis Supervisor

Chair, Department of Chemistry

Carleton University

June, 1991

ABSTRACT

A series of 4-coordinate, neutral, approximately square planar (1,3-bis(2'-pyridylimino)isoindolato)Ni(II)(phenylcyanamido) complexes (i.e. (PVP)Ni(pcyd)) have been prepared and characterized by ^1H NMR, electronic absorption, and infrared spectroscopies and X-ray crystallography. Increasing the π -donating ability of the phenylcyanamido ligand results in a diamagnetic to paramagnetic change in magnetic properties of the complexes. Tetrahedral distortion from the square plane is demonstrated by a crystal structure of (PVP)Ni(2-Clpcyd) which also shows ordered molecular stacking in the crystal lattice.

The $\text{PVP}^\ominus$ centered $\pi-\pi^*$ electronic transitions of the (PVP)Ni(pcyd) complexes in low donating solvents shows a "*mixing*" effect attributed to an extension of conjugation resulting from π donation of the phenylcyanamido ligand mediated by a common Ni(II) π symmetry orbital within a square planar geometry.

Temperature dependent, reversible solvent coordination equilibria exist for the (PVP)Ni(pcyd) complexes. The proportions of non-solvated and solvated complexes are characterized by changes in the apparent π -*mixing* effect from which thermodynamic parameters are derived.

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"Not to have edges that catch
But to remain untangled,
Unblinded,
unconfused,
Is to find balance,
And he who holds balance beyond sway of love or hate,
Beyond reach of profit or loss,
Beyond care of praise or blame,
Has attained the highest post in the world"

LAO TZO

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CHAPTER 1

INTRODUCTION

1.1 Background

1.1.1 Molecular Metals

Electronically conductive molecular materials or, "molecular metals" derived from coordination compounds have historically required the fulfilment of two fundamental criteria: 1) the complex molecules must be arrayed in close proximity in an ordered or, "stacked" fashion within the crystal lattice, and 2) the complex must adopt a non-integral formal oxidation state [1–3]. The mixed valency or incomplete charge transfer can be achieved chemically or electrochemically by oxidation or reduction of components of the delocalized stack. Both criteria require that the metal complex possesses ligands which are conjugated and relatively planar [1–4].

The phenylcyanamide ligand has shown a recent resurgence in importance with the discovery of highly conducting copper(II) cations bridged by the radical anion form of N,N'-dicyanoquinonediimine (DCNQI) (i.e. in particular the 2,5-dimethyl substituted quinone form, Figure 1.1) by Hünig *et al* [5,6].

Figure 1.1 Perspective view of (2,5-dimethyl-DCNQI)₂Cu crystal lattice [5]

The DCNQI molecule shown in Figure 1.1 is planar with the bending at the amine nitrogens occurring in the plane. The copper salt has slight tetrahedral distortion in regards to the nitrile nitrogen coordination to Cu(II) [5]. Conduction was suggested to occur through the overlapping π system of the planar DCNQI molecules as a result of intimate stacking and transversely through the NCN—Cu—NCN bridges [7–9]. Partial negative charge was imparted to the π -accepting DCNQI radical anion bridge resulting in a non-integral oxidation state on the copper. It was suggested that the mixed valent state of the copper was accomplished through the mixing of copper d orbitals and DCNQI $p\pi$ orbitals [6–9]. The metallic like description of this salt is further enhanced by the sensitivity of electrical conduction to temperature (i.e. decreased temperature, increased conductivity).

This π conductive behavior has been seen before in other organic ligand–metal systems [10]. In particular, the class of neutral Ni(II) tetraammine (NiN_4) planar conjugated systems shown in Figure 1.2 have demonstrated interplanar π conductivity [1–4,11,12] similar to that seen in $\text{Cu}(\text{DCNQI})_2$ systems.

The one dimensional stacked lattice of conjugated metallomacrocylic complexes can be partially oxidized by the addition of the oxidant $\text{I}_3^\ominus$. Chains of triiodide counterions co-occupy the lattice with the now conductive partially oxidized metallomacrocylics as shown for Ni(II)(phthalocyanine) ($\text{NiPcI}_{1.0}$) (i.e. NiPc carries a positive +0.33 charge) in Figure 1.3a. $\text{I}_3^\ominus$ can accommodate itself to channels of the one dimensional lattice [4] creating fractionally occupied valence shells on the macrocyclic complex [11]. Figure 1.3b depicts a valence band approach to partial filling of the highest occupied band of the metal complex in the lattice with the subsequent enhancement of molecular π

Figure 1.2 Metallomacrocycles ($M = \text{Ni}$) which display molecular conductivity via the π stacks [3]

Figure 1.3 a) A simple schematic representation of molecular stacking for partially oxidized $\text{NiPcI}_{1.0}$ (i.e. metallomacrocycle represented by circle) [4]. b) Enhancement of charge mobility via the molecular π interaction as a result of partial oxidation of the macrocycle.

conduction within the stacks. In addition, EPR (electron paramagnetic resonance) studies of $\text{NiPcI}_{1.0}$ have confirmed the oxidation is predominantly ligand centered [4]. Therefore, inter-stack electron delocalization provides the extended path for electron movement via $d-\pi$ and $\pi-\pi$ interactions [1-4,11,12].

This class of partially oxidized metallomacrocycles represent the first examples of highly conducting molecular systems of first row transition metals. In addition, the electrical conductivity is temperature dependent which enhances the metallic description of these materials [3-5]. Metallocyanines (Figure 1.2c) have shown the greatest variance in electrical conductivity when doped with electron acceptors such as halogens, quinones, or nitrosyl salts [1,12]. These conductive polymers range in charge transport characteristics from molecular metals to semi-conductors depending on the doped oxidant.

It is apparent that potential exists for conductive behavior in other planar, metal complexes which contain conjugated ligands. Phenylcyanamide is a potential candidate in light of conductive behavior exhibited by the analogous DCNQI metal salts.

1.1.2 Phenylcyanamide Anion-Metal Systems

The phenylcyanamide anion ($\text{pcyd}^{\ominus}$) is both a π and σ donating ligand and prefers coordination to π -acid metals [13]. Metal coordination generally takes place through the nitrile nitrogen for steric and electronic reasons [14-19]. The anion is resonance stabilized (Figure 1.4a) where structure Y gives rise to the two molecular orbitals shown in Figure 1.4b.

Figure 1.4a The $\text{pcyd}^{\ominus}$ ligand, resonance stabilized [13,20,21]

Figure 1.4b Orthogonal π -symmetry molecular orbitals resulting from the delocalization of two non-bonding electron pairs as in resonance form Y.

The cyanamide anion has been classified as a pseudo-halide and a range of metal complexes have been documented [19].

In this lab, there has been a concerted effort to understand the nature of the interaction between the anionic phenylcyanamide and the metals Cu(II) and Ru(III) [13,20–23]. Elucidation of the bonding interaction between the $\text{pcyd}^{\ominus}$ and Cu(II) and Ru(III) is necessary in order to gauge the potential of the

1,4-dicyanamidobenzene dianion (dicyd^{2-}) as an electron-transfer moderator in bridged dinuclear complexes containing mixed-valent metals (i.e. Ru (II/III) and Cu (I/II)) [13,20,21]. The bonding interaction between metal and ligand has been shown to be influenced by changes in the substituents on the phenyl ring of $\text{pcyd}^{\ominus}$ for both Ru(III) and Cu(II). There is extensive conjugation between the phenyl ring and cyanamide π systems and substituents on the ring effectively "tune" the extent of electronic interaction between the $\text{pcyd}^{\ominus}$ and the metal.

Pentaammine ruthenium(III)–phenylcyanamide complexes have demonstrated this sensitivity and have been monitored by noting changes in the electronic ligand to metal charge transfer (LMCT) spectroscopic transitions and redox properties of the Ru(III) metal center [13,21,22]. It was demonstrated that within $\text{pcyd}^{\ominus}$, the cyanamide moiety and the phenyl ring are coplanar when bound to Ru(III), suggesting that a strong π interaction exists. The Ru(III)– $\text{pcyd}^{\ominus}$ bonding interaction is therefore influenced by the phenyl ring substituents via the conjugated π system of $\text{pcyd}^{\ominus}$. The filled π symmetry orbitals of $\text{pcyd}^{\ominus}$ take advantage of the favorable π -acceptor properties of Ru(III).

Aquino *et al* [23] recently constructed a dicyd^{2-} system composed of the 1,4-dicyanamido-2,3,5,6-tetrachlorobenzene dianion (L^{2-}) bridging two Ru(III) pentaammine metal centers. To induce metal to metal coupling, selective reduction of one Ru(III) center to Ru(II) was expected to create π -donor (Ru(II)) and π -acceptor (Ru(III)) centers which could couple through the easily oxidized conjugated dicyd^{2-} π -donor bridge. The existence of a low intensity electronic IT (intervalence transfer) band indicated that this mixed valent system was weakly coupled. The justification for weak electronic coupling hinged upon the discontinuity of π coupling between Ru(III) and dicyd^{2-} .

The mononuclear systems of $\text{pcyd}^{\ominus}$ and $[\text{Cu(II)(bipy)}_2]^{2+}$ have been recently studied by Crutchley *et al* [20] to interpret the $\text{Cu(II)}-\text{pcyd}^{\ominus}$ bonding interaction. As with $\text{Ru(III)}-\text{pentaammine}$ systems [13,21], the analysis is made possible by monitoring the electronic influence on the metal-ligand interaction resulting from phenyl ring substituent changes with electronic absorption spectroscopy, cyclic voltammetry, and X-ray crystallography. It was noted that both the intensity and energy of the electronic LMCT bands involving π type orbitals on Cu(II) and $\text{pcyd}^{\ominus}$ are significantly lower and higher, respectively than with Ru(III) [13,21]. The orbitals involved in the LMCT transition of the former are assigned as $p\pi-d_{x^2-y^2}$, where the singly occupied $d_{x^2-y^2}$ orbital is mostly σ anti-bonding in character. This interaction is described as formally forbidden but it was suggested that the low symmetry of $[(\text{bipy})\text{Cu}(\text{pcyd})]^+$ complexes mixed some π character into the $d_{x^2-y^2}$ orbital reducing the forbiddenness of the transition. Similar assignments have been made for copper(II) phenolato complexes [18] and dinuclear copper(II) ambidentate $\text{pcyd}^{\ominus}$ bridged systems [17-19]. The insensitivity of Cu(II) to the σ and π donor properties of the phenylcyanamide anion ligands was reflected in the somewhat invariant Cu (II/I) redox couple. The extension of these results to mixed valent dinuclear copper DCNQI type systems are presently underway in Dr. Crutchley's lab.

This prompted the study of $\text{pcyd}^{\ominus}$ interaction with Ni(II) . The only $\text{pcyd}^{\ominus}-\text{Ni(II)}$ complex known to exist was prepared by Hollebone [14,15] in which four $2-\text{Clpcyd}$ or $2,4,6-\text{Cl}_3\text{pcyd}$ anions were bound to Ni(II) . It was suggested that tetrahedral distortion is preferred over low-spin square planar since the apparently

strong π -donor properties of these ligands stabilize the tetrahedral or distorted tetrahedral geometry.

The d orbital splitting pattern for Ni(II) (i.e. as a result of square planar coordination) is similar to Cu(II) (d^9) and Co(II) [16,25]. The $d_{x^2-y^2}$ orbital of Ni(II) is empty when low-spin and can therefore be destabilized to a greater extent [17,18,20]. It is therefore of interest to study mono-pcyd[⊖], Ni(II) complexes to explore the significance of changing the pcyd[⊖] phenyl ring substituents in terms of the metal-ligand interaction via π -coupling since the filled, stabilized d orbitals have π symmetry.

It has been recently demonstrated by Brodie *et al* [17,24] that a number of metal coordination modes are available to the pcyd[⊖] ligand. Two Cu(II) systems were synthesized, namely [Cu(bipyridine)(pcyd)₂]₂ and [Cu(1,10-phenanthroline)(3-Clpcyd)(CH₃CO₂)₂•2H₂O], in which pcyd[⊖] displayed three distinctive bonding modes: 1) copper-copper bridging through the nitrile nitrogen alone (i.e. 3-Clpcyd used), 2) copper-copper bridging through the nitrile and amine nitrogens (i.e. unsubstituted pcyd used), and 3) terminal mono coordination to copper through the nitrile nitrogen. The suggestion was made that the versatility for bonding is dependent on the basicity of cyanamide and minimal steric hinderance especially in a bridging interaction. While the 3-Clpcyd and pcyd anions (stronger π -donors) demonstrate bridging with (bipy)Cu(II), 2,3-Cl₂pcyd does not [20].

It has been shown that the pcyd[⊖] ligand prefers to bind in a σ and π donating fashion to the cationic metal centers Cu(II), Ru(III), and Ni(II). In each case,

"tuning" of the conjugated pcyd[⊖] π system via the phenyl ring substituents influences the metal–NCN interaction. An extension of this behavior involves the dicyd²⁻ type ligands bridging two metal centers. In essence, the delocalizing bridge allows the metals to electronically sense one another.

Application of these materials as "*molecular conductors*" would rely on the potential for delocalization of metal charge via the organic ligand bridge. This has been demonstrated by planar π stacked Ni(II) macrocyclic complexes which are partially oxidized and by the DCNQI radical anion when bridging Cu(II) metal centers.

1.1.3 Factors Influencing Ni(II) 4–Coordinate Geometry

For 4–coordinate Ni(II) complexes, the coordination geometry (i.e. tetrahedral or square planar) is largely determined by the ligand field properties of the coordinating ligands. Strong field ligands give rise to square planar systems and are generally π –accepting in nature whereas weak field ligands result in tetrahedral geometries and are generally π –donating [14–16].

Nishida and Kida [25] have summarized, in a general description, the possible ligand π –donating influences on the square planar 4–coordinate geometry in terms of d orbital splitting of Ni(II). It is widely accepted that the most destabilized empty d orbital in a Ni(II) square planar arrangement is the $d_{x^2-y^2}$ orbital when the x, y Cartesian coordinates pass through the Ni–L bonds but has been labelled

d_{xy} when bidentate ligands are used (i.e. x,y cartesian coordinates are written as to bisect the bidentate ligands) [26a]. In either case, total spin pairing in the lower four d orbitals of Ni(II) d^8 is energetically favourable if the empty d orbital is appreciably separated by elevation to high enough energy. Conversely, Hund's rule becomes more predominant when the splitting is small.

Nishida and Kida classify ligands as two major types:

TYPE 1

- coordinating atom of the ligand is nitrogen or phosphorous and carries no charge
- tetraammine dianion macrocycles with well developed conjugated π systems

TYPE 2

- dianionic tetra-coordinate ligands containing 4 nitrogen or 2 nitrogen/2 oxygen ligating atoms having no or less developed π systems
-

Type 1 ligands have π -acid character and thus stabilize the symmetrically compatible $d\pi$ orbitals d_{yz} and d_{xz} , whereas Type 2 ligands are π -bases and thus destabilize these same orbitals so that spin pairing in the lower four orbitals becomes energetically less favourable as shown in Figure 1.5.

This general trend has been reinforced recently by the study of square planar Ni(II) complexes of tetradentate N,N'-ethylene, N,N'-trimethylene, N,N'-tetramethylenebis(methyl-2-amino-1-cyclopentenedithiocarboxylate)

Figure 1.5 π -donation effects on the d orbital splitting of square planar Ni(II) [25]

Figure 1.6 Lewis structure of neutral Ni(II) complexes of $[\text{N}_2\text{S}_2]^{2-}$ ligands [27]

(abbrev. $[\text{N}_2\text{S}_2]^{2-}$) ligands by Bereman *et al* [27] as shown in Figure 1.6. With a growing alkyl bridge, it was suggested that the σ -donating nitrogens are rotated as a result of tetrahedral distortion towards the z-axis (i.e. perpendicular to the square plane) whereas the two π donating sulfur atoms moved closer to the central metal within the square plane. This resulted in stabilization of the empty $d_{x^2-y^2}$ orbital and destabilization of the filled d_{xy} orbital. As in Figure 1.5, increased ligand π -donation destabilized symmetrically compatible $d\pi$ orbitals of Ni(II) increasing the probability of spin unpairing (i.e. a paramagnetic ground state).

Ligand π donation to Ni(II) in 4-coordinate square planar geometry may induce a tetrahedral distortion from the square plane as a result of the $d\pi-p\pi$ interaction since the ligand field splitting is reduced. Spin un-pairing may occur (Hund's rule) inducing a diamagnetic to paramagnetic spin transition of Ni(II). As part of this study, the effects of π -donation on novel neutral NiN_4 systems is explored incorporating $\text{pcyd}^\ominus$ as the π donating ligand.

1.1.4 Temperature Dependent Diamagnetic/Paramagnetic Equilibria in Ni(II) Tetraammine Complexes

In 1939, Lifschitz *et al* [28,29] observed for the first time the coexistence of diamagnetic and paramagnetic forms of a tetraammine Ni(II) complex, namely $\text{Ni}[1,2\text{-diphenylethylenediamine}]_2^{+2}$. It was not until 1957 when Jørgensen [30] studied by electronic absorption the equilibrium condition exhibited by the two forms in aqueous solution. The equilibrium could be perturbed as a result of temperature change or by the addition of an inert electrolyte and was attributed to axial interaction of either electrolyte anions or solvent molecules with the Ni(II) tetra-coordinated complex. A single broad electronic absorption band representing

three $d-d$ ligand field transitions (to be discussed) denotes low-spin, diamagnetic, square planar coordination by which many of these complexes can be described in solution [26a]. A change in the intensity of this band by either of the two perturbing mechanisms was reflective of the ratio of paramagnetic and diamagnetic species present.

Ballhausen and Liehr [31] were able to explain theoretically the observed equilibrium in terms of ligand field theory. Square planar geometry could be described as a strong tetragonal distortion of axial ligands in octahedral Ni(II) (d^8) complex (Figure 1.7a). It was possible to have a paramagnetic (i.e. $^3A_{2g}$ (Figure 1.7c), strong tetragonal distortion) or diamagnetic ground state (i.e. $^1A_{1g}$ (Figure 1.7b)) with a square planar geometry about Ni(II). Dissolution in a complexing solvent was said to lower Δ_2 , "the tetragonality parameter" so that $^3A_{2g}$ (Figure 1.7c) was the preferred ground state (i.e. paramagnetic).

Diamagnetic/paramagnetic equilibria of Ni(II) tetraamine (NiN_4^{2+}) complexes in solution has been suggested to arise from several mechanisms [32]:

Square planar-octahedral interconversion as a result of solvent coordination. The equilibrium is sensitive to temperature and ionic strength.

These equilibria are characterized by concentration and steric sensitivity

Figure 1.7 a) Ligand field splitting diagram for weak and strong tetragonal distortion along the z axis of an octahedral Ni(II) complex (the strong case exemplifies an approximately square planar geometry). The diamagnetic (b) and paramagnetic (c) ground state energy level diagrams as a result of strong tetragonal distortion of Ni(II) complexes [31].

[32-34]. The absence of temperature dependence of the equilibrium in non-coordinating solvent argues against the formation of associated species.

These equilibria are highly unlikely with amine ligands which are cyclic polydentate since gross distortion of the ligand is required on going to tetrahedral geometry.

There have been a number of studies on NiN_4^{2+} systems of EQUIL.1 in various solvent media which have been monitored by electronic absorption of the square planar $d-d$ band envelope [32]. It is this particular equilibria with respect to changing temperature which will be of concern in studies carried out on the neutral NiN_4 type complexes synthesized here.

The diamagnetic (desolvated)/paramagnetic (solvated) equilibria has associated with it an equilibrium constant, K_{eq} , which is temperature dependent. The thermodynamic parameters ΔH° (enthalpy) and ΔS° (entropy) of the solvent coordination equilibrium are dependent on both K_{eq} and temperature by the expression

$$(1) \quad \ln K_{eq} = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}$$

Both ΔH° and ΔS° can be obtained graphically by plotting $\ln K_{eq}$ vs $1/T$. ΔH° and ΔS° are generally constant over a relatively large temperature range [35].

Table 1.1 lists the enthalpy and entropy values of NiN_4^{2+} systems in various solvent media where there is coordination of two solvent molecules. In all cases, solvation of the NiN_4^{2+} complexes was exothermic (negative ΔH°) and solvent coordination gave negative entropies.

Fabbrizzi *et al* [36] noted that the Ni(II) cation undergoes a radial increase (i.e. orbital electron density expansion) when going from low to high spin and as a result the Ni-N bond lengths of the coordinated N_4 ligand increase. When steric factors on the N_4 ligands become significant, the enthalpic barrier increases accordingly [37]. From Table 1.1 this is evident because exothermicity decreases going from: substituted cyclic $\rightarrow$ cyclic $\rightarrow$ linear tetraamine complexes. In addition, ΔS° values become markedly less favourable (more negative) towards solvation going from: linear $\rightarrow$ cyclic $\rightarrow$ substituted cyclic tetraamine complexes. It has been suggested [35] that a spin state increase (diamagnetic to paramagnetic) does not necessarily require solvent coordination. Weak solvation is possible in which the solvent molecule is only "immobilized" in the axial positions. This was used to explain the less favourable solvation entropies in more sterically hindered NiN_4 environments.

Table 1.2 lists similar thermodynamic parameters for mono-solvent coordination of the $[\text{Ni}(\text{cis-tetramethylcyclam})]^{2+}$ complex in differing solvent media. In these examples significant steric restrictions imposed by the N_4 ligand are regarded as the barrier to a second solvent molecule coordination [38–40]. Note that when both the ΔH° and ΔS° values are normalized to 2 solvent coordination, there is close agreement with the corresponding values in Table 1.1.

Solvent dependence of the paramagnetic/diamagnetic equilibria is not entirely

Table 1.1 Thermodynamic parameters, ΔH° and ΔS° , for various NiN_4 complexes in differing solvent media according to the equilibria $\text{NiN}_4^{2+} + 2\text{Solvent} \rightleftharpoons [\text{NiN}_4(\text{Solvent})_2]^{2+}$

Complex [†]	$-\Delta H^\circ$ [†]	$-\Delta S^\circ$ [*]	Solvent ^b	Ref.
$[\text{Ni}(\text{CR})](\text{BF}_4)^a$	26.7	74.9	H_2O	32
$[\text{Ni}(\text{CR})](\text{BF}_4)^a$	17.1	51.0	CH_3OH	32
$[\text{Ni}(\text{CR})](\text{PF}_6)^a$	17.4	45.2	CH_3CN	32
$[\text{Ni}(\text{CRCH}_3)](\text{BF}_4)$	19.2	63.2	H_2O	32
$[\text{Ni}(\text{CRCH}_3)](\text{ClO}_4)$	20.3	52.7	DMF	32
$[\text{Ni}(\text{cyclam})](\text{ClO}_4)$	24.0	91.0	H_2O	37
$[\text{Ni}(\text{trans-TMcyclam})](\text{ClO}_4)$	43.8	146.0	H_2O	37
$[\text{Ni}(\text{trans-TMcyclam})](\text{ClO}_4)$	27.7	83.7	DMF	40
$[\text{Ni}(2,3,2\text{-tet})](\text{ClO}_4)$	14.2	42.6	H_2O	36
$[\text{Ni}(3,2,3\text{-tet})](\text{ClO}_4)$	18.4	62.8	H_2O	36
$[\text{Ni}(\text{isocyclam})](\text{ClO}_4)$	22.2	78.2	H_2O	56

[†] See Figure 1.8 for the corresponding Lewis structures. [†] Values in kJ mol^{-1} . ^{*} Values in $\text{J K}^{-1} \text{mol}^{-1}$. ^a Obtained from paramagnetic shifting in ^1H NMR. ^b DMF = N,N-dimethylformamide, DMSO = dimethylsulfoxide.

Table 1.2 Thermodynamic parameters, ΔH° and ΔS° , for $[\text{Ni}(\text{cis-TMcyclam})](\text{ClO}_4)$ in various solvent media according to the equilibria $\text{NiN}_4^{2+} + \text{Solvent} \rightleftharpoons [\text{NiN}_4(\text{Solvent})]^{2+}$

	$-\Delta H^\circ$ [†]	$-\Delta S^\circ$ [*]	Solvent	Ref.
	12.2	41.0	H_2O	37
	19.6	40.9	DMF	40
	16.8	32.0	CH_3CN	40

[†] Values in kJ mol^{-1} . ^{*} Values in $\text{J K}^{-1} \text{mol}^{-1}$.

(i)

(ii)

Figure 1.8 Lewis structural diagrams for NiN_4^{2+} systems displaying solvent coordination equilibria.

clear [31,32] despite the differences seen in the ΔH° and ΔS° values (Table 1.1). Rusnak and Jordan [32] suggested a number of compensating factors were responsible including solvating power and steric effects.

A major portion of this thesis is devoted to probing spin-state change due to solvent coordination in a series of novel neutral tetraammine Ni(II) complexes. Some unusual trends were observed in varying solvent media.

1.1.5 Influence of Metal Orbitals on Intra-Ligand Electronic Transitions

In 1984 Lever [26b] stated, " The variation in intra-ligand transitions, with change of metal ion, is often quite small and usually ignored ". There are several recent spectroscopic indications which signal the possibility of greater metal orbital influence on the ligand centered $\pi-\pi^*$ transitions. Lewis and Schröder [42] indicated the π^* orbitals of the metal bound pyridine nitrogen of conjugated diiminopyridine macrocycles can behave as π -acceptors to stabilize $d\pi$ orbital electron density on Ni(II). In addition, Nishida and Kida [25] showed that π -donating ligands bonded to Ni(II), including N_4 dianion systems, destabilized the filled $d\pi$ orbitals, d_{xz} and d_{yz} .

Symmetry compatibility of the forementioned π^* orbitals with the $d\pi$ metal orbitals is possible. Favorable energetics between these two types of orbitals is also possible in light of π -donor ligand destabilization of the d_{xz} and d_{yz} orbitals.

In this study, a series of neutral, 4-coordinate, square planar NiN_4 systems, namely (PVP)Ni(pcyd), are found to display peculiar spectroscopic behavior pertaining to $PVP^\ominus$ centered $\pi-\pi^*$ transition energy and intensity. The behavior appears to be uncommon and will be carefully scrutinized in this study.

1.2 System Design for a Mono-Phenylcyanamide Anion Ni(II) Complex

It was previously shown that $\text{pcyd}^{\ominus}$ binds to Ni(II). In this study, the exploration of the metal-ligand interaction between a $\text{pcyd}^{\ominus}$ and Ni(II) is of interest and the synthesis of such a system required a unique approach.

The molecular concept was planned to satisfy specific criteria: 1) a synthetic approach that would facilitate the substitution of only one $\text{pcyd}^{\ominus}$ ligand to Ni(II), 2) isolation of a four coordinate pcyd-Ni(II) complex in which the remaining 3 coordination sites were occupied by a tri-dentate ligand of a conjugated and planar nature, and 3) that the Ni(II) complex be a neutral species approximately square planar in geometry to gauge the intermolecular metal-ligand interactions in the solution and solid state and to explore the intermolecular sensitivity towards coordination of donating solvents.

The macrocyclic or polydentate nature of a ligand enhances the thermodynamic stability of a coordination complex relative to complexes of similar coordination number but with ligands of lesser denticity. The property was first noted by Cabbiness and Margerum [43] and was coined as the "*macrocyclic effect*". This property is advantageous with the use of 1,3-bis(2-pyridylimino)isoindoline anion ($\text{PVP}^{\ominus}$) (Figure 1.9) since it is capable of tridentate complexation.

The incorporation of $\text{PVP}^{\ominus}$ as a ligand was first realized during the metal assisted "template" synthesis of phthalocyanines [44-47]. The $\text{PVP}^{\ominus}$ ligand can function as a mono-anion tridentate ligand with a variety of transition metal ions [48-53]. The metal bound $\text{PVP}^{\ominus}$ ligand maintains planarity [48,49,51-53], except for a slight twisting seen in the five coordinate species

Figure 1.9 The 1,3-bis(2-pyridylimino)isoindolinato anion ligand

(dibenzoylmethanato)(1,3-bis((5-methyl-2-pyridyl)imino)isoindolinato)copper(II) [50].

The $\text{PVP}^\ominus$ ligand falls into a class of ligands which contain the conjugated iminopyridine moiety. Lewis and Schröder noted the ability of diiminopyridine macrocyclic ligands to stabilize the $d\pi$ orbitals of low valent transition metal species [42]. Energetically low lying π^* orbitals on the metal bound pyridine nitrogen characterized these ligands as good π acceptors. It would appear that this property would compliment the π -donating ability of $\text{pcyd}^\ominus$ especially if the $d\pi$ orbitals of the coordinated metal are filled.

Four-coordinate Ni(II) complexes of $\text{PVP}^\ominus$ are uncommon. Of the 4-coordinate species known to exist, namely $(\text{PVP})\text{Ni}(\text{CH}_3\text{CO}_2)$, $(\text{PVP})\text{NiCl}$, and $(\text{PVP})\text{Ni}(\text{N}_3)$, the proton nuclear magnetic resonance (^1H NMR) for the first two were found to be paramagnetic as indicated by broadening and shifting of the peaks (i.e. paramagnetic contact shift) [47,52-55]. One may suspect that square planar ligation is not the case considering Ni(II) is not low-spin (diamagnetic).

It is therefore suspected that the observed paramagnetism in 4-coordinate Ni(PVP)L complexes arises from a significant distortion from square planar towards tetrahedral geometry.

Dirk and Marks [12] have shown that the macrocyclic ligand, hemiporphrazine (hp^{2-}) (Figure 1.2d), forms square planar Ni(II) complexes. Close inspection reveals that it is strikingly similar to $\text{PVP}^\ominus$ except the conjugation is continuous. Partial oxidation of Nihp by doping the solid state with $\text{I}_3^\ominus$ uncovered preliminary indication that this material was electrically conductive.

Complexes of $\text{PVP}^\ominus$ have taken on even greater significance based on work pioneered by Siegl *et al* [53]. The planar dinuclear bis-chelating $\text{PVP}^\ominus$ shown in Figure 1.10, binds to two metals in an identical fashion as $\text{PVP}^\ominus$.

Figure 1.10 The dimetal-chelating 1,3,5,7-tetra(2-pyridylimino)benzodipyrrolo ligand (bis-PVP^{2-})

Several authors have reported dinuclear bridging of Ru(II) , Mn(II) , Fe(II) , Co(II) , Cu(II) , and Pd(II) [48,49,53-55]. Furthermore, it was suggested that

multi-electron transfer between the two metals in these polymeric metals compounds are facilitated by the extensive conjugation in the bridge. This behavior has been demonstrated in the cyclic voltammetry of $(4'-\text{MePVP})\text{Ru(II)}(\mu\text{-bis-PVP})\text{Ru(II)}(4'-\text{MePVP})$. If the metals are isolated from one another, two coincidental Ru II/III couples are expected. Although the separation was small, two couples existed suggesting the odd electron in the Ru(III)/Ru(II) mixed valent species was delocalized over both metals thus the bridging ligand is regarded as having a partial oxidation state [48,49].

1.3 Aims of the Thesis

1) The focal point of this thesis is the synthesis of a series of novel, neutral 4-coordinate Ni(II) complexes composed of tridentate PVP[⊖] and monodentate pcyd[⊖]. The systems are characterized using electronic absorption, infrared, and ¹H NMR spectroscopies as well as X-ray crystallography. To my knowledge the crystal structure of (PVP)Ni(2-Clpcyd) obtained in the course of this study represents the first known crystal structure of a phenylcyanamide-Ni(II) complex.

The nature of the metal-ligand bonding interaction is explored with regards to the data obtained and by comparing to analogous pcyd[⊖] complexes of Ru(III) and Cu(II). Ultimately, some insight is elucidated as to the potential for Ni(II) in dinuclear complexes of the dicyd²⁻ or bis-PVP²⁻ ligands and the subsequent possibility of solid state molecular conductivity.

2) The square planar diamagnetic spin state of these tetraammine systems in

non-coordinating solvent was found to be sensitive to the π -donating ability of the $\text{pcyd}^\ominus$ ligand. ^1H NMR is very sensitive to paramagnetic effects and thus the spin state perturbation could be monitored for appreciably soluble complexes. This will be discussed and spectral comparison will be made to other pseudo-halide anion ligands.

3) The electronic absorption spectra of the $(\text{PVP})\text{Ni}(\text{pcyd})$ complexes are dominated by ligand centered $\pi-\pi^*$ transition bands. There are large perturbations in energy and intensity of these bands in non-coordinating solvents and this is attributed to the possibility of $\text{Ni}(\text{II})$ mediated π mixing phenomena in the square planar systems. A discussion of factors pertaining to this effect will be presented in terms of a broad comparative study with anions other than $\text{pcyd}^\ominus$.

4) The neutral $(\text{PVP})\text{Ni}(\text{pcyd})$ systems are found to be coordinatively sensitive to solvent as seen for square planar NiN_4^{2+} complexes. An equilibrium condition is established between unsolvated (diamagnetic) and solvated (paramagnetic) species which was dependent on solvent donor strength and temperature. Unlike other NiN_4^{2+} studies in which the K_{eq} relied on changes in the square planar $d-d$ band envelope to calculate the thermodynamic parameters, ΔH° and ΔS° , the π -mixing perturbation on $\pi-\pi^*$ transitions is used in this study. To my knowledge this represents the first study of diamagnetic (desolvated)-paramagnetic (solvated), temperature dependent equilibria using *neutral* 4-coordinate tetraammine $\text{Ni}(\text{II})$ complexes. In addition, the $\pi-\pi^*$ transition energy and intensity dependence on solvent coordination provides a new spectroscopic tool for analysis of this type. Comparative discussion will be presented regarding this equilibrium condition in various solvent media.

CHAPTER 2

SYNTHESIS AND EXPERIMENTAL

2.1 Synthetic Description of the Ligands and Complexes

2.1.1 1,3-bis(2'-pyridylimino)isoindoline Ligand, PVPH

1,3-bis(2'-pyridylimino)isoindoline (PVPH) was initially prepared by R.P. Linstead and J.A. Elvidge [44] via method A (Scheme 2.1). Alternate synthetic approaches such as method B allowed for the formation of PVPH from simpler chemical reagents [54].

Scheme 2.1

In method A, the initial reaction is a condensation between di-iminoisoindoline and 2-aminopyridine. Similarly, method B denotes the reaction of phthalonitrile and 2-aminopyridine and is described as an intramolecular cyclization catalyzed by CaCl_2 . The monosubstituted intermediate A, common to both method A and B, is more reactive toward a second condensation and readily forms the PVPH ligand.

2.1.2 Thallium Salts of the Phenylcyanamide Anion Ligands, Tl(pcyd)

Preparation of the thallium salts of phenylcyanamide anions, Tl(pcyd), from their protonated dimer or monomer analogues, has been well documented [13,14]. The ease of monomer or dimer formation is highly influenced by the position, type, and number of substituents on the aromatic ring of the phenylcyanamide. In particular, increasing chloro substitution especially in ortho positions (i.e. relative to the cyanamide) renders the phenylcyanamide more sensitive to dimerization.

Initially, nucleophilic attack of the thiocyanate anion on the carbonyl carbon of benzoyl chloride occurs (Scheme 2.2a). The primary amine of the aniline adds across the C=N bond of the resulting benzoyl thiocyanate intermediate ending in the formation of thiourea derivative (Scheme 2.2b).

The previously isolated thiourea is transformed through a series of successive *in situ* reactions to give the neutral phenylcyanamide dimer or monomer.

Cleavage of the benzoyl moiety from the thiourea facilitates the desulfurization of intermediate A by lead acetate (Schemes 2.3a and 2.3b). The amine proton of the resulting pcydH (i.e. acidification of A, Scheme 2.3c) is generally acidic which is partially credited to resonance stabilization of the pcyd anion (Figure 1.4a) [13]. Greater chloro substitution on the phenyl ring rendered the ligands more sensitive to dimerization (i.e. Scheme 2.3d). In the presence of a weak base such as triethylamine, the dimer equilibrates between itself and its' anion monomer. Introduction of thallium acetate shifts the equilibrium to the monomer form by precipitation of Tl(pcyd).

Scheme 2.2

Scheme 2.3

2.1.3 (PVP)Ni(II)(pcyd) Complexes

In order to achieve a four coordinate nickel(II) system containing tridentate PVP and monodentate pcyd anions, the (PVP)NiBr complex was first synthesized. The use of bromide was advantageous since the reaction of (PVP)NiBr with Tl(pcyd) results in the formation of a stable TlBr precipitate which drives the metathesis reaction to completion [14]. Thallium(I) halide salts are insoluble in non-aqueous solvents and thus the TlBr byproduct was easily removed from the reaction mixture [30]. In Scheme 2.5 a simplified stepwise illustration of (PVP)Ni(II)(pcyd) complex formation is presented.

Scheme 2.4

2.1.4 Ni(PVP)₂

Synthesis of this compound had been accomplished previously by Siegl *et al* [53,54], J.A. Elvidge *et al* [44], and T.J. Hurley *et al* [49]. In general, Ni(II) underwent facile substitution of halide or psuedo-halide ligand for PVP anion. In a solution of excess PVP anion, Ni(PVP)₂ was generally the resultant product.

The ease with which Ni(PVP)₂ can be formed from Ni(PVP)X complexes is illustrated by the following recrystallization schemes (i.e. Scheme 2.6, a and b).

Scheme 2.5

In methods (a) and (b), 2 molecules of the (PVP)NiL complex appear to disproportionate slowly.

2.1.5 (PVP)NiCl·H₂O, (PVP)Ni(OAc), and (PVP)Zn(OAc)

Unlike the bromide analogue, the (PVP)NiCl has been prepared [55]. Synthesis of the latter involved a template type reaction using nickel(II) chloride, phthalonitrile, and 2-aminopyridine in methanol. It was suggested that the product mixture contained hydroxyl impurities as a result of partial anion exchange with the methanol. Scheme 2.6 illustrates the alternate method used here.

Scheme 2.6

Previous attempts in absence of triethylamine resulted in a metal bound protonated PVPH.

(PVP)Ni(OAc) and (PVP)Zn(OAc) (i.e. ${}^{\ominus}\text{OAc} = {}^{\ominus}\text{O}_2\text{CCH}_3$) were prepared in an identical fashion as used by Siegl *et al* [55] (Scheme 2.7)

Scheme 2.7

2.1.6 (PVP)Ni(NCS)

Synthesis was modelled after the (PVP)Ni(pcyd) complexes since an indepth search of the literature revealed that its' preparation appears not to have been previously attempted.

Scheme 2.8

This simple metathesis reaction (Scheme 2.8) yielded the desired product although triethylamine was required to maintain the deprotonated status of the PVP anion.

2.1.7 (PVP)Ni(N₃)

A detailed method of preparation was not available for (PVP)Ni(N₃), although its synthesis has been noted [55]. The metathesis reaction illustrated in Scheme 2.9 did not require triethylamine as with (PVP)Ni(NCS).

Scheme 2.9

2.1.8 (PVP)Cu(2,3-Cl₂pcyd)•0.5H₂O

This complex was prepared in a similar manner to the (PVP)Ni(pcyd) complexes. The (PVP)CuBr had been prepared previously [55], and thus a metathesis reaction was carried out with Tl(2,3-Cl₂pcyd) as shown in Scheme 2.10.

Scheme 2.10

2.2 Experimental

2.2.1 Starting Materials

2.2.1.1 Ligand Synthesis Reagents

1,3-bis(2'-pyridylimino)isoindoline

The reagents were obtained as follows: 1,3-diiminoisoindoline (Aldrich, 97%), 2-aminopyridine (Aldrich, 99%), anhydrous calcium chloride (Anachemia, reagent grade) and used without further purification. Phthalonitrile (Eastman-Kodak, reagent grade) was recrystallized from hot toluene prior to use.

Phenylcyanamides and their Thallium Salts

The following reagents were obtained commercially and used without further purification: ammonium thiocyanate (Fisher Scientific, 99.6%, reagent grade), benzoyl chloride (Aldrich, 99%, reagent grade), sodium hydroxide (Anachemia, lab grade), lead acetate trihydrate (Anachemia, reagent grade), glacial acetic acid (Anachemia, 99.7%, lab grade), 2,3-dichloroaniline (Aldrich, 99%), 2,6-dichloroaniline (Aldrich, 98%), 2,3,5,6-tetrachloroaniline (Aldrich, 99%), 2-chloroaniline (Aldrich, 98+%), 4-chloroaniline (Aldrich, 98%), 2,4,5-trichloroaniline (Aldrich, reagent grade), thallium acetate (Aldrich, 99.99%), and triethylamine (Aldrich, 99+%).

2.2.1.2 Metal Complex Synthesis Reagents

Nickel bromide hydrate (Aldrich, 98%, reagent grade), triethylamine (Aldrich, 99+%), nickel acetate tetrahydrate (Fisher Scientific, reagent grade), nickel chloride tetrahydrate (Fisher Scientific, reagent grade), sodium azide (British Drug House, 99+%), potassium thiocyanate (Fisher Scientific, reagent grade), potassium cyanide (Fisher Scientific, 99.2%), and zinc acetate dihydrate (Aldrich, 98+%, reagent grade) were all used without further purification.

2.2.1.3 Solvents

Chloroform (Caledon Labs, spectro grade), nitrobenzene (Aldrich, 99+%, reagent grade), anhydrous diethyl ether (Caledon Labs), methanol (Caledon Labs,

spectro grade), absolute ethanol (Consolidated Alcohols, 100%), propylene carbonate (Aldrich, 99%, reagent grade), anisole (a.k.a. phenyl methyl ether; Fisher Scientific, reagent grade), 2-methoxyethanol (Aldrich, 99+%, spectro grade), 1-butanol (Caledon Labs, 99.4%), and 1-methyl-2-pyrrolidinone (Aldrich, 99.4%, HPLC grade) were all used as received. Dimethyl sulphoxide (Caledon Labs, distilled in glass), n-hexanes (Caledon Labs, spectro grade), and benzonitrile (Aldrich, 99.9%, HPLC grade) were stored over activated 3A molecular sieves (heated to $\approx 500^\circ\text{C}$ for 16 hrs., cooled in a desiccator). Acetone (Caledon Labs, Spectro grade) was distilled and stored over activated 3A molecular sieves. Tetrahydrofuran (Anachemia, 99.7%, distilled in glass) underwent additional purification by refluxing (≈ 2 hrs.) with and fractionally distilling from lithium aluminum hydride (Aldrich, 99.5%) and finally storing over activated 3A molecular sieves. Concentrated hydrochloric acid (Anachemia, lab grade) was used as received. Deuterated dimethyl sulphoxide (MSD Isotopes, 99.9 atom % D) was stored over activated 3A molecular sieves. Deuterated chloroform (MSD Isotopes, 99.8 atom % D) was used as received.

2.2.1.4 Electrolytes

Tetrabutylammonium hexafluorophosphate (Aldrich, 98%) was recrystallized from hot absolute ethanol twice followed by high vacuum drying at 118°C for 18 h. Potassium chloride (Aldrich, 99+%) was used without further purification. Standard buffer solution $\text{pH} = 4.00 \pm 0.01$ (Anachemia) was used as received.

2.2.2 Ligand synthesis

2.2.2.1 Preparation of 1,3 bis(2'-pyridylimino)isoindoline, PVPH

The ligand was prepared by either of two methods depending on the availability of the required reagents.

Method A: The manner of preparation was similar to that of J.A. Elvidge and R.R. Linstead [44]. A mixture of 1,3-diiminoisoindoline (9.0g, 60 mmol), 2-aminopyridine (12.0g, 130 mmol), and 75 mL of 1-butanol was refluxed with stirring for a period of 4 h. During this time the solution became progressively dark green in color. Upon cooling, a fine, hair-like, lime green precipitate emerged from solution. This was filtered through a medium porosity frit and washed with fresh 1-butanol.

The crude product was recrystallized from a chloroform/hexane solvent mixture. This was accomplished by heating a sufficient amount of chloroform and PVPH to the point of total dissolution (i.e. just before boiling). Hexanes were then slowly added. When precipitation began to occur, the temperature was increased slightly to drive the precipitated PVPH back into solution. This was removed from heat and set aside to cool. Large, lime green needles were collected, washed with hexanes and air dried. Repeated preparation gave an average yield of 10.54g (57%, based on initial reagents).

Method B: The manner of preparation was similar to that of Siegl [55]. 2-aminopyridine (9.0g, 60 mmol), phthalonitrile (3.84g, 30 mmol), anhydrous calcium chloride (0.33g, 3.0 mmol), and 30 mL of 1-butanol were combined together and refluxed with stirring for 48 h. The solution changed from a colorless

suspension to a dark green solution during this time. Cooling yielded a fine, hair-like, lime green precipitate. Recrystallization was performed in an analogous manner to method A. Final yield was 3.14g (35%, based on initial reagents).

2.2.2.2 Preparation of the Neutral Phenylcyanamide Monomers (pcydH) and Dimers (pcydH)₂

Dimer ligand

N-(2,3,5,6-tetrachlorophenyl)-N'-cyano-N'-(2,3,5,6-tetrachlorophenyl)guanidine, (2,3,5,6-Cl₄pcydH)₂

Phenylcyanamide was prepared by initially synthesizing the thiourea derivative. Ammonium thiocyanate (7.61g, 100 mmol) and 100 mL of acetone were brought to a rapidly stirring reflux. A solution of benzoyl chloride (14.06g, 100 mmol) and 100 mL of acetone was added dropwise immediately producing a white ammonium chloride precipitate. Once the addition was complete, a 10 min. reflux proceeded. Dropwise addition of 2,3,5,6-tetrachloroaniline (23.06, 100 mmol) in 100 mL of acetone followed, after which the solution refluxed for 1 h. The milky yellow solution was then slowly poured into 1500 mL of rapidly stirring water yielding the pale yellow thiourea derivative. This was collected by filtration and washed with excessive amounts of distilled water followed by diethyl ether and allowed to air dry.

A mixture of thiourea (20.0g, 50 mmol) and ≈200 mL of 2.0 M sodium hydroxide (aqueous) were brought to a boil for 5 min. The transparent pale yellow solution was then gradually cooled to 65°C at which point 100 mL of aqueous lead acetate trihydrate (18.97g, 50 mmol) was added. The temperature was maintained at ≈60°C during which time black PbS formed. After 8 min. the slurry was judged

dark enough and suction filtered through a Buchner funnel. The clear filtrate was cooled on an ice bath and glacial acetic acid was added with swirling until litmus registered an acidic pH. Milky white product immediately precipitated. This was collected and washed with water. The crude product was considered pure enough for use in the synthesis of the thallium salt of the anion. Yield = 18.11g (71%, based on initial reagents).

2,4,5-trichlorophenylcyanamide monomer (2,4,5-Cl₃pcydH)

This was prepared in an analogous manner to (2,3,5,6-Cl₄pcydH)₂. Only small deviations from this preparation were required. Crude yield = 17.46g (79%, based on initial reagents).

Dimer ligand

**N-(2,6-dichlorophenyl)-N'-cyano-N'-(2,6-dichlorophenyl)guanidine
(2,6-Cl₂pcydH)₂**

This was prepared in an analogous manner to (2,3,5,6-Cl₄pcydH)₂ except desulfurization of thiourea required 9 min. Crude yield = 24.19g (69%, based on initial reagents).

2,3-dichlorophenylcyanamide monomer (2,3-Cl₂pcydH)

The preparation was similar to that of (2,3,5,6-Cl₄pcydH)₂. The only change to the procedure was a reduced desulfurization temperature of 60° C.

Crude yield = 16.84g (91%, based on initial reagents).

4-chlorophenylcyanamide monomer (4-ClpcydH)

This was prepared in an analogous manner to (2,3,5,6-Cl₄pcydH)₂. Changes included: reduction of the desulfurization temperature to 56° C for 5 min. and the final filtrate was allowed sit in an ice bath (i.e. after glacial acetic acid addition) for ≈1 hr. before filtration. Crude yield = 12.50g (82%).

2-chlorophenylcyanamide monomer (2-ClpcydH)

The preparation was similar to 4-ClpcydH except the final product solution was filtered shortly after the addition of glacial acetic acid. Crude yield = 14.17g (93%).

2.2.2.3 Preparation of Phenylcyanamide Anion Thallium Salts

Caution: thallium is extremely toxic and therefore should be handled with the utmost care in a well ventilated area.

Thallium salt of the 2,3-dichlorophenylcyanamide anion Tl(2,3-Cl₂pcyd)

Neutral 2,3-dichlorophenylcyanamide monomer (1.0g, 5.0 mmol) was dissolved into 25 mL of boiling 50/50 acetone/water. A second solution comprised of thallium acetate (2.2g, 8.0 mmol) and 25 mL 50/50 acetone/water was added to the initial mixture slowly enough to allow for maintenance of the boil. Triethylamine (0.7g, 7.0 mmol) addition immediately followed. Boiling was continued a further 1 min. after which time the solution was set aside to cool. Long white needles crystallized from the cooling solution. These were collected, washed with water, then acetone, and allowed to air dry at least 24 h. Yield = 1.75g (83%).

Thallium salt of 2,3,5,6-tetrachlorophenylcyanamide anion $\text{Tl}(2,3,5,6\text{-Cl}_4\text{pcyd})$

This was prepared in similar fashion to $\text{Tl}(2,3\text{-Cl}_2\text{pcyd})$ except the dimer form of the neutral starting compound was used yielding a fine white material. Yield = 2.35g (55%).

Thallium salt of the 2,6-dichlorophenylcyanamide anion $\text{Tl}(2,6\text{-Cl}_2\text{pcyd})$

This was prepared in a similar fashion to $\text{Tl}(2,3,5,6\text{-Cl}_4\text{pcyd})$ except a greater molar excess of thallium acetate was employed yielding large irregular shaped plates. Yield = 2.20g (76%).

Thallium salt of the 2,4,5-trichlorophenylcyanamide anion $\text{Tl}(2,4,5\text{-Cl}_3\text{pcyd})$

A similar preparation was used with respect to $\text{Tl}(2,3\text{-Cl}_2\text{pcyd})$ except crystallization required that the solution sit covered overnight. A fine, fiber-like, white precipitate was obtained. Yield = 1.80g (72%).

Thallium salt of the 4-chlorophenylcyanamide anion $\text{Tl}(4\text{-Clpcyd})$

This was prepared in a similar manner to $\text{Tl}(2,3\text{-Cl}_2\text{pcyd})$ except for the following: twice the molar amount of starting reagents were used and crystallization took 2 h before it was judged complete. The solution yielded small white needles. Yield = 2.22g (58%).

Thallium salt of the 2-chlorophenylcyanamide anion $\text{Tl}(2\text{-Clpcyd})$

This was prepared in a similar fashion to $\text{Tl}(2,3\text{-Cl}_2\text{pcyd})$. A slightly greater

proportion of acetone to water was required to fully dissolve the neutral 2-chlorophenylcyanamide monomer. The final solution was allowed to sit overnight at room temperature before collection. Small white needles were obtained. Yield = 2.10g (55%).

2.2.3 Metal Complex Synthesis

2.2.3.1 (1,3-bis(2'-pyridylimino)isoindolato)nickel(II) bromide, (PVP)NiBr

1.0g (4.2 mmol) of nickel bromide hydrate and 50 mL of 1-butanol were combined together in a 250 mL beaker. This was gradually heated with magnetic stirring to $\approx 100^{\circ}\text{C}$ at which point full dissolution had occurred giving a pale green-orange solution. In a separate 100 mL beaker was placed 1.12g (3.7 mmol) of 1,3-bis(2'-pyridylimino)isoindoline and 50 mL of 1-butanol. Gradual heating produced a transparent lime green solution at $\approx 60^{\circ}\text{C}$. Both solutions were allowed to cool to 70°C . Triethylamine (0.38g, 3.7 mmol) was added to the nickel bromide solution which rapidly turned light green. Immediately after, the PVPH solution was added while vigorously stirring the combining mixtures. This resulted in a rapid color change to deep red-orange. The temperature was maintained at 70°C for 5 min. over which time a dark suspension began to emerge. With continued stirring, the suspension was cooled to room temperature. Filtering separated out a dark mossy green precipitate which was washed with fresh 1-butanol followed by anhydrous diethyl ether and finally air dried. Crude yield = 1.25g (77%).

Recrystallization was achieved by first adding the total crude yield to 75 mL

of nitrobenzene. The mixture was brought to a boil (deep orange solution) followed by a rapid filtering through a hot ($\approx 120^\circ\text{C}$) medium frit into a receiver flask of the same temperature. Slow cooling for ≈ 7 hrs. produced a dark green–orange crystalline material which was collected and successively washed with fresh nitrobenzene and anhydrous diethyl ether (i.e. until the odor of nitrobenzene was barely noticeable). This was vacuum dried at room temperature overnight. Yield = 349mg (28%, based on initial crude product). Anal. calcd. (%) for $\text{C}_{18}\text{H}_{12}\text{N}_5\text{BrNi}$: C, 49.47; H, 2.75; N, 16.03. Found (%): C, 49.27; H, 3.02; N, 15.60.

2.2.3.2 Preparation of the Neutral (1,3-bis(2'-pyridylimino)isoindolinato)nickel(II)(phenylcyanamido) Complexes

(2,6-dichlorophenylcyanamido)nickel(II)(1,3-bis(2'-pyridylimino)isoindolinato) (2,6- Cl_2pcyd)Ni(PVP)

0.47g (1.2 mmol) of (PVP)NiBr and 100 mL of 2-methoxyethanol were heated to a gentle boil with stirring. To the transparent orange solution was added 0.42g (1.2 mmol) of $\text{Ti}(2,6\text{-Cl}_2\text{pcyd})$. The reaction mixture immediately turned a deep brown–orange color with a coagulating suspension of whitish TiBr . The heat of solution was maintained at a temperature of 100°C for 30 min. followed by careful gravity filtration into a round bottom flask. The solvent was taken off under reduced pressure at 40°C until $\approx 25\%$ of the original volume remained. A dark precipitate could be seen emerging from solution and the amount increased upon cooling to room temperature. Small, bronze–orange needles were collected and washed with fresh 2-methoxyethanol.

The crude product was recrystallized in two successive ways. First, 12 mL of

nitrobenzene was added to the entire amount of crude with stirring. Full dissolution occurred once a boil was reached. The solution was removed from heat and sat overnight after which time a dark crystalline precipitate could be seen. Bronze crystals were collected, washed with anhydrous diethyl ether, and vacuum dried overnight at room temperature. Yield = 380mg (58%, based on starting reagents); this material was not quite pure according to elemental analysis.

Further purification was performed by applying diffusion recrystallization. 50 mg of nitrobenzene recrystallized material was dissolved into 17 mL of chloroform. When dissolution was judged complete (≈ 10 min.), the solution was filtered through a millipore[®] 0.45 μ m membrane into a chloroform rinsed 30 mL beaker. This was placed into a diffusion chamber (i.e. a 500 mL screw top jar) along with 40 mL of diethyl ether. After 2 days long, jagged, bronze-orange crystals had grown. Vacuum drying at 118°C proceeded for 16 hrs. Yield = 32mg (64%, based on nitrobenzene recry. material). Anal. calcd.(%) for $C_{25}H_{15}N_7Cl_2Ni$: C, 55.30; H, 2.76; N, 18.06. Found (%): C, 55.21; H, 2.89; N, 18.29.

**(2,3-dichlorophenylcyanamido)nickel(II)(1,3-bis(2'-pyridylimino)isoindolinato)
(2,3-Cl₂pcyd)Ni(PVP)**

The manner of preparation was similar to (2,6-Cl₂pcyd)Ni(PVP). The starting reagent amounts used were; 1.00g (2.29 mmol) (PVP)NiBr, 0.89g (2.28 mmol) Tl(2,3-Cl₂pcyd), and 110 mL 2-methoxyethanol. Evaporation under reduced pressure to $\approx 10\%$ of the original volume was required for precipitation to commence. Purification from nitrobenzene gave 430mg (35%, based on starting reagents). Diffusion recrystallization differed slightly by using 40 mg of material in 25 mL of chloroform and extending the time to 4 days in the diffusion chamber.

Dark orange–brown microcrystalline material was produced of yield = 21mg (53%). Anal. calcd.(%) for $C_{25}H_{15}N_7Cl_2Ni$: C, 55.30; H, 2.76; N, 18.06. Found (%): C, 54.95; H, 2.79; N, 18.43.

**(2-chlorophenylcyanamido)nickel(II)(1,3-bis(2'-pyridylimino)isoindolinato)
(2-Clpcyd)Ni(PVP)**

The manner of preparation was similar to (2,6-Cl₂pcyd)Ni(PVP). The procedure was altered slightly using the following amounts of starting reagents; 0.83g (1.90 mmol) of (PVP)NiBr, and 0.68g (1.91 mmol) of Tl(2-Clpcyd). Initial purification employed 19 mL of nitrobenzene yielding 500mg (52%) of dark brown precipitate. The diffusion recrystallization procedure used 50 mg and 18 mL chloroform to give crystals in the form of small dark orange plates. Yield = 21mg (42%). Anal calcd. (%) for $C_{25}H_{16}N_7ClNi$: C, 59.04; H, 3.15; N, 19.29. Found (%): C, 59.07; H, 3.20; N, 19.31.

**(4-chlorophenylcyanamido)nickel(II)(1,3-bis(2-pyridylimino)isoindoline)
(4-Clpcyd)Ni(PVP)**

A similar method of preparation was used with respect to (2,6-Cl₂pcyd)Ni(PVP). The following initial reagent amounts were employed: 0.50g (1.14 mmol) of (PVP)NiBr and 0.41g (1.15 mmol) of Tl(4-Clpcyd). Nitrobenzene recrystallization yielded 368mg (64%). From diffusion recrystallization 31mg (67%) of small dark brown–orange plates were obtained. Anal. calcd. (%) for $C_{25}H_{16}N_7ClNi$: C, 59.04; H, 3.15; N, 19.29. Found (%): C, 58.50; H, 3.05; N, 19.34.

(2,4,5-trichlorophenylcyanamido)nickel(II)(1,3-bis(2'-pyridylimino)isoindolinato) (2,4,5-Cl₃pcyd)Ni(PVP)

The manner of preparation was similar to (2,6-Cl₂pcyd)Ni(PVP) except 0.50g (1.14 mmol) of (PVP)NiBr and 0.49g (1.15 mmol) of Tl(2,4,5-Cl₃pcyd) represented the starting reagent amounts. The crude product displayed greater insolubility in 2-methoxyethanol therefore 150 mL were required. Evaporation under reduced pressure was not needed since the crude product precipitated out of the cooling reaction solution. Insolubility in chloroform prevented further purification beyond nitrobenzene recrystallization. Yield = 450mg (68%, vacuum dried at 118°C for 14 hrs.). Anal. calcd. (%) for C₂₅H₁₄N₇Cl₃Ni: C, 52.00; H, 2.43; N, 16.99. Found (%): C, 51.55; H, 2.50; N, 16.16.

(2,3,5,6-tetrachlorophenylcyanamido)nickel(II)(1,3-bis(2'-pyridylimino)isoindolinato) (2,3,5,6-Cl₄pcyd)Ni(PVP)

The preparation of this complex deviated significantly from the previous systems. The acute insolubility of the crude product in 2-methoxyethanol limited the use of this solvent after the initial reaction. The starting reagent amounts consisted of 0.50g (1.14 mmol) of (PVP)NiBr and 0.53g (1.16 mmol) of Tl(2,3,5,6-Cl₄pcyd). Both TlBr and the crude product precipitated from solution. This mixed precipitate was added to 50 mL of 1-methyl-2-pyrrolidinone and heated to 70°C. A dark orange solution resulted and was gravity filtered removing insoluble TlBr. While maintaining the filtrate at 70°C, 12 mL of water was gradually added. Cooling produced copious amounts of bright orange precipitate. Collection proceeded followed by successive washings of water, methanol, and anhydrous diethyl ether.

Recrystallization of the crude product was accomplished by first dissolving the material in 19 mL of boiling nitrobenzene. Slow cooling produced precipitate almost immediately. The hair-like, bright orange material was collected, washed with anhydrous diethyl ether, and vacuum dried at 118°C for 16 h. Yield = 295mg (42%, based starting reagents). Anal calcd. (%) for $C_{25}H_{13}N_7Cl_4Ni$: C, 49.00; H, 2.12; N, 16.00. Found (%): C, 49.02; H, 2.04; N, 15.98.

Note: of the various recrystallization techniques mentioned, not one was able to produce crystals suitable for crystallographic analysis. This was finally achieved for (4-Clpcyd)Ni(PVP) as a result of slow evaporation of a dilute chloroform solution of the complex. A millipore[®] filtered solution of $\approx 10^{-3}$ M (≈ 5 mL) was transferred to a new sample vial and sealed with its' accompanying plastic cap. Over a 3 week period chloroform evaporation reduced the volume by $\approx 50\%$ and large deep orange plate clusters had formed in the supersaturated solution.

2.2.3.3 Di(1,3-bis(2'-pyridylimino)isoindolato)nickel(II) Ni(PVP)₂

Method A: 64mg (0.11 mmol) of (2,4,5-Cl₃pcyd)Ni(PVP) was combined with 4 mL of dimethyl sulphoxide and heated gently. When the solution had warmed to $\approx 50^\circ\text{C}$, full dissolution occurred giving a deep red-orange color. This was allowed to cool and sit overnight. Red-orange microcrystalline material was collected, ether washed, and vacuum dried at 118°C for a period of 21 h. Yield = 48mg (67%, based on starting material). Anal. calcd. (%) for $C_{36}H_{24}N_{10}Ni$: C, 65.98; H, 3.66; N, 21.38. Found (%): C, 64.91; H, 3.75; N, 20.94.

Method B: 40mg (0.09 mmol) of (PVP)NiBr was dissolved into 20 mL of chloroform. This was gravity filtered into a clean 30 mL beaker. The green–orange filtrate was placed into a diffusion chamber along with 50 mL of anhydrous diethyl ether, sealed, and allowed to sit for 1 day. Red–orange crystals were collected, washed with ether, and vacuum dried at 118°C for 14 h. Yield = 41mg (69%, based on starting material). Anal. calcd. (%) for $C_{36}H_{24}N_{10}Ni$: C, 65.98; H, 3.66; N, 21.38. Found (%): C, 65.30; H, 3.65; N, 21.32.

2.2.3.4 (1,3-bis(2'-pyridylimino)isoindolinato)nickel(II) chloride monohydrate (PVP)NiCl·H₂O

This compound was prepared in a similar manner to Siegl [55]. Nickel chloride hexahydrate (1.75g, 7.36 mmol) and PVPH (1.10g, 3.68 mmol) were placed into a 125 mL erlenmeyer flask along with 60 mL of methanol. The bright orange–green suspension gradually turned moss green with stirring over a 24 h period. To ensure full deprotonation of PVPH, 1.81g (17.89 mmol) of triethylamine was added rapidly turning the suspension orange. Stirring continued for 45 min. after which time the material was collected, washed with copious amounts of methanol, and vacuum dried at room temperature for 12 h. Orange–green microcrystalline product yield = 1.15g (80%, based on starting reagents). Anal. calcd. (%) for $C_{18}H_{14}N_5OClNi$: C, 52.67; H, 3.41; N, 17.07. Found (%): C, 52.75; H, 3.08; N, 17.22.

**2.2.3.5 (1,3-bis(2'-pyridylimino)isoindolinato)nickel(II) acetate
(PVP)Ni(OAc)**

The preparation of this compound was identical to Siegl *et al* [55]. Nickel acetate tetrahydrate (0.50g, 2.0 mmol) and PVPH (0.30g, 1.0 mmol) were stirred for 24 h in 15 mL of methanol to give green-yellow needles. These were filtered, methanol washed, and vacuum dried at room temperature overnight. Yield = 350mg (84%, based on starting reagents). Anal. calcd. (%) for $C_{20}H_{15}N_5O_2Ni$: C, 57.73; H, 3.61; N, 16.84. Found (%): C, 57.98; H, 3.50; N, 17.12.

**2.2.3.6 (1,3-bis(2'-pyridylimino)isoindolinato)nickel(II)(isothiocyanato)
(PVP)Ni(NCS)**

Metathesis of (PVP)NiBr (0.22g, 0.51 mmol) and potassium thiocyanate (0.04g, 0.46 mmol) in 15 mL of methanol took place over a 24 hr. period. Triethylamine (2.03g, 20.06 mmol) was also added to prevent re-protonation of coordinated PVP. During this period of time the initial dark orange solution changed to a green-yellow suspension. Golden yellow needles were isolated and successively washed with methanol and anhydrous diethyl ether followed by vacuum drying for 12 h. Yield = 151mg (87%, based on starting reagents). Anal. calcd. (%) for $C_{19}H_{12}N_6SNi$: C, 54.97; H, 2.89; N, 20.25. Found (%): C, 54.54; H, 2.83; N, 20.46.

2.2.3.7 (1,3-bis(2'-pyridylimino)isoindolinato)nickel(II)(azido) (PVP)Ni(N₃)

Preparation of this compound was similar to (PVP)Ni(NCS) except that the

starting reagents were 0.23g (0.52 mmol) of (PVP)NiBr and 0.03g (0.53 mmol) sodium azide and triethylamine was not used. Recrystallization was achieved by dissolving 100mg of the bright orange crude into 15 mL of chloroform. The resulting deep red solution was carefully decanted from the small amount of insoluble green-orange material which had settled out. The former was filtered through a millipore[®] 0.45 μ m membrane and evaporated under reduced pressure until deep red needles could be seen coming out of solution. These were filtered, diethyl ether washed, and dried under high vacuum overnight. Yield = 81mg (81%, based on starting crude). Anal. calcd. (%) for C₁₈H₁₂N₈Ni: C, 54.18; H, 3.01; N, 28.09. Found (%): C, 53.66; H, 3.04; N, 27.62.

2.2.3.8 (1,3-bis(2'-pyridylimino)isoindolato)zinc(II) acetate (PVP)Zn(OAc)

The method of synthesis was similar to that of Siegl *et al* [55]. Zinc acetate dihydrate (0.88g, 4.0 mmol) was first dissolved in 30 mL of methanol followed by rapid addition of PVPH (0.59g, 2.0 mmol). The fluorescent green suspension was stirred overnight over which time it transformed to a bright yellow-green material. This was filtered, washed with methanol, and vacuum dried for 7 h. Crude yield = 820mg (97%, based on starting reagents).

The method of recrystallization involved adding 600mg of crude to 30 mL of nitrobenzene and heating to a boil. This was quickly filtered through a medium frit (pre-heated to $\approx 120^\circ\text{C}$) and allowed to slowly cool. A fluorescent yellow-green precipitate was obtained which was collected, washed with diethyl ether, and vacuum dried at 118°C overnight. Anal. calcd. (%) for C₂₀H₁₅N₅O₂Zn: C, 56.82; H, 3.55; N, 16.57. Found (%): C, 56.98; H, 3.63; N, 16.44.

2.2.3.9

(1,3-bis(2'-pyridylimino)isoindolino)copper(II)(2,3-dichlorophenylcyanamido)
(PVP)Cu(2,3-Cl₂pcyd)•0.5H₂O

The method of synthesis was analogous to the general preparation of (1,3-bis(2-pyridylimino)isoindoline)nickel(II)(phenylcyanamide) complexes. (PVP)CuBr [53] (0.50g, 1.13 mmol) and 80 mL of 2-methoxyethanol were heated with stirring to $\approx 100^{\circ}\text{C}$ giving a greenish-brown solution. At this point Tl(2,3-Cl₂pcyd) (0.44g, 1.13 mmol) was added which immediately turned the solution deep green with a fine suspension of whitish TlBr. The heat was maintained for 5 min. followed by hot gravity filtration. The filtrate was evaporated under reduced pressure until $\approx 20\%$ of the original volume remained. Cooling to room temperature yielded green-yellow microcrystalline precipitate.

Recrystallization was achieved by dissolving 40mg of crude into 18 mL of chloroform, stirring for 2 h, and filtering through a millipore[®] 0.45 μm membrane into a clean 30 mL beaker. This was placed in a diffusion chamber with 65 mL of diethyl ether; after 1 day small, pale green-yellow needles had formed. These were collected, washed with anhydrous diethyl ether, and vacuum dried overnight. Yield = 33mg (82%, based on initial crude). Anal. calcd. (%) for C₂₅H₁₆N₇O_{0.5}Cl₂Cu: C, 53.93; H, 2.87; N, 17.62. Found (%): C, 53.88; H, 2.83; N, 17.93.

2.2.4 Physical Measurements

2.2.4.1 Infrared Spectra

Infrared spectral analysis was carried out using a Perkin–Elmer 1600 Series FTIR spectrophotometer. An inter-connected Hewlett–Packard Colorpro plotter provided hardcopy reproductions of the recorded data. All samples were prepared within a KBr matrix (oven dried at 120°C) in disc form and referenced against an air background (i.e. run just prior to the sample).

2.2.4.2 Proton Nuclear Magnetic Resonance (NMR) Spectra

^1H NMR spectroscopy was performed on either a Varian XL200 (Gemini) or XL300 NMR spectrometer at ambient temperature. Hardcopies were obtained from an online Hewlett–Packard 7550 Colorpro plotter and an instrumentally incorporated plotting system, respectively. Sample solubility and the paramagnetic nature of some complexes determined which instrument was more appropriate.

Samples (vacuum dried) were dissolved into CDCl_3 or d_6 -dimethyl sulphoxide and analyzed within a 5 mm NMR tube. Standard sample preparation was performed with 2–3mg unless solubility was a limiting factor. In these cases a saturated solution was first prepared by stirring an excess of compound with ≈ 0.75 mL of appropriate deuterated solvent. The solution was filtered through a dispo-pipette plugged with glass wool and allowed to flow directly into a NMR tube. Chemical shifts were derived from solvent peak positions or from an internal TMS reference.

2.2.4.3 Electronic Absorption Spectroscopy

General Description

Electronic Spectra were recorded on a Cary 5 UV-vis/NIR spectrophotometer interfaced with a Raven 386/16 computer online to both a Hewlett-Packard Laserjet IID printer and Colorpro plotter. Matched quartz or glass cells were used for sample analysis; use of the latter was restricted when scans <300 nm were required. Prior background correction using the appropriate medium was carried out for each run.

Quantitative spectra required knowledge of precise solution concentrations. To accomplish this, samples were weighed to five decimal places on either a Sartorius Research R160P or Mettler AE163 enclosed top loading balance. Meticulous cleaning of volumetric flasks guarded against interference from soluble impurities. The general procedure for cleaning involved successive overnight sittings in concentrated nitric acid and water followed by thorough water rinsing. A final rinse of methanol and acetone followed by air drying completed the procedure. The flasks were rinsed with the appropriate solvent just prior to use.

Solid absorbance spectra were carried out using the same apparatus except the reference beam was attenuated with a Riik IT-04 attenuator. Samples were finely ground in an agate mortar and prepared as Nujol mulls. Analysis was performed on a thin film situated between two KBr plates.

Temperature Variable Apparatus

Variance of the sample cell temperature was achieved by using a temperature thermostated cell holder. The holder used was for a Perkin-Elmer Lambda 4B

spectrophotometer in absence of a similar accessory for the Cary 5. An elevated base and subsequent beam alignment was required to modify the cell holder. The temperature was controlled using a Haake D8-G circulatory bath system which contained pure water or a water/ethylene glycol mixture. The rubber tubing which connected the cell holder and circulatory bath was insulated with high density foam tape. The tubing prevented complete closure of the cell compartment and therefore the area was protected from stray light with a dark cloth. Temperature of the cell solution was precisely monitored with a model 425C YSI Co. tele-thermometer/thermocouple assembly. After each temperature change, the cell temperature was allowed to stabilize before scanning. At temperatures below 15°C, the cell compartment was continually flushed with a dry argon stream to prevent moisture condensation on the cell windows. When using more volatile solvents at higher temperatures, the meniscus of the cell solvent level was marked to assure evaporation was not an erroneous contributor to extinction coefficient calculation.

Variable pH Apparatus

Qualitative spectra for pH variable, methanol sample solutions were obtained. A Fisher Accumet[®] pH meter, model 620, was standardized with pH=4.00±0.01 buffer solution. Before each reading of the cell pH (i.e. the probe was inserted directly into the cell), the instrument was first checked with the buffer. The cell was filled ~60% to allow for the gradual addition of dilute HCl/ethanol.

2.2.4.4 Conductivity

Conductance measurements were carried out on $\approx 10^{-3}$ M solutions. The temperature was thermostated at $25.0 \pm 0.1^\circ\text{C}$ by means of a double-walled glass container connected to a Haake D8-G temperature variable bath and circulator. The resistance measurements were made with a conductivity bridge manufactured by Industrial Instruments Inc., model RC16B2 at a frequency of 1000 Hz (changing the frequency had no noticeable effect on the resistance reading). To complete the circuit electrodes consisting of parallel platinum plates (1 cm^2 surface area separated by $\approx 1\text{ cm}$) were submerged directed into the thermostated solution. The cell constant was calculated to be $0.3164 \pm 0.0017\text{ cm}^{-1}$. Conductivity of the THF and DMSO solvents used had resistance values $> 2.000 \times 10^6$ ohms and thus had negligible contributions to the overall conductivity values. The molar conductivities of potassium chloride, tetrabutylammonium hexafluorophosphate, and previously known 1:1 electrolytes provided suitable reference.

2.2.4.5 X-Ray Structure Determination

Credit for the crystal structure determination goes to Corinne Bensimon at the National Research Council (NRC) of Canada. For single crystal of (PVP)Ni(2-Clpcyd) complex with dimensions $0.3\text{mm} \times 0.3\text{mm} \times 0.05\text{mm}$, measurement of the diffracted intensities were made on a Nonius diffractometer using Cu K α radiation with a nickel filter. Data was collected at 23°C using omega 2θ scan technique and corrected for absorption as well as Lorentz-polarization effects [92]. No decay of the crystal was observed.

The structure was solved by direct methods including a final cycle

full-matrix least-squares refinement. Anisotropic refinement was required for the nickel, chloride, and nitrogen atoms whereas all other non-hydrogen atoms were refined isotropically. The hydrogen atom positions were calculated. The absolute structure was determined using the approach developed by Lepage, Gabe, and Gainsford [93]. All the computations were performed using the NRCVAX crystallographic software package [94].

2.2.4.6 Elemental Analysis

The elemental analysis of all samples were performed by Canadian Microanalytical Services Ltd.. Notation of the analytically calculated and experimentally found percent values for C, H, and N are located at the end of the appropriate compound preparation in section 2.2.3.

CHAPTER 3

Physical Characterization of the Ligands and (PVP)Ni(pcyd) Complexes

3.1 Introduction

Four coordinate tetraammine Ni(II) complexes (NiN_4^{2+}) are an interesting class of systems which exhibit a wide range of intra and intermolecular phenomena which ranges from geometrical perturbation to solvent coordination [36–39,56]. Ni(II) (d^8) has a strong tendency to form diamagnetic square planar systems as a consequence of total spin pairing of d orbital electrons when bound to sufficiently strong field ligands [57b]. Nishida and Kida [25] have shown that if the ligands possess significant π donating ability, tetrahedral distortion generally occurs resulting in a paramagnetic Ni(II) complex.

The following discussion is meant to provide rationale toward the elucidation of the molecular structure of a series of neutral Ni(II) N_4 complexes illustrated in Figure 3.1 using X-ray crystallography and the spectroscopies of electronic absorption, ^1H NMR, and infrared. Both solution state, and to a lesser extent, solid state properties are explored.

($R_x = 2\text{-Cl}, 4\text{-Cl}, 2,3\text{-Cl}_2, 2,6\text{-Cl}_2, 2,4,5\text{-Cl}_3, 2,3,5,6\text{-Cl}_4$)

Figure 3.1 General structure of the (PVP)Ni(pcyd) complexes.

The pcyd[⊖] ligand possesses π donating ability which can be "tuned" by the substituents on the phenyl ring. It is therefore of interest to see how these electronic nuances manifest themselves on the geometrical and magnetic properties of the neutral (PVP)Ni(II)(pcyd) systems.

3.2 Data

Infrared spectroscopy

Diagnostically, the infrared region reveals the presence of both coordinated anionic monodentate (i.e. pcyd[⊖]) and tridentate (i.e. PVP[⊖]) ligand in the six (PVP)Ni(pcyd) complexes. Relevant vibrational frequencies for the PVP anion are listed in Table 3.1 along with appropriate comparative data. The corresponding spectra for the (PVP)Ni(pcyd) complexes are presented in Figures 3.2 to 3.8.

Table 3.1 IR Data for PVP Anion of the (PVP)Ni(pcyd) Complexes†

pcyd anion complex	PVP [⊖] $\nu_{\text{C}=\text{N}}$	pyridyl skeletal vibrations
2-Clpcyd	1637(w)	1576, 1532, 1482, 1460, 1433(m)
4-Clpcyd	1646(w)	1585, 1530, 1488, 1459, 1432(m)
2,6-Cl ₂ pcyd	1637(w)	1574, 1521, 1490, 1463, 1430
2,3-Cl ₂ pcyd	1638(w)	1575, 1532, 1459, 1432(m)
2,4,5-Cl ₃ pcyd	1648(w)	1588, 1533, 1474, 1461, 1433(m)
2,3,5,6-Cl ₄ pcyd	1646(w)	1587, 1534, 1501(m), 1460, 1434(m)

Comparative Data

(PVP)NiBr	1647(w)	1585, 1522, 1466, 1431(m)
PVPH	1626	1579, 1533, 1457, 1430

† KBr discs, in cm⁻¹, peaks are strong unless indicated otherwise. (w) denotes weak, (m) denotes medium.

Figure 3.2 Infrared spectrum (KBr) for (PVP)Ni(2,6-Cl₂pcyd).

Figure 3.3 Infrared spectrum (KBr) for (PVP)Ni(2,3-Cl₂pcyd).

Figure 3.4 Infrared spectrum (KBr) for (PVP)Ni(4-Clpcyd).

Figure 3.5 Infrared spectrum (KBr) for (PVP)Ni(2,4,5-Cl₃pcyd).

Figure 3.6 Infrared spectrum (KBr) for (PVP)Ni(2,3,5,6-Cl₄pcyd).

Figure 3.7 Infrared spectrum (KBr) for (PVP)Ni(2-Clpcyd).

Figure 3.8 Infrared spectrum (KBr) for 1,3-bis(2'-pyridylimino)isoindoline, PVPH.

Electronic Absorption Spectroscopy

The assignments of quantitative transitions observed in the 300–700 nm range for the (PVP)Ni(pcyd) complexes (i.e. Figures 3.9 through 3.14) are listed in Table 3.2. Expansion of the 600–700 nm region allows the weak *d–d* band to be more readily observed. Relevant comparative data is also listed which includes (PVP)Zn(OAc) and PVPH (i.e. Figure 3.15). The qualitative diffuse reflectance spectrum for (PVP)Ni(2-Clpcyd) is shown in Figure 3.16 where it is contrasted with the analogous CHCl₃ solution spectra.

Proton NMR Spectroscopy

The ¹H NMR data obtained is presented in Tables 3.3a and 3.3b along with the proton numbering scheme in Figure 3.17. Comparative data is also included. Spectra for (PVP)Ni(2,6-Cl₂pcyd) (i.e. CDCl₃ and *d*₆-DMSO (inset)), (PVP)Ni(4-Clpcyd) (i.e. CDCl₃), and (PVP)Ni(2-Clpcyd) (i.e. CDCl₃) are shown in Figures 3.18, 3.19, and 3.20, respectively. PVPH and (PVP)Zn(OAc) ¹H NMR can be found in Appendix 3 (Figures A1 and A2, respectively).

X-Ray Crystallography

Crystallographic data for (PVP)Ni(2-Clpcyd) is extensive. Crystal structure data is listed in Table 3.4. An ORTEP structural drawing is displayed in Figure 3.21 including the atomic numbering scheme. Table 3.5 contains dihedral angles between ideal planes within the molecule. Table 3.6 lists selected bond lengths and angles. A stereoview of the unit cell is illustrated in Figure 3.22. The atomic parameters in terms of Cartesian coordinates of the central molecule are listed in Tables 3.7 and 3.8.

Table 3.2 Electronic Absorption Data for the (PVP)Ni(pcyd) Complexes†‡

pcyd anion complex	$\pi-\pi^*$	$d-d$ transitions
4-Clpcyd	≈ 476 (≈ 6600) 349 (18100)	629 (789), [15900]
2,6-Cl ₂ pcyd	476 (7170) 348 (20220)	625 (551), [16000]
2,3-Cl ₂ pcyd	473 (7390) 348 (20080)	620 (557), [16120]
2,4,5-Cl ₃ pcyd	472 (7020) 346 (19140)	621 (500), [16090]
2,3,5,6-Cl ₄ pcyd	470 (7500) ^c 346 (19400) ^c	615 (700) ^c , [16250]
2-Clpcyd	≈ 476 (≈ 6800) 348 (18960)	627 (650), [15940]
2-Clpcyda	508, 353	—

Comparative Data

(PVP)Zn(OAc) ^b	440 (15260) 414 (19210) 391 (13190)	—
PVPH ^b	410 (9730) 387 (17010) 367 (15660)	—
1,3-diiminoisoindolined	256 (11200) 308 (3300)	—
2-aminopyridined	295 (8000)	—

† In CHCl₃ unless stated otherwise, 10⁻⁴–10⁻⁵ M. ‡ In nm, parentheses: (), ϵ in M⁻¹cm⁻¹; [], band energy max. in cm⁻¹. ^a Qualitative nujol mull between NaCl plates, attenuated for minimum reflection contribution. ^b More $\pi-\pi^*$ bands in UV region. ^c Non-zero baseline, as a result of marginal solubility in CHCl₃. ϵ corrected for estimated baseline contribution. ^d In absolute methanol.

Figure 3.9 Visible electronic absorption spectrum of (PVP)Ni(4-Clpcyd) in CHCl_3 . The complex concentration is 1.03×10^{-4} M.

Figure 3.10 Visible electronic absorption spectrum of (PVP)Ni(2-Clpcyd) in CHCl_3 . The complex concentration is 8.18×10^{-5} M.

Figure 3.11 Visible electronic absorption spectrum of (PVP)Ni(2,6-Cl₂pcyd) in CHCl₃. The complex concentration is 8.77×10^{-5} M.

Figure 3.12 Visible electronic absorption spectrum for (PVP)Ni(2,3-Cl₂pcyd) in CHCl₃. The complex concentration is 1.13×10^{-4} M.

Figure 3.13 Visible electronic absorption spectrum for (PVP)Ni(2,4,5-Cl₃pcyd) in CHCl₃. The complex concentration is 8.32×10^{-5} M.

Figure 3.14 Visible electronic absorption spectrum for (PVP)Ni(2,3,5,6-Cl₄pcyd) in CHCl₃. The complex concentration is 6.54×10^{-5} M.

Figure 3.15 Visible electronic absorption spectra for PVPH (dashed line) and (PVP)Zn(OAc) (solid line) in CHCl_3 . The concentrations are 5.35×10^{-5} M for the former and 5.20×10^{-5} M for the latter.

Figure 3.16 Visible electronic absorption spectra (8.18×10^{-5} M CHCl_3 solution, solid line and 9.59×10^{-5} M THF solution, dash-dot line) and qualitative diffuse reflectance spectra (solid in nujol mull, dashed line) for (PVP)Ni(2-Clpcyd).

Table 3.3a ^1H NMR Data of the (PVP)Ni(pcyd) Complexes and Comparative Data[†]

Compound	H ₁	H ₂	H ₃	H ₄	H ₅	H ₆	H ₇	H ₈
(in CDCl_3)								
PVPH ^a	8.63	7.13	7.77	7.47	8.08	7.66	—	—
4-Clpcydg ^h	9.27 ^c	7.23	7.87	$\approx 7.6^{\text{d}}$	8.02	7.62	7.03	6.54
2,6-Cl ₂ pcydg	8.87	$\approx 7.0^{\text{e}}$	7.76	7.37	7.97	7.57	7.05	6.56
2-Clpcydg ^h	—	≈ 7.3	≈ 8.3	≈ 7.9	8.29	7.92	7.08 ⁱ	6.65 ^j
(in d_6 -DMSO)								
PVPH ^a	8.74	7.29	7.93	7.46	8.05	7.75	—	—
(PVP)Zn(OAc)	8.60	7.21	$\approx 7.9^{\text{b}}$	7.43	7.90	7.62	—	—
2,6-Cl ₂ pcydg ^{fg}								

[†] Values in ppm (median calculated if proton coupled) referenced against deuterated solvent peak. Proton numbering correlates with positions in figures. ^a Pyrrole amine proton $\delta = 14.00$ ppm. ^b Underneath H₅ quartet. ^c Poorly resolved. ^d Underneath H₆ quartet. ^e Underneath H₇ doublet. ^f Paramagnetic broadening and shifting made peaks at 12.41, 7.31, and 6.16 ppm difficult to assign. No other complex peaks downfield up to 150 ppm. ^g Anion complexed to [(PVP)Ni(II)]⁺ moiety. ^h Progressive broadening and shifting made peak assignment difficult. ⁱ Most likely combined with H₁₀. ^j Most likely combined with H₉.

Figure 3.17 Proton numbering schemes:

- a) free PVPH and Ni(II) complexed PVP^- ligand
 b) Ni(II) complexed pcyd anion

Table 3.3b ^1H NMR Data of Other Mono-Anion (L) (PVP)NiL Complexes[†]

L anion	H ₁	H ₂	H ₃	H ₄	H ₅	H ₆
Diamagnetic^c						
N ₃	8.72	7.11	7.80	7.39	8.01	7.61
NCS [‡]	8.72	7.11	7.81	7.41	7.97	7.59
Paramagnetic^d						
Cl ^{a,c}	8.02, 7.64					
Br ^e	13.72, $\approx$ 13.5, $\approx$ 12.7					
PVP	13.70, $\approx$ 13.5, $\approx$ 12.7					
OAc ^b	13.73, $\approx$ 13.4, $\approx$ 12.6, 8.21, 7.82					

[†] Values in ppm, CDCl₃ spectra. [‡] Nitrogen bound. ^a Elemental analysis indicated 1 H₂O associated with each complex molecule. ^b OAc = O₂CCH₃ anion. ^c Coupling pattern may be observed in Figures 3.25 and 3.26. ^d Paramagnetic broadening and shifting made assignment difficult. All values represent the center point of a broad peak. No other peaks were observed up to 150 ppm downfield. ^e Spectra shown in Figures 3.27 and 3.28.

Figure 3.18 ^1H NMR spectra of $(\text{PVP})\text{Ni}(2,6\text{-Cl}_2\text{pcyd})$ in a saturated CDCl_3 solution (inset in $d_6\text{-DMSO}$).

Figure 3.19 ^1H NMR spectrum of $(\text{PVP})\text{Ni}(4\text{-Clpcyd})$ in a saturated CDCl_3 solution.

Figure 3.20 ^1H NMR spectrum of $(\text{PVP})\text{Ni}(2\text{-Clpcyd})$ in a saturated CDCl_3 solution.

Figure 3.21 ORTEP drawing of the complex (PVP)Ni(2-Clpcyd). The diagram includes the appropriate numbering scheme. The hydrogens have been excluded for clarity.

Table 3.4 Crystal Structure Data for (PVP)Ni(2-Clpcyd)

empirical formula	NiN ₇ ClC ₂₅ H ₁₆
formula weight	508.61
crystal shape	plate
crystal system	monoclinic
space group	A a
lattice parameters (Å)	a, 7.7824(7); b, 28.2194(23); c, 9.8306(12)
β (deg.)	103.720(8)
volume, Å ³	2097.3(4)
Z	4
cal. density (g/cm ³)	1.611
cryst. dim. (mm ³)	0.30 × 0.30 × 0.05
radiation (λ , Å)	Cu K α_1 (1.540 56) with Ni filter
$m\mu$ (mm ⁻¹)	2.77
hkl ranges	-7 ≤ h ≤ 7, 0 ≤ k ≤ 27, 0 ≤ l ≤ 9
2 θ max.	99.7
no. of reflns. measd.	3343
no. of unique reflns	2142
no. of reflns with I > 2.5 σ	2111
trans. factor range	0.397111 – 0.621227
R factor†	0.061
R _w factor‡	0.064
Goodness-of-fit	13.24

† $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$; $R_w = \text{sqroot}(\Sigma(w|F_o| - |F_c|)^2 / \Sigma w|F_o|^2)$

Table 3.5 Crystal Structure Data† for (PVP)Ni(2-Clpcyd): Dihedral Angles

Equations of Selected Least-Squares Planes ^b						
plane no.		plane atoms				
1	Ni-N1-N3-N5-N6					6.967x+7.24y+1.39z=7.34
2	N1-C1-C2-C3-C4-C5					6.54x+1.85y+3.17z=4.00
3	N5-C14-C15-C16-C17-C18					6.870x-4.25y+2.19z=1.61
4	C8-C9-C10-C11-C12-C13					6.81x+1.45y+2.57z=5.20
5	C20-C21-C22-C23-C24-C25					0.30x+19.53y+6.79z=17.59

Distance of Atoms to the Least-Squares Plane, Å								
1	Ni	0.000(3)	N1	0.250(16)	N3	-0.239(16)	N5	0.256(16)
	N6	-0.266(17)						
5	C20	-0.003(19)	C21	0.015(20)	C22	-0.018(21)	C23	0.004(23)
	C24	0.012(14)	C25	0.011(23)				

Angle deviation on Nitrogens from Least-Squares Coordination Plane, deg. [†]								
1	Ni	0.0	N1	7.4	N3	-7.6	N5	7.5
	N6	-8.1						

Dihedral Angle Between Planes A and B, deg. ^a					
A	B	Angle	A	B	Angle
1	2	21.3(5)	2	4	7.7(5)
1	3	24.0(5)	2	5	68.0(5)
1	4	13.6(5)	3	4	11.8(5)
1	5	61.6(5)	3	5	75.5(5)
2	3	7.6(5)	4	5	65.3(6)

† Estimated standard deviations in parentheses. † Calculated using distance of nitrogen from the least-squares plane and Ni-N bond lengths in the equation $\sin \theta = \text{opposite/hypotenuse}$ of a right angle triangle. ^a Planes 2 (N1-C1-C2-C3-C4-C5), 3 (N5-C14-C15-C16-C17-C18), and 4 (C8-C9-C10-C11-C12-C13) are all essentially planar. ^b Estimated standard deviations range from 0.017 to 0.19 for equation values.

Table 3.6 Crystal Structure Data† for (PVP)Ni(2-Clpcyd)
Selected Bond Lengths and Angles

Bond Lengths, Å			
Ni-N1	1.950(10)	N6-C19	1.186(22)
Ni-N3	1.817(11)	N7-C20	1.350(20)
Ni-N5	1.963(10)	N7-C19	1.289(21)
Ni-N6	1.890(12)		
Bond Angles, deg.			
N1-Ni-N5	165.4(5)	Ni-N6-C19	163.5(11)
N1-Ni-N3	88.4(5)	N6-C19-N7	169.3(16)
N1-Ni-N6	92.4(4)	C19-N7-C20	118.9(13)
N3-Ni-N5	92.4(4)	N5-Ni-N6	90.5(5)
N3-Ni-N6	165.5(5)		

† Estimated standard deviations in parentheses

Table 3.7 Calculated Atomic Parameters and B_{iso} for the Hydrogen Atoms of
(PVP)Ni(2-Clpcyd)

Atom	X	Y	Z	B_{iso}
H1	0.443	0.606	0.732	3.9
H2	0.527	0.578	0.514	4.0
H3	0.515	0.496	0.455	4.1
H4	0.438	0.436	0.618	4.0
H9	0.157	0.438	1.366	3.7
H10	0.177	0.352	1.358	4.5
H11	0.251	0.310	1.153	4.0
H12	0.332	0.360	0.967	4.1
H15	0.136	0.587	1.414	3.7
H16	0.189	0.671	1.422	3.7
H17	0.290	0.710	1.221	4.3
H18	0.318	0.661	1.022	3.5
H22	-0.348	0.769	0.383	4.7
H23	-0.582	0.738	0.496	5.9
H24	-0.0499	0.673	0.677	5.3
H25	-0.194	0.665	0.743	4.6

Figure 3.22 3-Dimensional stereoview of the unit cell for the complex (PVP)Ni(2-Clpcyd). Note the numbering assignment for the 4 molecules contained in the unit cell on the right. The positions of the molecules 2, 3, and 4 relative to molecule 1 in terms of Cartesian coordinates are $(x+0.5, y+0.5, z+0.5)$, $(x+0.5, -y, z)$, and $(x+1.0, -y+0.5, -z)$, respectively.

Table 3.8 Atomic Parameters and $B_{iso}^{\dagger\dagger}$ for (PVP)Ni(2-Clpcyd)

Atom	X	Y	Z	B_{iso}
Ni	0.27954	0.56432(7)	0.93633	3.06(11)
Cl	0.0118(7)	0.75333(14)	0.4316(5)	5.59(24)
N1	0.3738(17)	0.5354(4)	0.7881(10)	3.1(6)
N2	0.3458(16)	0.4531(4)	0.8453(11)	3.2(6)
N3	0.2879(17)	0.5067(4)	1.0178(11)	3.2(6)
N4	0.1868(16)	0.5284(4)	1.2301(11)	3.1(6)
N5	0.2492(17)	0.5978(4)	1.1019(10)	3.1(6)
N6	0.2081(19)	0.6196(4)	0.8269(12)	3.7(7)
N7	0.0805(19)	0.6773(40)	0.6441(11)	4.0(7)
C1	0.4319(19)	0.5681(5)	0.7030(15)	3.5(3)
C2	0.4842(20)	0.5533(5)	0.5826(15)	3.8(3)
C3	0.4772(21)	0.5064(5)	0.5506(15)	3.7(3)
C4	0.4336(20)	0.4726(5)	0.6379(15)	3.7(3)
C5	0.3828(21)	0.4885(5)	0.7657(16)	2.8(3)
C6	0.3034(21)	0.4640(5)	0.9656(13)	3.1(8)
C7	0.2291(22)	0.4976(5)	1.1468(15)	3.4(8)
C8	0.2268(19)	0.4471(4)	1.1684(15)	3.2(3)
C9	0.1976(20)	0.4204(5)	1.2779(15)	3.7(3)
C10	0.2054(21)	0.3715(5)	1.2726(15)	4.3(4)
C11	0.2460(21)	0.3490(5)	1.1569(15)	3.7(3)
C12	0.2885(18)	0.3762(5)	1.0521(14)	3.3(3)
C13	0.2739(19)	0.4228(5)	1.0564(14)	2.9(3)
C14	0.2075(19)	0.5751(5)	1.2152(15)	3.0(3)
C15	0.1816(20)	0.6040(5)	1.3292(15)	3.2(3)
C16	0.2104(18)	0.6507(4)	1.3355(14)	3.3(3)
C17	0.2627(21)	0.6718(5)	1.2207(15)	4.3(4)
C18	0.2788(19)	0.6439(5)	1.1070(14)	3.1(3)
C19	0.1342(21)	0.6458(5)	0.7424(15)	3.3(8)
C20	-0.0920(20)	0.6903(5)	0.6099(14)	3.2(3)
C21	-0.1480(20)	0.7264(4)	0.5040(14)	3.4(3)
C22	-0.3161(21)	0.7424(5)	0.4660(15)	4.2(4)
C23	-0.4451(23)	0.7232(5)	0.5247(17)	5.2(4)
C24	-0.3968(23)	0.6884(5)	0.6267(16)	4.9(4)
C25	-0.2238(22)	0.6721(5)	0.6637(16)	4.0(3)

† Estimated standard deviations in parentheses. ‡ Hydrogens not included in this table.

3.3 Results and Discussion

3.3.1 1,3-bis(2'-pyridylimino)isoindoline Ligand

Identification of PVPH was accomplished using IR, ^1H NMR, and electronic absorption spectroscopy. Figure 3.8 shows the IR spectrum of PVPH and the corresponding peak energies are listed in Table 3.1. A very strong $\nu_{\text{C}=\text{N}}$ occurs in the 1600–1650 cm^{-1} region and four moderate–strong bands appear in the 1600–1400 cm^{-1} area which can be ascribed to pyridyl skeletal vibrations [48]. A similar band pattern is observed for a variety PVPH ligands with varying substitution on the pyrrole and pyridyl ring systems [48,52–55]. The presence of $\nu_{\text{N-H}}$ confirmed the protonated nature of the pyrrole amine.

The planar PVPH ligand was expected to give a ^1H NMR spectrum (Appendix 3, Figure A1) containing 7 chemical shifts as indicated by the equivalency of protons on either side of the mirror plane denoted by the y-axis shown in Figure 3.17 (Table 3.3 for shift values) [48]. For the pyridyl protons the order of increasing downfield shift was $\text{H}_1 > \text{H}_3 > \text{H}_4 > \text{H}_2$ based on the similar trend seen in a large number of metal bound pyridyl ring–alkylated $\text{PVP}^\ominus$ systems [48,51,52,55]. The phenyl protons are ordered $\text{H}_5 > \text{H}_6$ with respect to the degree of downfield shift. It has been suggested that deshielding of H_5 by the nearby imino π -electron cloud is responsible for this order [52].

The relative positions of pyridyl and phenyl protons were determined by ^1H – ^1H vicinal and longer range coupling. The phenyl protons stood out as well resolved doublet of doublets with identical coupling values. The pyrrole proton had a larger downfield shift and integration of one relative to all other protons which had integrations for 2 protons. The remaining pyridyl shifts (i.e. $\text{H}_1 > \text{H}_3 > \text{H}_4 > \text{H}_2$) are labelled according to the predescribed order.

The electronic absorption spectrum (Figure 3.15) and corresponding band maxima in Table 3.2 reflect the $\pi-\pi^*$ band pattern similarly observed in literature for metal bound PVP[⊖] [44,48,52,54]. The multiple band structure is partially attributed to vibrational fine structure inherit to aromatic systems [58]. Increasing conjugation of π systems generally leads to bathochromic shifting of $\pi-\pi^*$ bands which explains the coloured nature of this ligand (i.e. tails into the visible range). A more complete analysis of $\pi-\pi^*$ transition origins is discussed in Chapter 4 (see section 4.3.2).

3.3.2 Thallium Salts of the Phenylcyanamide Anion Ligands Tl(pcyd)

Characterization of the anion ligand thallium salt is straightforward in that IR spectroscopy in conjunction with literature comparisons is definitive proof of its' presence. The IR spectrum is distinctive from both pcydH ($\nu_{\text{C}\equiv\text{N}}$, $\approx 2250\text{ cm}^{-1}$) or (pcydH)₂ ($\nu_{\text{C}\equiv\text{N}}$, $\approx 2250\text{ cm}^{-1}$; $\nu_{\text{C}=\text{N}}$, $\approx 1670\text{ cm}^{-1}$). Carbo-diimides contain the N=C=N moiety which has a stretching mode in the 2100–2150 cm^{-1} range [14]. Table 3.10 shows that Tl(pcyd) peak values are in the $\approx 2100\text{ cm}^{-1}$ range which suggests a $\nu_{\text{N}=\text{C}=\text{N}}$ assignment is reasonable [13,20,21].

3.3.3 (PVP)Ni(pcyd) Complexes

The ORTEP drawing of neutral (PVP)Ni(2-Clpcyd) shown in Figure 3.21 illustrates the 4-coordinate nature of the complex in the solid state. According to literature, crystal structures of anionic cyanamide bound metal complexes are uncommon [17,18,20,21] and to my knowledge a crystal structure which contains the 2-Clpcyd anion has not yet been attained. Besides 4-coordinate ligation, the

complex appears to be approximately square planar. Close inspection of Figure 3.21 in conjunction with the stereoview of the unit cell in Figure 3.22, reveals that tetrahedral distortion from the square plane exists. The least-squares plane N1–N3–N5–N6–Ni (Table 3.5) has an average nitrogen distortion of 0.253Å (7.6°) (i.e. the two opposing nitrogens are up and the two other are down relative to the ideal square plane). The dihedral angle between the two planes defined by Ni–N1–N3 and Ni–N5–N6 can be approximated to be roughly 15° (i.e. Table 3.5, addition of two adjacent nitrogen angle deviations from the ideal square plane). An exhaustive search of the literature failed to uncover a N_4 dianion square planar Ni(II) complex with tetrahedral distortion of this size in which the diamagnetic, low-spin integrity of Ni(II) is maintained. The largest found was 0.08Å [59].

Berman *et al* [27] recently observed a dihedral angle of 18.9° for the tetrahedrally distorted $Ni(N_2S_2^{2-})$ complex illustrated in Figure 1.6 (i.e. $n = 3$ for the alkyl bridge). Both solution and solid state ^{13}C NMR displayed no contact shifts as a result of a paramagnetic Ni(II) ground state. This would suggest that the (PVP)Ni(2–Clpcyd) complex is diamagnetic since its' dihedral angle is approximately 15° . Further study is required to confirm the apparent diamagnetic nature of (PVP)Ni(2–Clpcyd) in the solid state. A magnetic susceptibility study of all six, elementally pure (PVP)Ni(pcyd) complexes would clarify the nature of the Ni(II) spin state.

Further structural evidence supporting a diamagnetic square planar description comes from the average value of 1.905Å observed for the Ni–N bond lengths (Table 3.6). Typical Ni–N bond lengths for paramagnetic NiN_4 complexes (i.e. as a result of tetrahedral distortion) are $\approx 2.13\text{Å}$ [60] whereas diamagnetic

systems are generally shorter ranging from 1.86 Å to 1.94 Å [59–61]. The increased bond length for high-spin cases stems from the occupation of the $d_{x^2-y^2}$ orbital which has been described as anti-bonding due the degree of energy destabilization, in square planar or pseudo-square planar Ni(II) complexes [57b]. This results in an expanded Ni(II) radius and subsequently the Ni–N bond lengths increase. The Ni–N bond length range for diamagnetic NiN₄ systems is consistent with that found for (PVP)Ni(2-Clpcyd).

The nature of the Ni(II) spin-state in the (PVP)Ni(pcyd) systems in solution was explored using ¹H NMR. The chemical shift, intensity, and peak width in NMR are sensitive to paramagnetic effects. The magnetic moment and hence the angular momentum are enormous for an electron as compared to a proton for example (i.e. $\approx 1000\times$). The unpaired electron is a potent mechanism for relaxation of resonant nuclei [62] and extensive conjugation within a transition metal complex allows the unpaired electron to circulate which influences the chemical shifts of nuclei throughout the complex. Paramagnetism is expected if Ni(II) has lost diamagnetic spin-paired properties, the latter characterizes an ideally square planar complex.

The CDCl₃ ¹H NMR of adequately soluble (PVP)Ni(II)(pcyd) complexes (Table 3.3a, Figures 3.18, 3.19, and 3.20) illustrate what appears to be a progression toward paramagnetic broadening (i.e. 2,6-Cl₂pcyd $\rightarrow$ 4-Clpcyd $\rightarrow$ 2-Clpcyd). This suggests that a high-low spin equilibria may exist as a result of tetrahedral distortion which is dependent on the phenyl ring substituents of pcyd⁹.

The diamagnetic d^{10} (PVP)Zn(OAc) complex (elementally pure) provides a good model for ¹H NMR changes when the PVP anion has coordinated to the

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metal (Appendix 3, Figure A2). The shifts are upfield and generally not more than 0.1 ppm (Table 3.3a). The CDCl_3 spectrum of $(\text{PVP})\text{Ni}(2\text{-Clpcyd})$ also displayed diamagnetic behavior and on average had downfield shifts, especially the pyridyl ring protons. The innermost H_1 of PVP anion underwent the largest shift which may be attributed to its' proximity to anisotropic effects from the neighboring cyanamide π electron cloud [28] since diamagnetic electronic circulation around the linear axis results in deshielding perpendicular to that axis. Both $(\text{PVP})\text{Ni}(2\text{-Clpcyd})$ and $(\text{PVP})\text{Ni}(4\text{-Clpcyd})$ ^1H NMR spectral peaks are not as clearly resolved suggesting paramagnetic effects are present.

It is known that for 4-coordinate $\text{Ni}(\text{II})$ complexes tetrahedral distortion from the square plane induces a spin state change from diamagnetic to paramagnetic. At some critical point of distortion this magnetic "*cross-over*" occurs [57b]. If paramagnetic/diamagnetic equilibria exists, it is most likely susceptible to perturbation. Temperature dependent variability of structure or "*thermochromism*" is known for 4-coordinate $\text{Ni}(\text{II})$ complexes [63]. If the effect exists, it would be interesting to study this phenomena by temperature dependent ^1H NMR. The Evan's method [63] uses NMR techniques to obtain the actual magnetic susceptibility values of paramagnetic complexes. This may be applied to the $(\text{PVP})\text{Ni}(\text{pcyd})$ complexes. The apparent high-low spin equilibria may result in a magnetic susceptibility value between diamagnetic (0) and paramagnetic (some real number) at a given temperature which would allow the ratio of the two to be calculated.

A ^1H NMR spectrum of $(\text{PVP})\text{Ni}(2,6\text{-Cl}_2\text{pcyd})$ in $d_6\text{-DMSO}$ is shown in Figure 3.18 (inset) and illustrates severe broadening and shifting on going from

non-donating to strongly donating solvent media. The geometrical sensitivity of the (PVP)Ni(pcyd) complexes to solvent media is the subject of discussion in Chapter 5. The complete ^1H NMR study of the remaining (PVP)Ni(pcyd) complexes (i.e. 2,3,5,6- $\text{Cl}_2\text{pcyd}^\ominus$, 2,4,5- $\text{Cl}_3\text{pcyd}^\ominus$, and 2,3- $\text{Cl}_2\text{pcyd}^\ominus$) in low donating CDCl_3 was not possible as a result of solubility limitations.

The electronic absorption spectrum (CHCl_3) of (PVP)Ni(2- Clpcyd) (Figure 3.10), is dominated by the $\pi-\pi^*$ bands of the PVP anion. One broad band centered at 627 nm with an extinction coefficient (ϵ) of $650 \text{ M}^{-1}\text{cm}^{-1}$ suggests the geometry in solution is square planar [26c]. In square planar Ni(II) (d^8) systems, three overlapping $d-d$ transitions occur as a result of the ligand field splitting shown in Figure 3.23.

Figure 3.23 d orbital splitting in a square planar environment for Ni(II) (d^8)

It is common in square planar NiN_4 systems that the lower four d orbitals are closely spaced in energy so that the resulting transitions to the $d_{x^2-y^2}$ orbital are indistinguishable [26c]. In addition, the E_{max} for the broad band is generally higher than is observed for (PVP)Ni(2- Clpcyd). The energy range for NiN_4 complexes is

generally from 400 to 550 nm which suggests that reduced ligand field strength exists in the case of (PVP)Ni(2-Clpcyd). The electronic absorption spectra of the remaining (PVP)Ni(pcyd) complexes (Figures 3.9, 3.11–3.14) display similar broad $d-d$ bands which implies the coordination geometry is probably very similar to the distorted square planar (PVP)Ni(2-Clpcyd) complex.

The CDCl_3 ^1H NMR spectra for both (PVP)Ni(2-Clpcyd) and (PVP)Ni(4-Clpcyd) suggests a high spin, paramagnetic isomer as a result of tetrahedral distortion may exist in equilibrium with a diamagnetic isomer. The electronic absorption spectra of tetrahedral or pseudo-tetrahedral 4-coordinate Ni(II) (d^8) systems results in three ligand field transitions at $\lambda > 550$ nm [26d]. The general order of those bands with increasing energy is as follows: $^3\text{T}_1(\text{F}) \rightarrow ^3\text{T}_1(\text{P})$ (≈ 650 nm, $\epsilon \approx 200$) $>$ $^3\text{T}_1(\text{F}) \rightarrow ^3\text{A}_2(\text{F})$ (≈ 1250 nm, $\epsilon \approx 40$) $>$ $^3\text{T}_1(\text{F}) \rightarrow ^3\text{T}_2(\text{F})$ (≈ 2500 nm, $\epsilon \approx 20$). No identifiable bands above ≈ 700 nm (i.e. up to 1600 nm) are observed in the spectra of the (PVP)Ni(pcyd) complexes which suggests that the apparent tetrahedrally distorted, paramagnetic Ni(II) ground state isomer is a relatively insignificant contributor. In addition, the Gaussian shape of the $d-d$ band envelope suggests that the more intense $^3\text{T}_1(\text{F}) \rightarrow ^3\text{T}_1(\text{P})$ transition is relatively insignificant since a large presence of paramagnetic isomer would most likely result in a low energy shoulder on the square planar $d-d$ band. This further suggests that the equilibrium position for diamagnetic and paramagnetic isomers favours the former. Further studies are required as to the ratio of isomers and may be accomplished by the forementioned Evan's method [63].

The $\pi-\pi^*$ band pattern for the (PVP)Ni(pcyd) complexes in CHCl_3 are unusual in contrast to (PVP)Zn(OAc) and PVPH (Figure 3.15). There is

profound broadening, intensity reduction, and bathochromic shifting. The origins of this effect are discussed in greater detail in Chapter 4, but it is important at this point to introduce general factors on which the effect appears to be depend.

The $\pi-\pi^*$ band pattern is highly sensitive to the solvent donating ability. In solvents of higher donor strength, the $\pi-\pi^*$ band pattern resembles that observed in (PVP)Zn(OAc) (Figure 3.15). Figure 3.16 illustrates this dramatic change by comparison with THF (tetrahydrofuran) and CHCl_3 solution spectra of (PVP)Ni(2-Clpcyd). In solvents of intermediate donor strength, an equilibrium is established between solvated and desolvated forms which can be perturbed by temperature change. Desolvation occurs at higher temperature, not unlike that observed in NiN_4^{2+} solvent coordination studies [36-39,56], resulting in a $\pi-\pi^*$ perturbed band pattern similar to that observed for (PVP)Ni(pcyd) in CHCl_3 solution. This phenomena is explored in greater depth in Chapter 5.

An "associated" or dimeric, 5-coordinate N-(n-alkylsalicylaldiminato)Ni(II) complex was found to exist when dissolved in a low donating solvent such as CHCl_3 [57b]. It was initially suspected that similar self-association was occurring for the (PVP)Ni(pcyd) complexes and was responsible for the $\pi-\pi^*$ effect. The $\pi-\pi^*$ effect is lifted as a result of THF solvent coordination (Figure 3.16) and is re-established when the temperature is increased (Chapter 5). It is not likely that self-association can compete with adduct formation at higher temperatures which suggests the $\pi-\pi^*$ effect originates from the monomer form.

If the $\pi-\pi^*$ band pattern is geometrically dependent, a valuable spectroscopic tool is now available for structural elucidation of the (PVP)Ni(pcyd) complexes. For this reason the solid state and CHCl_3 solution electronic absorption spectra of

(PVP)Ni(2-Clpcyd) are compared (Figure 3.16). In the solid state (i.e. nujol mull) spectra, diamagnetic, square planarity could not be confirmed since a broad band in the 600 to 650 nm range is not distinguishable due to the strong baseline contribution (i.e. correction was difficult). The $\pi-\pi^*$ band pattern however, is similar to the CHCl_3 solution spectrum. This suggests that the geometrical integrity is approximately maintained in the solid and solution state. In Chapter 4, an attempt is made to more clearly establish the dependence of the $\pi-\pi^*$ band pattern on tetrahedral distortion of the (PVP)Ni(pcyd) complexes.

The infrared spectra (Figures 3.2 to 3.7) of the (PVP)Ni(pcyd) systems reinforce the coordinated nature of $\text{pcyd}^\ominus$ and $\text{PVP}^\ominus$ to Ni(II). Characteristic peak changes in the $1650-1400\text{ cm}^{-1}$ range occurs when PVP anion binds to a metal centre in a tridentate fashion (Table 3.1). The $\nu_{\text{C=N}}$ at 1626 cm^{-1} weakens considerably upon coordination and occurs only if accompanied by deprotonation of the pyrrole amine [9,11].

In the pyridyl stretching region, the peak at 1579 cm^{-1} shifts to slightly higher energy and new peaks appear around 1640 and 1520 cm^{-1} [9]. The peak at $\approx 1640\text{ cm}^{-1}$ is of particular interest since its intensity, as with the 1626 cm^{-1} peak, reflects the protonated status of the pyrrole amine. If both peaks are weak, deprotonation is implied which corroborates with the absence of $\nu_{\text{N-H}}$. These IR spectral changes appear to be consistent with a variety of metal centres [6,8,9,13] and are maintained going from (PVP)NiBr (Appendix 3, Figure A3) to any one of the six (PVP)Ni(pcyd) complexes (Figures 3.2 to 3.6).

It has been noted that octahedral $(\text{PVP})_2\text{Ni}$ readily forms from either (PVP)NiBr or other halide and pseudo-halide (PVP)NiL systems [9] and displays

identical IR spectral changes in the $\text{PVP}^{\ominus}$ peak region. The elemental analysis is markedly different between the di- and mono-substituted PVP nickel(II) complexes. Both $(\text{PVP})\text{NiBr}$ and the $(\text{PVP})\text{Ni}(\text{pcyd})$ complexes give elemental analyses which are consistent with a mono-PVP complex (see Chapter 2 under the appropriate compound).

The pcyd anion generally coordinates to transition metals, "end-on" through the nitrile nitrogen which is less sterically hindered than the aryl-substituted amine nitrogen [13,20,21]. Table 3.9 compares the $\nu_{\text{N}=\text{C}=\text{N}}$ of pcyd anions under study when bound to various metal complex fragments including the $[(\text{PVP})\text{Ni}]^{2+}$ moiety. Changes in this stretch energy depend on the relative contribution of resonance forms X and Y (Figure 1.4a) which in turn is influenced by the nature of the metal and the substituents on the pcyd anion phenyl ring (Table 3.9) [20,21].

Table 3.9 IR Data for the $\nu_{\text{N}=\text{C}=\text{N}}^{\dagger}$ of the pcyd Anion-Metal Complexes

pcyd anion(L)	Complexes [†]			
	Tl(L)	(PVP)NiL	(bipy) ₂ CuL ⁺	(NH ₃) ₅ RuL ²⁺
2-Clpcyd	2098	2154	2108	2115
4-Clpcyd	2078	2148	2122	2109
2,6-Cl ₂ pcyd	2092	2188	2109, 2149w	2121
2,3-Cl ₂ pcyd	2102	2146	2154, 2117w	2111
2,4,5-Cl ₃ pcyd	2085	2184	2155, 2125	2111
2,3,5,6-Cl ₄ pcyd	2097	2196	2151	2137

[†] In cm^{-1} , absorptions are strong unless stated otherwise.

[‡] The Tl^{+}L and $(\text{PVP})\text{Ni}^{2+}\text{L}$ are neutral complexes, run as KBr discs. The $(\text{bipy})_2\text{Cu}^{2+}\text{L}$ and $(\text{NH}_3)_5\text{Ru}^{3+}\text{L}$ complexes are PF_6^- salts, run as nujol mulls.

The $[(\text{NH}_3)_5\text{Ru(III)}]^{3+}$ moiety is a strong π -acceptor and is expected to favour resonance form Y (Figure 1.4a) to take advantage of the two filled orthogonal π_{nb} molecular orbitals that arise (Figure 1.4b) [13,20,21]. Both Cu(II) (d^9) and Ni(II) (d^8) are expected to be much poorer π -acids as a result of filled $d\pi$ orbitals (Figure 3.23). The energy of $\nu_{\text{N}=\text{C}=\text{N}}$ is inconsistent with the π -acid nature of the ligating metal. One might expect the Ru(III) coordinated pcyd[⊖] to have the lowest $\nu_{\text{N}=\text{C}=\text{N}}$ energy in comparison to Tl(I), Ni(II), and Cu(II) since the bond order within the cyanamide should undergo the largest reduction when bound to the most effective π -acid metal. However, other influences such as cyanamide polarization by the metal ion, electronegativity, and coordination number of the metal may also contribute. This exposes the difficulty in assessing the true origin(s) of the difference between the $\nu_{\text{N}=\text{C}=\text{N}}$ of the metal cyanamide complexes.

It is possible to assess the strength of bonding within pcyd[⊖] by evaluating the structural characteristics of the Ni(II) bonded 2-Clpcyd anion in the solid state by way of its' crystal structure. Figure 1.4a illustrates two extremes of amine lone pair delocalization. With resonance form Y, a M-N-C bond angle of 180° is expected if the metal is π -accepting since the orientation will maximize both σ and π bonding (i.e. maximize $d\pi$ - $p\pi$ overlap of two π symmetry orbitals containing electron pairs). If the interaction was purely σ -bonding, an angle of 120° would be anticipated as a result of the sp^2 hybridized nitrile nitrogen. With resonance form X, the sp hybridized nitrile nitrogen would require a M-N-C bond angle of 180° for maximum σ -bonding overlap [20].

The Ni-Nb- C19 bond angle of 163.5° for (PVP)Ni(2-Clpcyd) (Table 3.6) suggests that the π -bonding contribution is relatively weak and subsequently

resonance form X is most likely a greater contributor to the bonding interaction. The (bipyridine)Cu(2,3-Cl₂pcyd)₂ system [20] had a similar bonding angle which was attributed to the weak π -accepting ability of the metal. Greater linearity should arise from the interaction of pcyd anion with a good metal π -acid (i.e. resonance form Y being the greater contributor). In (2,3-Cl₂pcyd)Ru(III)(NH₃)₅, the bond angle was found to be 171.4° as a result of the favourable π -accepting properties of Ru(III) and thus a preference for resonance form Y [21].

The N7-C20 bond length of 1.350 Å (Table 3.6) is double bond in character when considering a typical C=N bond is 1.35 Å [64]. Of the known cyanamide anion bound metal complex crystal structures, this bond is the shortest [17,20,21a] and suggests that conjugation of the amine lone pair to the phenyl ring is significant. This is reasonable considering the poor π -acid nature of Ni(II).

It has been shown that the 4-coordinate geometry about Ni(II) in low donating CHCl₃ for the (PVP)Ni(pcyd) complexes is not a simple rigid description. From the ¹H NMR there appears to be a paramagnetic isomer present whose proportion of the total concentration is most likely small relative to the diamagnetic isomer since the electronic absorption spectra (CHCl₃) is consistent with square planar geometry for all six (PVP)Ni(pcyd) complexes.

The range of square planar *d-d* band energies for the (PVP)Ni(pcyd) complexes is small (i.e. ≈ 13.5 nm or ≈ 350 cm⁻¹, Table 3.2). This suggests that the strength of the ligand field (i.e. greater field strength, greater splitting as shown in Figure 3.23) is weakly affected by chloro substituents. In addition, the field strength demonstrated by *d-d* electronic absorption is low in energy relative to other NiN₄ square planar systems (i.e. 400 to 550 nm) [26c]. (PVP)Ni(2-Clpcyd) and (PVP)Ni(4-Clpcyd) show the weakest field (Table 3.2) and demonstrate

paramagnetic effects in their ^1H NMR (Figures 3.19 and 3.20) which may represent a temperature dependent high–low spin Ni(II) complex equilibrium.

This may be corroborated by relatively weaker and stronger field cases. In Figures 3.25 and 3.26, ^1H NMR are shown for (PVP)Ni(NCS) and (PVP)Ni(N_3), respectively. Both gave well resolved PVP⁹ peaks indicative of a diamagnetic Ni(II) while (PVP)NiBr (Figures 3.27) is severely broadened and shifted making assignments exceedingly difficult (Table 3.3b). The general relationship in Figure 3.24 appears to hold.

Figure 3.24 Ni(II) spin–state / ligand field strength relationship

A reasonable explanation requires attention to two important points: 1) spin pairing in the stabilized d orbitals is favorable when the $d_{x^2-y^2}$ orbital has been raised to sufficiently high energy and 2) the d – d band energy for the (PVP)Ni(pcyd) complexes is quite low when compared to most N_4 square planar Ni(II) systems [26c] which implies the d orbital splitting is smaller (i.e. $d_{x^2-y^2}$ is less destabilized).

The above points suggest that the paramagnetic isomer contribution is most likely small but significant enough to induce some broadening in the ^1H NMR in the marginally weaker field cases (i.e. (PVP)Ni(2-Clpcyd) and

(PVP)Ni(4-Cipcyd)) and dominates in the weakest field cases (i.e (PVP)NiBr). This further suggests that the field strength threshold for "cross-over" from diamagnetic to paramagnetic due to tetrahedral distortion from the square plane is found within the small $d-d$ transition energy range of the six chloro substituted (PVP)Ni(pcyd) complexes. The $d-d$ bands of (PVP)NiBr in CHCl_3 were too weak to be identified (Figure 4.2) which implies low-spin square planar geometry is absent. The solid state tetrahedral distortion for (PVP)Ni(2-Clpcyd) appears to be justified as indicated by the slight paramagnetic contact shift in the CDCl_3 ^1H NMR. The field strength required to maintain diamagnetism appears to have been met. In light of the narrow square planar $d-d$ band energy shift observed in the (PVP)Ni(pcyd) complexes, it is worthwhile to determine if this shift is random or if the phenyl ring substituent change is influential in a predictable manner.

A series of seventeen pentaammine-ruthenium(III) complexes of $\text{pcyd}^\ominus$ ligands were prepared by Crutchley *et al* [21]. The Ru III/II reduction couple was obtained using cyclic voltammetry. Substituents on the phenyl ring of $\text{pcyd}^\ominus$ influence the electron density on the Ru(III) bound terminal nitrogen of the cyanamide. When the substituents are electron withdrawing, π donation to the π symmetry d orbitals of Ru(III) is reduced. Since the LUMO (i.e. lowest occupied molecular orbital) of Ru(III) is of π symmetry, electrochemical reduction is influenced by the π donating ability of $\text{pcyd}^\ominus$ (i.e. reduction becomes more negative with increasing π donation from $\text{pcyd}^\ominus$).

The isothiocyanate anion is known to be a π donor when bound through nitrogen but also has weak π accepting ability [65]. The corresponding pentaammine-ruthenium(III) complex has a Ru III/II reduction couple less negative than the analogous chloro substituted $\text{pcyd}^\ominus$ complexes which reflects the

Figure 3.25 ^1H NMR spectrum for $(\text{PVP})\text{Ni}(\text{NCS})$ in a saturated CDCl_3 solution.

Figure 3.26 ^1H NMR spectrum for $(\text{PVP})\text{Ni}(\text{N}_3)$ in a saturated CDCl_3 solution.

Figure 3.27 ^1H NMR spectrum for (PVP)NiBr in a saturated CDCl_3 solution.

decreased π donating ability of the former.

The $d-d$ band envelope E_{max} of the (PVP)Ni(pcyd) complexes and of (PVP)Ni(NCS) are plotted against the corresponding pentaammine ruthenium(III)(L) Ru (III/II) reduction couples (Figure 3.28) establishing an approximately linear relationship. Increasing π -donating ability equated to a decreasing E_{max} (i.e. decreasing field strength). It has been suggested that increasing π donor strength in square planar Ni(II) complexes destabilizes the in plane d_{xz} and d_{yz} orbitals resulting in lower $d-d$ transition energies [25] which corroborates with what is observed for the (PVP)Ni(pcyd) complexes. This is consistent with the apparent paramagnetic effects observed in the CDCl_3 ^1H NMR of (PVP)Ni(2-Clpcyd) and (PVP)Ni(4-Clpcyd) which are attributed to increasing tetrahedral distortion. 2,6-Cl₂pcyd^o is less π donating as indicated by its' less negative Ru III/II reduction couple (Figure 3.28). This is consistent with the greater ligand field strength (i.e. square planar $d-d$ band is higher energy) in (PVP)Ni(2,6-Cl₂pcyd) and hence the diamagnetic nature of the complex in the CDCl_3 ^1H NMR.

The broadness of the (PVP)Ni(II)(L) bands combined with a narrow range of energy change reduces the credibility of this plot. Although it is roughly linear, it represents only a portion of a greater trend which may be quite different therefore the apparent linearity must be considered with caution.

The plot may also provide qualitative elucidation of the Ru(III/II) redox couple for $[(\text{NH}_3)_5\text{Ru}(\text{N}_3)]^{2+}$ which is too unstable to be physically isolated [66]. The corresponding (PVP)Ni(N₃) was obtained and appears to be low-spin square planar having a $d-d$ band energy of $\approx 16070 \text{ cm}^{-1}$ ($\approx 622 \text{ nm}$). From Figure 3.28, this corresponds to a Ru(III/II) reduction couple potential of $\approx -0.1 \text{ V}$.

Figure 3.28 Plot of $(\text{PVP})\text{Ni(II)L } d-d$ square planar transition energy (cm^{-1}) vs the III/II reduction couple for the corresponding $(\text{NH}_3)_5\text{Ru(III)L}$ complexes (volts).

In the (PVP)Ni(II)(L) complex series, ligand field strength may be approximated with respect to the spectrochemical series [67]. It has been demonstrated by ^1H NMR (CDCl_3) and electronic absorption (CHCl_3) that a chloro substituted range of (PVP)Ni(pcyd) complexes have ligand field strengths that lie intermediate to the stronger (PVP)Ni(NCS) but higher than the halide analogues. The latter are known to be weak field ligands and it appears reasonable that the ligand field strengths of the pseudo-halide (PVP)Ni(pcyd) complexes studied here are also relatively weak field.

A wider range of phenyl substituted (PVP)Ni(pcyd) complexes are required to test the validity of the plot in Figure 3.28. Phenylcyanamide anions of greater π donating ability such methoxy and methyl substituted derivatives are a logical choice but one may suspect these complexes to be tetrahedrally distorted, high spin since both the (PVP)Ni(2-Clpcyd) and (PVP)Ni(4-Clpcyd) complexes (i.e. the better π donors of the chloro substituted pcyd⁻ ligands) displayed evidence of paramagnetism.

3.3.4 Crystal Packing Properties of the (PVP)Ni(2-Clpcyd) Complex

Careful observation of the unit cell in Figure 3.22 reveals that the molecules are stacked such that the 2-Clpcyd anion alternates in a mirror-like fashion between adjacent molecules. It is suggested that in this orientation, contact between the PVP anion planes appears to be maximized.

From the space group (i.e. A_2), the positions of the atoms of a molecule within the unit cell can be equated in terms of Cartesian coordinates. In Table 3.7 the atomic parameters are listed for the molecule which lies closest to the middle of the cell. Equations defining the relative positions of the other three molecules are

noted in Figure 3.22. To obtain an approximate interplanar distance within the stacking formation, selected atoms which appear to line up along the x-axis were chosen. Using the relationship, $(x+0.5, -y, z)$ the correlating atomic positions of the molecule which lies directly below the cell centered molecule were calculated. In Table 3.10 the arrows represent the two atoms in molecule #1 (middle) and molecule #3 (below) which appeared to lie in line with each other along the x-axis. The interplanar distance could be approximated from ΔX Cartesian coordinates which are converted to Angstroms using the unit cell dimensions (Table 3.4).

Table 3.10 Selected Interplanar Atom Distances in the Unit Cell of (PVP)Ni(2-Clpcyd)[†]

molecule #1				molecule #3				$\Delta X(\text{\AA})$
atom	X	Y	Z	atom	X	Y	Z	
C8	0.2268	0.4471	1.1684	→ C14	0.7075	0.4249	1.2152	3.741
C13	0.2739	0.4228	1.0564	→ N5	0.7492	0.4022	1.1019	3.699
C14	0.2075	0.5751	1.2152	→ C8	0.7268	0.5529	1.1684	4.041
N5	0.2492	0.5978	1.1019	→ C13	0.7739	0.5772	1.0564	4.083
N1	0.3738	0.5354	0.7881	→ C5	0.8828	0.5115	0.7657	3.961
C5	0.3828	0.4885	0.7657	→ N1	0.8738	0.4646	0.7881	3.821

[†] Estimated standard deviation not included (see Table 3.8)

The interplanar separation represented by ΔX in Table 3.10 was relatively consistent ranging from 3.699 $\text{\AA}$ to 4.083 $\text{\AA}$. The corresponding Z and Y values were quite close but not identical which suggests the selected atoms in each YZ plane are not perfectly aligned along the X-axis. As a result, the interplanar

separation is probably a little less than the number calculated (therefore ΔX represents a slightly angled distance).

Neutral, planar 4-coordinate, macrocyclic N_4 square planar Ni(II) complexes which exhibit Ni- π and π - π interplanar interactions in a stacked lattice have interplanar separations which range from 3.235 Å to 3.350 Å [68]. In contrast, the (PVP)Ni(2-Clpcyd) range is high (i.e. 3.699 to 4.083 Å, Table 3.10) which suggests the ordered nature of the crystal lattice is more a consequence of efficient molecular packing rather than interplanar interaction.

One may postulate interplanar π interaction based on the difference of π - π^* transition energies between solid and solution electronic absorption [68]. Figure 3.16 illustrates what appears to be a mild bathochromic shifting of the π - π^* bands in the solid state (i.e. nujol mull) relative to $CHCl_3$ solution [45]. This suggests that interplanar π interaction may exist in the solid state.

The significance of this apparent interplanar π interaction lies in the potential for the complexes to behave as "*molecular conductors*" through the π stacks. Metallomacrocycles of Ni(II) (i.e. incorporating cyclic dianion tetraamine ligands) have demonstrated this behavior [1-4,11], but required partial oxidation. There appears to be conductive potential in the neutral (PVP)Ni(pcyd) systems which requires further study.

3.4 Summary

The 4-coordinate geometry of the (PVP)Ni(pcyd) complexes is not a simple rigid description. The solid state geometry of (PVP)Ni(2-Clpcyd) is that of a tetrahedrally distorted square plane. It is not certain whether the spin-state of

Ni(II) is diamagnetic or paramagnetic. The nature of the molecular packing in the crystal lattice appears to indicate potential for π conduction.

The solution state behavior of the (PVP)Ni(pcyd) systems was of primary concern. The paramagnetic (high-spin) or diamagnetic (low-spin) magnetic properties of the (PVP)Ni(pcyd) complexes appears to depend on the nature of the phenylcyanamido ligand. An increase in the π donor ability of the pcyd[⊖] ligand increases the magnitude of the paramagnetic contact shift in CDCl₃ (i.e. low donating solvent) ¹H NMR which suggested an isomeric spin-state equilibrium exists. The magnetic "*cross-over*" to a paramagnetic ground state appears to take place within the π donor range of the six chloro substituted (PVP)Ni(pcyd) complexes although the diamagnetic isomer predominates as indicated by the CHCl₃ electronic absorption spectra.

A similar paramagnetic contact shift occurs when the solvent donor strength is increased as indicated by the *d*₆-DMSO ¹H NMR of (PVP)Ni(2,6-Cl₂pcyd) which suggested the possibility of solvent coordination. There exists an unusual PVP[⊖] centered π - π^* band pattern in the CHCl₃ electronic absorption spectra for the (PVP)Ni(pcyd) complexes which appears to be dependent upon complex geometry since dissolution in coordinating THF (Figure 3.16) lifted the π - π^* effect.

The dynamic nature of the (PVP)Ni(pcyd) complex geometry and Ni(II) spin-state properties in solution as a result of intra and intermolecular influences, is the focus of Chapters 4 and 5.

CHAPTER 4

Unusual Electronic Transition Perturbations in (PVP)Ni(pcyd) Complexes

4.1 Introduction

It has been shown that the $\text{PVP}^\ominus$ centered $\pi-\pi^*$ transitions undergo unique changes characterized by decreases in intensity, loss of vibrational fine structure, and red shifts in band energy when $\text{PVP}^\ominus$ is bound in a tridentate fashion to Ni(II) as part of the approximately square planar (PVP)Ni(pcyd) systems. It was demonstrated in Chapter 3 that dissolution in donating solvent (i.e. DMSO spectra of (PVP)Ni(2-Clpcyd), Figure 3.16) disrupted the effect altering the band pattern to resemble a description characterized by (PVP)Zn(OAc) (Figure 3.15) and rendering the complex paramagnetic (d_6 -DMSO, ^1H NMR for (PVP)Ni(2,6-Cl₂pcyd), Figure 3.18). Such $\pi-\pi^*$ transition effects appear to be uncommon [26b] and it was therefore of interest to investigate the potential intramolecular sources by comparison to other mono-anion systems of (PVP)NiL (i.e. L = anion ligand other than pcyd[⊖]) in a low donating solvent such as CHCl_3 . The source of electronic $\pi-\pi^*$ transitional perturbation in square planar (PVP)Ni(pcyd) complexes appears to be a function of the singular or combined influence of metal type, complex geometry, loss of $\text{PVP}^\ominus$ planarity, and the π properties of the mono-chelating anion. The significance of each will be discussed in an attempt to elucidate this unique effect.

4.2 Data

Electronic Absorption Spectroscopy

CHCl_3 solution data pertaining to the (PVP)Ni(pcyd) complexes has already been listed in Table 3.2 (Figures 3.9 to 3.14). Table 4.1 shows data for the

(PVP)NiL complexes. Figures 4.1 to 4.8 illustrate the accompanying spectra which range from 300 to 900 nm (detailed insets are displayed where appropriate).

Table 4.1 Electronic Absorption Data for 4-Coordinate Ni(II) and Cu(II) Complexes Containing PVP Anion[†]

L anion	$\pi-\pi^*$ [†]	ligand field, $d-d$
(PVP) ₂ Ni	461 (34360) 433 (35770) 337 (23960)	≈850 (≈22)
(PVP)Ni(OAc)	459 (10300) 341 (16170)	693 (≈30) 656 (≈30)
(PVP)NiCl ^a	464 (3780) 347 (8630)	≈680 (≈50)
(PVP)Ni(NCS)	476 (15380) 340 (34960)	≈600 (≈270)
(PVP)Ni(N ₃)	482 (5280) 348 (13800)	≈620 (≈180)
(PVP)NiBr	459 (22400) 432 (27240) 339 (29490)	
(PVP)NiCN ^c	465 [451] 433 [422] 322 [328]	
(PVP)Cu(2,3-Cl ₂ pcyd) ^b	418 (10870) 352 (8590) 336 (11140)	674 broad (213)

[†] All spectra obtained from CHCl₃, 10⁻⁵–10⁻⁴ M solutions. Values in nm. Numbers in parentheses are extinction coefficients in M⁻¹ cm⁻¹. [†] PVP⁻ bands sensitive to π mixing perturbation. ^a Elemental analysis suggests 1 H₂O associated with complex, ϵ calculated accordingly. ^b Same as ^a except 0.5 H₂O. ^c Both the qualitative dimethylformamide (DMF) solution spectra and diffuse reflectance spectra (nujol mull, square brackets) band energies are listed. ^d Baseline subtracted (Figure 4.1 inset), assumed to be zero.

Figure 4.1 Electronic absorption spectrum of (PVP)Ni(OAc) in CHCl_3 . The complex concentration is $6.01 \times 10^{-5} \text{ M}$ (inset $9.71 \times 10^{-4} \text{ M}$).

Figure 4.2 Electronic absorption spectrum of (PVP)NiBr in CHCl_3 . The complex concentration is $5.00 \times 10^{-5} \text{ M}$.

Figure 4.3 Electronic absorption spectrum of $(\text{PVP})_2\text{Ni}$ in CHCl_3 . The complex concentration is $9.62 \times 10^{-5} \text{ M}$ (inset $1.15 \times 10^{-3} \text{ M}$).

Figure 4.4 Electronic absorption spectrum of $(\text{PVP})\text{Ni}(\text{N}_3)$ in CHCl_3 . The complex concentration is $1.33 \times 10^{-4} \text{ M}$ (magnification inset).

Figure 4.5 Electronic absorption spectrum of (PVP)Ni(NCS) in CHCl₃. The complex concentration is 1.64×10^{-4} M (magnification inset).

Figure 4.6 Electronic absorption spectrum of (PVP)NiCl·H₂O in CHCl₃. The complex concentration is 6.58×10^{-5} M (magnification inset).

Figure 4.7 Electronic absorption spectra of (PVP)Cu(2,3-Cl₂pcyd)•0.5H₂O in CHCl₃. The complex concentration is 5.51×10^{-5} M (inset 1.06×10^{-3} M).

Figure 4.8 Qualitative electronic absorption spectra (DMF solution, (a)) and diffuse reflectance spectra (solid in nujol mull, (b)) of (PVP)NiCN.

¹H NMR Spectroscopy

The chemical shifts for the (PVP)NiL ($L = \text{OAc}^\ominus$, $\text{PVP}^\ominus$, $\text{Cl}^\ominus$, $\text{Br}^\ominus$, $\text{SCN}^\ominus$, $\text{N}_3^\ominus$) have been listed previously in Table 3.3b. Furthermore, spectra for several of these complexes can also be found in Chapter 3 (i.e. Figures 3.25 ($L = \text{SCN}^\ominus$), 3.26 ($L = \text{N}_3^\ominus$), and 3.27 ($L = \text{Br}^\ominus$)). Spectra for (PVP)₂Ni, (PVP)Ni(OAc), and (PVP)NiCl•H₂O can be found in Figures 4.9, 4.10, and 4.11, respectively.

Infrared Spectroscopy

Several of the complexes used in this study were previously unreported or not fully characterized, namely, (PVP)Ni(NCS), (PVP)Ni(N₃), (PVP)Cu(2,3-Cl₂pcyd), and (PVP)NiCN. Their infrared spectra are shown in Figures 4.12(a,b), 4.13, 4.14, and 4.16, respectively. In addition, the infrared spectra for (PVP)Ni(OAc), (PVP)NiCl•H₂O, and (PVP)₂Ni are shown in Figures 4.15, 4.17, and 4.18, respectively.

4.3 Results and Discussion

4.3.1 Characterization of the Mono-Anion (PVP)NiL Complexes

The complexes (PVP)Ni(OAc), (PVP)NiCl, and (PVP)₂Ni, were synthesized by previously developed methods [44–49,52,53]. Their elemental analysis were consistent with the assigned empirical formula except for (PVP)NiCl which required correction by the addition of one H₂O.

The bonding mode of acetate anion in (PVP)Ni(OAc) can be either:

A

B

Figure 4.9 ^1H NMR spectrum of $(\text{PVP})_2\text{Ni}$ in CDCl_3 .

Figure 4.10 ^1H NMR spectrum of $(\text{PVP})\text{Ni}(\text{OAc})$ in a saturated CDCl_3 solution.

Figure 4.11 ^1H NMR spectrum for $(\text{PVP})\text{NiCl}\cdot\text{H}_2\text{O}$ in a saturated CDCl_3 solution.

Figure 4.12a Infrared spectrum (KBr) for (PVP)Ni(NCS) ($\nu_{\text{C-N}}$ at 2091 cm^{-1}).

Figure 4.12b Infrared (KBr) spectral comparison of (PVP)NiBr (upper) and (PVP)Ni(NCS) (lower) in the 1000 to 500 cm^{-1} region.

Figure 4.13 Infrared spectrum (KBr) for (PVP)Ni(N₃) ($\nu_{\text{N}=\text{N}=\text{N}}$ at 2051 cm⁻¹).

Figure 4.14 Infrared spectrum (KBr) for (PVP)Cu(2,3-Cl₂pcyd) ($\nu_{\text{N}=\text{C}=\text{N}}$ at 2145 cm⁻¹).

Figure 4.15 Infrared spectrum (KBr) for (PVP)Ni(OAc).

Figure 4.16 Infrared spectrum (KBr) for (PVP)NiCN ($\nu_{\text{C}\equiv\text{N}}$ at 2169 cm^{-1}).

Figure 4.17 Infrared spectrum (KBr) for (PVP)NiCl·H₂O.

Figure 4.18 Infrared spectrum (KBr) for (PVP)₂Ni.

The infrared spectrum (Figure 4.15) suggests the binding mode A exists due to the absence of a distinctively strong infrared $\nu_{\text{C=O}}$ in the 1590–1650 cm^{-1} region which characterizes binding mode B [69]. This is also the case for the infrared spectrum of (PVP)Zn(OAc) (Appendix 3, Figure A4) which suggests both complexes are 5-coordinate. Since there is no ligand field stabilization in Zn^{2+} (d^{10}), the ligand geometry is determined by size, electrostatic forces, and covalent bonding forces [57d]. The trigonal bipyramidal or square pyramidal geometry of 5-coordinate (PVP)Zn(OAc) is probably distorted since the restricted bidentate ability of the small acetate anion most likely cannot span the ideal coordination sites of either geometry. The infrared spectra of (PVP)Ni(OAc), (PVP)NiCl $\cdot$ H $_2$ O, (PVP) $_2$ Ni, and (PVP)Zn(OAc) (Figures 4.15, 4.17, 4.18, and Figure A4, respectively) had a typical PVP $^{\ominus}$ peak pattern (i.e. in the 1500–1650 cm^{-1} region) which was consistent with tridentate coordination of deprotonated PVP $^{\ominus}$ [48,54,55].

The paramagnetically broadened and shifted ^1H NMR spectra for (PVP)NiCl $\cdot$ H $_2$ O (Figure 4.11), (PVP) $_2$ Ni (Figure 4.9), and (PVP)Ni(OAc) (Figure 4.10) in CDCl_3 indicated the presence of high-spin Ni(II) which implies non-square planar geometry.

The electronic absorption spectrum of (PVP) $_2$ Ni (Figure 4.3) contains an unsymmetrical band (inset) at 880 nm ($\epsilon \approx 30$). This is consistent with ligand field transitions of an octahedral Ni(II) complex (i.e. generally 3 spin allowed transitions: $^3\text{A}_{2g} \rightarrow ^3\text{T}_{1g}$ (1400–750 nm), $^3\text{A}_{2g} \rightarrow ^3\text{T}_{1g}$ (900–500 nm), and $^3\text{A}_{2g} \rightarrow ^3\text{T}_{1g}(\text{P})$ (530–370 nm) with extinction coefficients less than 30 $\text{M}^{-1} \text{cm}^{-1}$ [26d]). The two weak higher energy bands are most likely obscured by the $\pi \rightarrow \pi^*$ transitions. (PVP)Ni(OAc) (Figure 4.1) exhibited two weak sharp bands (inset) at

693 nm and 656 nm (i.e. both having $\epsilon \approx 120 \text{ M}^{-1} \text{ cm}^{-1}$). One would expect that a high-spin, 5-coordinate species most likely exists due to the infrared and ^1H NMR (CHCl_3) data. It was difficult to make an absolute geometrical assignment from the electronic absorption spectra. The $d-d$ band pattern is somewhat different from both 5-coordinate high-spin square pyramidal (i.e. generally there is multiple weak transitions, the number dependent on the level of symmetry) and tetrahedral (i.e. generally one band, $^3\text{T}_1(\text{P}) \rightarrow ^3\text{T}_1(\text{F})$, 600 – 850 nm, ϵ 100 – 1000 $\text{M}^{-1} \text{ cm}^{-1}$ [26a]). In the spectrum of $(\text{PVP})\text{NiCl} \cdot \text{H}_2\text{O}$ (Figure 4.6) only one weak broad band (i.e. $\approx 680 \text{ nm}$, $\epsilon \approx 50 \text{ M}^{-1} \text{ cm}^{-1}$) is observed beyond the $\pi \rightarrow \pi^*$ transitions (i.e. in the 500 to 1600 nm range). It is unclear to whether the H_2O molecule is actually coordinated to the complex but the energy and intensity of the band suggests that tetrahedral geometry exists (i.e. one band 600–850 nm, ϵ 100–1000 $\text{M}^{-1} \text{ cm}^{-1}$ [26a]) which implies the complex is 4-coordinate. Caution is taken in discussing the $\pi \rightarrow \pi^*$ transition properties in relation to other 4-coordinate species.

The complexes $(\text{PVP})\text{Ni}(\text{NCS})$, $(\text{PVP})\text{Ni}(\text{N}_3)$, and $(\text{PVP})\text{NiBr}$ were prepared using methods developed in conjunction with this study and their formulation is consistent with elemental analysis. The 1500–1650 cm^{-1} region of the infrared is diagnostic of coordinated, deprotonated $\text{PVP}^\ominus$ in all three cases. The infrared spectrum for the azido ($\text{N}_3^\ominus$) complex (Figure 4.13) has a strong $\nu_{\text{N}=\text{N}=\text{N}}$ at 2051 cm^{-1} (compared to 2122 cm^{-1} for NaN_3) which suggests the ligand is metal coordinated. Bonding through a terminal nitrogen is the general metal bonding mode for the azido ligand [70,71].

The infrared spectrum of the isocyanato ($\text{SCN}^\ominus$) complex (Figure 4.12a) possesses an intense $\nu_{\text{C}-\text{N}}$ at 2091 cm^{-1} suggesting that the nitrogen end is metal

bound since the sulfur bound isomer is generally much less intense [72]. Differentiation between linkage isomers is also indicated by the energy position of $\nu_{\text{C-S}}$. When the sulfur bound, the peak ranges from 720–690 cm^{-1} whereas the nitrogen bound isomer is 860–780 cm^{-1} . The 1000–500 cm^{-1} region for (PVP)Ni(NCS) is shown in Figure 4.12b and compared to (PVP)NiBr to demonstrate the difficulty in assigning $\nu_{\text{C-S}}$.

The ^1H NMR for (PVP)Ni(NCS) (Figure 3.25), and (PVP)Ni(N_3) (Figure 3.26) in CDCl_3 , are both diamagnetic as all peaks of $\text{PVP}^\ominus$ were assignable and well resolved (Table 3.3b). In addition, both displayed broad bands (Figures 4.4 and 4.5) in their electronic absorption spectra which is indicative, in terms of energy and intensity, of square planar geometry (Table 4.1) [26a]. The CDCl_3 ^1H NMR (Figure 3.27) for (PVP)NiBr is paramagnetically broadened and shifted which suggests the 4-coordinate complex (i.e. formulation is consistent with elemental analysis) is high-spin as a result of tetrahedral distortion from the square plane. The electronic absorption spectrum (Figure 4.2) is featureless at wavelengths above 500 nm except for a shoulder at approximately 500 nm (i.e. adjacent to the $\pi\text{--}\pi^*$ transitions).

The (PVP)NiCN complex was recently prepared by Dr. Crutchley in this lab. The degree of purity is not entirely certain and at present is the subject of further analysis (i.e. elemental analysis). The infrared spectrum (Figure 4.16) contains a strong singular peak at 2169 cm^{-1} assigned as $\nu_{\text{C}\equiv\text{N}}$. The 1650–1500 cm^{-1} region has a peak pattern consistent with deprotonated, coordinated $\text{PVP}^\ominus$. The broad band at 3426 cm^{-1} is attributed to H_2O (i.e. $\nu_{\text{O-H}}$) originating in the KBr matrix since a nujol mull (i.e. hydrophobic) spectrum of the

same material did not contain the band. Cyanide anion is a strong field ligand [73,57e] and one would therefore anticipate the (PVP)NiCN complex to be square planar since both the $\text{SCN}^\ominus$ and $\text{N}_3^\ominus$ (i.e. weaker field ligands [67]) (PVP)NiL complexes are square planar (diamagnetic). The electronic absorption solution (DMF, dimethylformamide) spectrum (Figure 4.8) is devoid of any identifiable bands other than the $\pi-\pi^*$ transitions of the $\text{PVP}^\ominus$ ligand. If the complex is square planar, the strong field $d-d$ band is most likely higher energy relative to the corresponding band in square planar (PVP)Ni(NCS) (i.e. ≈ 600 nm, Figure 4.5) and therefore is obscured by the $\pi-\pi^*$ bands.

The (PVP)Cu(2,3- Cl_2pcyd) complex is synthetically novel and to my knowledge this formulation has not been previously reported. Elemental analysis is consistent with $0.5\text{H}_2\text{O}$ associated with each complex molecule. The associated H_2O appeared not to be metal bound as indicated by the invariance of all bands (i.e. especially bands assigned to $d-d$ transitions) in the electronic absorption spectrum (Figure 4.7) to temperature increase (i.e. low donating toluene spectra of the complex heated up to 95°C). If weakly bound, the H_2O would most likely have dissociated at these temperatures suggesting that a 4-coordinate as opposed to a 5-coordinate (i.e. as a result of complexed H_2O) description is more appropriate. The infrared spectrum in Figure 4.14 has a $1500\text{--}1650\text{ cm}^{-1}$ region peak pattern indicative of coordinated, deprotonated $\text{PVP}^\ominus$ and a strong peak at 2145 cm^{-1} which is assigned as a coordinated $\nu_{\text{N}=\text{C}=\text{N}}$ (Ti(2,3- Cl_2pcyd) has a similar stretch at 2102 cm^{-1}).

The electronic spectrum (Figure 4.7) contains a broad slightly structured band at 674 nm ($\epsilon\ 200$) and assigned as a $d-d$ transition. There is an odd bump on the

$d-d$ band originally thought not to be attributed to the complex. The change in its intensity is proportional with changes in concentration which indicated it was real. Most copper(II) complexes have $d-d$ bands which consist of a poorly resolved single broad band in the visible region for reasons attributed to distorted stereochemistries (i.e. low symmetry) [74]. Square planar tetraammine copper(II) complexes (CuN_4) generally have one broad band showing little structure in the 555–470 nm range. Tetrahedral CuN_4 systems also show a single transition at relatively low energy [26c]. Five-coordinate CuN_5 complexes have a $d-d$ band envelope which ranges from 850–650 nm [26c]. It is therefore difficult to make an absolute assignment from the electronic absorption spectrum. Perhaps Jahn–Teller effects influence $d-d$ transitions as a result of the geometrical distortion [75]. The apparent presence of H_2O further reduces the confidence of assignment. A crystallographic analysis of elementally pure compound is required to confirm the coordination geometry.

4.3.2 Origins of the $\pi-\pi^*$ Transitions of PVPH

In Chapter 3 it was demonstrated that the $\pi-\pi^*$ transitions of PVPH were influenced by the act of tridentate coordination of the anion form to a dicationic metal center. Figure 3.15 illustrated the effect by comparison of the electronic $\pi-\pi^*$ spectra of PVPH to the established complex $(\text{PVP})\text{Zn}(\text{OAc})$ [54,55]. It was shown that an even greater energy and intensity perturbation came about when $\text{PVP}^\ominus$ is bound to $\text{Ni}(\text{II})$ along with $\text{pcyd}^\ominus$ in a square planar complex geometry (i.e. in a low donating solvent such as CHCl_3). It is therefore of interest to more clearly define the origin of the $\pi-\pi^*$ bands on $\text{PVP}^\ominus$ so that we may further

understand changes as a result of metal complexation.

The discussion begins by considering the $\pi-\pi^*$ spectra of the parent reactants. 1,3-Diiminoisoindoline (Figure 4.19) displays two lower energy bands. The intensities (Table 3.2) suggests they originate from $\pi-\pi^*$ transitions [58]. Using the labelling designation employed by Braude [76], the more intense band at 256 nm (ϵ 11200) is labelled "K" type and the 308 nm (ϵ 3300) broad band "B" type. These assignments are reasonable considering that the direct attachment of an unsaturated group (chromophore) to benzene induces bathochromic shifting and increased intensity of the B band (originally at 256 nm, ϵ 200) and the appearance of a K band with $\epsilon > 10,000$ in the 200–250 nm region [58].

Altering the pH of a methanol solution of 1,3-diiminoisoindoline was undertaken to observe the effects of nitrogen protonation on the $\pi-\pi^*$ transitions (Figure 4.20). No noticeable change occurred until a pH $\approx$ 1.0 at which point the K band experienced a slight increase in intensity and bathochromic shift, and a weak low energy shoulder on the B band appeared. When an additional pair of electrons from an auxochromic group such as NH_2 interact with a conjugated π system, bathochromic shifting of $\pi-\pi^*$ transitions is known to occur [58]. The imine lone pair is most likely perpendicular to the π cloud as a result of sp^2 hybridization whereas the sp^3 hybridized pyrrole amine has an electron lone pair which is more symmetrically compatible with the conjugated π cloud. This would suggest that the imine nitrogen is protonated since the resulting positive charge would enhance interaction of the amine nitrogen lone pair with the conjugated π cloud. Greater conjugation generally results in a bathochromic shift of $\pi-\pi^*$ transitions [58]. This explanation appears to be reasonable but it is not certain that mono-protonation

Figure 4.19 Visible electronic absorption spectra of PVPH (solid line), 2-aminopyridine (dashed line), and 1,3-diiminoisoindoline (dash-dot line) in absolute methanol.

Figure 4.20 Qualitative visible electronic absorption spectra of 1,3-diiminoisoindoline in absolute methanol (solid line) and subsequent addition of a methanol/conc. HCl solution to pH $\approx$ 3.0 (dashed line).

is occurring therefore interpretation should be made with caution.

Pyridine possesses a B band at 257 nm (ϵ 2750 M⁻¹ cm⁻¹) which is bathochromically shifted as a result of direct attachment of an auxochromic group such as NH₂ [58]. 2-Aminopyridine (Figure 4.19) displays one band at $\approx$ 300 nm (ϵ 8000) which is consistent with a pyridine B type π - π^* transition.

Aromatic systems are characterized by fine structure which originates from sub-levels of vibrational absorption which are superimposed by electronic absorptions [58]. The planar PVPH ligand (Figure 4.19) possesses extensive conjugation as indicated by the bathochromic shifting of π - π^* transitions where each aromatic ring is inter-connected by an unsaturated bridge. A similar situation exists for trans-stilbene where bathochromic shifting of the K band results in a spreading out of vibrational fine structure [58]. This suggests that the low energy π - π^* band pattern of PVPH results from the maintenance of extensive conjugation between the isoindoline benzene and pyridine rings.

Linstead *et al* [44-46] have prepared variations of PVPH where the 2-aminopyridine group is altered. When one or both imine protons on 1,3-diiminioisoindoline are replaced by a phenyl group, 4 intense bands appear in the 300-360 nm range ($\epsilon \approx$ 9000) which most likely arise from extended conjugation. Replacement by two 3-pyridine groups intensifies these bands (i.e. $\epsilon \approx$ 12000). When the imine substituents are 2-pyridine (PVPH) all four bands are shifted to lower energy (330-385 nm) accompanied by a large growth in intensity ($\epsilon \approx$ 20000). This suggests that the π - π^* transitions are shifted to lower energy as a result of extended conjugation since the proximity of the pyridine nitrogens in the 1 position as opposed to the 2 position relative to diiminioisoindoline allows for more effective conjugation.

4.3.3 Origins of the $\pi\text{--}\pi^*$ Transition Perturbations in (PVP)Ni(pcyd) Complexes

The electronic $\pi\text{--}\pi^*$ transition pattern of the (PVP)Ni(pcyd) complexes (Figures 3.9–3.14) contains two broad bands, one centered at ≈ 480 nm ($\epsilon \approx 7000$) and the other at ≈ 350 nm ($\epsilon \approx 20000$) and are highly perturbed in contrast to the band pattern characterized by (PVP)Zn(OAc) (Figure 3.15) which has two multiple band sets, a three band set centered at 414 nm (ϵ 19200) and a multiple set at 334 nm (ϵ 12000). In either case, the PVP anion ligand most likely remains planar since a number of metal complex crystal structures containing PVP anion ligand show this to be true [48,49,51–53]. The apparent maintainance of $\text{PVP}^\ominus$ planarity in both 5-coordinate (PVP)Zn(OAc) and 4-coordinate (PVP)Ni(pcyd) complexes suggests that $\text{PVP}^\ominus$ planarity is not a requirement for the $\pi\text{--}\pi^*$ effect to occur. Furthermore, the spectra of the octahedral $(\text{PVP})_2\text{Ni}$ complex (Figure 4.3) is devoid of the $\pi\text{--}\pi^*$ effect where it is likely that the two $\text{PVP}^\ominus$ ligands are bound to Ni(II) in a planar perpendicular fashion (Figure 4.21).

When $\text{PVP}^\ominus$ is planar, conjugation should be maximized. If the $\text{PVP}^\ominus$ ligand was non-planar conjugation would be reduced and the probability of transition or "forbiddenness" would increase since the dipole moment of transition is proportional to the change in electronic distribution during excitation [58]. This in turn may increase the $\pi\text{--}\pi^*$ transition energy as well as decrease the intensity.

Self-association of planar conjugated systems is a possible explanation of the observed red shift or $\pi\text{--}\pi^*$ effect. However, as shown in Chapter 5, the (PVP)Ni(pcyd) form 6-coordinate adducts in THF. Upon raising the temperature, the $\pi\text{--}\pi^*$ effect is re-established. It is highly unlikely that self-association can compete with THF adduct formation at these temperatures and therefore

self-association cannot be the origin of the $\pi-\pi^*$ effect.

The $\text{pcyd}^\ominus$ ligands are good π -donors as shown in Chapter 3 and therefore comparison to other π -donating ligands in the $(\text{PVP})\text{Ni}(\text{L})$ system is of interest to elucidate the role of this mono-anion property. The only reasonable explanation for the $\pi-\pi^*$ effect would appear to be related to the nature of the ligand occupying the 4th coordination site in the $(\text{PVP})\text{Ni}(\text{L})$ complexes. The origin of the $\pi-\pi^*$ effect is suggested to be an extension of conjugation involving the 4th ligand. The conditions for extension are square planarity of the complex and a good energy match between π -symmetry orbitals.

For example, the $(\text{PVP})\text{Ni}(\text{NCS})$ (Figure 4.5) and $(\text{PVP})\text{Ni}(\text{N}_3)$ (Figure 4.4) complexes contain the good π donor ligands $\text{N}_3^\ominus$ [65] and $\text{SCN}^\ominus$ [57] and are diamagnetic (^1H NMR) square planar and also show the $\pi-\pi^*$ effect. The structure of the paramagnetic $(\text{PVP})\text{NiBr}$ complex is suggested to be distorted square planar. The $\pi-\pi^*$ band pattern (Figure 4.2) for the $\text{Br}^\ominus$ complex contains a low energy shoulder (Figure 4.2) which may be attributed to a π -mixing complex isomer. However, the $(\text{PVP})\text{NiCl}$ complex is also paramagnetic and likely significantly distorted from square planar geometry. Its UV-vis spectrum does not show the $\pi-\pi^*$ effect (Figure 4.6).

It is apparent that the low-spin, diamagnetic square planar $(\text{PVP})\text{Ni}(\text{L})$ systems demonstrate the $\pi-\pi^*$ effect whereas the tetrahedrally distorted, paramagnetic high-spin systems do not. The ligands $\text{SCN}^\ominus$, $\text{N}_3^\ominus$, $\text{Cl}^\ominus$, and $\text{Br}^\ominus$ all have π donating ability [57,65,78].

The $\pi-\pi^*$ effect appears to have a geometrical dependence since octahedral 6-coordinate, 5-coordinate, and tetrahedrally distorted 4-coordinate $\text{Ni}(\text{II})$

complexes containing planar $\text{PVP}^\ominus$ do not demonstrate the effect. The combined factors of π donation and square planarity appear to be of significance.

It is interesting to note that the octahedral $(\text{PVP})_2\text{Ni}$ complex has a square equatorial plane but displayed no $\pi-\pi^*$ perturbation effect. Like the square planar $(\text{PVP})\text{Ni}(\text{pcyd})$ complexes, the π -donating nitrogen anions are *trans* in $(\text{PVP})_2\text{Ni}$. The π orbitals in the latter are most likely *orthogonal* considering the perpendicular nature of the bound $\text{PVP}^\ominus$ ligands and therefore unable to mix and extend conjugation whereas the pyrrole amine anion of $\text{PVP}^\ominus$ and the nitrile nitrogen of $\text{pcyd}^\ominus$ in the $(\text{PVP})\text{Ni}(\text{pcyd})$ systems have parallel π symmetry orbitals (Figure 4.21). This suggests that π donation in the square plane by the mono-anion is responsible for some sort of " π -mixing" mediated by Ni(II) $d\pi$ orbitals.

Figure 4.21 Schematic diagram of molecular structure and orbital interaction in $(\text{PVP})_2\text{Ni}$ and $(\text{PVP})\text{Ni}(\text{pcyd})$

The significance of π donation by the mono-anion is emphasized by the π -accepting cyanide anion [79]. The (PVP)NiCN complex was found to be completely insoluble in low donating solvents (CHCl_3 in particular). The $\pi-\pi^*$ band energies in DMF (i.e. a strongly donating solvent) (Figure 4.9, Table 4.1) are consistent with $(\text{PVP})_2\text{Ni}$ which suggests that π -mixing is not occurring. This may be misleading when one considers the absence of π -mixing could be a function of solvent interaction with the complex. Comparison to the qualitative solid state spectrum (nujol mull, Figure 4.8) illustrates the absence of change in the energy position of the $\pi-\pi^*$ bands which suggests the lack of π -mixing in the apparently square planar (PVP)NiCN complex results from the absence of π donation from the mono-anion.

It has yet to be proven that the (PVP)NiCN complex is indeed diamagnetic (i.e. low-spin, square planar) and therefore interpretation of this data may be premature. Its' overall insolubility (slight solubility in stronger donating solvents such as DMF and dimethyl sulfoxide) made simple ^1H NMR spectra difficult to attain. EPR (electron paramagnetic resonance) is a possible alternative for Ni(II) spin-state confirmation in solution since the technique gives best results at much lower concentrations [80]. Further study is required as to the significance of π properties of the mono-anion in (PVP)NiL complexes in terms of π -mixing. Other π accepting ligands such as carbon monoxide and nitrosyl oxide [57c,81] may provide confirmation that π donation is indeed necessary for π -mixing to occur. Difficulties may arise since these ligands are neutral and therefore would result in positively charged (PVP)NiL complexes (i.e. would require a counter-anion to

satisfy electrostatic neutrality which may interfere with the π -mixing effect). If the π properties of the mono-anion are truly influential, the π -mixing must be mediated by the Ni(II) which raises the question to whether Ni(II) is unique in this regard.

The structural assignment of the (PVP)Cu(2,3-Cl₂pcyd) complex was difficult as previously noted. The possible association of an H₂O molecule further complicated the validity of the data. Further study is required which would begin with the purification of the complex. Confirmation of the coordination geometry is necessary which could be obtained by X-ray crystallography. If the complex is indeed square planar or approximately square planar, comparison of the π - π^* band pattern to the analogous Ni(II) complex should determine whether the π -mixing phenomenon is restricted to Ni(II). Similar PVP[⊖] complexes of Pt(II) and Pd(II) would be interesting to explore to compare to the Ni(II) systems obtained in this thesis. Both the size and energy of the $d\pi$ orbitals would most likely influence the metal mediated π - π^* effect.

4.4 Summary

The attempt here has been to present evidence which suggests the assignment of " π -mixing" to describe the unique π - π^* effect seen in the (PVP)Ni(pcyd) complexes (i.e. in low donating solvent). It has been shown that both square planar geometry and π donation by the 4th ligand is necessary for the observance of the π - π^* effect. In the absence of π donation by the 4th ligand (i.e. (PVP)NiCN), where square planar geometry is likely retained, the π - π^* effect is

not seen. Where π donor orbitals are orthogonal to the $\text{PVP}^\ominus$ conjugated system (i.e. $(\text{PVP})_2\text{Ni}$), the $\pi-\pi^*$ effect is absent. In the following chapter (i.e. Chapter 5), the geometrical dependence of the π -mixing effect is utilized to study solvent adduct formation.

CHAPTER 5

Solvent Coordination Equilibria in Neutral (PVP)Ni(pcyd) Complexes

5.1 Introduction

The sensitivity of NiN_4^{2+} complexes to solvent coordination has been observed by several authors [32–34,36–40,56,82]. In all cases, an equilibrium condition ensues between the solvated (paramagnetic) and desolvated (diamagnetic) complex forms (i.e. equation (1)). The diamagnetic/paramagnetic ratio is dependent on properties inherent to the solvent as well as steric and bonding aspects of the N_4 ligand.

$$(2) \quad K_{\text{eq}} = \frac{[\text{NiN}_4(\text{Solvent})_x]}{[\text{NiN}_4]} = \frac{[\text{par a magnetic}]}{[\text{diam a gnetic}]}$$

The equilibrium is defined by K_{eq} (equilibrium constant) which equates to the concentration ratio of diamagnetic to paramagnetic species and can be converted to the former by either: a) addition of inert electrolyte (i.e. ions are thought to compete for the solvent molecules coordinated to the Ni(II) ion [36]), or b) increasing the temperature [36–40,56,82,83]. The shift in equilibrium can be monitored by changes in the intensity of the square planar $d-d$ transition (i.e. a single broad band).

To obtain K_{eq} , two methods have been applied which adhere to the condition that one or both extremes of the extinction coefficients of the $d-d$ band is known

(i.e. the maximum is 100% desolvated and the minimum is 0% desolvated). The relationship developed in equation (3) requires knowledge of the maximum intensity limit [36,56].

$$(3) \quad K_{eq} = \frac{\epsilon}{\epsilon_{limit} - \epsilon} \quad (\epsilon = \text{molar extinction coefficient})$$

The extinction coefficient, ϵ , may vary in intensity and is calculated by considering the absorbance at a given position and dividing by the NiN_4^{+2} concentration (i.e. solvated or desolvated, the NiN_4^{+2} concentration remains the same).

The K_{eq} has also been found using the method by Tregloan *et al* [39] where both intensity extremes were determined for the complex $[Ni(cis\text{-tetramethylcyclam})](ClO_4)_2$. The minimum absorbance is obtained from low temperature spectra of an acetonitrile complex solution (maximum solvent coordination, $\approx 0\%$ diamagnetic species). Conversely, the maximum absorbance is obtained from increased temperature spectra of an acetonitrile/nitromethane complex solution (minimum solvent coordination, $\approx 100\%$ diamagnetic species). Intermediate absorbance values of the $d-d$ band could be achieved with temperature change and thus the diamagnetic/paramagnetic ratio could be obtained (i.e. equation (2)). It is this method which is applied in the present analysis involving solvent coordination of neutral (PVP)Ni(pcyd) complexes.

The appearance of isosbestic points in the temperature dependent $d-d$ electronic spectra is indicative of a single step process concerning interconversion of diamagnetic and paramagnetic complex forms [37]. Figure 5.1 illustrates this for

$[\text{Ni}(\text{cis-tetramethylcyclam})](\text{ClO}_4)_2$. The band at ≈ 500 nm originates from $d-d$ transitions out of the square planar diamagnetic ground state ($^1A_{1g}$) and decreases with decreasing temperature. Conversely, the band at ≈ 600 nm arises from the paramagnetic ground state ($^3A_{2g}$) and increases with decreasing temperature (i.e. solvated complex forming).

The paramagnetic/diamagnetic K_{eq} has also been calculated using ^1H [82,84]

Figure 5.1 Temperature variant electronic absorption spectra for $[\text{Ni}(\text{cis-tetramethylcyclam})](\text{ClO}_4)_2$ in acetonitrile/nitromethane solution (i.e. 74.8°C to 14.5°C). Arrows indicate direction of band change with decreasing temperature [39].

and ^{17}O [40] NMR spectroscopy (i.e. paramagnetic contact shift) as well as magnetic susceptibility [32]. These methods have an advantage over the forementioned electronic absorption technique since the presence of intense ligand centered $\pi-\pi^*$ bands may obscure the square planar $d-d$ ligand field band.

Unique to this study is the application of variable intensity $\pi-\pi^*$ bands as a result of the apparent π -mixing effect. Two sets of $\pi-\pi^*$ bands arise which are inversely proportional in intensity. One set represents the solvent coordinated

complex which displays no π -mixing and the other set represents the desolvated square planar which demonstrates π -mixing.

The K_{eq} is a dynamic variable which is directly proportional to changes in temperature. The thermodynamic parameters, ΔH° (enthalpy) and ΔS° (entropy), can be obtained graphically from the relationship between K_{eq} and temperature by using equation (7) (i.e. derived from equations 4 and 5).

$$(4) \quad \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad \text{Gibbs free energy equation}$$

$$(5) \quad \Delta G^\circ = -RT \ln K_{eq} \quad (R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1})$$

$$(6) \quad \Delta H^\circ - T\Delta S^\circ = -RT \ln K_{eq}$$

$$(7) \quad \ln K_{eq} = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}$$

A plot of $\ln K_{eq}$ vs. $1/T$ gives a slope of $-\Delta H^\circ/R$ and y-intercept of $\Delta S^\circ/R$. This expression was developed from the dependence of free energy (ΔG°) on K_{eq} and temperature. Both ΔH° (enthalpy) and ΔS° (entropy) are generally constant over relatively large temperature ranges [35].

Indication that the *neutral* (PVP)Ni(pcyd) complexes are electronically sensitive to solvent interaction was exposed during characterization (Chapter 3). Diamagnetic to paramagnetic conversion of (PVP)Ni(2,6-Cl₂pcyd) was noted by paramagnetic effects in the ¹H NMR on going from CDCl₃ to d₆-DMSO solvent media. This result prompted a more in depth exploration of the solvent-complex relationship in these *neutral* (PVP)Ni(pcyd) systems.

The ΔH° and ΔS° values found for the (PVP)Ni(pcyd) systems differ as a function of the pcyd⁹ substituents and are sensitive to changes in the donor

properties of the coordinating solvent. In this chapter, these effects are discussed and compared to similarly calculated thermodynamic parameters for NiN_4^{2+} systems.

5.2 Data

Electronic Absorption Spectroscopy

The $(\text{PVP})\text{Ni}(\text{pcyd})$ complexes were found to undergo solvent coordination. The $\text{PVP}^\ominus$ centered $\pi-\pi^*$ transitions displayed two distinct sets of $\pi-\pi^*$ bands which appear to be dependent on the coordination. Table 5.1 lists the $\pi-\pi^*$ bands and their extinction coefficients for the $(\text{PVP})\text{Ni}(2,6\text{-Cl}_2\text{pcyd})$ complex in solvent media of increasing donor strength (i.e. donor number). The accompanying spectra are shown in Figures 5.2 to 5.7 (the CHCl_3 spectra was shown previously in Figure 3.11) and are ordered from the weakest to the strongest donating solvent.

Figures 5.8 to 5.11 show the variable temperature spectra for representative examples of $(\text{PVP})\text{Ni}(\text{pcyd})$ complexes in each of the solvents in which temperature dependent equilibria is demonstrated, namely, benzonitrile, tetrahydrofuran (THF), acetone, and propylene carbonate (PC), respectively.

Molar Conductivity

In Table 5.2 the molar conductivity values are tabulated for $(\text{PVP})\text{Ni}(2,6\text{-Cl}_2\text{pcyd})$ in DMSO and THF. Also listed are values for well known 1:1 electrolytes obtained using the same apparatus, for comparison.

Table 5.1 Electronic Absorption Data for (PVP)Ni(2,6-Cl₂pcyd) in Increasingly Donating Solvent Media at Room Temperature†

Solvent	DN†	solvated $\pi-\pi^*$	desolvated $\pi-\pi^*$	$d-d$
A)				
CHCl ₃	≈0	————	476 (7170) 348 (20220)	625 (551)
Toluene	0.1	————	487 (6220) 350 (17150)	623 (569)
B)				
Benzonitrile	11.9	463 (9390) 436 (10460)	≈480 (st.sh)	625 (370)
PC ^a	15.1	458 (9530) 432 (10100)	≈480 (st.sh)	622 (246)
Acetone	17.0	456 (8300) 428 (9220)	≈480 (st.sh)	618 (526)
THF ^b	20.0	458 (18760) 431 (19800)	————	≈613 (≈100)
C)				
DMSO ^c	29.8	462 (18030) 434 (20290)	————	————

‡ Values in nm with the extinction coefficient indicated in parentheses ($M^{-1} \text{ cm}^{-1}$).

† DN = donor number from reference [85]. ^a Propylene carbonate.

^b Tetrahydrofuran. ^c Dimethyl sulfoxide.

Figure 5.2 Electronic absorption spectrum for (2,6-Cl₂pcyd)Ni(PVP) in toluene. The complex concentration is 1.29×10^{-4} M.

Figure 5.3 Electronic absorption spectrum for (2,6-Cl₂pcyd)Ni(PVP) in benzonitrile. The complex concentration is 1.16×10^{-4} M.

Figure 5.4 Electronic absorption spectrum of (2,6-Cl₂pcyd)Ni(PVP) in propylene carbonate. The complex concentration is 1.05×10^{-4} M.

Figure 5.5 Electronic absorption spectrum of (2,6-Cl₂pcyd)Ni(PVP) in acetone. The complex concentration is 1.29×10^{-4} M.

Figure 5.4 Electronic absorption spectrum of (2,6-Cl₂pcyd)Ni(PVP) in propylene carbonate. The complex concentration is 1.05×10^{-4} M.

Figure 5.5 Electronic absorption spectrum of (2,6-Cl₂pcyd)Ni(PVP) in acetone. The complex concentration is 1.29×10^{-4} M.

Figure 5.6 Electronic absorption spectrum of (2,6-Cl₂pcyd)Ni(PVP) in tetrahydrofuran (THF). The complex concentration is 1.28×10^{-4} M.

Figure 5.7 Electronic absorption spectrum for (2,6-Cl₂pcyd)Ni(PVP) in dimethyl sulfoxide (DMSO). The complex concentration is 9.59×10^{-5} M.

Figure 5.8 Variable temperature electronic absorption spectra of (4-Clpcyd)Ni(PVP) in benzonitrile (1.06×10^{-4} M). Arrows indicate spectral change from decreasing temperature (83.8°C to 23.7°C).

Figure 5.9 Variable temperature electronic absorption spectra of (2,4,5-Cl₃pcyd)Ni(PVP) in THF (8.49×10^{-5} M). Arrows indicate spectral change from decreasing temperature (60.4°C to 27.3°C).

Figure 5.10 Variable temperature electronic absorption spectra of (2,3-Cl₂pcyd)Ni(PVP) in acetone (4.42×10^{-5} M). Arrows indicate spectral change from decreasing temperature (29.2°C to 11.7°C).

Figure 5.11 Variable temperature electronic absorption spectra of (2-Clpcyd)Ni(PVP) in propylene carbonate (7.68×10^{-5} M). Arrows indicate spectral change from decreasing temperature (58.2°C to 8.9°C).

Table 5.2 Molar Conductivity Measurements for (PVP)Ni(2,6-Cl₂pcyd)
Thermostated at 25°C†

Solvent	Compound	Molar Conductance, Λ_m
DMSO ^a	(PVP)Ni(2,6-Cl ₂ pcyd)	10.2
	(<i>t</i> -Bu ₄ N)(PF ₆)‡	32.2
	KCl	36.2
THF ^a	(PVP)Ni(2,6-Cl ₂ pcyd)	<0.099 ^b
	(<i>t</i> -Bu ₄ N)(PF ₆)‡	6.8

† Values in ohms⁻¹mol⁻¹cm² using a cell constant of 0.3164 cm⁻¹.

‡ Tetrabutylammonium hexafluorophosphate. ^a Dimethyl sulfoxide (DMSO) and tetrahydrofuran (THF) both had pure solvent conductance <1.0 × 10⁻⁷ ohm⁻¹cm⁻¹, therefore a negligible contribution. ^b Resistance beyond upper range of 2.0 × 10⁶ ohm.

5.3 Results and Discussion

5.3.1 The Nature of the (PVP)Ni(pcyd)–Solvent Interactions

It has been recognized that, for macrocyclic square planar NiN_4^{+2} systems, there is a tendency to undergo axial solvent coordination if the solvent possesses sufficient donating properties. As a result of solvent coordination, these complexes become paramagnetic from an initially unsolvated diamagnetic form. It was previously demonstrated that a change of pcyd⁹ to other anions had a profound effect on the electronic $\pi-\pi^*$ band pattern of the neutral (PVP)Ni(pcyd) complexes. A similar perturbation can be brought about by altering the type of coordinating solvent. It was found in this study that two separate sets of $\pi-\pi^*$ transitions originating from solvated (paramagnetic) and desolvated (diamagnetic) forms of a (PVP)Ni(pcyd) complex existed simultaneously in solvents of moderate donor strength.

Table 5.1 lists the range of donating solvents used for this study. Figures 3.11 and 5.2 to 5.7 illustrate the progressive change in the $\pi-\pi^*$ band pattern of (2,6- Cl_2pcyd)Ni(PVP) on going to solvents of greater donor strength. The figures show a progressive increase in the three band pattern in the 450 nm region attributed to the solvated (i.e. paramagnetic) complex and a subsequent decrease in the broad band at ≈ 480 nm associated with the desolvated (i.e. diamagnetic) form. In the strongest donating solvent DMSO, the ≈ 480 nm band is essentially non-existent. This suggests that solvent coordination to the complex is essentially 100% (i.e. no unsolvated complex remains). The influence of solvent polarity is not known to decrease the intensity of $\pi-\pi^*$ bands in aromatic chromophores [57] which suggests solvent effects do not significantly contribute to changes in $\pi-\pi^*$ intensity.

The extinction coefficients (Table 5.1) of the two $\pi-\pi^*$ band sets reflect the diamagnetic to paramagnetic complex change as a result of solvent coordination. The assigned square planar $d-d$ band at ≈ 625 nm gradually decreases along with the broad band at ≈ 480 nm. These two bands were shown earlier to be associated with the square planar complex form (i.e. in CHCl_3). This suggests there is a progressive decrease in the concentration of the desolvated, square planar (diamagnetic) species with increasing solvent donor strength. The inversely proportional intensities of the two $\pi-\pi^*$ band sets indicate an equilibrium condition may exist in which the concentration sum of the desolvated and solvated complexes is constant. The resulting geometry of the solvent coordinated complex is discussed in the following section.

In highly donating solvents such as DMSO and pyridine, solvent substitution of a coordinated anion in Ni(II) systems is possible [86,87] resulting in an electrolytic solution. DMSO (donor number = 29.8) is known to substitute for halides on Ni(II) [86]. In Table 5.2 the electrolytic behavior represented by molar conductance, Λ_m , of a DMSO solution of $(\text{PVP})\text{Ni}(2,6\text{-Cl}_2\text{pcyd})$ is consistent with partial dissociation of $2,6\text{-Cl}_2\text{pcyd}^\ominus$. Comparison of Λ_m to the known 1:1 electrolytes KCl and $(t\text{-Bu}_4\text{N})(\text{PF}_6)$ revealed that the value for $(\text{PVP})\text{Ni}(2,6\text{-Cl}_2\text{pcyd})$ is less than the suggested 1:1 electrolyte Λ_m range. Furthermore, the lowest Λ_m reported for 1:1 electrolytes thermostated at 25°C was $\approx 23 \text{ ohm}^{-1} \text{ mol}^{-1} \text{ cm}^2$ for potassium octadecylsulphate [88] which suggests that the following dissociated equilibrium condition may exist:

In THF (donor number = 20.0), similar molar conductance measurements give non-conductive values which suggest the $\text{pcyd}^{\ominus}$ of $(\text{PVP})\text{Ni}(2,6\text{-Cl}_2\text{pcyd})$ is not dissociated. This may explain the inconsistency of the $\pi\text{-}\pi^*$ band intensity in the 450 nm region (i.e. for the solvated complex). Going from THF to DMSO these bands decreased slightly in extinction coefficient which opposed the increasing trend observed for increased solvent donor strength. This suggests that a solvent donor number in excess of 20 results in $2,6\text{-Cl}_2\text{pcyd}^{\ominus}$ dissociation. In addition, recrystallization of either $(\text{PVP})\text{Ni}(2,4,5\text{-Cl}_3\text{pcyd})$ or $(\text{PVP})\text{NiBr}$ from DMSO resulted in the formation of $(\text{PVP})_2\text{Ni}$ which strongly indicated dissociation was indeed occurring. A variable temperature electronic absorption study is required to confirm the existence of dissociated $\text{pcyd}^{\ominus}$ equilibria in strongly donating solvents.

In acetone, the intensities of the $(\text{PVP})\text{Ni}(2,6\text{-Cl}_2\text{pcyd})$ complex band pattern also shows inconsistent behaviour. The square planar $d\text{-}d$ band at 618 nm has an abnormally high extinction coefficient and conversely the $\pi\text{-}\pi^*$ bands in the 450 nm region are low compared to the trend observed with increasing donor strength trend. The donor number of acetone, which is lower than THF, would argue against any electrolytic behavior (i.e. dissociation) and point toward a solvent-complex interaction which differs from that seen for other solvents exhibiting solvent coordination equilibria.

From the solvents studied there appears to be three distinct solvent-complex interaction types at ambient temperature (Table 5.1): A) normal solvation (i.e. weak solvent-complex interaction), B) coordinated solvent-desolvated equilibria, and C) $\text{pcyd}^{\ominus}$ dissociated-nondissociated equilibria. Type B (i.e. solvent coordination) is highly probable as compared to simple solvent induced distortion of the 4-coordinate complex (i.e. reminiscent of tetrahedral distortion in Chapter

4) since Ni(II) is coordinatively unsaturated [26d,57] and that the closely related NiN_4^{2+} complexes are susceptible to solvent coordination in sufficiently donating solvents [36–38,56]. The inversely related intensity ratio of the apparent type B solvated–desolvated $\pi-\pi^*$ bands (Table 5.1) in benzonitrile, propylene carbonate (PC), tetrahydrofuran (THF), and acetone suggests the equilibrium in equation (1) exists for the *neutral* (PVP)Ni(pcyd) complexes.

The application of π -mixing of ligand centered $\pi-\pi^*$ bands in the (PVP)Ni(pcyd) complexes as it pertains to the equilibrium between two geometrical forms as in equation (1) is a novel and unique approach to studying equilibria of this type. In terms of electronic absorption spectroscopy, previous studies have relied on ligand field transitions which are usually weak and are easily obscured by intense $\pi-\pi^*$ and charge transfer type bands. In the following section, the solvated–desolvated equilibria is explored in a series of neutral (PVP)Ni(pcyd) complexes by way of variable temperature electronic absorption spectra of the $\pi-\pi^*$ bands.

5.3.2 Thermodynamic Aspects of (PVP)Ni(pcyd) Complex–Solvent Equilibria

The nature of the solvent coordinated complex equilibria is of interest considering that such associations exist between solvents and NiN_4^{+2} complexes [32–34, 36–40,56,82] and to my knowledge similar studies have not been done on *neutral* NiN_4 systems. One would expect the ΔH° values for solvent coordination to neutral (PVP)Ni(pcyd) complexes to be reduced in magnitude relative to dicationic NiN_4^{2+} solvent adduct complexes because of complex charge effects. The apparent desolvated (diamagnetic)–solvated (paramagnetic) equilibrium is reversibly shifted by temperature change as indicated by the inverse intensity

change of the $\pi-\pi^*$ bands sets ascribed to the two complex forms. The temperature variable electronic absorption spectra are displayed for representative complexes in four solvents of intermediate donor strength, namely benzonitrile, THF, acetone, and PC (propylene carbonate) (Figures 5.8 to 5.11). Each possesses isosbestic points suggesting the conversion between the complex forms is a simple one step process [37]. The isosbestic points are more clearly defined in benzonitrile (i.e. b.p. 190.7°C, m.p. -13°C) and PC (i.e. b.p. 240°C, m.p. -55°C) since variable temperature studies in these solvents were less hampered by limitations imposed by an unfavourable liquid range of the solvent. Acetone (i.e. b.p. 56.2°C, m.p. -95.3°C) and THF (i.e. b.p. 67°C, f.p. -108°C) were more difficult to work with as a result of their volatility at higher temperatures. In addition, the intensity of the solvated complex $\pi-\pi^*$ band pattern (i.e. 450 nm region) at room temperature suggested that the solvated form is more favoured and therefore reduction of the ambient temperature resulted in only a moderate change of the $\pi-\pi^*$ spectra. The arrows on each spectra indicate the direction of intensity change with decreasing temperature. These changes are consistent with the spectra of NiN_4^{+2} systems (Figure 5.1) where the solvent coordinated complex is preferred at lower temperatures [32-34,36-40,56,82].

Thusfar we have implied that only two species are in equilibrium. The isosbestic points suggested this to be true and the method developed by Coleman *et al* [46], a simple graphical technique, provides further evidence. Figures 5.12 to 5.15 illustrate the method as it is applied to the representative variable temperature spectra shown in Figures 5.8 to 5.11. In each case, a family of linear plots passing through the origin indicates that two absorbing species are present whose concentration summation is constant. Other plots were attempted

Figure 5.12 Coleman graphical test for 2 absorbing species with a constant concentration sum for (4-Clpcyd)Ni(PVP) in benzonitrile. Reference $\lambda = 434 \text{ nm}$ (i). Each j represents the electronic absorption spectra at a different temperature. A = absorbance (see Figure 5.8).

Figure 5.13 Coleman graphical test for 2 absorbing species with a constant concentration sum for (2,4,5- Cl_3pcyd)Ni(PVP) in THF. Reference $\lambda = 430 \text{ nm}$ (i). Each j represents the electronic absorption spectra at a different temperature (see Figure 5.9).

Figure 5.14 Coleman graphical test for 2 absorbing species with a constant concentration sum for (2,3-Cl₂pcyd)Ni(PVP) in acetone. Reference $\lambda = 430 \text{ nm}$ (i). Each j represents the electronic absorption spectra at a different temperature (see Figure 5.10).

Figure 5.15 Coleman graphical test for 2 absorbing species with a constant concentration sum for (2-Clpcyd)Ni(PVP) in propylene carbonate. Reference $\lambda = 432 \text{ nm}$ (i). Each j represents the electronic absorption spectra at a different temperature (see Figure 5.11).

incorporating different sets of conditions (i.e. different number of absorbing species and non-constant concentrations) but did not exhibit linear relationships. A sample calculation of Coleman plot data for (PVP)Ni(4-Clpcyd) in benzonitrile is presented in Appendix 1. Similar Coleman plots were found for the temperature dependent spectra of the remaining (PVP)Ni(pcyd) complexes in PC, THF, acetone, and benzonitrile.

The K_{eq} , and hence the thermodynamic parameters, are calculated in a similar manner as used by Tregloan *et al* [39] for acetonitrile coordination to [Ni(*cis*-tetramethylcyclam)]²⁺ which has been previously outlined. The method incorporated a monitoring of the square planar *d-d* band of the desolvated complex. High and low intensity extremes representing 0% solvated and 100% solvated complex, respectively, were used to calculate the ratios of the two forms at a given temperature (i.e. intermediate intensities). Our method utilized the temperature dependent intensity of the solvated complex form $\pi-\pi^*$ band at ≈ 430 nm (see Figures 5.8 to 5.11). This band underwent the largest intensity fluxuation as a function of temperature and therefore was considered to be the most sensitive.

The maximum intensity was obtained from low temperature spectra of the (PVP)Ni(pcyd) complexes in THF (donor number = 20.0). Below $\approx 10^\circ\text{C}$ the spectra is temperature invariant suggesting that maximum solvation ($\approx 100\%$) had been reached. The minimum intensity was obtained from the CHCl_3 spectra in which the characteristic solvated complex $\pi-\pi^*$ band structure is not seen. Furthermore, the CHCl_3 spectra were temperature invariant from $\approx 5^\circ\text{C}$ to $\approx 40^\circ\text{C}$ which corroborated with the presence of 100% desolvated complex. In benzonitrile, acetone, PC, and higher temperature THF solutions, the absorbances of the ≈ 430 nm band are considered representative of intermediate concentration ratios of

desolvated and solvated complex as compared to the two absorbance extremes. The concentration change of the neat solvent as a result of coordination to the complex was assumed to be negligible since the change would be on the order of the complex concentration (i.e. 10^{-4} – 10^{-5} M). Therefore the percent ratio of the two complex forms at any given temperature could be equated to the K_{eq} calculated in equation (2).

A sample calculation of K_{eq} values at given temperatures in the range 83.8°C to 23.7°C for (4-Clpcyd)Ni(PVP) in benzonitrile is presented in Appendix 2.

Both ΔH° (enthalpy) and ΔS° (entropy) were calculated using equation (7). Representative plots are shown in Figures 5.16 to 5.19 for selected complexes in acetone, THF, benzonitrile, and PC. The resulting ΔH° and ΔS° values are listed in Table 5.3 and a sample calculation for (PVP)Ni(4-Clpcyd) in benzonitrile is presented in Appendix 2.

The $\ln K_{eq}$ vs. $1/T$ plots display remarkable linearity which is corroborated by the correlation coefficients (i.e. all values were ≥ 0.990) (Table 5.3). The temperature spread of data points for benzonitrile and PC solutions as compared to THF and acetone, are larger owing to lower volatility of the former solvents at higher temperatures. Since ΔS° was obtained from the y-intercept, a less than ideal correlation coefficient equates to greater possible error. This suggests that one should interpret the ΔS° values for acetone and THF with caution.

The ΔH° values for benzonitrile, THF, and PC complex solutions (Table 5.3) are within the range of values found for NiN_4^{2+} systems exhibiting two solvent coordination equilibria (i.e. Table 1.1, ΔH° range, 17.1 to 43.8 KJ mol⁻¹). This suggests that for the *neutral* (PVP)Ni(pcyd) complex solutions, two solvent

Figure 5.16 Plot of $\ln K_{eq}$ vs $1/T$ for the solvent coordination equilibria of (PVP)Ni(4-Clpcyd) in benzonitrile ($1.06 \times 10^{-4} \text{ M}$). Each point was derived from the electronic absorption spectra at a given temperature (see Figure 5.8).

Figure 5.17 Plot of $\ln K_{eq}$ vs $1/T$ for the solvent coordination equilibria of (PVP)Ni(2,4,5-Cl₃pcyd) in THF ($8.49 \times 10^{-5} \text{ M}$). Each point was derived from the electronic absorption spectra at a given temperature (see Figure 5.9).

Figure 5.18 Plot of $\ln K_{eq}$ vs $1/T$ for the solvent coordination equilibria of (PVP)Ni(2,3-Cl₂pcyd) in acetone (4.40×10^{-5} M). Each point was derived from the electronic absorption spectra at a given temperature (see Figure 5.10).

Figure 5.19 Plot of $\ln K_{eq}$ vs $1/T$ for the solvent coordination equilibria of (2-Clpcyd)Ni(PVP) in propylene carbonate ($7.68 \times 10^{-5} \text{ M}$). Each point was derived from the electronic absorption spectra at a given temperature (see Figure 5.11).

Table 5.3 Thermodynamic Parameters, ΔH° and ΔS° †, Derived from Temperature Dependent Solvation Equilibria of the (PVP)Ni(pcyd) Complexes

$-\Delta H^\circ$				
pcyd anion	PhCN DN=11.9	THF DN=20.0	PC DN=15.1	Acetone DN=17.0
2,3,5,6-Cl ₄ pcyd	35.7±1.9	34.2±3.5	27.0±2.3	^a
2,4,5-Cl ₃ pcyd	38.2±1.4	35.1±2.5	28.3±1.0	12.1±2.8
2,6-Cl ₂ pcyd	44.2±2.3	30.1±3.7	29.5±1.7	17.0±1.4
2,3-Cl ₂ pcyd	43.2±2.5	37.7±5.0	30.4±1.4	12.6±3.4
2-Clpcyd	43.8±2.6	30.5±5.2	23.9±0.3	13.0±2.0
4-Clpcyd	31.3±1.6	35.2±3.0	25.9±1.2	15.6±1.4
$-\Delta S^\circ$				
2,3,5,6-Cl ₄ pcyd	127.3±6.1	96.6±10.9	92.1±7.1	^a
2,4,5-Cl ₃ pcyd	131.0±4.3	101.7±8.0	95.3±3.0	44.9±9.6
2,6-Cl ₂ pcyd	156.0±7.5	85.1±11.5	110.1±5.7	71.2±4.1
2,3-Cl ₂ pcyd	151.2±7.8	110.7±15.7	110.9±4.6	56.6±11.6
2-Clpcyd	151.7±8.2	84.7±16.5	84.6±1.1	55.2±6.9
4-Clpcyd	102.8±4.8	102.7±9.6	93.4±3.8	63.8±4.6

† ΔH° in kJ mol⁻¹, ΔS° in J mol⁻¹ K⁻¹. Correlation coefficients for all values > 0.99. All errors calculated by linear regression with a confidence level of 95%.

^a Completely insoluble.

molecules undergo complex coordination. In addition, solvent coordination as a result of a right shift in equation (1) is an *exothermic* process (negative ΔH°) which is consistent with diamagnetic (desolvated) to paramagnetic (solvated) conversion in NiN_4^{2+} systems [36–38,56].

Enthalpy values for acetone are dissimilar to the other three solvents. The negative ΔH° values (i.e. exothermic) ranged from 12.1 to 17.0 KJ mol⁻¹ which is roughly half in comparison to the other three solvents studied. This is consistent with ΔH° values obtained for mono-solvent coordination to $[Ni(cis\text{-tetramethylcyclam})]^{+2}$ (Table 1.2) [82,40] which suggests only one acetone coordinates to the (PVP)Ni(pcyd) complexes.

Comparison of ΔH° values found for the solvent coordinated (PVP)Ni(pcyd) equilibria are explored in two ways: 1) constant solvent, variable pcyd[⊖] and 2) constant pcyd[⊖], variable solvent.

In Chapter 4, it was concluded that the $\pi\text{-}\pi^*$ band pattern change is a manifestation of structural (coordination geometry) and/or π -donating influence by the mono-anion mediated by Ni(II). The apparent tetrahedral distortion from square planarity of the (PVP)NiL complexes resulted from steric and/or field strength influences. It is relatively clear that this is followed by a diamagnetic to paramagnetic spin-state change of Ni(II) as suggested by ¹H NMR in non-coordinating CDCl₃. The act of solvent coordination to the (PVP)Ni(pcyd) complexes, changes the coordination geometry which implies that there is also a diamagnetic to paramagnetic spin state change of Ni(II). Such a spin state change was seen for (PVP)Ni(2,6-Cl₂pcyd) in *d*₆-DMSO (Figure 3.18).

The ΔH° values (Table 5.3) are not consistent with the trend in solvent donor strength (i.e. increasing donor strength, increasingly negative ΔH°) which suggests

that solvent properties other than the donor strength contribute to the interaction with Ni(II).

benzonitrile

THF

PC

Benzonitrile has π -acceptor properties when bound terminally through the nitrile nitrogen as well as σ -donor ability [89], whereas both THF and PC are purely σ -donors when oxygen bound (i.e. through the lone pairs on oxygen) [57,90]. In general, there is an increase in the exothermicity of solvent coordination going from PC (donor number = 15.1) to THF (donor number = 20.0) which suggests that the donor strength is the predominant factor in determining the complex-solvent bond strength of the solvated form. Both solvents should be relatively unhindered by the substituents of the planar (PVP)Ni(pcyd) complexes.

Benzonitrile (donor number = 11.9) coordinated complexes have values which are comparable to that of THF (donor number = 20) even though their donor numbers are quite different. Benzonitrile is a "rod-like" molecule [39] which is most likely less sterically hindered than both THF and PC when bound to the (PVP)Ni(pcyd) complexes. Herron and Moore [37] also observed unusual

bis-solvent complex coordinated ΔH° values for acetonitrile bound to $[\text{Ni}(\text{trans-tetramethylcyclam})]^{2+}$ and none compare to more strongly donating DMSO and DMF coordinated complex. It was suggested that the more exothermic ΔH° of the acetonitrile coordinated complex was a direct consequence of steric limitations imposed by the macrocyclic ligand on the coordinating solvent molecules. The π accepting nature of benzonitrile can also be noted as a contributor to the solvent-complex bond strength if one considers the advantages of a *trans* relationship between benzonitrile and a π -donor ligand such as the amine anions on $\text{pcyd}^\ominus$ (nitrile nitrogen) and $\text{PVP}^\ominus$ (pyrrole nitrogen). For bis-solvent coordination we can consider two possible isomers owing to the preference of $\text{PVP}^\ominus$ to remain essentially planar [48,49,51,54,55]. Form B would satisfy the *trans* effect but would require that $\text{pcyd}^\ominus$ be distorted out of the plane. It has been shown that desolvated to solvated complex interconversion is a simple one step process as indicated by the isosbestic points in

Figure 5.20 Isomers of the bis-solvent coordinated (PVP)Ni(pcyd) complexes

Figures 5.8 to 5.11. This suggests that if isomer B does indeed exist, the distortion of $\text{pcyd}^\ominus$ and the coordination of two solvent molecules must take place rapidly. Further evidence is required to confirm the existence of this isomeric form. Perhaps a lower temperature benzonitrile (i.e. not too low as benzonitrile solidifies at 13°C) infrared study would be appropriate. If the $\nu_{\text{C}\equiv\text{N}}$ of coordinated benzonitrile is sufficiently isolated from the $\nu_{\text{N}=\text{C}=\text{N}}$ of $\text{pcyd}^\ominus$, a split peak would be expected owing to the differing coordination interactions of benzonitrile in isomer B.

Fabrizzi *et al* [36] have put forward that diamagnetic to paramagnetic conversion of the Ni(II) as a result of solvent coordination to macrocyclic NiN_4^{2+} systems results in a radial increase of the Ni(II) ion (i.e. the result of becoming high spin) with a subsequent increase in the Ni-N bond lengths. If the N_4 macrocycle is bulky, the enthalpic barrier to solvent coordination increases since the ligand experiences distortional strain due to the Ni-N bond length increases. If the (PVP)Ni(pcyd) complexes experience the same diamagnetic to paramagnetic Ni(II) spin state change, the in-plane steric strain may be relieved by out of plane distortion on the mono dentate $\text{pcyd}^\ominus$. This also suggests isomeric form B is possible.

Judging from the ΔH° values, acetone only mono-coordinates to the (PVP)Ni(pcyd) complexes. In NiN_4^{2+} systems where mono-solvent coordination has occurred (Table 1.2) [39,82,40], it has been suggested that bulky substituents on the N_4 ligand prevents the normal in-plane distortion (i.e. buckling of the N_4 ring)

that results from increased Ni-N bond lengths due to the Ni(II) ionic radial increase (i.e. on going from diamagnetic to paramagnetic). The Ni(II) ion lifts out of the plane as a consequence of in plane steric repulsion and as a result only mono-solvent coordination can take place. It remains unclear as to why the acetone apparently mono-coordinates to the (PVP)Ni(pcyd) complexes. Perhaps the methyl groups of acetone are too bulky even though the pcyd[⊖] appears to be able to distort out of the square plane.

Comparison of ΔH° values where the solvent is constant and the type of pcyd[⊖] is varied, is difficult to interpret. It is apparent that changes in the substituents on the phenyl ring of pcyd[⊖] have a definite effect on the ΔH° of solvent coordination (Table 5.3). One would anticipate that a stronger π -donating pcyd[⊖] would render solvent coordination less exothermic for THF and PC (σ -donors) since the build up of electron density on Ni(II) would most likely be greater. This is not the case (i.e. 2-Clpcyd[⊖] and 4-Clpcyd[⊖] are the better π -donors [21]) which would suggest the presence of differing number and the position of chloro substituents may contribute a possible steric dimension to solvent coordination. In addition, the likelihood of bis-solvated isomer B may account for randomness of ΔH° for the (PVP)Ni(pcyd) complexes in a given solvent if one considers that an equatorial to axial distortion of pcyd[⊖] would probably be sensitive to the position of the bulky chloro substituents on the phenyl ring.

The same can be said for benzonitrile coordination. Its rodlike description when bound through the nitrile nitrogen [57] would suggest simple bis-axial

coordination would be relatively unhindered (i.e. this may also account for ΔH° values comparable to the bulkier THF). Therefore the irregular ΔH° values (i.e. as a function of the π -donor ability of $\text{pcyd}^\ominus$) may be accounted for by equatorial to axial distortion of $\text{pcyd}^\ominus$. Further study is required, incorporating a wider range of $\text{pcyd}^\ominus$ ligands. Any trends in ΔH° may become more apparent in the wake of an expanded study.

The apparent bis-solvent coordinated $(\text{PVP})\text{Ni}(\text{pcyd})$ systems have large negative ΔS° values (Table 5.3) with a range of 85 to 156 $\text{J K}^{-1} \text{mol}^{-1}$ which is consistent with the range of ≈ 50 to $\approx 150.0 \text{ J K}^{-1} \text{mol}^{-1}$ (most values fall within the 65 to 146 $\text{J K}^{-1} \text{mol}^{-1}$ range, Table 1.2) for similar NiN_4^{2+} systems [36–39,56,82]. The ΔS° values for acetone (i.e. 45 to 71 $\text{J K}^{-1} \text{mol}^{-1}$) are roughly in the range of that obtained for mono-solvent coordination which is 32.0 to 41.0 $\text{J K}^{-1} \text{mol}^{-1}$, (only 3 values, Table 1.2).

The parallels in the ΔS° values for the $(\text{PVP})\text{Ni}(\text{pcyd})$ (Table 5.3) and NiN_4^{2+} (Table 1.1) complexes reinforces the mono and bis-solvent coordination assignments made previously from ΔH° values. According to Hinz and Margerum [91], the large range of ΔS° values for solvent coordination to NiN_4^{2+} complexes stems from the "degree" to which the solvent is coordinated to the complex. Spin interconversion between diamagnetic and paramagnetic does not necessarily require that the solvent be absolutely coordinated or non-coordinated, respectively. The interaction can range from totally bonded to weakly "mobilized" which reflects the degree of freedom, or entropy, of the solvent molecule. The degree of steric repulsions between the N_4 ligand and the solvent was also suggested to be largely responsible for the degree of solvent-complex bonding.

The ΔS° values of the bis-solvent coordinated, $(\text{PVP})\text{Ni}(\text{pcyd})$ complex

equilibria appear to be consistent with the above rationale. The benzonitrile values demonstrated the largest decrease in entropy which is most likely a result of stronger bonding, whereas THF and PC are generally lower and may be more adequately described as "intimately mobilized".

5.4 Summary

Through this study it has been shown that the *neutral* (PVP)Ni(pcyd) complexes undergo solvent coordination in appropriate media with subsequent establishment of coordinated (paramagnetic)/non-coordinated (diamagnetic) equilibria which is reversibly shifted as a function of temperature. Unique to studies of this type is the application of π -mixing seen in the π - π^* transitions of the (PVP)Ni(pcyd) complexes. The effect is lifted when the complex is solvent coordinated and can therefore be used to monitor the reversible change of the desolvated and solvated forms. The K_{eq} is used to calculate the thermodynamic parameters ΔH° and ΔS° which are then used to deduce the bis-solvated and mono-solvated status of the complexes and partially elucidate the role of solvent properties which govern the bonding interaction. Solvent coordination equilibria of dicationic NiN_4^{2+} systems had ΔH° and ΔS° values similar to neutral (PVP)Ni(pcyd) complex-solvent equilibria which suggested that the charge was not a significant factor to the solvent-complex interaction. If charge effects were important one would expect less negative ΔH° and ΔS° values resulting from solvent coordination for the neutral complexes. Distortion of $pcyd^\ominus$ from an equatorial to an axial position is suspected for solvents undergoing bis-coordination.

CHAPTER 6

CONCLUSIONS AND FUTURE STUDIES

The work amassed in this thesis has covered a range of interesting properties attributed to the (PVP)Ni(pcyd) complexes. The crystal structure obtained for (PVP)Ni(2-Clpcyd) appears to be the first such structure for a phenylcyanamide Ni(II) complex. The tetrahedral distortion observed for this complex in the solid state suggested the ligand field about Ni(II) is relatively weak. Intramolecular bond lengths and angles implied the complex retains low-spin diamagnetic integrity despite the tetrahedral distortion. The solid state work is preliminary and requires magnetic susceptibility (χ_m) measurements to confirm the Ni(II) spin state. It would be interesting to compare χ_m values for the (PVP)Ni(pcyd) series since paramagnetic/diamagnetic ground state equilibria may exist and would be reflected in the χ_m values. Intermediate values between the ideal diamagnetic (i.e. $\chi_m = 0$, low-spin) and paramagnetic (i.e. $\chi_m = 2$ unpaired electrons, high-spin) would imply isomeric equilibria. This may also be seen in crystal structure comparisons. Decreasing pcyd⁹ π donation would most likely result in decreased tetrahedral distortion (i.e. diamagnetic).

The orientation of the (PVP)Ni(2-Clpcyd) molecules in the unit cell indicated that there may be inter-stack π interaction based on the distances between the molecular planes. The potential for molecular conductivity via the π stacks opens up a whole new area of potential study for these systems especially if one considers the extension to a possible dicyd²⁻ planar complex. It was previously noted that well conjugated, partially oxidized Ni(II) dianion macrocyclic complexes are electrically conductive. If a mixed valent, Ni (III/II)

dicyd²⁻ complex could be obtained there is a strong possibility electrical conduction may occur through the conjugated π stacks. Ni(III) is known to be stabilized by the π anti-bonding orbitals of macrocyclic tetraammine ligands and iminopyridine moieties (i.e. when bound through the pyridine nitrogen) [42,95,96].

The focus of this thesis was the dynamics of the (PVP)Ni(pcyd) systems in solution. By changing substituents on the phenyl ring of the phenyl¹⁻ amide anion ligand, it was possible to "tune" the π donating properties. The influence of this property in low donating CDCl₃ was indicated by the ¹H NMR where diamagnetic to paramagnetic conversion of the complex appears to take place (i.e. (PVP)Ni(2,6-Cl₂pcyd), (PVP)Ni(4-Clpcyd), and (PVP)Ni(2-Clpcyd)). This behaviour suggested the establishment of equilibria between the paramagnetic and diamagnetic isomers. A temperature variable ¹H NMR study is required to confirm the existence of the equilibria. In addition, the paramagnetic isomer contribution should be reflected in the solution state magnetic susceptibility values. The method used by Evans [63] would be an appropriate follow-up study for obtaining these values. EPR (electron paramagnetic resonance) data would also be useful for

spin state evaluation for the less soluble (i.e. in low donating solvent) complexes, (PVP)Ni(2,3-Cl₂pcyd), (PVP)Ni(2,4,5-Cl₃pcyd), and (PVP)Ni(2,3,5,6-Cl₄pcyd) since much lower concentrations are required for measurement [80]. The CHCl₃ electronic absorption spectra denoted square planar geometry (i.e. *d-d* band) which suggested the diamagnetic isomer was more favoured. In addition, the E_{max} of the square planar band decreases (i.e. decreasing ligand field) in energy with increasing pcyd[⊖] π donation which corroborates with the conversion to a paramagnetic ground state.

The $\pi-\pi^*$ effect seen in the electronic absorption spectra (i.e. in low donating solvent) has been characterized as a " π -mixing" effect between filled π -symmetry orbitals of PVP[⊖] and pcyd[⊖] anion nitrogens mediated by a common *d* π orbital of Ni(II) which essentially extends the conjugation of the PVP[⊖] anion. Confirmation of the assignment has yet to be obtained but the geometrical dependence (i.e. square planar) of the $\pi-\pi^*$ effect on the π donation of the mono-anion appears to hold. This is based on comparisons to other 4-coordinate complexes which contain mono-anion ligands that are π donating (i.e. Cl[⊖], Br[⊖], N₃[⊖], and SCN[⊖]), have alternate coordination geometries (i.e. 5-coordinate (PVP)Ni(OAc) and 6-coordinate (PVP)₂Ni), and to the apparently square planar (PVP)NiCN complex in which the cyanide anion is π accepting [79]. Work is continuing on the (PVP)NiCN complex as to the confirmation of the diamagnetic, square planar assignment. The (PVP)NiCl complex requires further purification to be absolutely sure that the absence of the $\pi-\pi^*$ effect is the result of tetrahedral distortion. The (PVP)Cu(2,3-Cl₂pcyd) complex requires also requires further purification and may provide insight into the significance of the ligated metal center on

the " π -mixing" effect if it is indeed a square planar complex. $\text{PVP}^\ominus$ complexes of Pt(II) and Pd(II) are also of interest since they would most likely form square planar systems.

To my knowledge temperature dependent solvent coordination equilibria for neutral tetraamine, square planar Ni(II) systems (NiN_4) has not been attempted. In addition, the tetraammine ligation in the $(\text{PVP})\text{Ni}(\text{pcyd})$ complexes are not macrocyclic and therefore greater ligand distortion is possible (i.e. from the square plane). The thermodynamic parameters, ΔH° and ΔS° , which define the degree of solvent coordination, for the $(\text{PVP})\text{Ni}(\text{pcyd})$ complexes (Table 5.3) are similar to the values for the dicationic NiN_4^{2+} systems (Table 1.1) which suggested solvated (paramagnetic)/ desolvated (diamagnetic) equilibria was occurring and the dicationic charge of the NiN_4^{2+} complexes was not a significant influence on the coordinated solvent bond strength. The ΔH° and ΔS° values for benzonitrile, propylene carbonate, and THF solvent coordination to the $(\text{PVP})\text{Ni}(\text{pcyd})$ complexes corroborated with two coordinating solvent molecules and that of acetone to one. Factors other than solvent donor strength contribute to the exothermicity of solvent coordination as indicated by the lack of correlation to the thermodynamic parameters. For the bis-solvent systems, two possible isomers were suggested. Isomer B (Figure 5.20) appeared to be the preferred structure due to the unusually negative ΔH° and ΔS° values for benzonitrile, a good π accepting molecule (i.e. trans to the anionic, π donating nitrogens). This corroborated with the absence of a consistent trend in the values of ΔH° and ΔS° for the series of complexes in a given solvent since intramolecular steric repulsions as a result of equatorial to axial distortion of $\text{pcyd}^\ominus$ would be a prerequisite to the formation of

isomer B. Confirmation of the mode of solvent coordination may come from a solution infrared study. If the $\nu_{C\equiv N}$ of benzonitrile is sufficiently isolated from $\nu_{N=C=N}$ of pcyd⁹, a band splitting may suggest different coordination modes exist for benzonitrile (Figure 5.20, isomer B). The (PVP)Ni(pcyd) complexes were found to be insoluble in a number of solvents of intermediate donor strength (i.e. 10–16 [85], eg. acetone and acetonitrile) which made expansion of this study to a larger range of solvents difficult.

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APPENDIX 1 – Sample Calculation for a Graphical Point on a Coleman Plot

The Coleman plot of solvent coordination equilibria for (PVP)Ni(4-Clpcyd) in benzonitrile (Figure 5.12) assumes there are two absorbing species present (i.e. solvent coordinated and non-coordinated forms) in which the concentration sum is constant.

Equation (1) had been derived previously [41] for a solution absorption spectrum with the above conditions. Absorbance values were obtained from temperature dependent spectra.

$$(1) \quad A_{ij} - A_{ij'} = \text{constant} (A_{i'j} - A_{i'j'})$$

i = reference λ (436 nm)

j' = reference solution of temperature 23.7°C

i' = another λ (eg. 323 nm)

j = another solution at a given temperature (eg. 53.3°C)

Therefore:

$$A_{ij} = 1.2194$$

$$A_{i'j} = 1.8328$$

$$A_{ij'} = 1.5594$$

$$A_{i'j'} = 2.0607$$

$$A_{ij} - A_{ij'} = -0.3400$$

$$A_{i'j} - A_{i'j'} = -0.2279$$

Plot $A_{ij} - A_{ij'}$ vs $A_{i'j} - A_{i'j'}$.

APPENDIX 2 – Sample Calculation for K_{eq} , ΔH° and ΔS° for Solvent Coordination Equilibrium

The method used for (PVP)Ni(4-Clpcyd) in benzonitrile was similar to that of Tregloan *et al* [43].

1) Equilibrium Constant K_{eq}

- a) Calculation of two absorbance extremes (i.e. minimum and maximum) for $\lambda = 436 \text{ nm}$.

$$(2) \quad A = \epsilon bc \quad (\text{Beer's Law}) \quad b = 1 \text{ cm}$$

- b) Maximum absorbance (100% solvent coordination)

$$\epsilon_{\max}(\text{THF}) = \frac{1.6170}{8.46 \times 10^{-5} \text{M}} = 19110 \text{ M}^{-1}\text{cm}^{-1}$$

$$\text{Abs. max. (benzonitrile)} = (19110 \text{ M}^{-1}\text{cm}^{-1})(1.06 \times 10^{-4} \text{M}) = \underline{2.0260}$$

- c) Minimum absorbance (0% solvent coordination)

$$\epsilon_{\min}(\text{CHCl}_3) = \frac{0.8393}{1.03 \times 10^{-4} \text{M}} = 8150 \text{ M}^{-1}\text{cm}^{-1}$$

$$\text{Abs. max (benzonitrile)} = (8150 \text{ M}^{-1}\text{cm}^{-1})(1.06 \times 10^{-4} \text{M}) = \underline{0.8637}$$

$$\text{Absorbance Range} = 2.0260 - 0.8637 = \underline{1.1623}$$

d) K_{eq} at 83.8°C

$$\text{Abs(at } \lambda=436 \text{ nm}) = 1.0246$$

$$\text{Decrease from Abs. max.} = 2.0260 - 1.0246 = 1.0014$$

$$\text{Therefore } \frac{1.0014}{1.1623} \times 100 = \underline{86.16\%} \text{ non-solvent coordinated complex A}$$

$$100\% - 86.16\% = \underline{13.84\%} \text{ solvent coordinated complex B}$$

$$\text{From (1)} \quad K_{eq} = \frac{13.84\%}{86.16\%} = \underline{0.161} \quad (\text{i.e. } [\text{PhCN}] \text{ assumed constant})$$

2) Thermodynamic Parameters ΔH° and ΔS°

$$(3) \ln K_{eq} = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}$$

$$\text{Plot } \ln K_{eq} \text{ vs } 1/T, \quad \text{slope} = \frac{-\Delta H^\circ}{R}, \quad \text{y-intercept} = \frac{\Delta S^\circ}{R}$$

$$\text{e.g. } K_{eq} \text{ at } 83.3^\circ\text{C} = 0.161$$

$$\ln K_{eq} = -1.83$$

Table A1

$T(^{\circ}\text{C})$	$1/T (\times 10^{-3})(\text{K}^{-1})$	$\ln K_{eq}$
83.8	2.80	-1.83
68.3	2.93	-1.31
64.1	2.97	-1.19
58.4	3.02	-1.02
53.3	3.06	-0.86
42.7	3.17	-0.50
32.7	3.27	-0.10
27.8	3.32	0.15
23.7	3.37	0.39

Therefore from Figure 5.16

$$\text{slope} = \frac{-\Delta H^\circ}{R}$$

$$\Delta H^\circ = -(\text{slope})R$$

$$\Delta H^\circ = -(3.76 \times 10^3 \text{ K}) \times$$

$$(8.3144 \text{ J/mol} \cdot \text{K})$$

$$\Delta H^\circ = -31300 \text{ J/mol}$$

$$\Delta H^\circ = \underline{-31.3 \text{ KJ/mol}}$$

$$\text{y-intercept} = \frac{\Delta S^\circ}{R}$$

$$\Delta S^\circ = (\text{y-intercept})R$$

$$\Delta S^\circ = (-12.36)(8.3144 \text{ J/mol} \cdot \text{K})$$

$$\Delta S^\circ = \underline{-10.3 \text{ J/mol} \cdot \text{K}}$$

APPENDIX 3 – Additional Spectral Data

Figure A1 ¹H NMR spectrum for PVPH in *d*₆-DMSO Figure A2 ¹H NMR spectrum for (FVP)Zn(OAc) in *d*₆-DMSO

Figure A3 Infrared spectrum (KBr) for (PVP)₂NiBr

Figure A4 Infrared spectrum (KBr) for (PVP)₂Zn(OAc)

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