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Notes

Intervalence Absorption, Ligand Interchange, and Redox Reactivity in Binuclear Cyanopyridine-Bridged Complexes Containing Pentacyanoruthenate(II) and Pentaammineruthenium(II) or -(III)

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Introduction

Metal−metal interactions in mixed-valence, asymmetric binuclear compounds of the $[(NC)_5Fe{-}L{-}Ru(NH_3)_5]^n$ series show weak-coupling behavior,[1] independent of which electronic isomer is predominant. $Fe^{II}{-}L{-}Ru^{III}$ distributions have been found for L = CN^-,[2] pyrazine (pz),[3] pyridinecarboxamido,[4] and imidazolato,[5] and an $Fe^{III}{-}L{-}Ru^{II}$ distribution, for L = cyanopyridine (CNpy).[6] The calculated values for the electronic coupling factor, H_{ab}, were in the range 400−600 cm^{-1}, with the exception of cyanide showing a greater value, 1500 cm^{-1}. On the other hand, no coupling or IV absorption occurred with the $[(NC)_5Fe^{II}{-}bpa{-}Ru^{III}(NH_3)_5]$ complex,[7] featuring a noncommunicating ligand (bpa = 1,2-bis(4-pyridyl)ethane). An extension to analogous complexes with $Ru(CN)_5^{3-}$ showed reasonable results for L = CN^-,[8,9] but surprisingly, no intervalence transitions were detected for L = pz,[10] 4,4′-bipyridine (4,4′-bpy),[9] or even dicyanogen (NCCN),[9] a ligand which promotes a large interaction and strong delocalization in the bis(pentaammine) complex.[11] This was assigned to a very weak through-space overlap between the dπ orbitals in $Ru(CN)_5^{3-}$ and the Ru^{III} acceptor, associated with the competitive influence of cyanides as electron-withdrawing coligands.[9,10]

The electronic interactions are controlled by the type of metal and by both the bridging and nonbridging ligands.[1] In view of the contrasting results obtained with the pz-bridged pentacyanoferrates[3] and ruthenates,[10] it seemed worthwhile to extend our work with the CNpy bridging ligand;[6] thus, we report herein the preparation and chemical properties of the fully reduced (II,II; R) and mixed-valence (II,III; M) CNpy-bridged complexes containing pentacyanoruthenate and pentaammineruthenium fragments.

Experimental Section

Materials. $[Ru(NH_3)_5(4\text{-}NCpy)](PF_6)_2$ and $K_4[Ru(CN)_6]$ were prepared according to literature.[12,13] Dilute solutions of $Ru(CN)_5H_2O^{3-}$ ($\sim10^{-4}$ M) were prepared by reaction of a solution of $Ru(CN)_6^{4-}$ with equimolar bromine;[14] the mixture was kept for 5 min under argon and was immediately used. All the solution experiments were performed at pH 5.5 (buffer edta−NaOAc), I = 0.1 M ($NaNO_3$, unless otherwise indicated), in deoxygenated media. Dimethyl sulfoxide (Baker) and acetone (Mallinckrodt) were used as supplied. Other chemicals (potassium peroxydisulfate, bromine, ascorbic acid, potassium nitrate, lithium chloride, sodium acetate, and Na(edta)) were analytical grade reagents.

Preparation of the Binuclear Complexes. The R compound was obtained by mixing a solution of $[Ru(CN)_5H_2O]^{3-}$ (0.06 mol of $K_4[Ru(CN)_6]$ in 10 mL of water, as described before) with an equimolar solution of $[Ru(NH_3)_5(4\text{-}NCpy)](PF_6)_2$. After 1 h, precipitation was induced with cold ethanol; the solid was isolated, washed with ethanol, and dried in vacuo under silica gel. Anal. Calcd for $K[(NC)_5Ru(4\text{-}pyCN)Ru(NH_3)_5]\cdot H_2O$: H_2O, 3.1; K, 6.7; NH_3, 14.7; Ru, 34.9. Found: H_2O, 3.2; K, 6.8; NH_3, 14.4; Ru, 35.0. The mixed-valence solid was isolated after mixing equimolar solutions of $Ru(CN)_5H_2O^{3-}$ and $Ru(NH_3)_5(4\text{-}NCpy)^{3+}$; the latter was freshly prepared by oxidation of $Ru(NH_3)_5(4\text{-}NCpy)^{2+}$ with chlorine and was used immediately to minimize hydrolytic reactions.[4] The precipitate was washed and dried as before. Anal. Calcd for $[(NC)_5Ru(4\text{-}pyCN)Ru(NH_3)_5]\cdot H_2O$: H_2O, 3.3; NH_3, 15.8; Ru, 37.5. Found: H_2O, 3.6; NH_3, 15.2; Ru, 37.0.

Spectral, Electrochemical, and Analytical Measurements. The visible−UV and IR spectra were measured on a Shimadzu UV 210A and a Perkin-Elmer 599 spectrophotometer, respectively. The cyclic voltammograms of R, $Ru(NH_3)_5(4\text{-}NCpy)^{2+}$, and $Ru(CN)_5(4\text{-}pyCN)^{3-}$ were obtained as recently described.[6] Potassium, ruthenium, water, and ammonia were determined for the analytical characterization of the binuclear complexes.[6]

Kinetic Measurements. The kinetics of the formation reactions of R and M were studied by measuring the absorbance increases at 460 and 380 nm, respectively, with $[Ru(CN)_5H_2O^{3-}] = 2 \times 10^{-5}$ M, pH 5.5, I = 0.1 M (LiCl), T = 25.0 °C, and $Ru(NH_3)_5(4\text{-}NCpy)^{2,3+}$ in the range $(0.6{-}2) \times 10^{-4}$ M. Values of k_{obs} (s^{-1}) were obtained by fitting a pseudo-first-order rate law, up to 3 half-lives. The second-order formation rate constants (k_1, k_2) were calculated from the slopes of the plots of k_{obs} against the concentration of $Ru(NH_3)_5(4\text{-}NCpy)^{n+}$ (n = 2, 3). The kinetics of the dissociation reaction of R (5×10^{-5} M) was studied by adding 0.2 M dimethyl sulfoxide and following the subsequent absorption decrease at 460 nm, in the range 40−60 °C. The fittings were obtained only to 1 half-life because of precipitation at longer times. The rate constant at 25.0 °C and the activation parameters were estimated by use of an Eyring plot. The rate constant of the dissociation reaction of M was estimated by using a thermodynamic cycle[15] and redox potentials for oxidation at the $Ru^{II}(NH_3)_5(4\text{-}NCpy)^{2+}$ center in the mononuclear and R complexes, as well as the stability constant of the latter complex, $K_{st} = k_1/k_{-1} = (5 \pm 1) \times 10^5$ M^{-1}. The kinetics of the reaction of R ($\sim10^{-4}$ M) with peroxydisulfate was studied under stopped-flow conditions with a Hewlett-Packard

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Table 1. UV–Visible and IR Absorptions, Reduction Potentials, and Rate Constants for Peroxydisulfate Oxidation of $Ru^{II}(CN)_5$ and $Ru^{II,III}A_5$ (A = Ammine) Complexes with Bridging 4-Cyanopyridine[a]

complex	λ, nm	$10^{-3}\epsilon$, M^{-1} cm^{-1}	ν, cm^{-1}	E, V (NHE)	k, M^{-1} s^{-1}
$[Ru^{II}(CN)_5(4\text{-pyCN})]^{3-}$ [b]	388	5.9	2250,[c] 2040[d]	1.00[a]	10^{-5} [e]
$[Ru^{II}A_5(4\text{-NCpy})]^{2+}$ [f]	425	5.4	2180,[g] 1268[h]	0.62[a]	$(2.3 \pm 0.1) \times 10^3$ [a]
$[(NC)_5Ru^{II}(4\text{-pyCN})Ru^{II}A_5]^-$	380, 460	4.5, 7.3	2180,[g] 2055,[d] 1280[h]	0.55[i]	$(8.7 \pm 0.4) \times 10^2$
$[(NC)_5Ru^{II}(4\text{-pyCN})Ru^{III}A_5]$	400, 700	5.1, 0.5	2200,[g] 2068,[d] 1300[h]	1.15[j]	10^{-5} [e]

[a] This work; at 25 °C, $I = 0.1$ M (KNO_3), pH 5.5 (H_2EDTA^{2-}, CH_3COO^-). IR data are for solids in KBr disks. [b] Reference 18; potassium salt. [c] Nitrile stretching, with pyCN bound through the pyridine nitrogen. [d] Cyanide stretching. [e] See text. [f] Reference 14; hexafluorophosphate salt. [g] Nitrile stretching, with NCpy bound through N at the nitrile group. [h] Ammine deformation. [i] Oxidation at the $Ru^{II}A_5$ center. [j] Oxidation at the $Ru^{II}(CN)_5$ center.

8452-A diode-array instrument, interfaced with a rapid-mixing device (Applied Photophysics, Model 7004B), by following the absorbance decrease at 460 nm with an excess of oxidant (range (1−5) × 10^{-3} M). With $Ru^{II}(NH_3)_5(4\text{-NCpy})^{2+}$, the oxidation reaction was followed by measuring the absorbance decrease at 425 nm. A good pseudo-first-order behavior was obtained, and the second-order rate constants were calculated as before.[5,6]

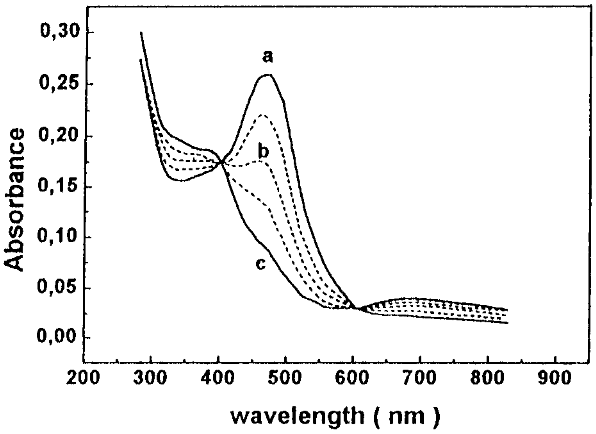

Figure 1. Spectrophotometric titration of the $[(NC)_5Ru^{II}(4\text{-pyCN})Ru^{II}(NH_3)_5]^-$ complex (R) with bromine ([R] = 4 × 10^{-5} M, pH 5.5, 25.0 °C): (a) without addition of bromine; (b) with 0.5 equiv of bromine; (c) with 1 equiv of bromine.

Results and Discussion

The solution obtained by mixing $Ru^{II}(CN)_5H_2O^{3-}$ (10^{-4} M, λ_{max} = 315 nm)[14] with equimolar $Ru^{II}(NH_3)_5(4\text{-NCpy})^{2+}$ (λ_{max} = 425 nm)[12] displays a band at 460 nm ($\epsilon = 7.3 \times 10^3$ M^{-1} cm^{-1}) and a shoulder at 380 nm ($\epsilon = \sim 4.5 \times 10^3$ M^{-1} cm^{-1}). The spectral changes are completed in about 30 min and can be described by eq 1.

$$Ru(CN)_5H_2O^{3-} + Ru(NH_3)_5(4\text{-NCpy})^{2+} \rightleftharpoons [(NC)_5Ru^{II}(4\text{-pyCN})Ru^{II}(NH_3)_5]^- + H_2O \qquad k_1, k_{-1} \quad (1)$$

Solutions of R display the MLCT bands involving both $Ru^{II}(CN)_5$ and $Ru^{II}(NH_3)_5$ centers and the bridging ligand. Table 1 shows the values of the MLCT bands corresponding to the relevant mononuclear species. Additional supporting evidence in Table 1 is the IR results for the solids, which are diagnostic of oxidation state II at both ruthenium centers.[7] The value of k_1, 22.5 ± 0.5 M^{-1} s^{-1} (25 °C), is consistent with the entry of a dipositively charged ligand into $Ru(CN)_5H_2O^{3-}$.[16] For the dissociation reaction (reverse reaction in eq 1), spectral monitoring of the products showed the formation of $Ru(NH_3)_5(4\text{-NCpy})^{2+}$, indicating the cleavage of the $(NC)_5Ru{-}pyCN$ bond. The value of k_{-1}, (4 ± 1) × 10^{-5} s^{-1} (25 °C), is similar to the one obtained for the dissociation of 4-pyCN from the $Ru(CN)_5(4\text{-pyCN})^{3-}$ ion.[17] Both the values of k_1 and k_{-1} as well as the activation parameters for the dissociation reaction, $\Delta H^{\ddagger} = 100 \pm 20$ kJ mol^{-1} and $\Delta S^{\ddagger} = 79 \pm 17$ J K^{-1} mol^{-1}, reflect the onset of dissociative-type mechanisms for ligand interchange.[16−19]

The M complex was obtained in solution by a stoichiometric oxidation of R with peroxydisulfate or bromine. In a spectrophotometric titration experiment, the spectrum of R (Figure 1a) evolved to the one shown in Figure 1c with addition of 1 equiv of oxidant; Figure 1b shows a spectrum of the mixture with addition of 0.5 equiv. The plots of absorbance at 460 or 700 nm against the concentration of oxidant showed definite breakpoints for the 1-equiv relation. The latter results and the well-defined isosbestic points in Figure 1 confirm that a mixed-valence species is formed. Because the MLCT band of $Ru^{II}(NH_3)_5$ disappears, while the one for $Ru^{II}(CN)_5$ is conserved, we infer that localized valences are as shown in Table 1. Thus, the band at 700 nm is assigned to the intervalence (IV) transition from $d\pi(Ru^{II}(CN)_5)$ to $d\pi(Ru^{III}(NH_3)_5)$. The energy is displaced to higher values by 3600 cm^{-1} (0.45 V) compared to that of the IV transition band measured for the $[(NC)_5Fe(4\text{-pyCN})Ru(NH_3)_5]$ complex;[20] this shift agrees with the difference in redox potentials for $Ru^{III,II}(CN)_5(4\text{-pyCN})^{2-,3-}$ and $Fe^{III,II}(CN)_5(4\text{-pyCN})^{2-,3-}$, 1.00 and 0.53 V,[4] respectively. Fresh solutions of M could be reduced with ascorbic acid, and the spectral changes were consistent with the recovery of R.

That M has the $[(NC)_5Ru^{II}(4\text{-pyCN})Ru^{III}(NH_3)_5]$ distribution is confirmed by the cyclic voltammetric results shown in Table 1 (see also the illustration). The shifts of E values for the binuclear complex with respect to values for the mononuclear species agree with previous results obtained for related complexes with L = pz.[3]

For the formation and dissociation reactions of M, eq 2, the values of k_2, 31 ± 3 M^{-1} s^{-1}, and k_{-2}, (4 ± 1) × 10^{-6} s^{-1} (25 °C), also suggest dissociative pathways.

$$Ru(CN)_5H_2O^{3-} + Ru(NH_3)_5(4\text{-NCpy})^{3+} \rightleftharpoons [(NC)_5Ru^{II}(4\text{-pyCN})Ru^{III}(NH_3)_5] + H_2O \qquad k_2, k_{-2} \quad (2)$$

The M complex is unstable on the minute time scale, as shown by the slow increase of absorbance at 400 nm obtained after the fast R → M conversion. The results were fitted to a pseudo-first-order rate law, with the following values of 10^3k (s^{-1}) at the indicated pH's in parentheses (25 °C, $I = 0.1$ M): 1.8 ± 0.1 (4); 1.5 ± 0.1 (5.5); 1.3 ± 0.1 (7); 2.6 ± 0.1 (10).

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(19) The value of $\Delta H^{\ddagger}$ is similar to those obtained for the dissociation of $[Ru(CN)_5L]^{n-}$ (L = 4-CNpy and others).[16,17] The positive value of $\Delta S^{\ddagger}$ agrees with that for $[Ru(CN)_5(4\text{-pyCN})]^{3-}$,[17] in contrast with values near zero (positive and negative) found for other L ligands.[16]

(20) In fact, the predominant electronic isomer was $[(NC)_5Fe^{III}(4\text{-pyCN})Ru^{II}(NH_3)_5]$, and λ_{max} of the IV band transition was found at 938 nm; the IV transition energy for the Fe^{II},Ru^{III} isomer should be very close to ~0.05 V (cf. ref 6).

By taking samples periodically and treating them with ascorbic acid, we obtained decreasing amounts of R for increasing times after the generation of M. The picture reflects a hydrolytic process at the Ru(III)−NCpy bond. The rate constants (pH range 4−7) are lower than the values obtained for the $Ru^{III}(NH_3)_5(4\text{-}NCpy)^{3+}$ ion, 2.85×10^{-3} s^{-1},[4] and for the fully oxidized binuclear species, $[X_5M^{III}{-}pyCN{-}Ru^{III}(NH_3)_5]^n$, with $X_5M^{III} = (NC)_5Fe^{III}$ or $(NH_3)_5Ru^{III}$, $\sim 2 \times 10^{-2}$ s^{-1}.[6,21] The stabilization relates to the back-bonding influence of the $Ru^{II}(CN)_5^{3-}$ moiety, which lowers the positive charge at the electrophilic nitrile group. The small rate increase when pH is decreased from 7 to 4 may be ascribed to the influence of hydrolysis of protonated $[Ru^{III}(NH_3)_5NCpy]^{3+}$, which overlaps with the dissociation reaction of M.[4] On the other hand, the rate increase at pH 10 may be ascribed to enhanced nucleophilic attack of the OH^- species instead of water.[4]

The value of the specific rate constant for the one-electron oxidation of R with peroxydisulfate (Table 1) shows that oxidation at the $Ru^{II}(NH_3)_5$ center is operative; the value of k fits nicely in the LFE plot for the oxidation of different binuclear complexes of the $[X_5M{-}L{-}Ru^{II}(NH_3)_5]$ series with peroxydisulfate.[5,6] Table 1 also shows the large differences in reactivity toward peroxydisulfate displayed by the mononuclear Ru(II) species with cyano and ammine coligands. The oxidation of the $Ru^{II}(CN)_5$ center in the M complex to the fully oxidized III,III species could not be obtained chemically with excess peroxydisulfate; instead, hydrolysis occurred. In addition, no reaction could be detected with the $Ru(CN)_5(4\text{-}pyCN)^{3-}$ ion (Table 1). With bromine as oxidant, decomposition ensues with formation of blue precipitates.[22] Because the $Fe^{II}(CN)_5^{3-}$ centers react with peroxydisulfate with $k = \sim 1$ M^{-1} s^{-1} or even lower,[23] and considering the redox potential at the $Ru^{II}(CN)_5^{3-}$ centers (Table 1), we estimate, on the basis of LFE calculations, that the oxidation of M to the III,III complex (through direct electron transfer at the $Ru^{II}(CN)_5$ center) should be $\sim 10^{-5}$ M^{-1} s^{-1}. On the other hand, we also predict an effective rate of the same order if the intramolecular assistance path becomes available owing to the presence of the reactive $[(NC)_5Ru^{III}{-}pyCN{-}Ru^{II}(NH_3)_5]$ electronic isomer.[24]

On the basis of the Hush model,[25] we calculate values of 345 cm^{-1} for H_{ab} and 5.8×10^{-4} for α^2, the delocalization factor in the ground state. The first value is similar to those measured for related complexes of the same series.[3−6] The value of α^2 is consistent with the proposed valence-trapped formulation. In summary, the coordination of pentacyanoruthenate *vs* pentacyanoferrate fragments in the binuclear complexes under consideration leads to predictable results and interpretation. In a revisited experiment, the pz-bridged complex also shows a weak IV transition band, probably related to a less efficient orbital overlap of pz compared to CNpy at the Ru(III) acceptor site.[26]

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(22) No decay of the absorption in the IV transition region was observed with excess bromine; instead, spectral changes in the near-UV region suggest the release of cyanides, probably through oxidation. Decomposition of the pentaammine fragment is also feasible.[9] The persistence of absorption and the formation of precipitates probably relate to the onset of Prussian blue-type compounds.

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(24) Haim, A. Taube Insights: From Electron Transfer Reactions to Modern Inorganic Chemistry. *Adv. Chem. Ser.*, in press. According to the intramolecular assistance mechanism, the observed second-order rate constant should be $k_{obs} = 2\,K_{et}k_{Ru}$, where K_{et} is the equilibrium constant for the formation of the unstable electronic isomer and k_{Ru} is the second-order rate constant for oxidation at the Ru(II) center;[5] the latter is controlled by the redox potential (∼0.65 V) and thus we estimate $k_{Ru} = 270$ M^{-1} s^{-1} (according to the LFE plot; cf. ref 5). By considering a thermodynamic cycle as described elsewhere,[6] we obtain $K_{et} = 2.3 \times 10^{-8}$. Thus, k_{obs} should be $\sim 10^{-5}$ M^{-1} s^{-1}.

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(26) We again performed the oxidation of the pyrazine-bridged II,II complex with bromine.[10] The II,II complex showed absorptions at 365 and 504 nm, associated with MLCT transitions from the pentacyanoruthenate(II) and pentaammineruthenium(II) fragments, respectively, in addition to the pz-centered band at 260 nm. Upon oxidation with 1 equiv, the bands at 260 and 365 nm shifted to 265 and 380 nm, respectively, as expected from oxidation at the $Ru(NH_3)_5$ center. The band at 504 nm nearly disappeared, with a weak broad absorption remaining in the 450−500 nm region. A careful inspection of the near-IR region showed a weak band centered at 963 nm ($\epsilon = \sim 100$ M^{-1} cm^{-1}), which decayed upon addition of excess bromine (cf. ref 22). The energy shift of this band compared to the one measured for the $[(NC)_5Fe^{II}{-}pz{-}Ru^{III}(NH_3)_5]$ species[3] is as expected from the difference in reduction potentials for the mononuclear iron and ruthenium pentacyanometalates (∼0.5 V). However, the intensity is unexpectedly low. Precipitation is probably induced upon formation of the neutral mixed-valence complex.