(1,3-Bis(2′-pyridylimino)isoindolinato)nickel(II) complexes of phenylcyanamido ligands: crystal structure, electronic absorption spectroscopy and solvent adduct studies

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Abstract

Complexes of the formula Ni(L)X, where L = 1,3-bis(2′-pyridylimino)isoindolinato and X = Cl, Br, N_3, NCS, 2-Clpcyd, 4-Clpcyd, 2,3-Cl_2pcyd, 2,6-Cl_2pcyd, 2,4,5-Cl_3pcyd and 2,3,5,6-Cl_4pcyd, have been synthesized and characterized by elemental analysis, and IR, ^{1}H NMR and UV–Vis spectroscopies. A crystal structure determination of Ni(L)(2-Clpcyd) showed nickel in a distorted square planar coordination sphere of nitrogen donor atoms in which the phenylcyanamido ligand is coordinated to Ni(II) via the terminal nitrogen. The solvent coordination equilibria of Ni(L)(pcyd) complexes was also investigated and the results suggest that both electronic and steric factors play important roles in determining the stability of the solvated complex.

Introduction

The properties of transition metal complexes that incorporate phenylcyanamide ligands have gone largely unexplored, since their initial investigation over 20 years ago [1]. Recent interest [2, 3] has been stimulated by the discovery of Hunig and co-workers of novel hybrid molecular metals with stoichiometry $Cu(DCNQI)_2$ where DCNQI is a dicyanoquinonediimine derivative [4]. The two electron reduction product of DCNQI, the 1,4-dicyanamidobenzene dianion, has been shown to be a powerful antiferromagnetic superexchange mediator when bridging two Ru(III) ions [5]. The extent of antiferromagnetic exchange observed at a metal–metal separation of approximately 13 Å is unprecedented and has been suggested to occur via a continuous π interaction between Ru(III) πd orbitals and the π HOMO of the bridging ligand.

In our exploration of the transition metal coordination chemistry of cyanamide ligands, we are interested in the electronic properties of the metal–cyanamide bond in the hopes that this information will be useful in the construction of molecular materials. In this study, the nature of the Ni–NCN bond has been characterized by X-ray crystallography and UV–Vis electronic absorption spectroscopy.

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Experimental

Physical measurements

IR spectra of samples in KBr discs were taken on a Perkin-Elmer 1600 Series FTIR spectrophotometer. ^{1}H NMR spectroscopy was performed on either a Varian XL200 or XL300 NMR spectrometer at ambient temperature. Electronic absorption spectra were recorded on a Cary 5 UV–Vis NIR spectrophotometer. The temperature of the sample cell was varied by using a sample cell holder connected to a Haake D8-G circulating bath. A model 425C YSI Co. tele-thermometer/thermocouple assembly was used to determine the sample cell's exact temperature ($\pm$0.1 °C). Conductance measurements were carried out on approximately 1 mM solutions at 25 °C. The resistance measurements were made with a conductivity bridge manufactured by Industrial Instruments Inc., model RC16B2. Elemental analyses were performed by Canadian Microanalytical Services Ltd.

Materials

The methods of Elvidge and Linstead [6] and Siegl [7] were used to prepare 1,3-bis(2′-pyridylimino)-isoindoline (LH). The crude ligand LH was recrystallized from chloroform/hexane solution as large, lime-green needles. The preparation of the phenylcyanamide derivatives and their conversion to thallium salts has already been described [3]. The nickel, copper, zinc and palladium salts and organic compounds were re-

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agent grade or better and used as received. $Ni(L)_2$ [6, 8], $Ni(L)Cl \cdot H_2O$ [9], Cu(L)Br [9] and Zn(L)(acetate) [10] were prepared according to the literature and their purity checked by elemental analysis. Benzonitrile (Aldrich, HPLC grade) was stored over activated 3 Å molecular sieves. Acetone (Caledon, spectro grade) was distilled and in the short term before use, stored over activated 3 Å molecular sieves. Tetrahydrofuran was fractionally distilled from lithium aluminum hydride and stored over 3 Å molecular sieves. Propylene carbonate (Aldrich) and dimethyl sulfoxide (Caledon, glass distilled) were used as received.

Syntheses

{Bromo[1,3-bis(2'-pyridylimino}isoindolinato]-nickel(II)}, Ni(L)Br

Triethylamine (0.38 g, 3.7 mmol) was added to a green–orange solution of nickel bromide hydrate (1.0 g, 4.2 mmol) in 1-butanol (50 cm^3) at 70 °C. The resulting light green solution was then added to a lime green solution of LH (1.12 g, 3.7 mmol) in 1-butanol (50 cm^3) at 70 °C. After 5 min, the deep red–orange reaction mixture was cooled to room temperature precipitating dark green microcrystals of the product. The product was filtered, washed with 1-butanol and ether and then recrystallized from nitrobenzene (0.35 g, 22%). *Anal.* Found: C, 49.3; H, 3.02; N, 15.6. Calc. for $C_{18}H_{12}N_5BrNi$: C, 49.5; H, 2.75; N, 16.0%.

{[1,3-Bis(2'-pyridylimino)isoindolinato](2,6-dichlorophenylcyanamido)nickel(II)}, Ni(L)(2,6-Cl_2pcyd)

Ni(L)Br (0.47 g, 1.2 mmol) was dissolved in boiling 2-methoxyethanol (100 cm^3). To the resulting orange solution was added Tl(2,6-dichlorophenylcyanamide) (0.42 g, 1.2 mmol). The reaction mixture immediately turned a deep brown–orange and precipitated TlBr. After 30 min at 100 °C, the reaction mixture was gravity filtered and the filtrate reduced to 25% of its original volume and cooled to room temperature. The bronze–orange needles of the product were collected and recrystallized from nitrobenzene and finally by ether diffusion into a chloroform solution (0.24 g, 37%). *Anal.* Found: C, 55.2; H, 2.90; N, 18.3. Calc. for $C_{25}H_{15}N_7Cl_2Ni$: C, 55.3; H, 2.76; N, 18.1%. IR (KBr): ν(NCN) = 2188 cm^{-1}.

{[1,3-Bis(2'-pyridylimino)isoindolinato](2,3-dichlorophenylcyanamido)nickel(II)}, Ni(L)(2,3-Cl_2pcyd)

The manner of preparation was similar to Ni(L)(2,6-Cl_2pcyd). Reagents used were Ni(L)Br (1.0 g, 2.29 mmol), Tl(2,3-dichlorophenylcyanamide) (0.89 g, 2.28 mmol) and 2-methoxyethanol (110 cm^3). The filtered reaction mixture was reduced to 10% of its original volume. Recrystallization as before yielded dark orange–brown microcrystals of the product (0.23 g, 18%). *Anal.* Found: C, 54.95; H, 2.79; N, 18.4. Calc. for $C_{25}H_{15}N_7Cl_2Ni$: C, 55.3; H, 2.76; N, 18.1%. IR(KBr): ν(NCN) = 2146 cm^{-1}.

{[1,3-Bis(2'-pyridylimino)isoindolinato](2-chlorophenylcyanamido)nickel(II)}, Ni(L)(2-Clpcyd)

The manner of preparation was similar to Ni((L)(2,6-Cl_2pcyd). Reagents used were Ni(L)Br (0.83 g, 1.9 mmol), Tl(2-chlorophenylcyanamide) (0.68 g, 1.9 mmol) and 2-methoxyethanol (100 cm^3). Recrystallization as before yielded dark orange plates of the complex (0.21 g, 22%). *Anal.* Found: C, 59.1; H, 3.2; N, 19.3. Calc. for $C_{25}H_{16}N_7ClNi$: C, 59.0; H, 3.15; N, 19.3%. IR (KBr): ν(NCN) = 2154 cm^{-1}.

{[1,3-Bis(2'-pyridylimino)isoindolinato](4-chlorophenylcyanamido)nickel(II)}, Ni(L)(4-Clpcyd)

The manner of preparation was similar to Ni((L)(2,6-Cl_2pcyd). Reagents used were Ni(L)Br (0.5 g, 1.14 mmol), Tl(4-chlorophenylcyanamide) (0.41 g, 1.15 mmol) and 2-methoxyethanol (100 cm^3). Recrystallization as before yielded dark brown–orange plates of the complex (0.23 g, 40%). *Anal.* Found: C, 58.5; H, 3.05; N, 19.3. Calc. for $C_{25}H_{16}N_7ClNi$: C, 59.0; H, 3.15; N, 19.3%. IR (KBr): ν(NCN) = 2148 cm^{-1}.

{[1,3-Bis(2'-pyridylimino)isoindolinato](2,4,5-trichlorophenylcyanamido)nickel(II)}, Ni(L)(2,4,5-Cl_3pcyd)

The manner of preparation was similar to Ni((L)(2,6-Cl_2Pcyd). Reagents used were Ni(L)Br (0.5 g, 1.14 mmol), Tl(2,4,5-trichlorophenylcyanamide) (0.49 g, 1.15 mmol) and 2-methoxyethanol (150 cm^3). The crude product precipitated out of cooled 2-methoxyethanol without the need for reduction in volume. Recrystallization from nitrobenzene, followed by drying under vacuum at 118 °C for 14 h, afforded brown–orange microcrystals of the product (0.45 g, 68%). *Anal.* Found: C, 51.55; H, 2.5; N, 16.2. Calc. for $C_{25}H_{14}N_7Cl_3Ni$: C, 52.0; H, 2.4; N, 17.0%. IR (KBr): ν(NCN) = 2184 cm^{-1}.

{[1,3-Bis(2'-pyridylimino)isoindolinato](2,3,5,6-tetrachlorophenylcyanamido)nickel(II)}, Ni(L)(2,3,5,6-Cl_4pcyd)

The manner of preparation was similar to Ni(L)(2,6-Cl_2pcyd). Reagents used were Ni(L)Br (0.5 g, 1.14 mmol), Tl(2,3,5,6-tetrachlorophenylcyanamide) (0.53 g, 1.16 mmol) and 2-methoxyethanol (100 cm^3). Both TlBr and the product precipitated from the reaction solution. This mixed precipitate was added to 1-methyl-2-pyrrolidinone (50 cm^3) and heated to 70 °C. The dark orange solution was gravity filtered to remove the insoluble TlBr and, while still maintaining the temperature at 70 °C, water (12 cm^3) was gradually added. The bright orange product precipitated as the solution cooled. Recrystallization from nitrobenzene afforded

fine orange needles of the product that were vacuum dried at 118 °C for 16 h (0.3 g, 42%). *Anal.* Found: C, 49.0; H, 2.04; N, 16.0. Calc. for $C_{25}H_{13}N_7Cl_4Ni$: C, 49.0; H, 2.12; N, 16.0%. IR (KBr): ν(NCN) = 2196 cm^{-1}.

{[1,3-Bis(2'-pyridylimino)isoindolinato]-(isothiocyanato)nickel(II)}, Ni(L)(NCS)

Metathesis of Ni(L)Br (0.22 g, 0.51 mmol) and potassium thiocyanate (0.04 g, 0.46 mmol) in the presence of triethylamine (2.0 g, 20 mmol) in methanol (15 cm^3) afforded golden-yellow needles of the product. These were isolated, washed with methanol and ether and finally vacuum dried (0.15 g, 87%). *Anal.* Found: C, 54.5; H, 2.83; N, 20.5. Calc. for $C_{25}H_{12}N_6SNi$: C, 55.0; H, 2.89; N, 20.25%. IR (KBr): ν(NCS) = 2091 cm^{-1}.

{Azido[1,3-bis(2'-pyridylimino)isoindolinato]-nickel(II)}, Ni(L)(N_3)

Metathesis of Ni(L)Br (0.23 g, 0.52 mmol) and sodium azide (0.03 g, 0.53 mmol) in methanol (15 cm^3) yielded a bright orange crude product. Recrystallization by the slow evaporation of a chloroform solution afforded deep red needles (0.08 g, 37%). *Anal.* Found: C, 53.7; H, 3.04; N, 27.6. Calc. for $C_{18}H_{12}N_8Ni$: C, 54.2; H, 3.01; N, 28.1%. IR (KBr): ν(NNN) = 2051 cm^{-1}.

{Chloro[1,3-bis(2'-pyridylimino)isoindolinato]-palladium(II)}, Pd(L)Cl

Palladium chloride (1.24 g, 7 mmol) was added to 2-methoxyethanol (150 cm^3) and the mixture brought to a boil. The resulting solution was filtered and the filtrate combined with a refluxing solution of the ligand LH (1.8 g, 6 mmol) in 2-methoxyethanol (100 cm^3). The reaction mixture was then refluxed for 20 h and allowed to cool to room temperature, precipitating the orange product. Recrystallization from 2-methoxyethanol yielded orange needles of the product (1.67 g, 63%). *Anal.* Found: C, 49.5; H, 2.71; N, 16.3. Calc. for $C_{18}H_{12}N_5ClPd$: C, 49.1; H, 2.75; N, 15.9%.

{[1,3-Bis(2'-pyridylimino)isoindolinato](2,3-dichlorophenylcyanamido)copper(II)}·0.5H_2O, (Cu(L)(2,3-Cl_2pcyd)

The manner of preparation was similar to Ni((L)(2,6-Cl_2pcyd). Reagents used were Cu(L)Br (0.5 g, 1.13 mmol), Tl(2,3-dichlorophenylcyanamide) (0.44 g, 1.13 mmol) and 2-methoxyethanol (80 cm^3). Recrystallization as before yielded pale green–yellow needles of the complex (0.27 g, 43%). *Anal.* Found: C, 53.9 H, 2.83; N, 17.9. Calc. for $C_{25}H_{16}N_7O_{0.5}Cl_2Cu$: C, 53.9; H, 2.87 N, 17.6%. IR (KBr): ν(NCN) = 2145 cm^{-1}.

X-Ray crystallography

Dark bronze crystal plates of Ni(L)(2-Clpcyd) suitable for X-ray analysis were grown by the slow evaporation of a dilute chloroform solution of the complex. Measurement of the diffracted intensities were made on a Rigaku diffractometer using Mo Kα radiation. The data was collected at the temperature of −175 °C with the omega 2θ scan technique to a maximum 2θ value of 46.9. The data collection at low temperatures is routine and is done to reduce thermal motion and to avoid solvent loss if solvent is incorporated in the crystal lattice. Cell constants and an orientation matrix for data collection were obtained from least-squares refinement by using the setting angles of 25 reflections in the range $40 < 2\theta < 46°$. Based on systematic absences, the space group was determined to be *Cc*. The space group *Cc* was chosen instead of *C2/c* because at lower symmetries there is no disorder. In addition, the NRCVAX crystallographic software package [11] found no symmetry missing. A total of 1651 reflections was collected. The unique set contains only 1554 reflections. The standards were measured every 150 reflections and the data were corrected for Lorentz and polarization effects [12]. No decay of the crystal was observed.

The structure was solved by direct methods. All of the atoms were refined anisotropically except the hydrogen atoms which were calculated. The final cycle of full matrix least-squares refinement was based on 1244 observed reflections ($I > 2.5\ \sigma(I)$) and 306 variable parameters. Weights based on counting statistics were used. The maximum and minimum peaks on the final differences Fourier map corresponded to 0.530 and −0.730, respectively. All the computations were performed by using the NRCVAX crystallographic software package [11]. Crystal data and experimental details are collected in Table 1. Atomic parameters are compiled in Table 2.

Results and discussion

Synthesis of complexes

The synthetic chemistry of Ni(L)Br, where L is the tridentate anion ligand 1,3-bis(2'-pyridylimino)-isoindolinato, is complicated by the substitutional lability of the Ni(II) coordination sphere and the apparent stability of $Ni(L)_2$. Indeed, when ethyl ether was allowed to diffuse over a period of 24 h into a solution of Ni(L)Br in chloroform, red–orange crystals of $Ni(L)_2$ were obtained. This competing side reaction necessitated a synthetic strategy that involved moderate reaction conditions. For the preparation of the complexes of this study, a metathesis reaction using thallium salts of phenylcyanamide derivatives and alkali salts of azide and thiocyanate anions gave the best results.

$$Ni(L)Br + MX \longrightarrow Ni(L)X + MBr$$

where for $M = Tl^+$, X is 2-Clpcyd, 4-Clpcyd, 2,3-Cl_2pcyd, 2,6-Cl_2pcyd, 2,4,5-Cl_3pcyd or 2,3,5,6-Cl_4pcyd, for M = K, X is azide and for M = Na, X is thiocyanate. These novel complexes appeared to be more stable than Ni(L)Br with respect to the formation of $Ni(L)_2$. Nevertheless, an attempt to recrystallize Ni(L)(2,4,5-Cl_3pcyd) from hot DMSO solution did result in the precipitation of $Ni(L)_2$. A conductance measurement of Ni(L)(2,6-Cl_2pcyd) in DMSO showed that significant ionization had occurred (for Ni(L)(2,6-cl$_2$pycd), $\Lambda_m = 10.2$ while for tetrabutylammonium iodide, $\Lambda_m = 34.2$ ohm^{-1} mol^{-1} cm^2 [13]). A tetrahydrofuran solution of the same complex had essentially zero conductance. The chemistry of these complexes in DMSO was not pursued and it is important to note that for the solution studies to follow, the observation of isosbestic points and the reversibility of temperature dependent absorption spectra indicated complex integrity was maintained.

The IR spectrum of the isothiocyanato complex possesses an intense ν(CN) at 2091 cm^{-1}. Since the sulfur bound linkage isomer has a generally less intense ν(CN), this supports the nitrogen bound assignment [14]. Differentiation between linkage isomers can also be achieved by the position of ν(CS). Unfortunately, this absorption region is obscured by the ligand L, preventing an unambiguous assignment.

NMR studies

The ^{1}H NMR spectral data of the protonated free ligand LH and the nickel and palladium complexes are shown in Table 3. The ^{1}H NMR assignments of the free ligand have already been published and we have adopted the numbering scheme of Siegl [9]. The poor solubility of Ni(L)(2,3-Cl_2pcyd), Ni(L)(2,4,5-Cl_3pcyd) and Ni(L)(2,3,5,6-Cl_4pcyd) in chloroform prevented NMR characterization. The ^{1}H NMR spectra of the free ligand and coordinated L should look identical with the exception of the pyrrole nitrogen proton if the ligand's plane of symmetry is maintained upon coordination. As shown by the data of the complexes in Table 3, this appears to be the case. Interestingly, the ^{1}H NMR spectrum of Ni(L)(2-Clpcyd) from 0 to 10 ppm showed only four broad singlets at 8.15, 7.79, 6.91 and 6.62 ppm and a doublet at 7.21 ppm. The loss of hyperfine coupling is suggestive of paramagnetism and since this complex is pure and solvent adduct formation in chloroform is unlikely, we suggest that the complex may be in a square planar–tetrahedral equilibrium as is commonly seen in four-coordinate Ni(II) complexes [15]. The concentration of tetrahedral

TABLE 1. Crystal data for Ni(L)(2-Clpcyd)

Formula	$NiClN_7C_{25}H_{16}$
Molecular weight	508.61
Crystal system	monoclinic
Space group	*Cc*
a (Å)	9.836(4)
b (Å)	28.219(10)
c (Å)	7.7886(18)
β (°)	103.71(3)
V (Å^3)	2100.2(13)
Z	4
D_c (g/cm^3)	1.609
Crystal dimensions (mm)	0.05 × 0.20 × 0.30
Radiation (λ, Å)	Mo Kα (0.70930)
mμ (mm^{-1})	1.08
No. reflections measured	1651
No. unique reflections	1554
No. significant reflections ($I > 2.5\sigma$)	1244
R factor[a]	0.062
R_w factor[a]	0.037
Goodness-of-fit ratio	3.08

[a]$R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_w = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2)^{1/2}$.

TABLE 2. Atomic parameters and B_{iso} for Ni(L)(2-Clpcyd)[a]

	x	*y*	*z*	B_{iso}[b]
Ni	0.68975	0.43557(6)	0.47713	2.51(7)
Cl	1.1914(5)	0.24646(14)	0.7439(6)	4.84(21)
N1	0.8365(11)	0.4643(4)	0.3863(13)	3.0(5)
N2	0.7774(11)	0.5460(4)	0.4091(13)	3.4(6)
N3	0.6054(10)	0.4934(4)	0.4717(13)	2.7(5)
N4	0.3925(10)	0.4724(4)	0.5643(12)	2.9(6)
N5	0.5195(11)	0.4015(4)	0.5094(15)	3.4(6)
N6	0.7943(11)	0.3807(4)	0.5519(14)	3.2(6)
N7	0.9817(11)	0.3244(4)	0.6765(14)	3.7(7)
C1	0.9257(13)	0.4320(5)	0.3293(15)	3.4(7)
C2	1.0418(14)	0.4466(5)	0.2744(17)	3.9(8)
C3	1.0723(13)	0.4943(5)	0.2785(16)	3.4(8)
C4	0.9870(13)	0.5275(5)	0.3198(15)	3.5(8)
C5	0.8634(14)	0.5098(4)	0.3726(16)	2.8(7)
C6	0.6599(13)	0.5349(4)	0.4486(16)	2.6(7)
C7	0.5689(13)	0.5755(5)	0.4839(16)	2.7(7)
C8	0.5724(13)	0.6242(5)	0.4708(18)	4.0(8)
C9	0.4642(14)	0.6497(5)	0.5132(22)	4.7(8)
C10	0.3519(13)	0.6282(5)	0.5515(17)	3.3(7)
C11	0.3440(13)	0.5800(5)	0.5643(16)	3.4(8)
C12	0.4545(13)	0.5528(5)	0.5236(16)	3.1(7)
C13	0.4779(12)	0.5030(5)	0.5232(16)	2.5(7)
C14	0.4043(14)	0.4238(5)	0.5477(16)	3.3(7)
C15	0.2969(13)	0.3960(5)	0.5721(17)	3.0(7)
C16	0.2923(13)	0.3500(5)	0.5479(17)	3.3(7)
C17	0.4022(14)	0.3285(5)	0.4979(20)	4.1(8)
C18	0.5133(14)	0.3559(5)	0.4800(20)	3.8(8)
C19	0.8833(13)	0.3557(4)	0.6212(15)	2.6(7)
C20	1.0136(13)	0.3095(4)	0.8523(15)	2.7(7)
C21	0.9602(14)	0.3300(5)	0.9813(20)	4.0(8)
C22	0.9980(15)	0.3114(5)	1.1533(18)	4.3(9)
C23	1.0991(15)	0.2768(5)	1.2014(17)	4.5(9)
C24	1.1569(13)	0.2571(5)	1.0753(17)	4.2(8)
C25	1.1170(13)	0.2739(4)	0.9004(16)	2.8(7)

[a]e.s.d.s are in parentheses. [b]B_{iso} is the mean of the principal axes of the thermal ellipsoid, Å^2.

TABLE 3. ^{1}H NMR data of complexes and free ligand LH[a]

Compound	H_α	H_β	H_3	H_4	H_5	H_6	pcyd$^-$	
LH	8.08q	7.66q	7.47d	7.77t	7.13t	8.63d		
Ni(L)(N_3)	8.01q	7.61q	7.39d	7.80t	7.11t	8.72d		
Ni(L)(NCS)	7.97q	7.59q	7.41d	7.81t	7.11t	8.72d		
Ni(L)(2,6-Cl_2pcyd)	7.97q	7.57q	7.37d	7.76t	≈7.0	8.87d	7.05d	6.56t
Ni(L)(4-Clpcyd)	8.02q	7.62q	≈7.6	7.87t	7.23t	9.27bs	7.03d	6.54bs
Pd(L)(2-Clpcyd)	8.05q	7.64q	7.66d	7.90t	7.17t	9.41d	7.22d	7.09d
							7.01t	6.74t

[a]All spectra were performed in deuterated chloroform at ambient temperature. bs, broad singlet; d, doublet; t, triplet; q, quartet.

complex would have to be a very small to explain the lack of significant paramagnetic chemical shift.

Crystal structure

Figure 1 shows the ORTEP drawing of the complex Ni(L)(2-Clpcyd) and Tables 1 and 2 give the crystal data and significant atomic coordinates, respectively. Bond lengths and angles have been compiled in Table 4. As seen in Figs. 1 and 2, the NiN_4 coordination sphere is that of a tetrahedrally distorted square plane with two opposing nitrogen atoms up and the other two down relative to the ideal square plane. The distances to the ideal plane from the atoms in the plane are Ni −0.001(3), N(3) 0.219(20), N6 (0.299(23), N1 −0.253(22) and N5 −0.211(21) Å.

TABLE 4. Selected bond lengths (Å) and angles (°) for Ni(L)(2-Clpcyd)[a]

Bond lengths			
Ni–N1	1.931(11)	Ni–N3	1.827(10)
Ni–N5	1.998(11)	Ni–N6	1.874(10)
N6–C19	1.154(16)	N7–C20	1.395(15)
N7–C19	1.306(16)		
Bond angles			
N1–Ni–N5	166.0(4)	N1–Ni–N3	89.4(4)
N1–Ni–N6	93.4(5)	N3–Ni–N5	92.5(4)
N3–Ni–N6	163.4(4)	Ni–N6–C19	161.8(10)
N6–C19–N7	171.4(13)	C19–N7–C20	120.3(11)
N5–Ni–N6	88.7(5)		

[a]The atom numbers are shown in Fig. 1 and e.s.d.s are in parentheses.

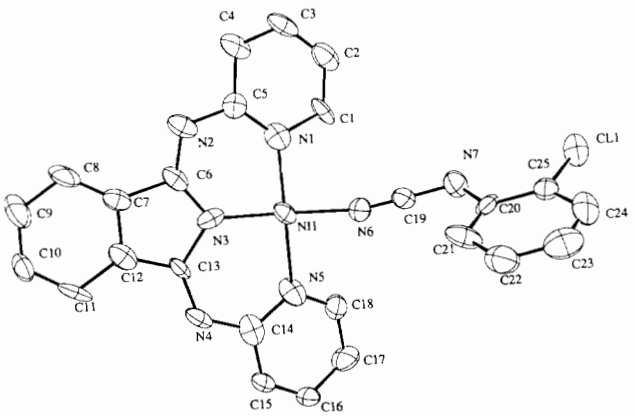

Fig. 1. ORTEP drawing of the complex Ni(L)(2-Clpcyd).

The tridentate anion ligand L retains an approximately planar geometry when coordinated to Ni(II) and, as shown in Table 4, the Ni–N bond distances to the pyridine nitrogen atoms N1 and N5 are significantly longer than that to the pyrrole nitrogen N3. This same pattern of bond lengths and geometry was also seen in Cu(II) complexes of a dimethyl derivative of the ligand L [16]. It is important to note that the hydrogen atoms on pyridine carbons C18 and C1 sterically hinder square planar coordination of monodentate ligands. This factor together with the ligand field properties of a given monodentate ligand may well determine the degree of tetrahedral distortion about Ni(L) complexes.

The 2-chlorophenylcyanamide ligand is coordinated to Ni via the terminal nitrogen of the cyanamide group. The coplanarity of the cyanamide group with the phenyl ring is a common feature of phenylcyanamide complexes [2, 3c, 5b], and is suggested to result from weak π coupling. The phenyl ring is perpendicular to the plane of the ligand L (Figs. 1 and 2) and it seems probable that this conformation has the least steric hinderance.

Figure 2 shows a stereoview of the unit cell and reveals intimate pairing of planar ligand groups. The interplane separation has an average value of 3.9 Å which is far larger than that found for Ni(II) complexes of macrocyclic ligands (interplanar separations range from 3.235 to 3.350 Å) [17]. The separation between nickel ions was found to be 5.328 Å. It is possible that the pairing seen in Fig. 2 has more to do with efficient crystal packing than with interplanar π interactions.

Electronic absorption spectroscopy

Spectral data for the free ligand and complexes have been compiled in Table 5 and representative spectra are shown in Fig. 3. The spectra are dominated by the π–π^* transitions of the ligand L. Deprotonation of the pyrrole nitrogen and the enforcement of approximately planar geometry upon coordination of L is expected to reduce the difference in energy between occupied

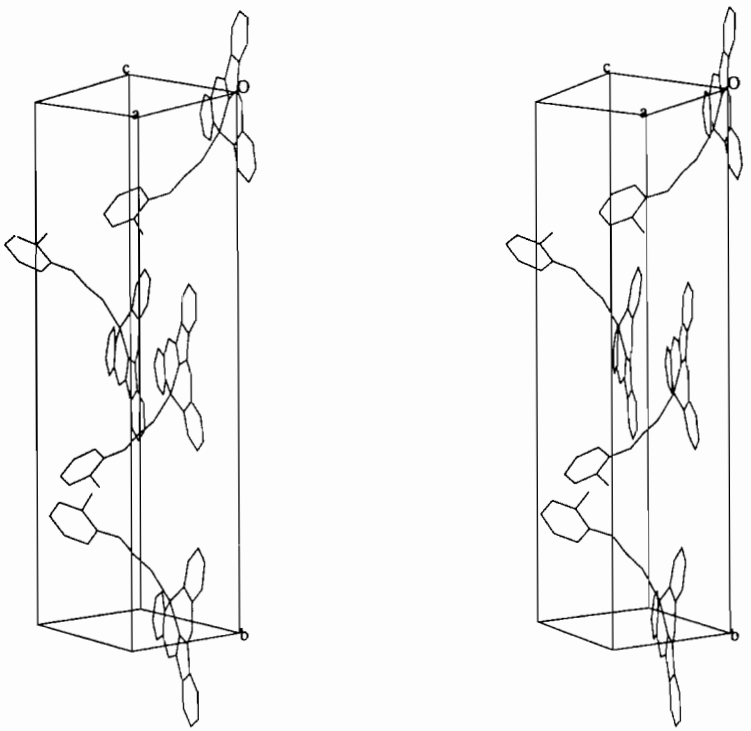

Fig. 2. Stereoview of the unit cell for the complex Ni(L)(2-Clpcyd).

TABLE 5. Electronic absorption data[a] of the free ligand HL and M(L)X complexes

Compound	$\pi \rightarrow \pi^*$	d–d
HL	24390 (3.99) 25840 (4.23)	
	27250 (4.19)	
Ni(L)(4-Clpcyd)[b]	21000 (3.82) 28650 (4.26)	15900 (2.90)
Ni(L)(2-Clpcyd)[b]	21000 (3.83) 28740 (4.28)	15940 (2.81)
Ni(L)(2,6-Cl_2pcyd)[b]	21010 (3.85) 28740 (4.30)	16000 (2.74)
Ni(L)(2,3-Cl_2pcyd)[b]	21140 (3.87) 28740 (4.30)	16120 (2.75)
Ni(L)(2,4,5-Cl_3pcyd)[b]	21190 (3.85) 28900 (4.28)	16090 (2.70)
Ni(L)(2,3,5,6-Cl_4pcyd)[b]	21280 (3.88) 28900 (4.29)	15940 (2.81)
$Ni(L)_2$	21690 (4.54) 23090 (4.55)	
	29670 (4.38)	11760 (1.34)
Zn(L)(acetate)	22730 (4.18) 24160 (4.28)	
	25580 (4.12)	
Cu(L)(2,3-Cl_2pcyd)	23920 (4.04) 28410 (3.93)	14840 (2.33)
	29760 (4.05)	
Pd(L)Cl	30120 (4.31) 22940 (4.17)	[c]
	21460 (4.17)	
Pd(L)(2-Clpcyd)	21790 (4.14) 23150 (4.15)	[c]
	29590 (4.20)	
Ni(L)Br	21790 (4.35) 23150 (4.43)	[c]
	29500 (4.47)	
Ni(L)Cl	21550 (3.58) 28820 (3.94)	≈14710 (1.70)
Ni(L)(N_3)	20750 (3.72) 28740 (4.14)	≈16130 (2.25)
Ni(L)(NCS)	21010 (3.99) 29410 (4.34)	16450 (2.06)

[a]Data in cm^{-1} with the log of ϵ (M^{-1} cm^{-1}) in parentheses. [b]The presence of an underlying $\pi \rightarrow \sigma^*$ LMCT transition is suggested by the broadening of the low energy $\pi \rightarrow \pi^*$ bands. See text for details. [c]Obscured by ligand L $\pi \rightarrow \pi^*$ bands.

and unoccupied π-MOs of the ligand L and to result in a red shift of $\pi \rightarrow \pi^*$ transitions (compare the spectra of LH and Ni(L)Br). However, the degree of red shift and intensity of these two main absorption bands at approximately 29 400 and 22 200 cm^{-1} are dependent on the nature of the four-coordinate complex in chlo-

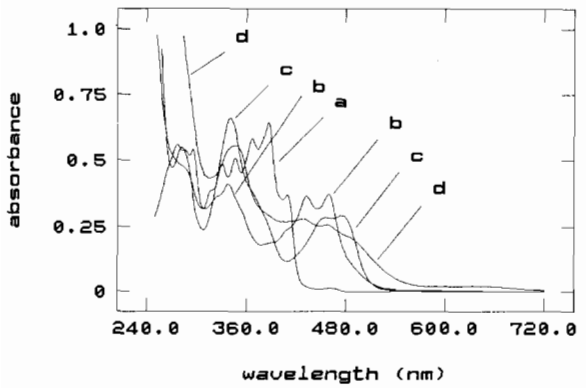

Fig. 3. UV–Vis spectra of the free ligand and Ni(L)X complexes in chloroform: (a) LH, (b) Ni(L)Br, (c) Ni(L)(NCS) and (d) Ni(L)(4-Clpcyd).

roform solution (Fig. 3): Zn(L)(acetate), Cu(L)(2,3-Cl_2pcyd), Pd(L)Cl and Pd(L)(2-Clpcyd) have spectra similar to that of Ni(L)Br, while the complexes Ni(L)Cl and Ni(L)(N_3) have spectra exemplified by that of Ni(L)(NCS), and finally the nickel phenylcyanamide complexes have spectra similar to that of Ni(L)(4-Clpcyd). The reason for this variation of $\pi \rightarrow \pi^*$ band energy and intensity is open to speculation.

Self-association of aromatic systems can result in a red shift of $\pi \rightarrow \pi^*$ bands. This possibility can be eliminated since the spectra of the Ni(II) phenylcyanamide complexes in chloroform are unaffected by changes in temperature (5–40 °C). If coordination of the ligand L to Ni(II) altered its degree of planarity, reduced conjugation would result in an increase in energy of the $\pi \rightarrow \pi^*$ transitions. We made the square planar Pd(L) complexes in the expectation that the planar geometry of the ligand L would be perturbed to the least extent. However, the Pd(L) complexes have high energy $\pi \rightarrow \pi^*$ bands as illustrated by Fig. 3(b) and do not support this line of argument. An alternative explanation is that the Ni(II) phenylcyanamide complexes have a low energy ligand to metal charge transfer LMCT transition that mixes with the $\pi \rightarrow \pi^*$ transition to create the broad absorption seen in Fig. 3(d).

There are few examples of LMCT bands in square planar Ni(II) complexes and in general the charge transfer bands are predicted to lie between 23 000 and 30 000 cm^{-1} [18a]. A number of [Cu(2,2'-bipyridine)$_2$(pcyd)]$^+$ complexes have been prepared [3g], whose absorption spectra show clearly resolved $\pi \rightarrow \sigma^*$ LMCT bands that range from 18 480 to 21 320 cm^{-1} depending on the basicity of the phenylcyanamide derivative. It is expected that the corresponding LMCT transitions for the complexes of this study should be blue shifted since Cu(II) has greater optical electronegativity than Ni(II). Importantly, tetrahedral [Ni(2-Clpcyd)$_4$]$^{2-}$ and [Ni(2,4,6-Cl_3pcyd)$_4$]$^{2-}$ were shown to have LMCT bands at 22 200 and 23 200 cm^{-1}, respectively [1].

Table 5 also gives d–d transitions observed for the novel complexes of this study. It is common in square planar NiN_4 systems that the lower four d orbitals are closely spaced in energy [18b]. The resulting transitions to the $d_{x^2-y^2}$ orbital (the x and y molecular axes pass through the Ni–N bonds) are indistinguishable and result in the observation of a single broad band usually in the range of 18 000 to 25 000 cm^{-1} [18c]. The lower energy of this band for the diamagnetic nickel complexes in Table 5, may be a reflection of a relatively weak square planar crystal field. 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 [19]. There is a slight trend in decreasing d–d energies in Table 5, that is consistent with the expected π donor properties of the phenylcyanamide ligands [3g].

Solvent coordination equilibria of Ni(L)(pcyd) complexes

The sensitivity of NiN_4 systems to solvent coordination has been known for a long time [20]. In all cases, an equilibrium condition ensues between the desolvated (diamagnetic) and solvated (paramagnetic) complexes.

$$[NiN_4] + n(\text{solvent} \overset{K_{eq}}{\rightleftharpoons} [NiN_4(\text{solvent})_n] \quad (1)$$

$n = 1$ or 2

The relative differences in equilibrium constant K_{eq} for a given complex with varying solvent is largely determined by the strength of the bonding interaction between Ni(II) and the solvent molecule which requires consideration of electronic and steric factors. The effect of temperature on the above equilibrium has been usually monitored by observing the changes in intensity of the square planar d–d transition. For the phenylcyanamide Ni(II) complexes of this study, a rather dramatic change in the absorption spectra involving not just the d–d band is seen when the complexes are dissolved in strongly coordinating solvents.

As shown by Fig. 4, the absorption spectrum at 23.7 °C of Ni(L)(4-Clpcyd) in benzonitrile is remarkably different from the same complex in chloroform (Fig. 3(d)) and closely resembles that of Ni(L)Br (Fig. 3(b)). As temperatures are raised to 83.8 °C, the $\pi \rightarrow \pi^*$ band drops in intensity and red shifts. The spectrum at 83.8 °C is beginning to resemble that of four-coordinate Ni(L)(4-Clpcyd) in chloroform (Fig. 3(d)). The temperature dependence of the absorption spectrum of Ni(L)(4-Clpcyd) in benzonitrile is completely reversible and is consistent with preferential solvent coordination to Ni(II) at low temperatures.

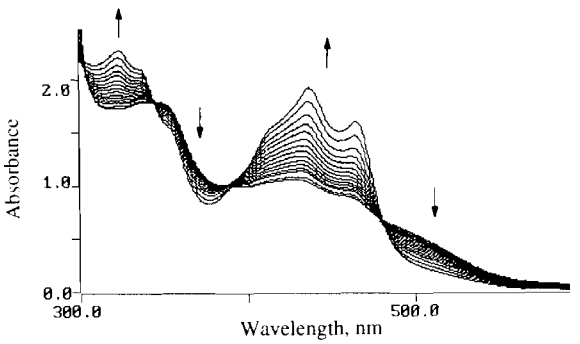

Fig. 4. Variable temperature electronic absorption spectra of Ni(L)(4-Clpcyd) in benzonitrile (1.06×10^{-4} M). Arrows indicate the direction of spectral change resulting from a change in temperature of 83.8 to 23.7 °C.

The spectral changes seen in Fig. 4 may be due to an increase in the forbiddeness of the $\pi\rightarrow\sigma^*$ LMCT transition or to a loss of planarity of the ligand L with solvent coordination. In any case, the effect can be used to determine the thermodynamics of solvent substitution and hence determine the likely coordination number of the solvated Ni(II) complex. The Ni(II) complexes of this study are neutral and are more soluble in a greater range of solvents than the charged Ni(II) complexes of previous studies [20]. This provides an opportunity to expand what is currently known concerning the solvent coordination thermodynamics of Ni(II) complexes.

Four solvents, benzonitrile, propylene carbonate, acetone and tetrahydrofuran, were chosen to study the solvent coordination equilibria of Ni(II) phenylcyanamide complexes. The assumption in eqn. (1) that only two species are in equilibrium was confirmed by graphical tests [21] by using absorbance data at several wavelengths. For solvents in which a six-coordinate adduct forms, it is likely that the concentration of five-coordinate Ni(II) is not significant. This would result if the activation barrier to form the five-coordinate adduct was far greater than that to form the six-coordinate adduct. K_{eq} and the thermodynamic parameters were calculated in a similar manner to those in a study by Tregloan and co-workers [20f]. For our study, the temperature dependent absorbance at 430 nm gave the greatest range. The spectra of all the complexes in tetrahydrofuran were invariant below 10 °C and these conditions were presumed to give the maximum absorbance at 430 nm for each fully solvated Ni(II) complex. The maximum absorbance at 430 nm of a four coordinate diamagnetic Ni(II) phenylcyanamide complex was obtained from its chloroform spectrum. At each temperature, K_{eq} was determined and the thermodynamic parameters were derived from plots of ln K_{eq} versus $1/T$. The results have been tabulated together with error limits in Table 6.

The four-coordinate diamagnetic complex $[Ni(A)][ClO_4]_2$ where A = 1,4,8,11-tetramethyl-1,4,8,11-tetra-azacyclotetradecane, can be readily prepared in two forms: *trans*-(I) and *trans*-(II) [20g]. In coordinating solvents, one of the axial coordination sites of *trans*-(I)-$[Ni(A)]^{2+}$ is sterically hindered and only five-coordinate species are formed. Under the same conditions *trans*-(II)-$[Ni(A)]^{2+}$ forms six-coordinate species. The thermodynamic data derived from equilibrium studies of these complexes reflect the extent of coordination [20g] and so for the five-coordinate *trans*-(I) complex

TABLE 6. Thermodynamic parameters $-\Delta H°$ and $-\Delta S°$ derived from temperature dependent solvation equilibria of the Ni(L)(pcyd) complexes[a]

Complex	Solvents[b]			
	BZ	THF	PC	AC
$-\Delta H°$ (kJ mol^{-1})				
Ni(L)(2,3,5,6-Cl_4pcyd)	35.7 ± 1.9	34.2 ± 3.5	27.0 ± 2.3	[c]
Ni(L)(2,4,5-Cl_3pcyd)	38.2 ± 1.4	35.1 ± 2.5	28.3 ± 1.0	12.1 ± 2.8
Ni(L)(2,6-Cl_2pcyd)	44.2 ± 2.3	30.1 ± 3.7	29.5 ± 1.7	17.0 ± 1.4
Ni(L)(2,3-Cl_2pcyd)	43.2 ± 2.5	37.7 ± 5.0	30.4 ± 1.4	12.6 ± 3.4
Ni(L)(2-Clpcyd)	43.8 ± 2.6	30.5 ± 5.2	23.9 ± 0.3	13.0 ± 2.0
Ni(L)(4-Clpcyd)	31.3 ± 1.6	35.2 ± 3.0	25.9 ± 1.2	15.6 ± 1.4
$-\Delta S°$ (J mol^{-1} K^{-1})				
Ni(L)(2,3,5,6-Cl_4pcyd)	127 ± 6	96.6 ± 11	92.1 ± 7	[c]
Ni(L)(2,4,5-Cl_3pcyd)	131 ± 4	102 ± 8	95.3 ± 3	44.9 ± 10
Ni(L)(2,6-Cl_2pcyd)	156 ± 8	85.1 ± 12	110 ± 6	71.2 ± 4
Ni(L)(2,3-Cl_2pcyd)	151 ± 8	111 ± 16	111 ± 5	56.6 ± 11
Ni(L)(2-Clpcyd)	152 ± 8	84.7 ± 17	84.6 ± 1	55.2 ± 7
Ni(L)(4-Clpcyd)	103 ± 5	103 ± 10	93.4 ± 4	63.8 ± 5

[a]All errors were calculated by linear regression with a confidence level of 95%. [b]BZ is benzonitrile (DN = 11.9), THF is tetrahydrofuran (DN = 20.0), PC is propylene carbonate (DN = 15.1), and AC is acetone (DN = 17.0). [c]Insoluble.

in DMF $\Delta H° = -19.6 \pm 1.3$ kJ mol^{-1} and $\Delta S° = -40.9 \pm 3.4$ J K^{-1} mol^{-1}. For the same complex in acetonitrile, $\Delta H° = -16.8 \pm 0.8$ kJ mol^{-1} and $\Delta S° = -32.0 \pm 2$ J K^{-1} mol^{-1}. For the six-coordinate *trans*-(II) complex in DMF, $\Delta H° = -27.7 \pm 0.4$ kJ mol^{-1} and $\Delta S° = -83.7 \pm 1.6$ J K^{-1} mol^{-1}.

Comparison of the $\Delta H°$ and $\Delta S°$ values of the $[Ni(A)]^{2+}$ complexes with those of the Ni(L)(pcyd) complexes in Table 6 supports six-coordinate Ni(L)(pcyd)(solvent)$_2$ complexes in benzonitrile, propylene carbonate and tetrahydrofuran and only five-coordinate solvated complexes in acetone. Acetone is a bulky ligand and it seems likely that its steric requirements are the limiting factor. The solvents were chosen to give a good range of electron donor properties as represented by their respective donor numbers (Table 6) [22]. Surprisingly, benzonitrile which has the smallest donor number forms the most stable solvated complex. It is possible that the π acceptor properties of benzonitrile add to the stability of the complex but it is also true that benzonitrile is the least bulky of all the solvents of this study and ought to experience the least steric hinderance. No trend in thermodynamic parameters was observed between Ni(L)(pcyd) complexes in Table 6. $\Delta H°$ was expected to increase in magnitude as Ni(II) became more electro-positive with increasing chloride substitution on pcyd$^-$. That this does not occur is again attributed to steric effects.

Supplementary material

A full listing of atomic parameters, thermal parameters and bond lengths and angles are available from R.J.C.

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References

1 (a) B.R. Hollebone and R.S. Nyholm, *J. Chem. Soc. A,* (1971) 332; (b) B.R. Hollebone, *J. Chem. Soc. A,* (1971) 481.
2 (a) M.L. Brader, E.W. Ainscough, E.N. Baker and A.M. Brodie, *Polyhedron, 8* (1989) 2219; (b) E.W. Ainscough, E.N. Baker, M.L. Brader, A.M. Brodie, S.L. Ingham, J.M. Waters, J.V. Hanna and P.C. Healey, *J. Chem. Soc., Dalton Trans.,* (1991) 1243.
3 (a) M.L. Naklicki and R.J. Crutchley, *Inorg. Chem., 28* (1989) 4226; (b) R.J. Crutchley and M.L. Naklicki, *Inorg. Chem., 28* (1989) 1955; (c) R.J. Crutchley, K. McCaw, F.L. Lee and E.J. Gabe, *Inorg. Chem., 29* (1990) 2576; (d) A.A. Saleh and R.J. Crutchley, *Inorg. Chem., 29* (1990) 2132; (e) R.J. Crutchley, A.A. Saleh, K. McCaw and M.A.S. Aquino, *Mol. Cryst. Liq. Cryst., 194* (1991) 93; (f) M.A.S. Aquino, A.E. Bostock and R.J. Crutchley, *Inorg. Chem., 29* (1990) 3641; (g) R.J. Crutchley, R. Hynes and E.J. Gabe, *Inorg. Chem., 29* (1990) 4921.
4 (a) A. Aumuller, P. Erk, G. Klebe, S. Hunig, J.U. von Schutz and H.-P. Werner, *Angew. Chem., Int. Ed. Engl., 25* (1986) 740; (b) R. Kato, H. Kobayashi and K. Kobayashi, *J. Am. Chem. Soc., 111* (1989) 5224, and refs. therein.
5 (a) M.A.S. Aquino, F.L. Lee, E.J. Gabe, J.E. Greedan and R.J. Crutchley, *Inorg. Chem., 30* (1991) 3234; (b) M.A.S. Aquino, F.L. Lee, E.J. Gabe, C. Bensimon, J.E. Greedan and R.J. Crutchley, *J. Am. Chem. Soc., 114* (1992) 5130.
6 J.A. Elvidge and R.P. Linstead, *J. Chem. Soc.,* (1952) 5000.
7 W.O. Siegl, *J. Heterocycl. Chem., 18* (1981) 1613.
8 M.A. Robinson, S.I. Trotz and T.J. Hurley, *Inorg. Chem., 6* (1967) 392.
9 W.O. Siegl, *J. Org. Chem., 42* (1977) 1872.
10 W.O. Siegl, *Inorg. Nucl. Chem. Lett., 10* (1974) 825.
11 E.J. Gabe, F.L. Lee and Y. Lepage, *J. Appl. Crystallogr., 22* (1989) 384.
12 D.F. Grant and E.J. Gabe, *J. Appl. Crystallogr., 11* (1978) 114.
13 P.G. Sears, G.R. Lester and L.R. Dawson, *J. Chem. Phys., 60* (1956) 1433.
14 K.F. Purcell and J.C. Kotz, *Inorganic Chemistry,* Saunders, Philadelphia, PA, 1977, p. 618.
15 J.K. Beattie, *Adv. Inorg. Chem., 32* (1988) 1, and refs. therein.
16 (a) R.R. Gagne, R.S. Gall, G.C. Lisensky, R.E. Marsh and L.M. Speltz, *Inorg. Chem., 18* (1979) 771; (b) A.W. Addison, P.J. Burke and K. Hendrick, *Inorg. Chem., 21* (1982) 60.
17 M.C. Weiss, G. Gordon and V.L. Goedken, *Inorg. Chem., 16* (1977) 305.
18 A.B.P. Lever, *Inorganic Electronic Spectroscopy,* Elsevier, Amsterdam, 2nd edn., 1984, (a) p. 536, (b) p. 221, (c) p. 534.
19 Y. Nishida and S. Kida, *Coord. Chem. Rev., 27* (1979) 275.
20 (a) R.H. Holm and K. Swaminathan, *Inorg. Chem., 1* (1962) 599; (b) E.K. Barfield, D.H. Busch and S.M. Nelson, *Q. Rev. Chem. Soc., 22* (1968) 457; (c) A. Anichini, L. Fabbrizzi and P. Paoletti, *Inorg. Chim. Acta, 24* (1977) L21; (d) N. Herron and P. Moore, *Inorg. Chim. Acta, 36* (1979) 89; (e) E.H. Curzon, N. Herron and P. Moore, *J. Chem. Soc., Dalton Trans.,* (1980) 574; (f) L. Helm, P. Meier, A.E. Merbach and P.A. Tregloan, *Inorg. Chim. Acta, 73* (1983) 1; (g) P. Moore, J. Sachinidis and R. Willey, *J. Chem. Soc., Dalton Trans.,* (1984) 1323; (h) L. Sabatini and L. Fabbrizzi, *Inorg. Chem., 18* (1979) 438; (i) P. Moore, J. Sachinidis and G.R. Willey, *J. Chem. Soc., Chem. Commun.,* (1983) 522; (j) L. Rusnak and R.B. Jordan, *Inorg. Chem., 10* (1971) 2199.
21 J.S. Coleman, L.P. Varga and S.H. Mastin, *Inorg. Chem., 9* (1970) 1015.
22 V. Gutmann, *The Donor–Acceptor Approach to Molecular Interactions,* Plenum, New York, 1978.