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Coordination Chemistry of Neutral Phenylcyanamide Ligands Bound to Pentaammineruthenium(II)

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A general synthesis of pentaammineruthenium(II) complexes of phenylcyanamide ligands is presented as well as a discussion of the conditions under which phenylcyanamide ligands autodimerize. Infrared ^{15}N-isotope labeling experiments strongly suggest that phenylcyanamide ligands coordinate "end-on" by the nitrile nitrogen. The pH dependence of the Ru(III/II) couple is consistent with a one electron/one proton equilibrium in the range pH 0.30–10.04. The pK_a of free (2,6-dichlorophenyl)cyanamide (4.90) rises to 7.13 upon coordination of Ru(II) and drops to 0.93 when there is coordination to Ru(III). These results can be understood by the preferred coordination of the π-donating anionic phenylcyanamide ligand to Ru(III) and the π-accepting neutral ligand to Ru(II).

Introduction

The coordination chemistry of phenylcyanamide ligands has taken on increased importance with the discovery of copper salts of radical anion *N,N'*-dicyanoquinonediimine derivatives (DCNQI).[1] Crystals of these copper compounds, with stoichiometry Cu(DCNQI)$_2$, show increasing conductivity as temperature is reduced with conductivity levelling off at $\sigma = 500000$ S cm^{-1} below 4 K. Crystal structures[1,2] of these compounds indicate that the dicyanoquinonediimine molecules are arranged in stacks linked together by tetrahedrally coordinated copper ions. The primary mechanism for conductivity was suggested to occur via π stacks of dicyanoquinonediimine molecules. This type of π stacking is a characteristic of other strongly conducting molecular metals.[3] In addition, transverse conductivity was proposed to occur via NCN–Cu–NCN bridges between the individual stacks. Transverse conductivity measurements[4] and ESCA studies[5] appear to support this suggestion. It is clear that if the properties of these compounds are to be fully understood, the coordination chemistry of phenylcyanamide ligands in both neutral and anionic forms should be investigated.

The linkage isomerism of the cyanamide group is best illustrated by the crystal structure of [Cr(CO)$_5$(η^1-diethylcyanamide)], in which the nitrile group is bound end-on,[6] and [W$_2$(OCH$_2$Bu-*t*)$_6$(μ-dimethylcyanamide)$_2$(η^2-dimethylcyanamide)], in which all of the cyanamide ligands are bound side-on to tungsten by the nitrile group.[7] Side-on coordination of a nitrile group is extremely rare[8] but is more common for cyanamide ligands due to the participation of the nitrile lone pair in a bridging interaction.[9] We have shown by infrared spectroscopy[10] and X-ray crystallography[11] that neutral or deprotonated phenylcyanamide ligands bind to Ru(III) end-on. We now present an infrared spectroscopic analysis using isotope labeling that strongly suggests end-on coordination of neutral (2,6-dichlorophenyl)cyanamide ligand to Ru(II). In addition, the nature of the bonding interaction between the cyanamide group and Ru(II) was investigated by electronic absorption and cyclic voltammetry.

Experimental Section

Equipment. The equipment used to perform nonaqueous cyclic voltammetry, infrared spectroscopy, and pK_a measurements has been described in a previous paper.[10] ^{13}C and ^{1}H NMR spectroscopy was performed on a Varian XL200 NMR spectrometer at ambient temperature. The determination of the pH dependence of the ruthenium(III/II) couple was performed at 25 °C, with a three-electrode system composed of glassy-carbon disk working, (BAS 3-mm diameter), platinum-wire counter, and saturated calomel reference electrodes, in buffered aqueous solution made up to a constant ionic strength of 0.5 with sodium perchlorate. In the pH range 10.04–9.04, a glycine/NaOH buffer was used.[12] In the pH range 8.01–2.02, a Na$_2$HPO$_4$/citric acid buffer was used.[13] One experiment was performed in 0.5 M perchloric acid.

Materials. All solvents and solid chemicals were reagent grade or better. Na^{15}NCS was obtained from MSD Isotopes and used without further purification. [(NH$_3$)$_5$Ru(H$_2$O)][PF$_6$]$_2$[14] and [(NH$_3$)$_5$RuCl][Cl]$_2$[15] were prepared by literature methods. Elemental analysis were performed by Canadian Microanalytical Services Ltd.

Preparation of (2,6-Dichlorophenyl)cyanamide (2,6-Cl$_2$Hpcyd). The preparation of this ligand is identical with the preparation of (2,3-dichlorophenyl)cyanamide.[10] The ligand appears to slowly dimerize in the solid state when stored at room temperature. Dimerization occurs much faster in nonaqueous polar solvents, and so recrystallization from acetone introduced dimer impurity. ^{13}C and ^{1}H NMR showed the initial product to be essentially free of impurities, and so it was used as recovered from the reaction mixture, after vacuum drying at room temperature. The ligand melted at 120 °C and then immediately solidified due probably to polymerization. Yield: 84%. Anal. Calcd for C$_7$H$_4$N$_2$Cl$_2$: C, 44.96; H, 2.16; N, 14.98. Found: C, 44.87; H, 2.21; N, 14.99. ^{13}C NMR data: a five-line spectrum with peaks at 112.05, 128.15, 129.08, 130.20, and 132.99 ppm.

Preparation of ^{15}N-Labeled (2,6-Dichlorophenyl)cyanamide. The above procedure was followed with the single exception of using Na^{15}NCS instead of NH$_4$NCS to prepare benzoyl thiocyanate.

Preparation of the Dimer Ligand, *N*-(2,6-Dichlorophenyl)-*N'*-cyano-*N'*-(2,6-dichlorophenyl)guanidine ((2,6-Cl$_2$Hpcyd)$_2$). The procedure for the (2,6-dichlorophenyl)cyanamide ligand was followed except that lead acetate was added to the reaction mixture at a reaction mixture temperature of 70 °C and the temperature was maintained at 65 °C for approximately 10 min during the desulfurization reaction. The crude ligand was recrystallized from acetone/water and then heated at 118 °C under vacuum for 17 h. The ligand initially melted at 169 °C and then solidified, due probably to polymerization. Yield: 43%. Anal. Calcd for C$_{14}$H$_8$N$_4$Cl$_4$: C, 32.85; H, 0.79; N, 10.95. Found: C, 32.83; H, 0.93;

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Table I. Infrared Data for Free Phenylcyanamide Ligands and Their Pentaammineruthenium(II) Complexes[a]

compd	$\nu(C{\equiv}N)$	$\nu(C{=}N)$
2,6-Cl_2Hpcyd	2249 (vs), 2231 (vs)	
2,6-Cl_2Hpcyd-^{15}N	2209 (vs)	
$[(NH_3)_5Ru(2,6\text{-}Cl_2Hpcyd)][PF_6]_2$	2287 (w)	
$[(NH_3)_5Ru(2,6\text{-}Cl_2Hpcyd\text{-}^{15}N)][PF_6]_2$	2264 (w)	
$(2,6\text{-}Cl_2Hpcyd)_2$	2245 (vs)	1667 (vs)
$[(NH_3)_5Ru((2,6\text{-}Cl_2Hpcyd)_2)][PF_6]_2$	2249 (m), 2234 (s)	1690 (s)

[a] In cm^{-1}. Abbreviations: vs, very strong; s, strong; m, moderate; w, weak. All spectra were taken from Nujol mulls pressed between sodium chloride plates.

N, 10.94. ^{13}C NMR data: a 10-line spectrum with peaks at 109.28, 124.49, 128.32, 128.75, 130.06, 130.42, 133.19, 135.50, 142.69, and 146.13 ppm.

Preparation of Tl(2,6-Cl_2pcyd). *Caution*! Thallium salts are toxic. The thallium salt of the anion ligand can be prepared from *either* monomer or dimer ligands (as confirmed by IR spectroscopy) in close to quantitative yields. For example, the thallium salt was prepared from the dimer ligand by a method already described.[10] White needles were collected and allowed to air dry. Yield: 85%. Anal. Calcd for $C_7H_3N_2Cl_2Tl$: C, 21.53; H, 0.77; N, 7.18. Found: C, 21.47; H, 0.81; N, 7.16.

Preparation of $[(NH_3)_5Ru(2,6\text{-}Cl_2Hpcyd)][PF_6]_2$. Reactions were carried out in a Vacuum Atmospheres Co. Model HE-493 drybox under an argon atmosphere owing to the sensitivity of this complex to oxidation. Freshly prepared $[(NH_3)_5Ru(H_2O)][PF_6]_2$ (0.25 g) was added to 5 mL of 9.60 × 10^{-3} M HPF_6 acetone solution, in the presence of 0.5 g of polished magnesium ribbon. After the mixture was stirred for 15 min, 0.095 g of (2,6-dichlorophenyl)cyanamide was added to the deep orange solution. After 30 min, the golden yellow solution was filtered and the product forced out of solution by the addition of excess ether. Recrystallization, by acetone/ether diffusion, in the presence of 0.1 g of magnesium ribbon, resulted in a yield of 0.22 g, 65%, after vacuum drying overnight. Anal. Calcd for $C_7H_{19}N_7F_{12}P_2Cl_2Ru$: C, 12.68; H, 2.89; N, 14.78; Cl, 10.69. Found: C, 13.03; H, 2.97; N, 14.46; Cl, 10.71. ^{13}C NMR data: a five-line spectrum with peaks at 112.03, 127.92, 128.02, 130.39, and 132.94 ppm.

Preparation of $[(NH_3)_5Ru((2,6\text{-}Cl_2Hpcyd)_2)][PF_6]_2 \cdot 0.81(C_2H_5)_2O$. The same procedure as above was followed except that after the addition of the dimer ligand (0.19 g) the solution was stirred for 1 h to complete the substitution reaction. Yield of yellow crystalline product: 0.26 g, 60%. The presence of ether in the vacuum-dried product was estimated by ^1H NMR spectroscopy (at least ±3% error). Attempts to drive off the ether by heating under vacuum decomposed the complex. Anal. Calcd for $C_{17.24}H_{31.1}N_9O_{0.81}F_{12}P_2Cl_4Ru$: C, 22.75; H, 3.44; N, 13.85; Cl, 15.58. Found: C, 22.53; H, 3.24; N, 14.07; Cl, 15.27. ^{13}C NMR data: a 10-line spectrum with peaks at 106.69, 124.45, 128.14, 128.75, 129.70, 131.98, 132.17, 135.13, 142.70, and 146.42 ppm.

Preparation of $[(NH_3)_5Ru(2,6\text{-}Cl_2pcyd)][ClO_4]_2$. *Caution*! Perchlorate salts are potentially explosive. This complex was prepared from the reaction of $[Ru(NH_3)_5Cl]^{2+}$ with the thallium salt of the anion ligand in a procedure described in ref 10. The product crystallizes as dark blue rectangular sheets of the perchlorate salt by diffusion of ether into an acetone solution. Yield: 57%. Anal. Calcd for $C_7H_{18}N_7O_8Cl_4Ru$: C, 14.72; H, 3.18; N, 17.17; Cl, 24.83. Found: C, 14.91; H, 3.20; N, 16.99; Cl, 24.58.

Preparation of $[(NH_3)_5Ru(2,6\text{-}Cl_2Hpcyd)][ClO_4]_3 \cdot 0.25(C_2H_5)_2O$. This complex was prepared by protonation of $[(NH_3)_5Ru(2,6\text{-}Cl_2pcyd)]^{2+}$ and isolated as its perchlorate salt in a procedure described in ref 10. Yield: 30%. Anal. Calcd for $C_8H_{21.5}N_7O_{12.5}Cl_5Ru$: C, 13.92; H, 3.14; N, 14.20; Cl, 25.69. Found: C, 13.69; H, 2.97; N, 13.74; Cl, 25.06.

Results

The elemental analyses of the phenylcyanamide ligands and complexes are consistent with their formulations as are the following spectroscopic and electrochemical characterizations.

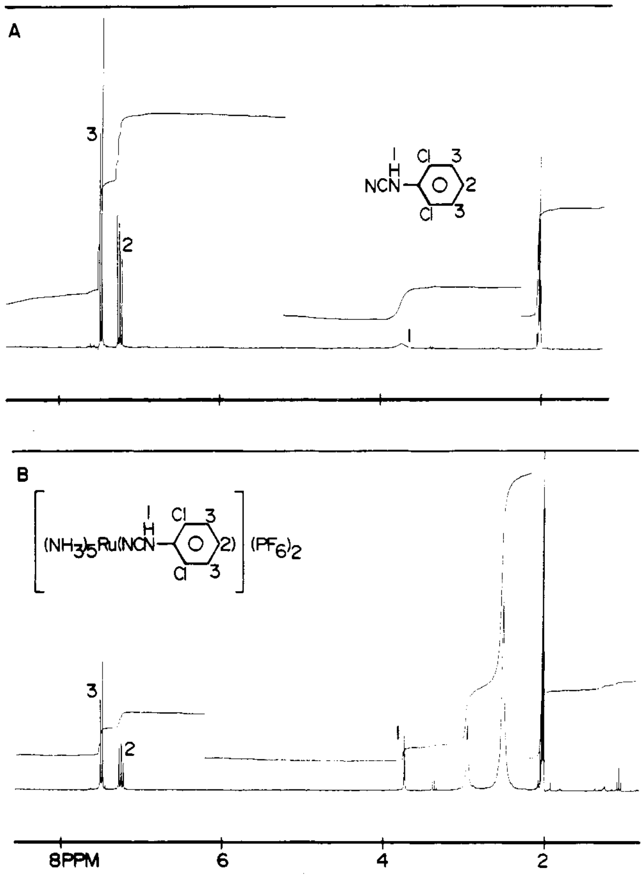

Figure 1. ^1H NMR spectra of (2,6-dichlorophenyl)cyanamide (A) with concentration 5.3 × 10^{-2} M and $[(NH_3)_5Ru(2,6\text{-}Cl_2Hpcyd)][PF_6]_2$ (B) with concentration 1.8 × 10^{-2} M, in acetone-d_6.

The infrared data of the free ligands and complexes are found in Table I. Nujol mulls of the air-sensitive complexes were prepared and pressed between sodium chloride plates in a Vacuum Atmospheres glovebox under argon and then their infrared spectra quickly determined, before oxidation could occur. ^{15}N-isotope labeling of the nitrile group of (2,6-dichlorophenyl)cyanamide was performed in order to distinguish between linkage isomers. Unfortunately, N–H bending modes occur in the region around 1600 cm^{-1} and it was possible that $\nu(C{=}N)$ would be obscured. Deuteration of the complex eliminated this possibility. Attempts to prepare the thallium salt of the dimer ligand only resulted in formation of the thallium salt of the monomer ligand, as supported by their identical infrared spectra and elemental analysis. It is important to note that the strong-intensity band at 1667 cm^{-1}, assigned to $\nu(C{=}N)$ in the spectrum of the dimer ligand, is not present in its thallium salt.

^1H NMR data assignments of the free ligands and complexes are compiled in Table II and illustrated in Figure 1 by a representative ^1H NMR spectra of (2,6-dichlorophenyl)cyanamide and its pentaammineruthenium(II) complex. The ^1H NMR spectrum of (2,6-dichlorophenyl)cyanamide shows an AA′X phenyl proton pattern and a single broad peak at 3.73 ppm that is assigned to the amine proton. The position of this amine peak proved extremely sensitive to concentration, shifting downfield with in-

Table II. ^1H NMR Spectra Data for Free Phenylcyanamide Ligands and Their Pentaammineruthenium(II) Complexes[a]

	phenylcyanamide			ammine	
compd	amine	imine	aromatic	cis	trans
2,6-Cl_2Hpcyd	3.73 (s)		7.27 (t),[b] 7.51 (d)[b]		
$[(NH_3)_5Ru(2,6\text{-}Cl_2Hpcyd)][PF_6]_2$	3.75 (s)		7.28 (t),[b] 7.53 (d)[b]	2.53 (s)	2.97 (s)
$(2,6\text{-}Cl_2Hpcyd)_2$	2.90 (s)	6.32 (s)	6.97 (t),[b] 7.31 (d),[b] 7.64 (m)[c]		
$[(NH_3)_5Ru((2,6\text{-}Cl_2Hpcyd)_2)][PF_6]_2$	3.80 (s)	6.38 (s)	7.01 (t),[b] 7.34 (d),[b] 7.65 (m)[c]	2.53 (s)	3.04 (s)

[a] In acetone-d_6; data in ppm vs TMS reference at 0.00 ppm. Abbreviations: s, singlet; d, doublet; t, triplet; m, multiplet. Integrations are consistent with assignments. [b] Part of an AA′X pattern. [c] An AA′B pattern.

Table III. Electronic Absorption Data[a] and Protonation Equilibrium Constants for Free Phenylcyanamide Ligands and Their Pentaammineruthenium(II) Complexes

compd	$\pi-\pi^*$	MLCT	$pK_a{}^b$
2,6-Cl_2Hpcyd	209 (4.40), 235 (3.68),[c] 285 (3.10)		4.90
$[(NH_3)_5Ru(2,6\text{-}Cl_2Hpcyd)]^{2+}$	205 (4.46), 225 (4.08)[c]	276 (3.71)	7.13[d]
(2,6-Cl_2Hpcyd)$_2$	201 (4.66), 236 (4.56),[c] 273 (3.30)[c]		
$[(NH_3)_5Ru((2,6\text{-}Cl_2Hpcyd)_2)]^{2+}$	200 (4.51), 238 (3.98),[c] 276 (3.65)[c]	313 (3.40)	

[a] λ in nm (log ϵ), in acetonitrile solution. [b] Aqueous solution, at 25 °C, μ = 0.5. [c] Shoulder. [d] Calculated by using the equation $pK_a(II) = \Delta E/59 + pK_a(III)$; see text for details.

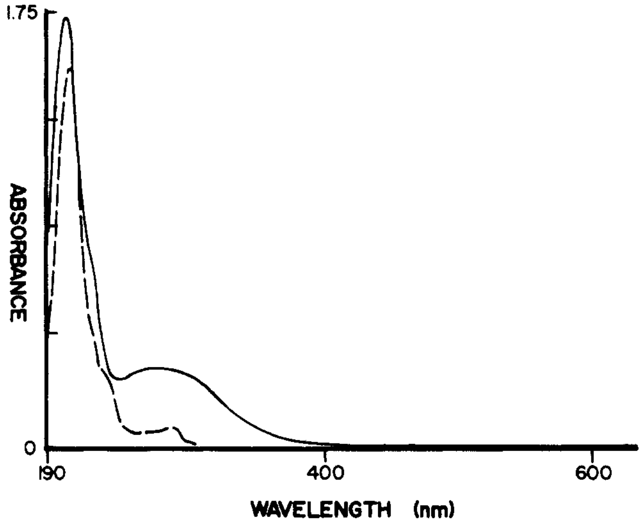

Figure 2. Electronic absorption spectra of $[(NH_3)_5Ru(2,6\text{-}Cl_2Hpcyd)][PF_6]_2$ (solid line) and (2,6-dichlorophenyl)cyanamide (dashed lined), both 5.9×10^{-5} M, in acetonitrile.

creasing concentration. The ligand's ^{13}C NMR spectrum shows the expected five-line pattern with the nitrile carbon assigned to the peak at 112.05 ppm.[16] Coordination of this ligand to pentaammineruthenium(II) has no significant effect on the chemical shifts of phenyl and amine protons. Importantly, the ratio of cis to trans ammine protons is consistent with the cyanamide ligand occupying only one coordination site of ruthenium(II). The ^{13}C NMR spectrum of this complex is essentially identical with that of the free ligand.

The ^1H NMR spectrum of the dimer ligand (Table II) shows two phenyl proton patterns (AA'X and AA'B), an amine proton at 2.90 ppm and an imine proton at 6.32 ppm. The ^{13}C NMR spectrum shows a 10-line pattern with the nitrile carbon assigned to the peak at 109.28 ppm.[16] The ^{13}C and ^1H NMR spectra of the complex dimer ligand are essentially identical with that of the free ligand.

The UV–vis data are assembled in Table III, and representative spectra are shown in Figure 2. The UV–vis spectrum of $[(NH_3)_5Ru(2,6\text{-}Cl_2Hpcyd)]^{2+}$, in Figure 2, shows intense absorptions at 205 and 225 nm that are present in the free ligand and are probably ligand-centered $\pi-\pi^*$ transitions.[10] The broad absorption band, centered at 276 nm, may be ligand field in origin. However, the intensity and energy of the absorption suggest a more accurate assignment may be metal to ligand charge transfer with minor contributions to band intensity due to underlying ligand field transitions.

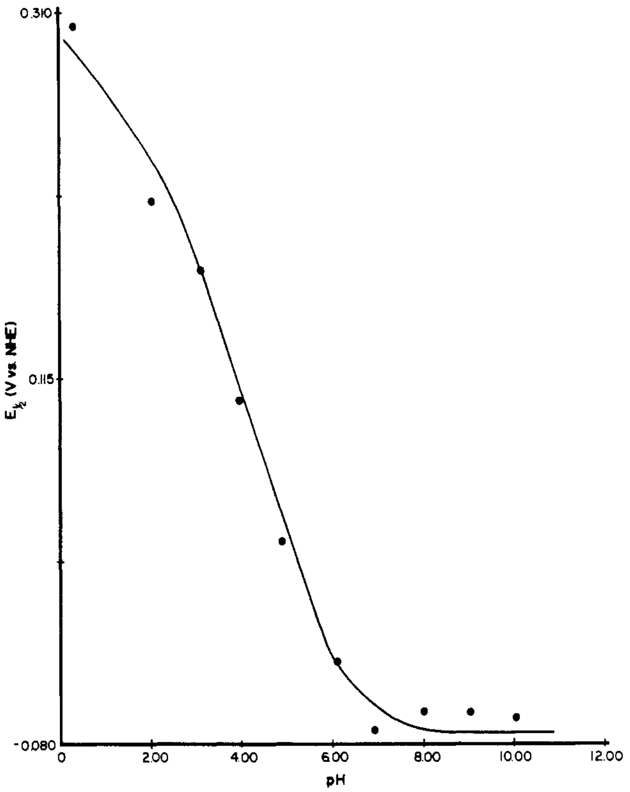

Figure 3. Dependence of the Ru(III/II) reduction couple of $[(NH_3)_5Ru(2,6\text{-}Cl_2pcyd)][ClO_4]_2$ on the pH of an aqueous buffered solution (see Experimental Section) maintained at a constant ionic strength of 0.5. The line drawn is a guide only.

Table IV. Formal Reduction Potentials of Pentaammineruthenium(III) Phenylcyanamide Complexes

complex	E_f[Ru(III/II)][a]
$[(NH_3)_5Ru(2,6\text{-}Cl_2Hpcyd)]^{3+/2+}$	0.380[b] 0.302[c]
$[(NH_3)_5Ru(2,6\text{-}Cl_2pcyd)]^{2+/+}$	−0.124[b] −0.064[d]
$[(NH_3)_5Ru((2,6\text{-}Cl_2Hpcyd)_2)]^{3+/2+}$	0.506[b]

[a] In volts vs NHE. [b] Acetonitrile with 0.1 M tetrabutylammonium hexafluorophosphate electrolyte. [c] Aqueous solution with 0.5 M perchloric acid. [d] Aqueous solution at pH 10.04, glycine/NaOH buffer;[12] ionic strength made up to 0.5 with sodium perchlorate.

The pH dependence of the ruthenium(III/II) couple for the complex $[(NH_3)_5Ru(2,6\text{-}Cl_2pcyd)]^{2+}$ is illustrated in Figure 3. In the pH range 3.10–6.13, the slope of the curve was determined by least-squares analysis to be −69 mV/pH unit. This is close to a theoretical slope of —59 mV/pH unit for a one electron/one proton equilibrium reaction.[17] Under strongly acidic conditions, the complex is not stable and a new reversible wave at more negative potentials increased in intensity, over a period of hours, at the expense of the cyanamide complex reduction wave. This reaction was not investigated further. Table IV summarizes the important electrochemical data.

Discussion

In the cyanamide group, the amine lone pair can delocalize into the nitrile π system, making the cyanamide ligand a σ and π donor of electron density.[10] Thus, cyanamide ligands have larger donor numbers[18] and are less sensitive to base hydrolysis than their nitrile analogues. Cyanamide ligands will autopolymerize when deprotonated or heated. The tendency of phenylcyanamide ligands to autopolymerize appears to increase with increasing chloride substitution of the benzene ring.[19] In addition, while (2,6-di-

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(16) The ^{13}C NMR resonances of organonitriles typically range from 112 to 126 ppm: Levy, G. C.; Nelson, G. L. *Carbon-13 Nuclear Magnetic Resonance Spectroscopy for Organic Chemists*; Wiley-Interscience: New York, 1972; p 129.

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chlorophenyl)cyanamide is stable for days in acetone, in dimethyl sulfoxide the ligand dimerizes in a few hours. The rate of dimerization in dimethyl sulfoxide can be significantly reduced by the addition of trace amounts of acid. These observations are consistent with a reaction mechanism in which the rate-determining step is deprotonation of the cyanamide amine followed by attack of the amide on the nitrile carbon of a neutral cyanamide ligand. The addition of thallium salt to a basic solution of the dimer precipitates $Tl(2,6\text{-}Cl_2pcyd)$ in close to quantitative yield, suggesting that the anion dimer ligand is probably in equilibrium with monomer ligand. The dimer ligand has a characteristic, strong absorption at 1667 cm^{-1}, assigned to $\nu(C{=}N)$, that can be used to determine the amount of dimer impurity in monomer ligand. The proposed structure (see Experimental Section) of the dimer ligand satisfies the requirements of its ^{13}C and ^{1}H NMR spectra and infrared data (see Tables I and II).

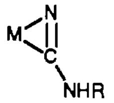
Phenylcyanamide ligands have a coordination configuration that depends primarily on the nature of the metal atom or ion and whether the ligand is neutral or anionic. Anionic phenylcyanamide ligands have been shown to coordinate to ruthenium(III) end-on[10,11] (see structure A). A crystal structure of $[Cr(CO)_5(\eta^1\text{-diethylcyanamide})]$ showed end-on coordination (structure B) of diethylcyanamide.[6] On the other hand, crystal structures of Mo(III)[7] and Ni(O)[20] complexes of cyanamide ligands demonstrated side-on coordination (structure C). The linkage isomerism of neutral cyanamide ligands can be distinguished readily by the $\Delta\nu(C{\equiv}N)$ from the infrared spectra of free relative to coordinated ligand. In type B coordination, $\Delta\nu(C{\equiv}N)$ shifts slightly positive, ranging from 32 to 47 cm^{-1}.[21] Type C coordination results in a large negative shift that is consistent with a change in CN bond order from a triple to a double bond. For example, in $[Mo_2(OCH_2CMe_3)_6(\mu\text{-dimethylcyanamide})]$,[9] $\nu(CN)$ occurs at 1552 cm^{-1} and in $[Ni(CO)(\mu\text{-}NCNC_5H_{10})]_3$,[20,22] $\nu(CN)$ occurs at 1790 cm^{-1}. Unlike the case for strong-intensity $\nu(C{\equiv}N)$ or $\nu(N{=}C{=}N)$ bands in the infrared spectra of respective neutral or anionic phenylcyanamide complexes of pentaammineruthenium(III),[10] identifying the $\nu(C{\equiv}N)$ band for the complex $[(NH_3)_5Ru(2,6\text{-}Cl_2Hpcyd)]^{2+}$ proved to be difficult because of its weak intensity. The weak-intensity band at 2287 cm^{-1} in this complex's infrared spectrum has been assigned to $\nu(C{\equiv}N)$ of cyanamide ligand end-on coordinated to ruthenium(II). This band was initially thought to be due to an impurity of ruthenium(III) complex bound to the neutral ligand. However, repeated recrystallizations did not diminish its intensity and finally a comparison of the infrared spectra of ^{15}N-labeled (at the nitrile nitrogen) and unlabeled deuterated complexes of $[(ND_3)_5Ru(2,6\text{-}Cl_2Hpcyd)]^{2+}$ showed no other band shifted to lower energy in the region, 1500–2300 cm^{-1}. The coordination of organonitrile ligands to pentaammineruthenium(II) has been shown to negatively shift $\nu(C{\equiv}N)$ by 15–59 cm^{-1}.[23] This negative shift in frequency has been ascribed to a net weakening of the nitrile bond due to a large π-back-bonding contribution in the synergistic interaction between ruthenium(II) and the nitrile group. Where π-back-bonding is not as significant, as in pentaammine-rhodium(III) organonitrile complexes,[24] a positive shift in $\nu(C{\equiv}N)$ is observed. The positive shift in $\nu(C{\equiv}N)$, observed for phenylcyanamide complexes of pentaammineruthenium(II), illustrates a previous observation[25] that cyanamide ligands are poorer π acids than their nitrile analogues.

M—N=C=NR

A

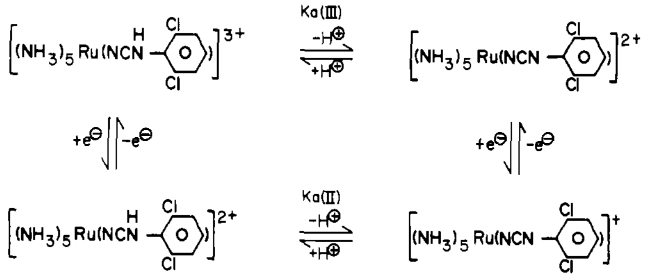
M—N≡CNHR

B



C

Scheme I



Neutral phenylcyanamide ligands are nevertheless significant π-acid ligands capable of stabilizing the ruthenium(II) oxidation state, even though they possess π-donor properties.[10] This is shown by the formal reduction potential of $[(NH_3)_5Ru(2,6\text{-}Cl_2Hpcyd)]^{3+}$ of 0.380 V vs NHE, which is comparable to that of $[(NH_3)_5Ru(4\text{-chlorobenzonitrile})]^{3+}$ of 0.505 V vs NHE.[26] In addition, the MLCT band at 276 nm in the UV–vis spectrum of $[(NH_3)_5Ru(2,6\text{-}Cl_2Hpcyd)]^{2+}$ (Figure 2) can be compared to the MLCT band at 376 nm of $[(NH_3)_5Ru(benzonitrile)]^{2+}$.[23] The greater energy of the MLCT band of the (cyanamide)ruthenium complex is a consequence of the destabilization of the nitrile group π* orbitals by the delocalization of the amine's lone electron pair.[10,27]

The pH dependence of the ruthenium(III/II) couple (Figure 3) is consistent with a one electron/one proton equilibrium, as illustrated in Scheme I. Complexing cyanamides to ruthenium(III) has a dramatic effect on the pK_a of the ligand. The $pK_a(III)$ of coordinated $2,6\text{-}Cl_2Hpcyd$ was determined to be 0.93 ± 0.05, a 3.97 pH unit shift from that of the free ligand. Similar effects have been observed for the complexation of purines or imidazoles to ruthenium(III).[28] Just as the π-acceptor properties of ruthenium(III) increase the acidity of the amine proton, the π-donor properties of ruthenium(II) decrease the acidity of the amine proton. It is possible to calculate the $pK_a(II)$ of the protonated ligand bound to ruthenium(II) by using the equation

$$pK_a(II) = \Delta E/59 + pK_a(III)$$

where ΔE, in millivolts, is the difference in reduction potential between pentaammineruthenium(III) complexes of neutral and anionic phenylcyanamide ligands, in aqueous solution. The $pK_a(III)$ of $[(NH_3)_5Ru(2,6\text{-}Cl_2Hpcyd)]^{3+}$ was determined experimentally to be 0.93 by monitoring the disappearance of the LMCT band at 605 nm of $[(NH_3)_5Ru(2,6\text{-}Cl_2pcyd)]^{2+}$ as acidity is increased.[10] Substituting the appropriate values (Table III and IV) yielded $pK_a(II) = 7.13$, a 6.2 pH unit shift in acidity of the coordinated phenylcyanamide ligand upon a single unit change in oxidation state.

In future studies, we intend to investigate the dependence of the π-acid properties of phenylcyanamide ligands on the nature of the substituents on the phenyl ring.

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(19) The (2,3,5,6-tetrachlorophenyl)- and (pentachlorophenyl)cyanamide ligands can only be prepared as dimer ligands via the thiourea derivative.[11]

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