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Pentacyanoruthenate(II)-Pentaammineruthenium(II/III) Binuclear Complexes Bridged by Cyanogen, Cyanide, and 4,4′-Bipyridine

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Binuclear complexes of the type $[(CN)_5RuLRu(NH_3)_5]^{n-}$, with L = 4,4′-bipyridine (4,4′-bpy), dicyanogen (NCCN), and cyanide ion (CN^-), have been prepared. The resulting (II,L,II) and (III,L,II) complexes have been characterized by infrared, UV–visible, near-IR, kinetic, and differential-pulse voltammetric methods. The (III,L,II) complexes with L = 4,4′-bpy and NCCN are found to be of the isolated valence type where coupling between the Ru^{III} and Ru^{II} metal centers is very weak. Like the previously characterized (III,pz,II) analogue (III,L,II), complexes with L = 4,4′-bpy and NCCN do not exhibit near-IR IT transitions. The (II,L,II) complexes appear to have significant electron-donating interaction between the Ru^{II} sites for L = NCCN and CN^-. An estimate of the π back-donation of $Ru(CN)_5^{3-}$ to NCCN in $(CN)_5Ru(NCCN)^{3-}$ of −3.8 kcal/mol has been made on the basis of its formation constant, 585 ± 70 M^{-1}. The π-donor ability of $Ru(CN)_5^{3-}$ is found to be about 40% of that of $Ru(NH_3)_5^{2+}$ toward nitrile functional groups; this estimate is consistent with prior results with pyrazine as the π-acceptor ligand. The rate of bond rupture for (II,CN^-,II) in forming the ion pair $\{(NH_3)_5RuOH_2^{2+},Ru(CN)_6^{4-}\}$ is found to be $(6.7 \pm 1.0) \times 10^{-6}\ s^{-1}$ with 2-methylpyrazine used as a scavenger for the dissociated $(NH_3)_5RuOH_2^{2+}$ fragment. (II,L,II) complexes exhibit new spectral MLCT maxima at 490 (4,4′-bpy) and 352 nm (NCCN) and a very weak one at 625 nm (CN^-). Their (III,L,II) derivatives have maxima at 380 (4,4′-bpy), <300 (NCCN), and 675 nm (CN^-), which are attributed to MLCT bands for 4,4′-bpy and NCCN and an intervalence transition for L = CN^-.

Introduction

We recently examined the properties of $[(CN)_5Ru(pz)Ru(NH_3)_5]^{0/-}$ complexes.[1] These unsymmetrical complexes, **1** = (II,III) and **2** = (II,II), are of interest due to the numerous studies of ligand-bridged mixed-valence binuclear complexes based on ruthenium ammines.[2-13] **1** is related to the famous Creutz-Taube ion $[(Ru(NH_3)_5)_2(pz)]^{5+}$, which exhibits an intervalence transition (IT) in the near-infrared region (1570 nm in D_2O).[2] Day included the Creutz–Taube ion in class II behavior of mixed-valence complexes. With class II systems the extent of electronic delocalization between the two Ru sites is rather small.[14] However, the communication in class II ions is still greater than in the strictly valence-localized class I ions. The existence of an intervalence transition has been exploited by Hush to calculate the extent of delocalization in mixed-valence complexes,[15] and his procedure has been routinely employed by others when intervalent bands are formed. Taube and Richardson have shown that the interaction energy between Ru^{II} and Ru^{III} sites will decrease with the distance of separation, which is achieved by replacing pyrazine with a variety of bridging ligands.[16] The interaction energy is particularly large with small ligand bridges including N_2 and dicyanogen (C_2N_2).[17-19] The delocalization is virtually complete for N_2 and C_2N_2 as implicated by the electrochemical behavior of $[(Ru(NH_3)_5)_2L]^{5+}$, L = N_2 or C_2N_2.[18,19]

The most striking aspect of the previous study of **1** = $[(CN)_5Ru^{II}(pz)Ru^{III}(NH_3)_5]$ was the absence of a detectable intervalent transition at wavelengths longer than the MLCT transition (λ_{max} = 450 nm).[1,21] The detection limits set by the solubility of **1** imply that no transition of $\epsilon > 50\ M^{-1}\ cm^{-1}$ exists beyond 800 nm. No IT band is observed for $(bpy)_2ClRu(BPA)Ru(NH_3)_5^{2+}$ with BPA = 1,2-bis(4-pyridyl)ethane, which loses coupling at the saturated ethane bridge.[22]

The absence of an IT band for **1** was surprising in view of similar redox potentials exhibited by **2** in comparison with $[Cl(bpy)_2Ru^{II}(pz)Ru^{III}(NH_3)_5^{4+}]$, characterized by Meyer et al.[22] Meyer's ion displays the IT band at 900 nm. Therefore the absence of the IT band for **1** is not a simple Franck–Condon effect. Also the $[(NH_3)_5Ru^{II}(pz)Ru^{III}(edta)]^+$ ion studied by Creutz and Sutin exhibits an IT band at 1020 nm.[23] Henderson and Shepherd offered one explanation for the loss of the IT transition in **1** or related systems, namely, that substantial Ru(II) d orbital–cyanide ion π^* orbital mixing competes with the π delocalization across the pyrazine ring and alters the metal orbital density in the direction of the $Ru^{III}(NH_3)_5$ site.[1] This phenomenon will reduce the probability of the IT transition through a lowered interaction energy.[16]

Complexes of the series $[(CN)_5Ru^{II}LRu^{III}(NH_3)_5]$, in which the L group promotes greater coupling than pyrazine, might restore the IT band. Dicyanogen, which promotes nearly complete delocalization in the $[(NH_3)_5Ru)_2L^{5+}]$ series, is a logical candidate for consideration in increasing the interaction energy between $(CN)_5Ru^{II}$ and $(NH_3)_5Ru^{III}$ sites. Cyanide ion, which can successfully compete with the other cyanides of $(CN)_5Ru^{II}$, is another logical choice. The CN^- bridged complex $[(CN)_5Ru(CN)Ru(NH_3)_5^-]$ has been prepared previously by thermal and photochemical paths.[24] However the $Ru^{II}Ru^{II}$ derivative has not been reported. Studies of the unsymmetrical $[(CN)_5RuLRu(NH_3)_5]^{n-}$ series in the $Ru^{II}Ru^{II}$ and $Ru^{II}Ru^{III}$ oxidation state levels with L = C_2N_2, CN^-, and 4,4′-bipyridine have been conducted in our laboratories and are reported here.

Experimental Section

$(NH_3)_5RuL^{2+}$ complexes (L = 4,4′-bpy and cyanogen) were prepared under Ar from $(NH_3)_5RuOH_2^{2+}$ and appropriate ligand. These com-

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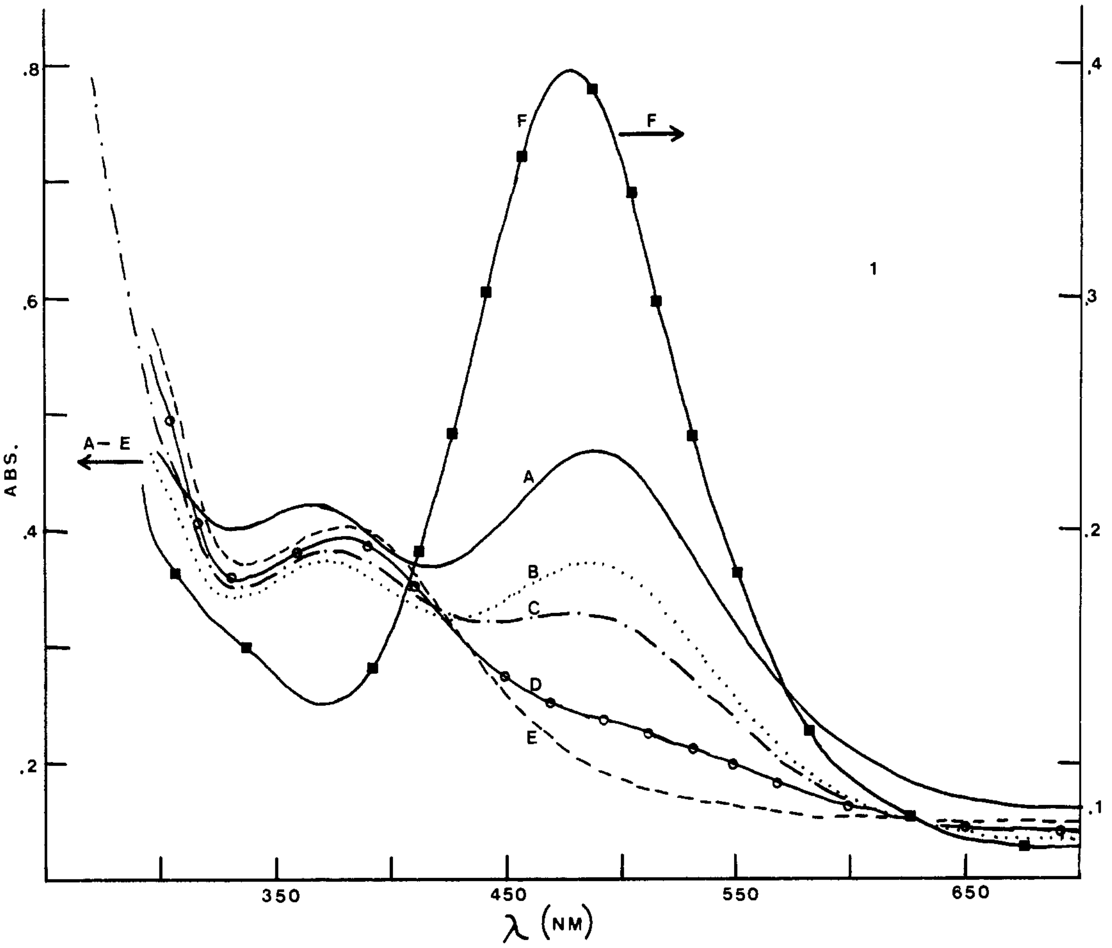

Figure 1. $S_2O_8^{2-}$ titration of $(CN)_5Ru(4,4'\text{-bpy})Ru(NH_3)_5^-$: (A) [(II,bpy,II)] = 1.0×10^{-5} M; (B) 0.10 equiv of $S_2O_8^{2-}$ added, (C) 0.20 equiv of $S_2O_8^{2-}$ added; (D) 0.50 equiv of $S_2O_8^{2-}$ added; (E) excess $S_2O_8^{2-}$; (F) $[(NH_3)_5Ru(4,4'\text{-bpy})^{2+}] = 1.0 \times 10^{-5}$ M. Conditions: 5.00-cm cells; T = 22 °C.

plexes were isolated as PF_6^- salts. $[(NH_3)_5Ru(4,4'\text{-bpy})][PF_6]_2$ and $[(NH_3)_5Ru(NCCN)][PF_6]_2$ salts were reasonably stable but decomposed slowly by light and air (~7 days). For this reason these complexes were freshly prepared for use. The isolated monomer solids were characterized by IR in KBr pellets. Dissolved samples of the solids were used in taking the UV–visible spectra.

A $(CN)_5RuOH_2^{3-}$ solution, prepared by the $Br_2/Ru(CN)_6^{4-}$ reaction as reported by Johnson and Shepherd,[23] was generated for immediate use in each procedure; the concentration was kept $<2.0 \times 10^{-4}$ M, to avoid complications from formation of cyanide-bridged binuclear cyanoruthenates.

In the case of the synthetically desired cyanide-bridged complex equimolar concentrations of $(NH_3)_5RuOH_2^{2+}$ and $Ru(CN)_6^{4-}$ solutions were mixed under Ar and spectra representative of $A_5Ru^{III}CNRu^{II}(CN)_5^-$ were obtained (A = NH_3). The dimer $A_5Ru^{II}CNRu^{II}(CN)_5^{2-}$ was hard to isolate as it is extremely air sensitive. A blue color developed from O_2 leaks in any syringe manipulation. Therefore solution transfers were carried out by using a Zwickel flask with spectrophotometric cells attached by means of a lightly greased ball joint and stopcock assembly. In this manner the cell could be purged with Ar gas and the desired solution could be transferred by application of Ar gas pressure. The cells were flushed with several volumes of solution before the stopcock assembly was placed in the Varian-Cary 118C spectrophotometer in order to record spectra with time. Even with these precautions, O_2 diffusion could be observed in the upper part of the stopcock assembly as a blue color change in the solution. Sometimes even this cell filling procedure was plagued by O_2 leaks. Under these conditions a blue precipitate of $K[(CN)_5RuCNRu(NH_3)_5]$ or $[(CN)_5RupzRu(NH_3)_5]$ was detected. A reasonable (II,II) spectrum was obtained under Ar with added Eu^{2+} as a reducing agent. However this system also changed to the (III,II) complex within several minutes.

Solids of binuclear complexes $[A_5Ru(4,4'\text{-bpy})Ru(CN)_5]^{-/0}$, $[A_5Ru(C_2N_2)Ru(CN)_5]^{-/0}$, and $[A_5RuCNRu(CN)_5]^0$ were isolated, and IR spectra were taken in KBr. The solids of the binuclear complexes were dissolved in D_2O to make saturated solutions and then near-IR spectra were taken with solvent correction.

Reagents. $(NH_3)_6RuCl_3$, 4,4'-bipyridine (4,4'-bpy), 2-methylpyrazine, $K_2S_2O_8$ (oxidizing agent), and $Na_2S_2O_4$ (reducing agent) were obtained from Aldrich. $K_4[Ru(CN)_6]$ was purchased from Alfa Inorganics; it was used without further purification. Cyanogen gas was purchased from Matheson and Br_2 from Baker.

Instrumentation. Spectra in the UV–visible region were obtained on a Varian-Cary 118C spectrophotometer using quartz cells. Spectra in the near-IR region were obtained on a Perkin-Elmer 330 spectrophotometer at Carnegie Mellon University, Pittsburgh, PA. The electrochemical studies were obtained on an IBM 225 electrochemical analyzer unit. Measurements for differential-pulse polarography were recorded at a glassy-carbon working electrode vs. a NaCl-replaced SCE standard; NaCl is used to avoid precipitation problems. A Pt wire served as the auxilliary electrode of the three-electrode assembly. The solution was purged with Ar inside a glass cell. The ionic strength was maintained with NaCl at the desired level. System response was calibrated with known lab standards such as $[Ru(NH_3)_6]Cl_3$ and the $[(CN)_5Ru(pz)Ru(NH_3)_5]^{0/-}$ system.[1]

Results

Formation of Binuclear Ions with 4,4'-Bpy or Cyanogen. When $(NH_3)_5Ru(4,4'\text{-bpy})^{2+}$ (λ_{max} = 482 nm)[25] and $(CN)_5RuOH_2^{3-}$ (λ_{max} = 315 nm)[26] are mixed in a 1:1 ratio, a new ion with maxima at 490 nm ($\epsilon = 7.44 \times 10^3$ M^{-1} cm^{-1}) and 365 nm ($\epsilon = 6.40 \times 10^3$ M^{-1} cm^{-1}) forms (Figure 1). If the concentration exceeds 8.33×10^{-5} M a purple-black solid precipitates as a K^+ salt. The monomer species were prepared separately as described in the Experimental Section and characterized by spectral matches to literature values.[25,26] On the basis of the previous chemistry in which $(NH_3)_5Ru(pz)^{2+}$ readily substitutes on $(CN)_5RuOH_2^{3-}$, the new ion is assigned as the (II,bpy,II) ion with 4,4'-bipyridine bridging the $(CN)_5Ru^{3-}$ and $(NH_3)_5Ru^{2+}$ sites. Additional support for this assignment is readily observed by the reaction of (II,bpy,II) with 0.5 molar equiv of $S_2O_8^{2-}$ or Br_2. A new complex with λ_{max} at 380 nm ($\epsilon = 6.0 \times 10^3$ M^{-1} cm^{-1}) grows in as the 500-nm region

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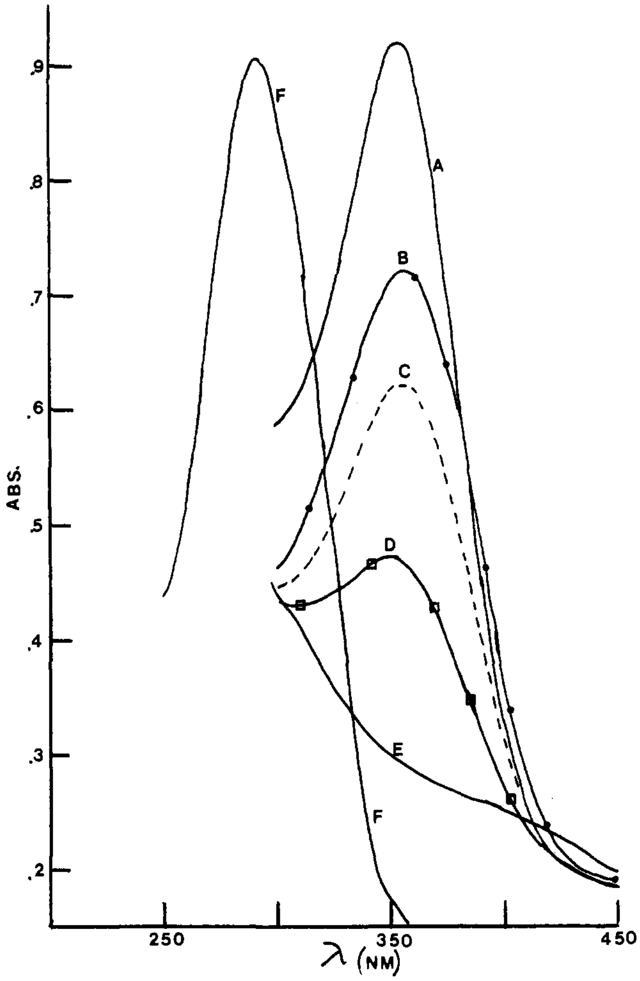


Figure 2. Br_2 titration of $(CN)_5Ru(NCCN)Ru(NH_3)_5^-$: (A) [(II,NCCN,II)] = 5.0 × 10^{-5} M; (B) 0.10 equiv of Br_2 added; (C) 0.50 equiv of Br_2 added; (D) 1.0 equiv of Br_2 added; (E) excess Br_2 added; (F) $[(NH_3)_5Ru(NCCN)^{2+}]$ = 5.0 × 10^{-5} M. Curve F has the zero suppressed by 0.10 absorbance unit for comparison on scale.

bleaches (Figure 1). The −1 charge of (II,bpy,II) is made neutral with oxidation of the $(NH_3)_5Ru^{2+}$ site to $(NH_3)_5Ru^{3+}$. A precipitate of the oxidation product (III,bpy,II) is isolated. The infrared spectra exhibit a number of diagnostic bands: for (II,bpy,II) ν_{CN} = 2055 cm^{-1} (strong) and a shoulder feature at 1995 cm^{-1}; (III,bpy,II) exhibits a broad, unsplit ν_{CN} at 2060 cm^{-1}. For comparison, ν_{CN} of $K_4Ru^{II}(CN)_6$ appears at 2045 cm^{-1}. The remaining bands indicative of the 4,4′-bpy moiety are assigned in Table I. The oxidation states at the $(NH_3)_5Ru$ sites are observed to be II in the primary product and III in the secondary, oxidized product as shown by the symmetric ammonia deformation frequencies at 1290 and 1305 cm^{-1}, respectively. Pentaammineruthenium(II) moieties exhibit the symmetric ammonia deformation in the range 1260–1290 cm^{-1}, while the Ru(III) counterparts exhibit this stretch between 1330 and 1360 cm^{-1}.[1,10]

$(NH_3)_5Ru(NCCN)^{2+}$ was prepared as the PF_6^- salt following a modified method of Taube et al.[20] $(NH_3)_5RuOH_2^{2+}$, formed by the Zn/Hg reduction of $[(NH_3)_5RuCl]Cl_2$, was transferred by gastight syringe techniques into a NCCN-saturated aqueous solution. A dark blue-violet solution was formed in 20 min. Addition of saturated NH_4PF_6 produced $[(NH_3)_5Ru(NCCN)](PF_6)_2$, which was isolated for the combination reaction with $(CN)_5RuOH_2^{3-}$. The isolated $[(NH_3)_5Ru(NCCN)](PF_6)_2$ solid gave two well-separated ν_{CN} stretches at 2092 ± 20 (sharp) and 2230 ± 20 cm^{-1} (broad). The ν_{CN} of free NCCN is 2200 cm^{-1}. The shift of the 2092-cm^{-1} band to lower frequency is indicative of π donation of Ru(II) into the adjacent $-C{\equiv}N$ functionality, leading to a reduced bond order to lower ν_{CN}. The result is the same as the well-known influence of low-valent metals on coordinated carbonyls.

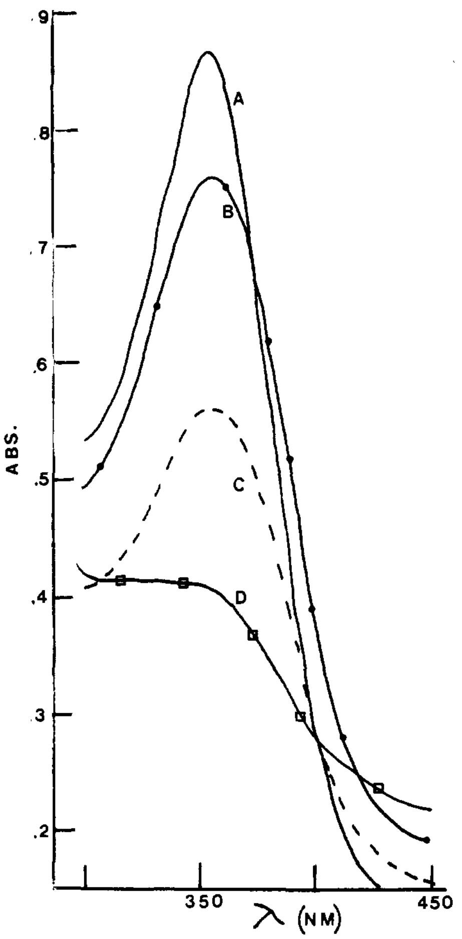


Figure 3. $S_2O_8^{2-}$ titration of $(CN)_5Ru(NCCN)Ru(NH_3)_5^-$: (A) [(II,NCCN,II)] = 5.0 × 10^{-5} M; (B) 0.10 equiv of $S_2O_8^{2-}$ added; (C) 1.0 equiv of $S_2O_8^{2-}$ added, spectrum obtained shortly after mixing (Note: compare curve D with Br_2 as oxidant; rate of Br_2 oxidation is greater than that of $S_2O_8^{2-}$; (D) excess $S_2O_8^{2-}$, spectrum at 12 h.

Combination for $(NH_3)_5Ru(NCCN)^{2+}$ with $(CN)_5RuOH_2^{3-}$ yielded $(CN)_5Ru^{II}(NCCN)Ru(NH_3)_5^-$, analogous to the pz and 4,4′-bpy-bridged complexes. This species exhibits a new UV band at 352 nm (ϵ = 1.24 × 10^4 M^{-1} cm^{-1}) (Figure 2). As with the 4,4′-bpy- and pz-bridged cases, a K^+ salt can be isolated, $K[(CN)_5Ru(NCCN)Ru(NH_3)_5]$, which shows infrared stretched at 2052 ± 2 and 2150 ± 50 cm^{-1}. The 2052-cm^{-1} band overlaps the stretches of the CN^- ligands (cf. 2055 cm^{-1} for the (II,bpy,II) case). Both bands are lowered in frequency for the NCCN ligand by about 80 cm^{-1} for the 2150-cm^{-1} band and ~40 cm^{-1} relative to that of the monomeric $[(NH_3)_5Ru(NCCN)](PF_6)_2$ complex. The influence of additional π delocalization due to the presence of two Ru(II) centers is implied. Other frequencies for (II,NCCN,II) are given in Table I, along with those of its oxidation products, (III,NCCN,II). As with the pz- and 4,4′-bpy-bridged complexes, addition of $S_2O_8^{2-}$ or Br_2 causes oxidation to (III,NCCN,II) with λ_{max} < 300 nm (Figures 2 and 3); however, the rate of the oxidation is very slow by comparison. The synthetic pathways for formation of 4,4′-bpy- and NCCN-bridged species and the oxidation of them to their (III,L,II) mixed-valence ions are summarized in eq 1 and 2, L = 4,4′-bpy, NCCN, or pz.

$$(NH_3)_5RuL^{2+} + (CN)_5RuOH_2^{3-} \rightleftharpoons \underset{\text{(II,L,II)}}{(NH_3)_5Ru^{II}LRu^{II}(CN)_5^-} \qquad (1)$$

$$\text{(II,L,II)} \xrightarrow{^1/_2S_2O_8 \text{ or } ^1/_2Br_2} \underset{\text{(III,L,II)}}{(NH_3)_5Ru^{III}LRu^{II}(CN)_5} \qquad (2)$$

No absorbance suggesting an intervalence transition (IT) was observed in the near-IR region out to 2500 nm for either (III,bpy,II) or (III,NCCN,II); the result is the same as for **1** = (III,pz,II). The solvent for these studies was the required D_2O.

Table I. IR Stretching Frequencies (cm^{-1}) Obtained for Bridged Complexes

$(NH_3)_5Ru(C_2N_2)Ru(CN)_5^-$	$(NH_3)_5Ru(C_2N_2)Ru(CN)_5^0$	$(NH_3)_5RuNCRu(CN)_5^0$	assignmt
3430, 3320, 3180 br	3430, 3250, 3160	3480, 3300 br	ν_{H_2O}
2210 s st	2210 s w		$\nu_{cyanogen}$
		2060 br st	ν_{CN}(bridging terminal)
2150, 2052	2030, 1980 w		$\nu_{C_2N_2} + \nu_{CN}$
1620	1605	1620	$\delta(deg)_{NH_3}$
1295	1305	1320	$\delta(sym)_{NH_3}$
780	785	810	ρ_{NH_3}

$(NH_3)_5Ru$-(4,4′-bpy)$Ru(CN)_5^-$	$(NH_3)_5Ru$-(4,4′-bpy)$Ru(CN)_5^0$	$(NH_3)_5Ru$-(pz)$Ru(CN)_5^{-a}$	$(NH_3)_5Ru$-(pz)$Ru(CN)_5^{0a}$	assignmt
3300 br	3250	3450, 3310, 3230	3480, 3250	ν_{H_2O}
2055, 1995 s, st	2050	2055 vs	2065, 2050 sh	ν_{CN}
1605 s	1620, 1535	1638, 1620	1650, 1632	$\delta(deg)_{NH_3}$
1490, 1472	1490, 1415	1465, 1430	1418	py, pz ring str
1290	1305	1302	1320	$\delta(sym)_{NH_3}$
1220 m	1220 m	1225 m	1227 w	py, pz δ_{CH} in-plane
1070, 1050	1070, 1050	1075, 1032	1075, 1032	py, pz ring str
820	820	820	820	py, pz τ_{CH} out-of-plane

[a] From ref 1.

Cyanide-Bridged Binuclear Ions. The CN^--bridged analogue of (III,L,II), L = 4,4′-bpy or NCCN, was readily prepared by several routes. The photochemical pathways have been described by Vogler.[24] The simplest procedure involves the thermal reaction at 60 °C in eq 3. A dark blue solution (λ_{max} = 675 nm) forms.

$$(NH_3)_5RuCl^{2+} + Ru(CN)_6^{4-} \xrightarrow[H_2O]{\Delta} (NH_3)_5RuNCRu(CN)_5^- + Cl^- \quad (3)$$

The band is broad, from 500 nm to greater than 800 nm. The K^+ salt of (III,CN^-,II) readily will precipitate. The solid can be used to prepare saturated solutions.

Reaction 3 is much slower at room temperature. However, $(NH_3)_5RuOH_2^{2+}$ readily reacts with $Ru(CN)_6^{4-}$; autoxidation forms (III,CN^-,II). In a separate experiment it was shown that $(NH_3)_5RuOH_2^{3+}$, which is prepared by oxidation of $(NH_3)_5RuOH_2^{2+}$ by O_2, also rapidly adds $Ru(CN)_6^{4-}$ in 10 s. Normally Ru(III) is substitution inert, reactions requiring hours to days. A significant rate enhancement occurs through the ion pair that forms between the 3+ and 4− reactants (eq 4 and 5).

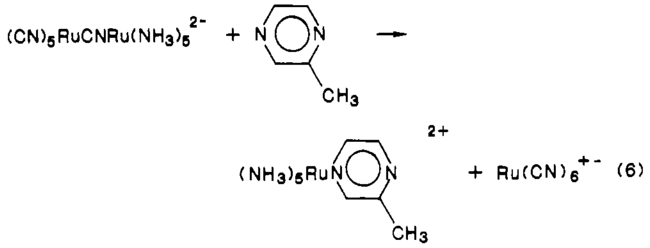
$$(NH_3)_5RuOH_2^{3+} + Ru(CN)_6^{4-} \underset{}{\overset{K_{IP}}{\rightleftharpoons}} \{(NH_3)_5RuOH_2^{3+},Ru(CN)_6^{4-}\} \quad (4)$$

$$\{(NH_3)_5RuOH_2^{3+},Ru(CN)_6^{4-}\} \xrightarrow[22\ ^\circ C]{k \sim 0.7\ s^{-1}} (NH_3)_5RuNCRu(CN)_5^- + H_2O \quad (5)$$

The infrared data for the product species appear in Table I. The ν_{CN} is broadened in the binuclear ion compared to that for $Ru(CN)_6^{4-}$, but the bridging CN^- is not resolved from the terminal CN^- frequencies.

Preparation of the (II,CN^-,II) complex proved to be more difficult. In principle, this complex was easily prepared by mixing 1:1 molar amounts at ca. 5 × 10^{-5} M of the $(NH_3)_5RuOH_2^{2+}$ and $Ru(CN)_6^{4-}$ stock solutions under Ar. The resulting solutions were exceedingly air sensitive (see Experimental Section). A suitable spectrum was obtained with the presence of a sacrificial reducing agent, $Eu(H_2O)_6^{2+}$. The $Eu(H_2O)_6^{2+}$ was introduced by the simultaneous reduction of $(NH_3)_5RuCl^{2+}$ and $EuCl_3$ over Zn/Hg. The (II,CN^-,II) species also exhibits a broad, very weak transition centered at 625 nm. The maximum shifts to 474 nm after 20 h. NH_3 is known to be displaced by CN^-, forming bridges in the related $(NH_3)_5Ru(py)^{2+}/Ru(CN)_6^{4-}$ system.[27] We assume the slow process, yielding the species absorbing at 474 nm, gives a similar CN^--bridged polymer. The initial solution absorbs at 612 nm, but the spectrum shifts rather rapidly to 625 nm. When $Ru(NH_3)_6^{2+}$ is mixed with $Ru(CN)_6^{4-}$, a weak transition is determined at 625 nm for the spectrum of the $[(NH_3)_6Ru^{2+},Ru(CN)_6^{4-}]$ ion pair. Therefore we conclude that the initial spectrum is a mixture of the $[(NH_3)_5RuOH_2^{2+},Ru(CN)_6^{4-}]$ ion pair and the bridged (II,CN^-,II) species. If the approach of $Ru(CN)_6^{4-}$ is on the side opposite the aqua ligand, a certain fraction may be tightly bound as the outer-sphere ion pair. Rearrangement, equivalent to an isomerism process, will place a cyanide group close enough to displace the aqua ligand. The improved coupling between Ru sites in the bridged (II,CN^-,II) ion causes a shift to modestly lower energy for this transition. The very low extinction coefficient (ϵ ~62) suggests the process is not a strongly allowed one. We assign it to a $\pi_{CN}^* \leftarrow d_\pi(Ru^{II}(NH_3)_5)$ transition. We also note that no band in the same region is observed for the ion pair formed between $Ru(NH_3)_6^{3+}$ and $Ru(CN)_6^{4-}$.

Dissociation of $(CN)_5RuCNRu(NH_3)_5^{2-}$. A number of studies were carried out concerning the rate of addition of 2-methylpyrazine ($2CH_3pz$) as a scavenger for $(NH_3)_5RuOH_2^{2+}$, eq 6, in



order to show that the (II,CN^-,II) binuclear ion was indeed bridged, and not simply an ion pair, $\{(NH_3)_5RuOH_2^{2+},Ru(CN)_6^{4-}\}$. The (II,$CN^-$,II) complex was prepared at 4.14 × 10^{-4} M by combining the 1:1 mononuclear reactants in a Zwickel flask under Ar. Ten minutes was allowed for formation of (II,CN^-,II), and an aliquot was taken for spectral study. The remaining solution was mixed with an Ar-purged solution containing $2CH_3pz$, and the slow formation of $(NH_3)_5Ru(2CH_3pz)^{2+}$ was followed by means of repetitive scans every 45 min from 750 to 350 nm over a 20-h period. The kinetics of the $(NH_3)_5Ru(2CH_3pz)^{2+}$ appearance was plotted by using the Guggenheim method since the calculated A_∞ value was higher than the spectrophotometer could accurately measure. A lower amount of (II,CN^-,II), which would seem to be an alternative way to reduce A_∞, was not feasible as this required too little initial mononuclear reagents to assure accurate delivery of a 1:1 stoichiometry by syringe methods. The added problem of equilibrium dissociation at very low levels of (II,CN^-,II) was another hazard of that approach. Therefore the Guggenheim procedure was imposed by reaction conditions. In the original set of experiments there was no Eu^{2+} present as a scavenger for O_2; the system was monitored in glass-closed cells (see Experimental Section). In a successful experiment, the 1.00-cm cell showed evidence of the trace O_2 diffusion in the stopcock assembly without contamination of the main cell contents.

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(27) Curtis, J. C.; Meyer, T. J. *Inorg. Chem.* **1982**, *21*, 1562. Shepherd, R. E.; Taube, H. *Inorg. Chem.* **1973**, *12*, 1392.

In a spoiled experiment, the cell would exhibit precipitation of K[(III,CN,II)] or an ion pair of $[(NH_3)_5Ru(2CH_3pz)]_2(Ru(CN)_6]$. The latter solid was isolated and characterized by matching its infrared spectrum to the sum of $[(NH_3)_5Ru(2CH_3pz)]Br_2$ and $K_4Ru(CN)_6$ salts. A sufficient number of successful kinetic runs were obtained to show that the rate of appearance of $(NH_3)_5Ru(2CH_3pz)^{2+}$ was independent of the initial $[2CH_3pz]$ in the range 1.21×10^{-3} to 1.24×10^{-2} M with $k = (6.7 \pm 1.0) \times 10^{-6}$ s^{-1}. By the law of microscopic reversibility, if the cyanide-bridged complex (II,CN$^-$,II) is made through the insertion of the CN$^-$ bridge ligand in place of H_2O in the ion pair, $\{(NH_3)_5RuOH_2{}^{2+},Ru(CN)_6{}^{4-}\}$, then the reverse process (eq 7) must

$$(NH_3)_5RuNCRu(CN)_5{}^{2-} \underset{}{\overset{k_d}{\rightleftarrows}} \{(NH_3)_5RuOH_2{}^{2+},Ru(CN)_6{}^{4-}\} \tag{7}$$

$$\{(NH_3)_5RuOH_2{}^{2+},Ru(CN)_6{}^{4-}\} \overset{1/K'_{IP}}{\rightleftarrows} (NH_3)_5RuOH_2{}^{2+} + Ru(CN)_6{}^{4-} \tag{8}$$

$$(NH_3)_5RuOH_2{}^{2+} + 2CH_3pz \rightleftarrows (NH_3)_5Ru(2CH_3pz)^{2+} \tag{9}$$

involve rupture of the $(NH_3)_5Ru^{II}\cdots NC$ bond to re-form the ion pair. This conclusion can be drawn because the rate constant for the process in eq 9. is 0.068 M^{-1} s^{-1}.[28] At 1.24×10^{-2} M $2CH_3pz$, a pseudo-first-order rate of 8.43×10^{-4} s^{-1} is predicted, which is 2 orders of magnitude faster than the process studied by the Guggeheim method. Therefore the forward rate of reaction 9 cannot be rate limiting. Furthermore, the process cannot be limited by the rate of dissociation of the ion pair in eq 8. Ion pairs of the general formula $[(NH_3)_5RuL^{3+},Ru(CN)_6{}^{4-}]$ have outer-sphere association constants, K_{IP}, of 3×10^3.[27] Therefore the outer-sphere association for $[(NH_3)_5RuOH_2{}^{2+},Ru(CN)_6{}^{4-}]$ must be about four-ninths as great, ca. $\sim 1 \times 10^3$. The rate of dissociation of step 8 must have a value of $\sim 1 \times 10^7$ s^{-1}, assuming a diffusion-controlled reverse reaction. Therefore the slow rate found in the $2CH_3pz$ scavenging experiment measures the bond rupture in reaction 7. The precision of this measurement was not high because of complications introduced by O_2 leakage. If O_2 diffusion competes to scavenge $(NH_3)_5RuOH_2{}^{2+}$, forming $(NH_3)_5RuOH_2{}^{3+}$, the increase in absorbance is attenuated and the rate constant would appear to be lower than the true value. An attempt to overcome the O_2 side reaction uncertainty was made by using Eu^{2+} as a reagent to restore the $(NH_3)_5RuOH_2{}^{2+}$ for full complexation by $2CH_3pz$. Unfortunately this procedure did not work because the bright-red salt $[Eu(H_2O)_6,(NH_3)_5Ru(2CH_3pz),Ru(CN)_6]$ precipitated from the reaction medium in the cell.

It is concluded that the (II,II) ion with $Ru(NH_3)_5OH_2{}^{2+}$ added to $Ru(CN)_6{}^{4-}$ is cyanide bridged. Perhaps the best evidence is that the Ru(III) derivative formed from $(NH_3)_5RuOH_2{}^{3+}$ is produced so rapidly within the ion pair ($k \sim 1 \times 10^{-3}$ s^{-1}). Since Ru(II) substitutions are generally much more rapid than Ru(III), the equilibrium constant for reaction 7 must be less than 1×10^{-2}, favoring the CN$^-$-bridged form.

Lability of the $(CN)_5Ru(NCCN)^{3-}$ Complex. The rate of substitution of $2CH_3pz$ on $(CN)_5RuOH_2{}^{3-}$ was measured at 1.50 $\times 10^{-3}$ M $2CH_3pz$ under pseudo-first-order reaction conditions by injecting $(CN)_5RuOH_2{}^{3-}$ into an Ar-purged $2CH_3pz$ solution. A 1.00-cm cell sealed by a rubber septum was filled, and the rate was monitored at 365 nm. A first-order rate was observed from which a substitution rate constant at 22 °C of 12.4 M^{-1} s^{-1} was determined. A literature comparison value has been measured by Macartney et al. for pyrazine with $(CN)_5RuOH_2{}^{3-}$, $k = 10.9$ M^{-1} s^{-1};[29] the two values are in reasonable agreement to justify the accuracy of our value for $2CH_3pz$. The substitution of NCCN was followed at 315 nm at [NCCN] = 3.0×10^{-3}M, 30-fold in excess of the $(CN)_5RuOH_2{}^{3-}$ complex. A second-order rate constant for formation of $(CN)_5Ru(NCCN)^{3-}$ was determined as 15.2 M^{-1} s^{-1}.

$(CN)_5Ru(NCCN)^{2+}$ was prepared in a cyanogen-saturated (~0.20 M) solution of NCCN by injection of 1.0×10^{-4} M $(CN)_5RuOH_2{}^{3-}$. After 30 min to allow for complexation by NCCN, an aliquot was taken and mixed with 1.0×10^{-3} M $2CH_3pz$. The reaction progress was also followed at 365 nm. The rate of appearance was nearly a factor of 10 slower than when NCCN was not present. Ligand exchange with X as the entering ligand and $Ru(CN)_5L^{3-}$ obeys eq 10.[30] In our study L = C_2N_2,

$$k_{obsd} = \frac{k_{-L}k_X[X] + k_{-X}k_L[L]}{k_L[L] + k_X[X]} \tag{10}$$

X = $2CH_3pz$, [X] = 5.0×10^{-4} to 1.00×10^{-3}, and [L] = 0.20 M. With the use of our measured value for $k_{C_2N_2} \cong 15$ M^{-1} s^{-1}, which is also the highest substitution rate for a neutral entering ligand in Macartney's studies of the substitution and dissociation kinetics of N-heterocyclic bases with $(CN)_5RuOH_2{}^{3-}$,[29,30] and with the assumption that k_d for $2CH_3pz \cong k_d$ for pz (1.77×10^{-5} s^{-1}), the data gave a fit for k_d of NCCN (k_{-L}) of 0.026 ± 0.003 s^{-1}. This value is 10^3 more rapid than the dissociation rates that were observed for the N-heterocycles.[30] Since the mechanism of ligand exchange for $(CN)_5RuL^{3-}$ is of the I_d type, it is logical that the much better σ bases of the N-heterocyclic ligands would suffer bond breaking less readily than the nitrile donor group of NCCN toward $(CN)_5RuOH_2{}^{3-}$. However, the nitrile functionality is potentially a better π acceptor than a pyridine ring; the π-bonding component could be stronger for NCCN relative to a pyridine ligand. The difference in σ basicity of NCCN vs. pyridine is ca. 10 p*K* units, which should translate into a 10^{10} more rapid rate if σ-only bonding were important. The otherwise unaccounted 10^7 difference in rate influence, which is found in the experimental results, shows significant π donation from $(CN)_5Ru^{3-}$ into NCCN. From a rate of forward and reverse rates the association constant of NCCN for $Ru(CN)_5{}^{3-}$ is 585 ± 70 M^{-1}.

The formation constants of $(CN)_5RuL^{3-}$ complexes are reported to be 5.9×10^5 M^{-1} (pz), 4.8×10^4 M^{-1} (imH), 7.5×10^5 M^{-1} (N-CH_3pz^+), and 15×10^5 M^{-1} (dmso).[30] This compares to our value of 585 M^{-1} for NCCN. One can conclude that the σ-only contribution to the binding of the very poor π-acceptor imidazole is nearly the entire additional free energy released on complexation;[28] ΔG_f is -6.4 kcal/mol. Similarly the complexation of NCCN, which is a poorer σ base by at least 17 orders of magnitude, is predominantly due to the π back-donation of -3.8 kcal/mol for NCCN from $(CN)_5Ru^{3-}$. One anticipates significantly less back-bonding in $(CN)_5Ru(pz)^{3-}$ than $(NH_3)_5Ru(pz)^{2+}$ to the pz ring; the value of the π back-bond in $(NH_3)_5Ru(pz)^{2+}$ was estimated as -13.6 kcal/mol by Wishart, Taube, Breslaw, and Isied.[31] The data of Johnson and Shepherd[26] suggest that in $(CN)_5Ru(pz)^{3-}$ the delocalization is about 40% of the value for $(NH_3)_5Ru(pz)^{2+}$, e.g. -5.4 kcal/mol. This is not far off the entire -7.9 kcal/mol for ΔG_f of the $(CN)_5Ru(pz)^{3-}$ complex (Macartney's data[30]). The σ component for L = pz is thus ca. 40% of the amount for the stronger σ base, L = imH. The ΔG_π value for $(NH_3)_5RuNCCH_3{}^{2+}$ is -8.8 kcal/mol.[31] Correcting for 40% poorer π interaction in $(CN)_5Ru(NCCH_3)^{3-}$ would give a predicted estimate of about -3.5 kcal/mol for the π back-bond in $(CN)_5Ru(NCCH_3)^{3-}$. This is surprisingly close to the estimate we have made here for the π back-donation to cyanogen (-3.8 kcal/mol), assuming the σ donation is small for this poor σ base.

Electrochemistry of Mononuclear and Binuclear Complexes. Differential-pulse polarography was performed at a glassy-carbon surface as described in the Experimental Section. The measured $E°$ values for the various species described in this work are given in Table II. The monomeric complexes of $(CN)_5Ru^{II}L^{n-}$, L = 4,4′-bpy, NCCN, and CN$^-$, have been examined as a function of pH. The protonation of the 4,4′-bpy, NCCN, and CN$^-$ ligands in competition with protonation of the remaining $(CN)_5Ru^{II}$ moiety has been studied in detail for L = 4,4′-bpy and CN$^-$. Protonation of the potential bridging L ligand causes the well-

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Table II. Differential Pulse Polarographic Data[a]

Ru^{II} complex	waves vs. NHE, V 1	waves vs. NHE, V 2
Monomeric Complexes		
$(NH_3)_5Ru(4,4'\text{-bpy})^{2+}$	0.331, 0.34,[b] 0.33[c]	
$(NH_3)_5Ru(NCCN)^{2+}$	0.898	
$(NH_3)_5Ru(pz)^{2+}$	0.52[d]	
$Ru(NH_3)_6{}^{2+}$	0.066[d]	
$(CN)_5RuOH_2{}^{3-}$		0.870[e]
$(CN)_5Ru(pz)^{3-}$		0.957[f]
$(CN)_5Ru(4,4'\text{-bpy})^{3-}$		0.652 (pH 11)
$(CN)_5Ru(4,4'\text{-bpyH})^{2-}$		0.707 (pH 6.1)
$(HCN)(CN)_4Ru(4,4'\text{-bpyH})^-$		0.672 (pH 2.8)
$(HCN)_3(CN)_2Ru(4,4'\text{-bpyH})^+$		0.612 (pH 2.0)
$(CN)_5Ru(NCCN)^{3-}$		1.03
$Ru(CN)_6{}^{4-}$		0.902 (pH 7.0)
$Ru(CN)_5(HCN)^{3-}$		1.07 (pH 3.5)
$Ru(CN)_4(HCN)_2{}^{2-}$		1.15 (pH 2.5)
$Ru(CN)_3(HCN)_3{}^-$		1.27 (pH 1.5)
Binuclear Complexes		
$(CN)_5Ru(4,4'\text{-bpy})Ru(NH_3)_5{}^-$	0.296	0.926
$(CN)_5Ru(NCCN)Ru(NH_3)_5{}^-$	−0.06	0.881
$(CN)_5Ru(pz)Ru(NH_3)_5{}^-$	0.529[f]	0.972[f]
$(CN)_5Ru(CN)Ru(NH_3)_5{}^{2-}$	−0.075 −0.060[g]	0.902 0.962[g]
$(NH_3)_5Ru(NCCN)Ru(NH_3)_5{}^{4+}$	0.046[h]	0.869[h]

[a] μ = 0.10 (NaCl), T = 22 °C, SCE reference, glassy-carbon working electrode. [b] Phillips, J.; Haim, A. *Inorg. Chem.* **1980**, *19*, 76. [c] Reference 13. [d] Lim, H. S.; Barclay, D. J.; Anson, F. *Inorg. Chem.* **1972**, *11*, 1460. [e] $(CN)_5Ru^{II}L$ complexes are listed as the second wave in the monomeric complexes to assist comparison with the second wave in the binuclear complexes. [f] Reference 1. [g] μ = 1.00 (NaCl). [h] Reference 19.

known shift of the reduction potential to more positive values: e.g. 0.652–0.707 V for 4,4′-bpy and 0.902–1.07 V for CN^-. Additional protonation of the remaining pentacyanoruthenate(II) fragment causes a steady increase in potential in the $Ru^{II}(CN)_n(HCN)_{6-n}$ series. Multiple waves attributable to mixtures of these ions were seen to grow in and shift with lower pH toward an increasingly more positive potential, culminating with $Ru(CN)_3(HCN)_3{}^{2-}$ at 1.27 V at the lowest pH of 1.50 in our study. The widths of the differential pulse waves are ca. 95 mV for the $Ru(CN)_n(HCN)_{6-n}$ series.

The situation for $(CN)_5Ru(4,4'\text{-bpy})^{3-}$ is similar for comparing the unprotonated to protonated terminal 4,4′-bpy ring position (shift to 0.707 V as above). However, additional protonation of three cyanides is seen to cause a reversal of the wave to less positive potentials. The reason for this shift is not obvious. However the widths of the differential pulse peaks (140–220 mV) implicate a significant kinetic overpotential component to the observed $E°$ value for the $(CN)_5Ru(4,4'\text{-bpy})^{3-}$system as a function of pH. Therefore kinetic factors at the electrode control the apparent $E°$ order, not thermodynamics.

These complications that have been observed for the monomeric complexes at low pH are less of a concern in the binuclear $(CN)_5Ru(L)Ru(NH_3)_5$ series because the bridging ligand position is blocked from protonation. The potentials were examined in the neutral pH domain where the $(CN)_5Ru^{II}$ moiety should remain unprotonated, based on the results with the monomeric species.

It has been noted previously for L-bridged $Ru^{II}Ru^{II}$ and $Fe^{II}Ru^{II}$ complexes of the sort described in these studies that the first wave of the binuclear complex is cathodically shifted due to the electron-donating influence of the second ruthenium(II) center.[9,13,27] The second wave appears as an anodically shifted wave due to the electron-withdrawing influence of the second ruthenium(III) center in the mixed oxidation species. References 9, 13, and 27 may be consulted for further discussion of these influences. On the basis of the infrared and UV–visible spectral evidences described earlier, it is assumed in the following discussion that the $(NH_3)_5Ru^{II}$ site is oxidized in the first step and $(CN)_5Ru^{II}$ is oxidized in the second step for the binuclear complexes examined in this work. In the bridged complex (II,bpy,II) both of these influences, cathodic shift relative to the $(NH_3)_5Ru(4,4'\text{-bpy})^{2+}$ monomer and anodic shift relative to the $(CN)_5Ru(4,4'\text{-bpy})^{3-}$ monomer, are seen in Table II. The case with NCCN as the bridging ligand is less easy to interpret. The binuclear complex is significantly less charged, 1− overall, compared with 2+ and 3− for its monomeric equivalents. The lower charge reduces the reduction potential of either the $(NH_3)_5Ru^{II}$ or the $(CN)_5Ru^{II}$ site significantly relative to that of the monomers. An important observation is that the first wave of $(CN)_5Ru(NCCN)Ru(NH_3)_5{}^-$ is even more cathodically shifted than the related wave in $(NH_3)_5Ru(NCCN)Ru(NH_3)_5{}^{4+}$. The probable influence is largely one of lower, more negative charge in oxidation of $(CN)_5Ru(NCCN)Ru(NH_3)_5{}^-$, because it is very unlikely that $(CN)_5Ru^{II}$ is a better π donor than $(NH_3)_5Ru^{II}$ in view of the equilibrium constant for formation of $(CN)_5Ru(NCCN)^{3-}$ of 585 M^{-1} compared to $>10^{10}$ for $(NH_3)_5Ru(NCCN)^{2+}$.[19] The second waves for both $(CN)_5Ru^{II}(NCCN)Ru^{III}(NH_3)_5$ and $(NH_3)_5Ru^{II}(NCCN)Ru^{III}NH_3)_5{}^{5+}$ occur at nearly the same value (0.881 vs. 0.869 V). This would seem to be fortuitous in that the decaammine is significantly delocalized as shown by its IT transition,[19] while the pentacyano/pentaammine bridged by NCCN exhibits no intervalent band detectable by us. This argues for a valence-localized assignment in (III,NCCN,II). The second wave also appears to experience a large cathodic shift; $(CN)_5Ru(NCCN)^{3-}$ at 1.03 V compared to the neutral ion $(CN)_5Ru^{II}(NCCN)Ru^{III}(NH_3)_5$ at 0.881 V. Both waves are ca. 125 mV broad.

No value for $E°$ of the $(NH_3)_5Ru^{II}(NC)^+$ complex exists in the literature because the $(NH_3)_5Ru(CN)^+$ linkage isomer is the stable entity and only the protonated $(NH_3)_5Ru(NCH)^{2+}$ species has been characterized in the solid state.[32] Furthermore, the trans labilization of NH_3 in this species results in rapid formation of cyanide-bridged polymers, preventing a suitable electrochemical study. The two waves exhibited by $(CN)_5Ru(CN)Ru(NH_3)_5{}^{2-}$ are consistent with the observations of the NCCN-bridged binuclear complex and the $Ru(CN)_6{}^{4-}$ monomer. Both $(CN)_5RuLRu(NH_3)_5{}^-$ complexes (L = NCCN and CN^-) exhibit waves near −0.06 V (−0.06 and −0.075 V, respectively). This result suggests both Ru centers are coupled extensively and to about the same amount as in the (II,L,II) complexes for L = NCCN and CN^-. The second wave at 0.902 V for the CN^--bridged binuclear ion appears to again experience the influence of an overall less charged ion at the electrode surface. The $[Ru(CN)_5(CN)]^{4-}$ center has its wave at greater than or equal to 0.90 V, shifting progressively positive upon addition of protonic charge. Yet in the (II,CN^-,III) binuclear ion the second wave appears at a potential comparable to that of $Ru(CN)_6{}^{4-}$ itself. This again suggests some special orientational effect brought about by the low-charged dipole of (III,CN^-,II) in contact with the glassy-carbon surface, which negates the presence of a high 3+ charge on the second wave. The influence may be due to a more easily achieved desolvation of the binuclear dipolar complexes compared to the more highly solvated, charged monomer components. Removal of solvent would increase the hydrophobic interaction at the glassy-carbon surface, reducing the observed reduction potentials relative to the monomers.

Conclusions

The absence of any observable intervalence transition (IT) for the (III,L,II) complexes with L = 4,4′-bpy and NCCN support a localized valence assignment for these mixed oxidation state species. The infrared spectrum of (II,NCCN,II) exhibits clear evidence for π back-donation from both $(NH_3)_5Ru^{2+}$ and $(CN)_5Ru^{3-}$. One $-C{\equiv}N$ unit (logically the one attached to $(NH_3)_5Ru)^{2+}$) has its frequency lowered more significantly by two factors; the nearby $(NH_3)_5Ru^{2+}$ plus the remote $(CN)_5Ru^{3-}$ for a combined 148-cm^{-1} lowering; the other $-C{\equiv}N$ is lowered about 70 cm^{-1} in the binuclear complex. Thus some delocalization occurs between both ruthenium sites across the NCCN bridge. This is confirmed by the low first wave in the differential-pulse voltammogram for (II,NCCN,II), which is nearly the same as

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(32) Isied, S.; Taube, H. *Inorg. Chem.* **1975**, *14*, 2561.

that for (II,CN^-,II). Both of these complexes have much more communication in the (II,L,II) complexes than for either (II,bpy,II) or (II,pz,II). These latter ions show the previously well-characterized small cathodic and small anodic shifts in waves 1 and 2, respectively, which have been attributed by Haim, et al.[9] and Petersen et al.[13] to isolated valence-type complexes. (II,NCCN,II) is slower to oxidize with $S_2O_8{}^{2-}$ or Br_2 than (II,bpy,II), which suggests a greater $d_\pi \rightarrow \pi^*$ interaction in the NCCN-bridged species than for 4,4′-bpy or pz. This is in keeping with the growing body of evidence that the nitriles are better π-acceptors than the pyridines. The absence of an intervalence band in (III,NCCN,II) and electrochemical evidence support loss of coupling between $(CN)_5Ru^{II}$ and $(NH_3)_5Ru^{III}$ sites upon oxidationof (II,NCCN,II). Therefore the idea that NCCN might lead to a larger delocalization than pz, as was found in the $(NH_3)_5Ru^{II}LRu^{III}(NH_3)_5{}^{5+}$ ions, is not realized to an extent that alters the main chemistry of the $(CN)_5Ru^{II}LRu^{III}(NH_3)_5$ series. For unsymmetric $Ru^{II}Ru^{III}$-bridged cationic ions the IT band for the 4,4′-bpy complex is between 265 and 540 nm at higher energy.[2,22,6] Therefore the absence of a band in the near-IR for the pz-bridged $(CN)_5RuLRu(NH_3)_5$ might predict a band in the visible or UV region. On the basis of the observation that as bridge length increases the IT transition energy increases (λ_{max} decreases), one might choose to examine the higher energy region at wavelenghts shorter than the 680-nm IT band of the CN^--bridged complex. A weak IT band would be hidden by MLCT transitions involving the cyanide $\sim$L bridge π–π^* bands. However, Haim has defended the idea that the low-charged dipole systems with $(CN)_5MLRu(NH_3)_5{}^-$, M = Fe^{II} or Ru^{II}, would have IT bands at lower energy.[10] We are forced to rely on the electrochemical data to infer isolated valences and complete loss of coupling in the mixed-valence NCCN-bridged complex. This probably implies free rotation of the C–C bond in (III,NCCN,II).

The shorter CN^- bridge introduces some significantly different character into both (II,CN^-,II) and (III,CN^-,II) that is not observed with other L bridges. (III,CN^-,II) displays the highly absorbing IT band at 675 nm ($\epsilon = 2.84 \times 10^3$).[24] Although this band appears at high energy compared to the IT band of Creutz–Taube ion or its similar derivatives, its existence implies more coupling than evidenced by the spectra of the complexes bridged by NCCN, 4,4′-bpy, or pz for the mixed oxidation state entities.

The distance of separation, d, in (III,CN^-,II) is approximately 5.22 Å, based on bond lengths in $Ru(CN)_6{}^{4-}$.[33] If the Hush equations[15] are used to calculate the extent of electronic interaction, values of α^2 equal to 0.013 and a resonance energy, H_{12}, of 4.0 kcal/mol is calculated for (III,CN^-,II). In this calculation $\bar{\nu}_{max}$ was taken to be 1.48 μm^{-1} and $\bar{\nu}_{1/2}$ was reduced by 1000 cm^{-1} for a spin–orbit correction to 0.452 μm^{-1}.[27] The calculated values of α^2 and H_{12} are respectively 1.8 times larger and 2.5 times smaller than those of the Creutz–Taube ion ($\alpha^2 = 0.009$, H_{12} = 9.0 kcal/mol).[22] The electron hole is more delocalized in (III,CN^-,II) than for the Creutz–Taube ion, but the extent of stabilization is less. Recently Weber et al.[34] prepared the $(CN)_5RuNCRu(CN)_5{}^{6-}$ species, which exhibits the IT transition at 0.909 μm^{-1} with $\bar{\nu}_{1/2}$ of ca. 0.316 μm^{-1} with the spin–orbit correction. The estimated ϵ_{max} value is between 3.5×10^3 and 7.0×10^3 M^{-1} cm^{-1}, which allows comparison values of α^2 = (0.019–0.038) and H_{12} (4.1–3.0) kcal/mol) to be calculated. This again supports an enhancement in charge delocalization supplied by the pentacyano environment, but it is achieved without a very large increase in separation of the ground-state–excited-state potential energy wells. This sets the interaction energy near 1400 cm^{-1} for bridging CN^- in (III,CN^-,II) compared to an energy of 3200 cm^{-1} for bridging pyrazine in the Creutz–Taube ion.[16]

A reliable estimate of about −3.8 kcal/mol for the back-donation of $(CN)_5Ru(NCCN)^{3-}$ into the π^* levels of NCCN has now been obtained, which is 43% of the π back-bond in $(NH_3)_5Ru(NCCH_3)^{2+}$ determined by calorimetric methods.[31] $Ru(CN)_5{}^{3-}$ is found to be about a 40% better π-donor center than $Ru(NH_3)_5{}^{2+}$ toward π-acceptor ligands.

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Registry No. $2CH_3pz$, 109-08-0; 4,4′-bpy, 553-26-4; $[(NH_3)_5Ru(4,4'\text{-bpy})][PF_6]_2$, 94070-17-4; $[(NH_3)_5Ru(NCCN)][PF_6]_2$, 109745-17-7; $(NH_3)_5RuOH_2{}^{2+}$, 21393-88-4; $(CN)_5RuOH_2{}^{3-}$, 74009-27-1; $Ru(CN)_6{}^{4-}$, 21029-33-4; $(CN)_5RuNCCN^{3-}$, 109764-49-0; $(CN)_5Ru(4,4'\text{-bpy})^{3-}$, 86260-22-2; $(NH_3)_5Ru(2CH_3pz)^{2+}$, 39003-89-9; $(CN)_5Ru(4,4'\text{-bpyH})^{2-}$, 109745-24-6; $(HCN)(CN)_4Ru(4,4'\text{-bpyH})^-$, 109745-25-7; $(HCN)_3(CN)_2Ru(4,4'\text{-bpyH})^+$, 109745-26-8; $Ru(CN)_5(HCN)^{3-}$, 109745-27-9; $Ru(CN)_4(HCN)_2{}^{2-}$, 109745-28-0; $Ru(CN)_3(HCN)_3{}^-$, 109745-29-1; $K[(CN)_5RuCNRu(NH_3)_5]$, 109745-18-8; $[(NH_3)_5RuCNRu(CN)_5]$, 109745-22-4; $[(CN)_5RuCNRu(NH_3)_5]^{2-}$, 109745-23-5; $[(NH_3)_5Ru(4,4'\text{-bpy})Ru(CN)_5]^-$, 109745-19-9; $[(NH_3)_5Ru(4,4'\text{-bpy})Ru(CN)_5]$, 109745-30-4; $[(NH_3)_5Ru(C_2N_2)Ru(CN)_5]^-$, 109745-20-2; $[(NH_3)_5Ru(C_2N_2)Ru(CN)_5]$, 109745-21-3; $[(NH_3)_5Ru(pz)Ru(CN)_5]^-$, 96455-65-1; C_2N_2, 460-19-5; CN, 57-12-5.

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