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Pentaammineruthenium(III) Complexes of Neutral and Anionic (2,3-Dichlorophenyl)cyanamide: Spectroscopic Analysis of Ligand to Metal Charge-Transfer Spectra

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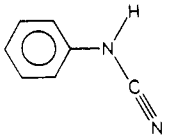
General synthetic methods are presented for neutral and anionic phenylcyanamide ligands and their pentaammineruthenium(III) complexes. A spectroscopic analysis of the complexes, in C_{2v} microsymmetry, details the origin of the ligand to metal charge-transfer bands observed in aqueous solution. For $[Ru(NH_3)_5(2,3\text{-}Cl_2Hpcyd)]^{3+}$, the LMCT band at 487 nm is assigned to an allowed $b_2^* \leftarrow b_2$ transition. For $[Ru(NH_3)_5Ru(2,3\text{-}Cl_2pcyd)]^{2+}$, the LMCT transitions at 356 and 629 nm are assigned to forbidden $b_1^* \leftarrow b_2$ and allowed $b_1^* \leftarrow b_1$ transitions, respectively.

Introduction

Our interest in cyanamide ligands began with the discovery by Hunig et al.[1] of a radical anion copper salt of 2,5-dimethyl-N,-N′-dicyanoquinonediimine with an extremely high electrical conductivity of 500 000 S cm^{-1} at 3.5 K. Further research has shown that both the nature of the cation and the substituents on *N,N′*-dicyanoquinonediimine have a dramatic effect on the electronic properties of the crystal salts.[2] Conduction was suggested to occur via stacks of *N,N′*-dicyanoquinonediimine π-electron systems with an additional contribution to conductivity via the copper ions that link individual stacks. If correct, this would make these novel electronic materials multidimensional conductors. In order to properly interpret the electronic properties of radical anion salts of *N,N′*-dicyanoquinonediimines, it is important that the coordination chemistry and electronic properties of the cyanamide group be fully explored.

The coordination chemistry of cyanamide ligands has been largely ignored with some exceptions.[3] This is probably due to the tendency of these ligands to undergo autopolymerization. Phenylcyanamide ligands are far more stable and can be prepared in high yields.[3h] When deprotonated, these ligands behave like pseudohalogens and prefer coordination to π-acid metal ions. Ligand to metal charge-transfer transitions, (LMCT), are seen in the electronic spectrum when either neutral or anionic phenylcyanamide ligands are coordinated to pentaammineruthenium(III). A spectroscopic analysis is presented that details the origin of these transitions.



Experimental Section

Equipment. UV–vis absorption spectra were taken on a Perkin-Elmer Lambda 4b spectrophotometer. Cyclic voltammetry was performed by using a PAR Model 170 electrochemistry system. The electrochemical cell consisted of a double-jacketed glass container with an inner volume of approximately 15 mL. Cell temperature was controlled by means of a Haake D8-G refrigerated bath and circulator (accuracy ±0.02 °C). The cell was fitted with a Teflon plug through which holes had been drilled to permit insertion of electrodes and argon gas inlet and outlet tubes. Non-aqueous cyclic voltammetry was performed in dry acetonitrile[4] (0.1 M. tetraethylammoniumhexafluorophosphate, TEAH), with a three-electrode system consisting of platinum-disk working (BAS 1.6 mm diameter) and wire counter electrodes and a silver-wire quasi-reference electrode. Ferrocene (E^0 = 0.400 V vs NHE) was used as an internal reference.[5] Infrared spectra of sample Nujol mulls were recorded on a Bomem Michelson-100 FT-IR spectrometer. Protonation equilibrium constants were determined, at ambient temperature, by measuring absorbance change as a function of pH (measured by a Fisher accumet pH meter, Model 620, equipped with a Fisher E-5M pH electrode). The magnetic susceptibility measurement of $[Ru(NH_3)_5(2,3\text{-}Cl_2pcyd)][PF_6]_2$ was determined, at room temperature, by the Evans method,[6] in 2% acetone/acetone-d_6 solution.

Materials. All chemicals and solvents were reagent grade or better. $[(NH_3)_5Ru(Cl)][Cl]_2$,[7] $[(NH_3)_5Ru(H_2O)][PF_6]_2$[8] and TEAH[9] were prepared by literature methods. Elemental analysis was performed by Canadian Microanalytical Services Ltd.

Preparation of (2,3-Dichlorophenyl)cyanamide (2,3-Cl_2Hpcyd). To a magnetically stirred solution of ammonium thiocyanate (0.1 mol), in 100 mL of refluxing acetone, was added dropwise benzoyl chloride, (0.1 mol in 100 mL of acetone). Ammonium chloride immediately precipitated. After addition was complete, the reaction mixture was allowed to reflux for an additional 10 min. Then, 2,3-dichloroaniline (0.1 mol in 100 mL of acetone) was added dropwise and the reaction mixture allowed to reflux for 1 h. The reaction mixture was slowly poured into 1500 mL of water with vigorous stirring. The yellowish benzoylthiourea derivative was collected on a Büchner funnel and washed with copious amounts of water. The wet benzoylthiourea derivative was dissolved in 250 mL of hot 2 M aqueous NaOH solution, and the resulting solution was then brought to a boil for 5 min. To the magnetically stirred solution, cooled to 60 °C, was added lead acetate, (0.1 mol in 100 mL of water). While the reaction mixture was maintained between 50 and 60 °C for 7 min, a deep black precipitate of PbS formed. Note: at temperatures much greater than 60 °C and/or longer reaction times after the addition of lead acetate, the product will polymerize. The PbS was filtered off and to the filtrate, cooled in an ice bath, was added approximately 25 mL of glacial acetic acid. White product immediately precipitates from solution. The product was collected by suction filtration and washed with water and allowed to air dry. Recrystallization was achieved by first dissolving the crude product in boiling acetone followed by the slow addition of an equal volume of water and then allowing the solution to cool. Yield: 13 g (83%) of white needles. Mp: 158 °C dec. $\nu(C{\equiv}N)$: 2245 cm^{-1}. Anal. Calcd for $C_7H_4N_2Cl_2$: C, 44.95; H, 2.15; N, 14.98. Found C, 44.78; H, 2.09; N, 14.85.

Preparation of Tl(2,3-Cl_2pcyd). *Caution*! Thallium is extremely toxic. The thallium salt of the anion ligand (2,3-Cl_2pcyd) was prepared by first dissolving 1.0 g of 2,3-dichlorophenylcyanamide in 25 mL of boiling 50/50 acetone/water solution. While the solution was maintained at a

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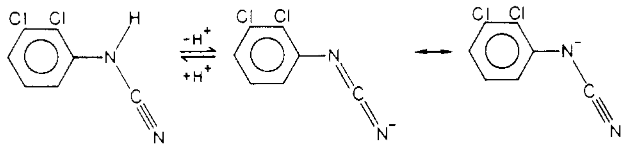
Scheme I



I Ia Ib

boil, a solution of 2.2 g of thallium acetate in 25 mL of 50/50 acetone/water was slowly added, followed by 0.7 g of triethylamine. The solution was allowed to boil for a further 1 min and then cooled to room temperature. White needles of the thallium salt slowly crystallized from solution. The product was washed with water and then acetone and allowed to air dry. Yield: 1.8 g (86%). ν(N=C=N): 2102 cm^{-1}.

Preparation of $[Ru(NH_3)_5(2,3\text{-}Cl_2pcyd)]^{2+}$. First Method. A 40-mL aliquot of acetone was transferred under argon gas to a reaction flask containing freshly prepared $[Ru(NH_3)_5(H_2O)][PF_6]_2$, (0.6 g) and (2,3-dichlorophenyl)cyanamide, (0.4 g). The greenish yellow solution was allowed to stir for 3 h during which time the solution became light blue with the production of the Ru(III) complex from trace oxidizing impurities. Full oxidation was achieved by bubbling air through the solution for 20 min. The intensely blue solution was then evaporated to dryness and then recrystallized by the careful addition of ether to a saturated solution of the complex in acetone. The blue crystalline product was vacuum dried at 78 °C for 2 h. Yield: 0.4 g (50%). Anal. Calcd for $C_7H_{18}N_7F_{12}P_2Cl_2Ru$: C, 12.70; H, 2.74; N, 14.81. Found: C 12.62, H 2.66, N 14.53.

Second Method. This method was found to be more reliable as it always gave analytically pure product. A 1.0-g sample of $[Ru(NH_3)_5(Cl)][PF_6]_2$ (prepared by metathesis of the chloride salt in aqueous solution) was dissolved in 80 mL of acetonitrile to which was added 3 mL of water. $Tl(2,3\text{-}Cl_2pcyd)$ (0.8 g) was added to the solution and the mixture magnetically stirred at 45 °C for 16 h. The deep blue solution was gravity filtered from the thallium precipitate, and to the filtrate was added 2.8 g of tetraethylammonium chloride. The resulting blue precipitate was filtered and washed with acetonitrile. The product was then purified by cation-exchange chromatography on Sephadex C25-120 and eluted with 1 M NaCl solution. For 0.6 g of the crude chloride product, the column dimensions were 22 cm height by 2.2 cm diameter. Elution of the blue product band was preceeded by yellow and purple bands. The product was forced out of the eluent solution by addition of $NaClO_4$, filtered, and washed with ice-cold water. The crude product was recrystallized by ether diffusion into an acetone solution of the product, and then vacuum dried at 78 °C. Yield: 0.4 g (36%). ν(N=C=N): 2111 cm^{-1}. Anal. Calcd for $C_7H_{18}N_7O_8Cl_4Ru$: C, 14.72; H, 3.18; N, 17.17; Cl, 24 83. Found: C, 14.89; H, 3.14; N, 17.11; Cl, 24.98.

Preparation of $[Ru(NH_3)_5(2,3\text{-}Cl_2Hpcyd)][ClO_4]_3\cdot 1.5H_2O$. *Warning!* Larger batches of this product are not advised as one of six batches exploded when scraped off a glass frit, after drying in a desiccator overnight. To an ice-cold solution of 0.06 g of $[Ru(NH_3)_5(2,3\text{-}Cl_2pcyd)][ClO_4]_2$ in 80 mL of water was added 80 mL of ice-cold 6.3 M $HClO_4$. Then, 48 g of $NaClO_4$ was dissolved in the orange-red solution, and after 1 h of cooling in an ice bath, the resulting orange precipitate was collected by suction filtration and washed with 6.3 M $HClO_4$ and ether (care should be taken not to let water condense onto the cold product). Forcing out the product from a dry acetonitrile solution by the addition of anhydrous ether yielded 0.03 g (32%) of product. ν(C≡N): 2287 cm^{-1}. Anal. Calcd for $C_7H_{22}N_7O_{13.5}Cl_5Ru$: C, 12.04; H, 3.17; N, 14.04; Cl, 25.38. Found: C, 11.63; H, 3.04; N, 14.33; Cl, 25.57.

Results and Discussion

As illustrated in Scheme I, the amine proton of the neutral phenylcyanamide ligand is unusually acidic, having a pK_a of 6.00 ± 0.05. Clearly, the anion is resonance stabilized and this increases the amine protons' acidity.[10] UV–vis spectral data for the neutral and anionic ligands are given in Table I. The cyanamide chromophore, whether neutral or anionic, does not significantly absorb at wavelengths greater than 200 nm.[11,12] The absorption bands are therefore assigned to π–π^* transitions associated with the benzene chromophore. The appearance of three absorption bands in the UV region is typical of a benzene chromophore to which an unsaturated group has been attached.[13] The infrared spectrum of the neutral ligand shows a strong band at 2245 cm^{-1} that is assigned to ν(C≡N) of the cyanamide group. Organic carbodiimides have ν(N=C=N) ranging from 2100 to 2150 cm^{-1}.[14] Thus, the strong band at 2102 cm^{-1} in the IR spectrum of the thallium salt of the anion ligand is assigned to ν(N=C=N).

Table I. Electronic Spectroscopic Data for Pentaammineruthenium(III) Complexes of Neutral and Anionic 2,3-Dichlorophenylcyanamide Ligands[a]

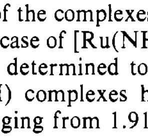
species	π–π^*	LMCT
$2,3\text{-}Cl_2Hpcyd$[b]	205 (4.60), 235 (3.85), 279 (3.01)	
$[2,3\text{-}Cl_2pcd]^-$[c]	219 (4.40), 264 (4.27), 298 (3.45)	
$[(NH_3)_5Ru(2,3\text{-}Cl_2pcyd)][ClO_4]_2$[d]	216 (4.46), 255 (4.16), 293 (3.54)[f]	356 (3.46), 629 (3.71)
$[NH_3)_5Ru(2,3\text{-}Cl_2Hpcyd)][ClO_4]_3$[e]	206 (4.52), 213 (4.06)[f], 275 (3.19)[g]	487 (3.12)

[a] All data were recorded in aqueous solution and are in nm (log ϵ in parentheses). [b] pH 4.12. [c] pH 9.85. [d] pH 5.70. [e] 2.5 M perchloric acid. [f] Shoulder. [g] Midpeak of fine structure.

Elemental analyses of the complexes are consistent with their formulation, and in the case of $[Ru(NH_3)_5(2,3\text{-}pcyd)][PF_6]_2$, the magnetic moment was determined to be 1.94 μ_B. Octahedral ammine ruthenium(III) complexes have been found to have magnetic moments ranging from 1.91 to 2.07 μ_B.[15]

Coordination of neutral and anionic phenylcyanamide ligands to metal cations can occur via amine or nitrile nitrogens, and there are examples in the literature of both types of coordination.[3] Transition metal complexes appear to prefer coordination to the nitrile nitrogen.[3b,h,i,11] This may be due to the π-back-bonding and donor properties of the nitrile group and the steric hindrance that would be experienced upon coordination to the amine of *N*-alkyl- or *N*-phenyl-substituted cyanamides. Crystal structure determinations of silver and copper salts of radical anion *N*,*N'*-dicyanoquinonediimines[2] and $[Cr(CO)_5(diethylcyanamide)]$[16] have all shown coordination of the cyanamide group by the nitrile nitrogen. Consistent with this is the positive shift of 42 cm^{-1} seen for ν(C≡N) upon coordination of the neutral cyanamide ligand to ruthenium(III). When hard cations bind to nitrile ligands a positive shift in ν(C≡N) is observed.[17-19]

The neutral cyanamide ligand has π-donor properties that are due to the delocalization of the amines' electron lone pair into a nitrile π-bond of the correct symmetry.[3a,20] The resulting three-centered π_{nb} molecular orbital in which atomic orbital size approximates[21] the magnitude of electron density is



Both the π_{nb} electron density and the σ lone electron pair on the nitrile nitrogen are available for interaction with cations, and this probably explains the greater donor number of cyanamides over their nitrile analogues.[22] It is important to note that while the interaction of the amine lone pair with a nitrile π orbital lowers

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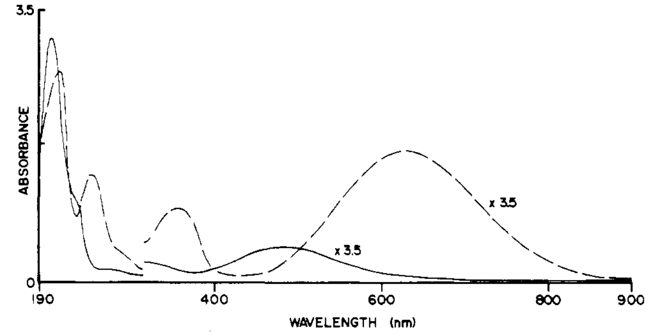
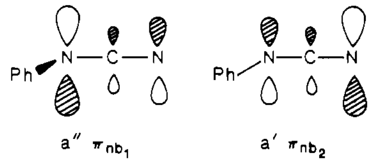


Figure 1. UV–vis absorption spectra of $[Ru(NH_3)_5(2,3\text{-}Cl_2Hpcyd)]^{3+}$ in 2.5 M perchloric acid, (solid line) and $[Ru(NH_3)_5(2,3\text{-}Cl_2pcyd)]^{2+}$ in distilled water, pH 5.8 (dashed line).

the π-orbitals' energy, it raises the antibonding π orbitals' energy. Thus, the π-acceptor properties of cyanamide ligands should be less than those of their nitrile analogues.[11] The anionic cyanamide ligand is expected to be a strong π-donor ligand because two lone electron pairs can delocalized into the nitrile π system. It is suggested that the resonance structure Ia (Scheme I) will dominate when the anion ligand is coordinated to pentaammineruthenium(III). If so, π_{nb_1} and π_{nb_2} molecular orbitals may appear as



The UV–vis spectra of pentaammineruthenium(III) complexes of neutral and anionic phenylcyanamide ligands are shown in Figure 1 and the data compiled in Table I. Ligand field transitions of $[Ru(NH_3)_6]Cl_3$ have been reported at ≃31 300 cm^{-1} ($\epsilon \simeq 100$) and 36 500 cm^{-1} ($\epsilon \simeq 473$).[23] Therefore, it would be difficult to resolve the ligand field transitions of ruthenium(III) phenylcyanamide complexes from the dominating ligand-centered π–π* transitions in the UV region. The absorption bands seen in the near-visible and visible regions are assigned to ligand to metal charge-transfer (LMCT) transitions that are characteristic of pseudohalide complexes of ruthenium(III).[24-27] The absorption spectrum of $[Ru(NH_3)_5(2,3\text{-}Cl_2Hpcyd)]^{3+}$ in Figure 1 shows a single LMCT band centered at 487 nm. This is consistent with the absorption spectra of osmium and ruthenium(III) pentaammine complexes of the halides, which also show a single LMCT band. However, the absorption spectrum of $[Ru(NH_3)_5(2,3\text{-}Cl_2pcyd)]^{2+}$ shows two LMCT bands. The reason for this is that π_{nb_1} and π_{nb_2} are nondegenerate in energy because π_{nb_1} can delocalize into the phenyl ring as well as the nitrile group. A spectroscopic analysis of this complex using C_{4v} microsymmetry[25] is inappropriate and a lower microsymmetry to C_{2v} is required. The coordination scheme and symmetry labels for this analysis were taken from a previously published study.[28] Figure 2 illustrates the π-bonding interactions and the resulting LMCT transitions of neutral and anionic phenylcyanamide ligands with pentaammineruthenium(III).

The possibility that the band at 356 nm in the absorption spectrum of $[Ru(NH_3)_5(2,3\text{-}Cl_2pcyd)]^{3+}$ (ν_1 in Figure 2), is due to a π–σ* LMCT transition is discounted as the energy separation between LMCT bands is only ≃12 200 cm^{-1} and a lower limit for Δ_0 has been estimated to be ≃36 000 cm^{-1}.[24,29] A σ–π* transition is symmetry forbidden and predicted to lie 30 000 cm^{-1} higher in energy than the π–π* (ν_1) transition.[30] The intensity of the ν_1 transition is inconsistent with its assignment as a symmetry-forbidden $b_1^* \leftarrow b_2$ transition. Because the π_{nb_1} cyanamide orbital can interact with a phenyl π system, it is suggested that the excess intensity arises by an intensity-stealing mechanism from the phenyl π–π* transitions.[26] This mechanism is supported by the data in Table I in which the intensity of the free anion ligand transition at 264 nm decreases upon coordination.

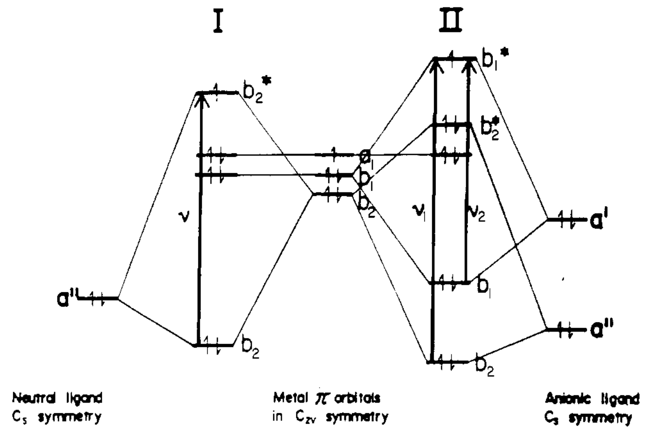


Figure 2. Origins of LMCT bands in pentaammineruthenium(III) complexes of neutral (I) and anionic (II) phenylcyanamide ligands. The figure represents a qualitative energy level scheme for the orbitals resulting from π interactions.

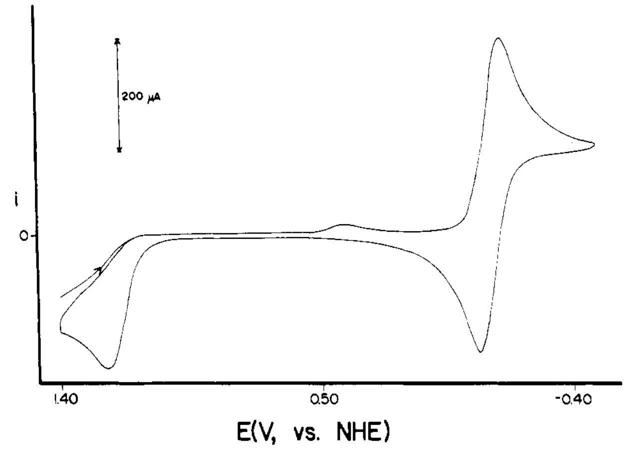


Figure 3. Cyclic voltammetry of 2 mM $[Ru(NH_3)_5(2,3\text{-}Cl_2pcyd)]^{2+}$ in dry acetonitrile (0.1 M TEAH) at 100 mV/s.

Figure 3 shows a cyclic voltammagram of $[Ru(NH_3)_5(2,3\text{-}Cl_2pcyd)]^{2+}$ in CH_3CN. Oxidation of the complex is irreversible with $E_{pa} = 1.245$ and $E_{pc} = 0.420$ V vs NHE at 100 mV/s sweep rate.[31] It seems probable that the coordinated ligand is irreversibly oxidized as the free anionic ligand undergoes irreversible oxidation at $E_{pa} = 0.617$ V vs NHE.[32] Reduction of the complex at $E° = -0.095$ V vs NHE showed quasi-reversible behavior between scanning rates of 50 and 500 mV/s, with the potential separation between anodic and cathodic peaks increasing from 60 to 80 mV, respectively. An electrochemical study of the complex $[Ru(NH_3)_5(2,3\text{-}Cl_2Hpcyd)]^{3+}$ was complicated by the ease with which it could be deprotonated, and care was taken to reduce basic impurities in acetonitrile. Reduction of this complex occurred at $E° = 0.451$ V vs NHE and was also quasi-reversible.

The Ru(III/II) reduction potentials of neutral and anionic cyanamide ligand complexes are compared against those of other

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Table II. Formal Reduction Potentials (V vs NHE) of Pentaammineruthenium(III) Complexes of σ- and π-Donor Ligands

complex	$E_f(Ru^{3+/2+})$
$Ru(NH_3)_6^{3+}$	0.050[a]
$Ru(NH_3)_5(OH_2)^{2+}$	0.067[a]
$Ru(NH_3)_5(imidazole)^{3+}$	0.079[b]
$Ru(NH_3)_5(cytidine)^{3+}$	0.09[c]
$Ru(NH_3)_5(2,3\text{-}Cl_2Hpcyd)^{3+}$	0.451[d]
$Ru(NH_3)_5(NCS)^{2+}$	0.133[e]
$Ru(NH_3)_5Cl^{2+}$	−0.040[a]
$Ru(NH_3)_5Br^{2+}$	−0.020[a]
$Ru(NH_3)_5(2,3\text{-}Cl_2pcyd)^{2+}$	−0.095[d]
$Ru(NH_3)_5(cytidine\ anion)^{2+}$	−0.30[f]
$Ru(NH_3)_5(OH)^{2+}$	−0.420[e]

[a] Aqueous solution of 0.10 M *p*-toluenesulfonic acid/0.10 M potassium *p*-toluenesulfonate: Matsubara, T.; Ford, P. C. *Inorg. Chem.* **1976**, *15*, 1107 and ref 34. [b] Aqueous solution of 0.1 M phosphate buffer plus 0.9 M $NaClO_4$: Johnson, C. R.; Shepherd, R. E. *Synth. React. Inorg. Met.-Org. Chem.* **1984**, *14*, 339. [c] Aqueous solution, 0.01 M $HClO_4$ + 0.09 M $LiClO_4$: Clarke, M. J. *J. Am. Chem. Soc.* **1978**, *100*, 5068. [d] Acetonitrile solution: this work. [e] Aqueous solution of 0.2–1 M NaOH: Lim, H. S.; Barklay, D. J.; Anson, F. C. *Inorg. Chem.* **1972**, *7*, 1460. [f] Aqueous solution, 0.1 M LiOH: Clarke, M. J. *J. Am. Chem. Soc.* **1978**, *100*, 5068.

pentaammineruthenium(III) complexes of π-donor ligands in Table II. Pentaammineruthenium(III) is a strong π acid, and its oxidation state should be stabilized by a strong π-donor ligand. Therefore, it should be possible to relate increasingly negative reduction potentials to the π-donor strength of a ligand. However, as the data in Table II illustrate, great care should be taken in interpretation. While NH_3 has no π-donor properties and water is a weak π donor, the reduction potential of $[Ru(NH_3)_6]^{3+}$ is more negative than that of $[Ru(NH_3)_5(H_2O)]^{3+}$. Clearly, the overall donicity of the ligand is important in determining reduction potential. The ligands thiocyanate and 2,3-Cl_2Hpcyd are π donors to ruthenium(III) but function as π acids to ruthenium(II). Thus, the reduction potentials in Table II reflect the stabilization of the ruthenium(II) oxidation state by π-acid ligands. The ligands Cl^-, Br^-, 2,3-Cl_2pcyd^-, cytidine anion, and OH^- are both σ and π donors with little π-acid properties. The slight anodic shift in reduction potentials in going from Cl^- to Br^- seems counterintuitive as Br^- is more polarizable and should be a better π donor. One possible explanation[34] is that the smaller size of the π orbitals of Cl^- compared to Br^- permits greater effective overlap with the ruthenium(III) πd orbitals. For the nitrogen-bound cytidine anion and OH^- ligands, the match in size between π orbitals may be far better. This is supported by pK_a measurements of coordinated water in $[Rh(NH_3)_5(H_2O)]^{3+}$ (pK_a = 6.8)[35] and $[Ru(NH_3)_5(H_2O)]^{3+}$ (pK_a = 4.2).[33] Rh(III) has a low-spin d^6 configuration in which all the πd orbitals are filled and, therefore, can only σ bond to H_2O or OH^-. The difference in pK_a of water coordinated to ruthenium and rhodium in these complexes is a measure of the importance of π bonding in the ruthenium(III) complex.[36] The anionic cyanamide ligand appears to be a significantly better π donor ligand than Cl^- and Br^- but less so than cytidine anion or OH^-. It should be possible to increase the cyanamide ligand π-donor properties by substituting electron-donor substituents on the phenyl ring. Future studies will attempt to quantitatively evaluate the importance of π bonding in phenylcyanamide ligands.

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Registry No. 2,3-Cl_2Hpcyd, 71232-27-4; $[(NH_3)_5Ru(Cl)][Cl]_2$, 18532-87-1; $[(NH_3)_5Ru(H_2O)][PF_6]_2$, 34843-18-0; $[(NH_3)_5Ru(2,3\text{-}Cl_2pcyd)][ClO_4]_2$, 120204-95-7; $[(NH_3)_5Ru(2,3\text{-}Cl_2pcyd)][ClO_4]_3$, 120204-97-9; Tl(2,3-$Cl_2$pcyd), 120204-98-0; ammonium thiocyanate, 1762-95-4; benzoyl chloride, 98-88-4; 2,3-dichloroaniline, 608-27-5.

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(35) Palmer, D. A.; Harris, G. M. *Inorg. Chem.* **1974**, *13*, 965.
(36) It is assumed that there is little difference in effective charge between Ru(III) and Rh(III).

Contribution from the Dipartimento di Chimica, Università di Firenze, Firenze, Italy, and Istituto per lo Studio della Stereochimica ed Energetica dei Composti di Coordinazione del CNR, Firenze, Italy

Crystal and Molecular Structure and Magnetic Properties of the μ-Azido-Bridged Low-Spin Cobalt(II) Complex $[(CH_3C(CH_2PPh_2)_3)Co(\mu\text{-}N_3)]_2(BPh_4)_2\cdot 2(CH_3)_2CO$

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The complex $[(triphos)Co(\mu\text{-}N_3)]_2(BPh_4)_2\cdot 2(CH_3)_2CO$, triphos = $CH_3C(CH_2PPh_2)_3$, crystallizes in the triclinic system, space group $P\bar{1}$, with a = 18.122 (9) Å, b = 14.025 (8) Å, c = 12.668 (7) Å, α = 92.95 (8)°, β = 103.77 (9)°, and γ = 108.12 (8)°. The molecular structure consists of discrete dinuclear $[(triphos)Co(\mu\text{-}N_3)]_2^{2+}$ cations with the cobalt atoms in a distorted P_3N_2 square-pyramidal environment. The compound is diamagnetic, and the observed diamagnetism has been related to the low-symmetry mixing of $d_{x^2-y^2}$ orbitals of cobalt with the ground d_{z^2} orbitals by using extended Hückel calculations. With the same model the magnetic properties of related azido-bridged nickel(II) complexes have been rationalized.

Introduction

During the last few years a number of μ-azido-bridged dinuclear complexes have been synthesized with the aim of investigating their magnetic properties.[2,3] The actual type of bridging arrangement that one can obtain from the azido ions is not easily predictable, but the magnetic properties of the resulting solid are strongly dependent on the bridging mode of N_3^-. The coordination chemistry of the N_3^- ion is, in this sense, rather different from that of other groups or ions that bridge transition-metal ions to form di- or polynuclear systems.[4] The oxalato ion, for example, always bridges two metals like a bis-chelating donor and transmits antiferromagnetic exchange interactions.[5] The largest number

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