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Unsymmetrical $Ru^{II}Ru^{II}$ and $Ru^{II}Ru^{III}$ Binuclear Ions: Properties of $(CN)_5Ru(pz)Ru(NH_3)_5{}^{0/-}$ Complexes

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The preparation and characterization of the unsymmetrical bridged binuclear complexes $(NH_3)_5Ru^{II}(pz)Ru^{II}(CN)_5{}^-$ and $(NH_3)_5Ru^{III}(pz)Ru^{II}(CN)_5$ are described. The MLCT band of the (III,II) complex (λ_{max} = 450 nm, $\epsilon = 5.8 \times 10^3$ M^{-1} cm^{-1}) and the stepwise one-electron couples determined by differential pulse voltammetry ($E(1)_{1/2}$ = 0.529 and $E(2)_{1/2}$ = 1.013 V; μ = 1.00, T = 25.0 °C) show that the $(NH_3)_5Ru$ moiety is the site of the first oxidation step. The (II,II) complex (λ_{max} = 500 nm, $\epsilon = 1.7 \times 10^4$ M^{-1} cm^{-1}) is cleanly oxidized with $K_2S_2O_8$ to the (II,III) complex. No intervalent transition (IT) is found at lower energy than the MLCT transition of (II,III). Reasons for the absence of this band, or its very low extinction coefficient, are presented on the basis of the polarizing influence of the pentacyanide environment around the Ru(II) site, which operates to reduce through-space coupling to the $Ru^{III}(NH_3)_5$ site, and hence lowers the interaction energy to an extent even greater than for ion pairs of the type $[(NH_3)_5RuL^{3+},Ru(CN)_6{}^{4-}]^-$. Comparisons are made to the Creutz–Taube ion, $(NH_3)_5Ru(pz)Ru(NH_3)_5{}^{5+}$, Meyer's ion, $(NH_3)_5Ru(pz)RuCl(bpy)_2{}^{4+}$, and $(NH_3)_5Ru(pz)Fe(CN)_5$ prepared separately by Toma and by Haim and Ludi.

Introduction

The metal–metal interactions in ligand-bridged mixed-valence complexes have been the subject of many studies for complexes based on ruthenium ammines.[1-12] The interest has originated with the Creutz–Taube ion, $[(Ru(NH_3)_5)_2(pz)]^{5+}$;[1] the assignment of this ion to valence-localized or -delocalized types remains controversial.[13] Day has included the Creutz–Taube ion in the class II group.[14a] Delocalization has been implicated for small ligand bridges such as N_2,[2] dicyanogen,[9] and pyrazine,[1] while extended bridging ligands and even saturated bridging ligands, such as dithianes,[3] promote weak metal–metal interactions. This latter group is of the valence-localized group, tending toward class I behavior by the Robin–Day assignment.[14c] The energies of intervalent transitions (IT), frequently observed for mixed-valence ions of the $[Ru^{II}Ru^{III}]$ type, have been treated by means of perturbation theory to calculate the interaction energy.[14] The calculated value decreases with distance between metal centers from 4900 cm^{-1} for the N_2-bridged case, 3200 cm^{-1} for pz, and 535 cm^{-1} for 4-cyanopyridine to 50 cm^{-1} for 1,3-dicyanobenzene as the bridge. In the Taube–Richardson study[14] it was noted that mixed-valence, ligand-bridged $[Ru^{II}Ru^{III}]$ species sometimes do not exhibit detectable IT bands (e.g. 1,6-dicyanonaphthalene and 2,7-dicyanonaphthalene) even though the species are of the mixed-valence type. In these cases the coupling is very weak. Cyclic voltammetry and differential-pulse voltammetry may be used to assess the comproportionation constant, K_c, for symmetrically coordinated mixed-valence [2,3] species at equilibrium with the isovalent [2,2] and [3,3] species.[12] Such data are particularly useful when the IT band has low extinction or remains undetected.[12] For near-zero interaction of metal centers in the [2,3] complex K_c = 4 and the difference in sequential one-electron-reduction potentials, $\Delta E_{1/2}$, is 36 mV. Greater interaction between $Ru^{II}Ru^{III}$ centers results in an increase in K_c and much wider separation of one-electron potentials.

There are fewer studies of binuclear mixed-valence ions where the local site symmetries are not identical. Meyer et al. have examined an intervalent case where the site of oxidation is localized on the $(NH_3)_5Ru$ portion of $(NH_3)_5Ru^{III}(pz)Ru^{II}Cl(bpy)_2{}^{4+}$.[15] The localized valence assignment is supported by a spectrum in the UV–visible region that is nearly a superposition of those for $(NH_3)_5Ru(pz)^{3+}$ and $(pz)RuCl(bpy)_2{}^+$. Stepwise one-electron electrochemistry for [2,2] → [2,3] → [3,3] oxidations at potentials nearly equivalent to those of their related monomer analogues also indicates a weak coupling case for this unsymmetrical system. The $(NH_3)_5Ru$ moiety is also the site of the higher oxidation state entity in the heterobinuclear complex $(NH_3)_5Ru^{III}(pz)Fe^{II}(CN)_5$.[18,34] The apparent absence of a near-IR transition remains a curious, unexplained feature in the properties of this heterobinuclear analogue of the Creutz–Taube ion. The $(NH_3)_5Ru$ moiety can be made to be the favored reducing site if $edta^{4-}$ complexes the oxidizing Ru^{III} partner. Creutz and Sutin were able to determine the back-electron-transfer rate from the less favorable $(NH_3)_5Ru^{III}(pz)Ru^{II}(edta)^+$ isomer by using flash photolysis techniques.[19] A rate of 8×10^9 s^{-1} was observed to restore the $(NH_3)_5Ru^{II}(pz)Ru^{III}(edta)^+$ ion, comparable to the decay rate of the radical ion, $(NH_3)_5Ru^{III}(pz^-)Rh^{III}(edta)^+$. These studies show that the site of oxidation in species of the general formula $(NH_3)_5Ru^{II}(pz)Ru^{II}L_n$ will be determined by the π-bonding properties of the chemical environment of L_n or the electrostatic ligand environment for harder ligands.

In this paper we describe the unsymmetrical $(NH_3)_5Ru^{II}(pz)Ru^{II}(CN)_5{}^-$ ion and its mixed-valence derivative $(NH_3)_5Ru^{III}(pz)Ru^{II}(CN)_5$. Our research group recently reported preparing the $(CN)_5Ru(pz)^{3-}$ complex.[17] The Ru(II)–pyrazine π back-bonding is substantially reduced in this monomer fragment relative to that of $(NH_3)_5Ru(pz)^{2+}$. The two new binuclear ions of this paper are clearly of interest in comparison with the Creutz–Taube ions and Meyer's $(NH_3)_5Ru(pz)RuCl(bpy)_2{}^{4+/3+}$ hybrids. In addition, a number of weak coupling cases have been observed through outer-sphere charge transfer (OSCT) for ion pairs including $[Ru^{II}(CN)_6{}^{4-},(NH_3)_5Ru^{III}Cl^{2+}]$ and $[Ru(CN)_6{}^{4-},(NH_3)_5Ru^{III}L]$ with L = an N-heterocyclic ligand.[20,21]

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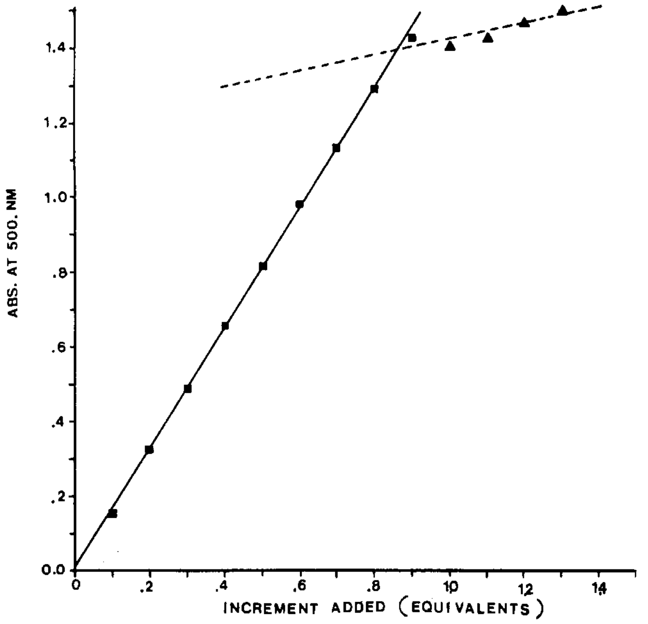

Figure 1. Job's plot titration of $(CN)_5RuOH_2^{3-}$ with $(NH_3)_5Ru(pz)^{2+}$. $[(CN)_5RuOH_2^{3-}]_i = 9.76 \times 10^{-5}$ M; titrant $[(NH_3)_5Ru(pz)^{2+}] = 5.309 \times 10^{-3}$ M; final [II,II] = 8.37×10^{-5} M at the intersection; $\epsilon = 1.67 \times 10^4$ M^{-1} cm^{-1} at 500 nm.

The ion pairing occurs across the minimum distance of the ammine to cyanide faces. Since NH_3 does not have low-lying orbitals to mediate the charge transfer as in the pyrazine-bridged systems, a direct metal orbital–metal orbital coupling is required for OSCT. Our newly prepared $(NH_3)_5Ru(pz)Ru(CN)_5^{0/-}$ ions are the bridged systems closest to those of the ion-paired $[Ru(CN)_6^{4-}$,-acceptor] type. Therefore these new ions should have a key position in relating the chemistry of a number of previously separate studies.

Experimental Section

$[(NH_3)_5Ru(pz)](PF_6)_2$. The pyrazine complex of $(NH_3)_5Ru^{2+}$ was prepared and characterized by literature methods.[1,23] Preparation of $(NH_3)_5Ru(pz)^{3+}$ was achieved by oxidation of $(NH_3)Ru(pz)^{2+}$ by bubbling Cl_2 through a solution at the desired concentration, followed by a purge with Ar.

$(CN)_5Ru(pz)^{3-}$ and $(CN)_5RuOH_2^{3-}$. Solutions for immediate use of $(CN)_5RuOH_2^{3-}$ were generated by the $Br_2/Ru(CN)_6^{4-}$ reaction as reported by Johnson and Shepherd.[17] The potassium salt $K_3Ru(CN)_5(pz)\cdot xH_2O$ was isolated previously.[17] $K_4Ru(CN)_6\cdot 3H_2O$ was used as supplied by Alfa Inorganics.

Instrumentation. Spectra in the UV–visible region were obtained on a Varian Cary 118C spectrophotometer using thermostated quartz cells. Spectra in the near-IR region were obtained on a Perkin-Elmer spectrophotometer at the Department of Chemistry, Carnegie Mellon University, and were repeated on a Cary 14 at the University of Pittsburgh. The electrochemical studies were obtained on an IBM 225 electrochemical analyzer unit. Measurements for differential-pulse polarography and cyclic voltammetry were recorded at a Pt–foil working electrode vs. an SCE standard. A Pt wire served as the auxiliary electrode of the three-electrode assembly. The solution was purged with Ar inside a glass-jacketed cell with $T = 25.0$ °C. Reversibility and proper response of the IBM 225 EC unit and the electrodes were determined by the behavior of chemically reversible standards: $Ru(NH_3)_6Cl_3$ and $K_4Fe(CN)_6$. The ionic strength was maintained with NaCl at the desired level between 0.10 and 1.00.

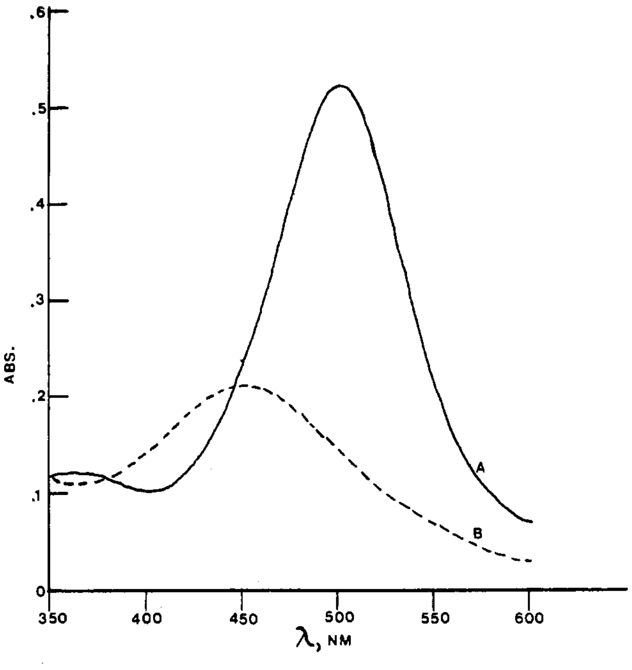

Figure 2. Visible spectra of the (II,II) and (II,III) binuclear ions: A, [II,II] = 2.90×10^{-4} M; B, 0.5 equiv of $S_2O_8^{2-}$ added. [II,III] = 2.90×10^{-4} M; ϵ_{450}(II,III) = 6.0×10^3 M^{-1} cm^{-1}.

Results

Formation of Binuclear Ions. When $(NH_3)_5Ru(pz)^{2+}$ and $(CN)_5RuOH_2^{3-}$ are mixed (eq 1) or if $(CN)_5Ru(pz)^{3-}$ is added to $(NH_3)_5RuOH_2^{2+}$ (eq 2), the same major product is formed.

$$(NH_3)_5Ru(pz)^{2+} + (CN)_5RuOH_2^{3-} \rightarrow (NH_3)_5Ru(pz)Ru(CN)_5^- + H_2O \quad (1)$$

$$(CN)_5Ru(pz)^{3-} + (NH_3)_5RuOH_2^{2+} \rightarrow (NH_3)_5Ru(pz)Ru(CN)_5^- + H_2O \quad (2)$$

A spectrophotometric titration of $(NH_3)_5Ru(pz)^{2+}$ by $(CN)_5RuOH_2^{3-}$, which may be generated by the $Br_2/Ru(CN)_6^{4-}$ reaction,[17] is shown in Figure 1. Equilibrium is reached after 10 min. The 1:1 stoichiometry of $(NH_3)_5Ru(pz)^{2+}$ to $(CN)_5RuOH_2^{3-}$ is supported by the experimental titration break at 0.87:1.00. The new ion is therefore the anticipated $(NH_3)_5Ru(pz)Ru(CN)_5^-$ complex, which exhibits its maximum at 500 nm (Figure 2). The intersection point of Figure 1 may be used to calculate an extinction coefficient of 1.7×10^4 M^{-1} cm^{-1} at 500 nm for $(NH_3)_5Ru(pz)Ru(CN)_5^-$.

Formation of the binuclear $Ru^{II}Ru^{II}$ ion via reaction 1 has the advantage that the potential complication of the cyano-bridged species of identical stoichiometry and composition (eq 3) is assured

$$(CN)_5Ru(pz)^{3-} + (NH_3)_5RuOH_2^{2+} \rightarrow (NH_3)_5RuNCRu(CN)_4(pz)^- + H_2O \quad (3)$$

to be avoided, even though the spectra indicate that some pyrazine-bridged product is formed from the combination of $(CN)_5Ru(pz)^{3-}$ and $(NH_3)_5RuOH_2^{2+}$.

The solubility of the resultant binuclear ion is very slight (~2×10^{-4} M). A low-resolution IR spectrum obtained in KBr for the potassium salt, which precipitates concomitantly with a de-

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Table I. IR Stretching Frequencies Obtained for the $(NH_3)_5Ru(pz)Ru(CN)_5^{0/-}$ System and Its $Fe(CN)_5^{3-}$ Analogue[a]

$Ru(NH_3)_5(pz)Ru(CN)_5^-$	$Ru(NH_3)_5(pz)Ru(CN)_5^0$	$Ru(NH_3)_5(pz)Fe(CN)_5^-$	$Ru(NH_3)_5(pz)Fe(CN)_5^0$	assignt
3450 br, s	3480 br, s	3400 br, s	3440 br, s	ν_{H_2O}
3310, 3230, 3180 br, vs	3250 br, s	3300 br, s	3250 br, s	ν_{H_2O}
	2065 s	2080 m (2100 sh[b])	2085 m (2100 sh[b])	ν_{CN}
2055 vs	2050 sh	2040 s (2040[b])	2045 s (2050[b])	
	(1960, 1920 s)		1700 s	δ_{deg} NH_3, δ_{H_2O}
1638 s, 1620 m	1650, 1632, 1620 m	1630 s	1640 m	
1595 s	1605 s	1590 m	1595 m	pz, ring str
		1485 m	1485 sh	
1465 m		1465 m		pz, ring str
1430 m	1418 m	1430 m	1430 m	
masked	1335 sh	1340 sh	1335 sh	pz, ring str
1302 br, m	1320 m	1280 s (1290[b])	1310 s (1340[b])	δ_{sym} NH_3
1225 m	1227 w	1225 m	1225 m	pz, δ_{CH} in plane
1170, 1180 w	1168 m	1190 w	1185 w	
1097 vw	1115 m	1095 w	1100 vw	pz, τ_{CH} in plane
1075 w	1075 w	1075 m	1075 m	
1032 sh	1032 m	1040 w	1030 m	pz, ring str
1013 m		1015 m	1015 s	
820 m	820 m	825 m	masked	pz, τ_{CH} out of plane
795 w, 765 w		770 m	800 s	ρ_{NH_3}
675 w	685 w	675 m	675 m	pz, ring def
		575 m	570 m	
		525 w	515 w	ν_{MC}, δ_{MCN}
		420 w	420 w	pz, ring def
		300 w	300 w	ν_{MN}, pz ring def

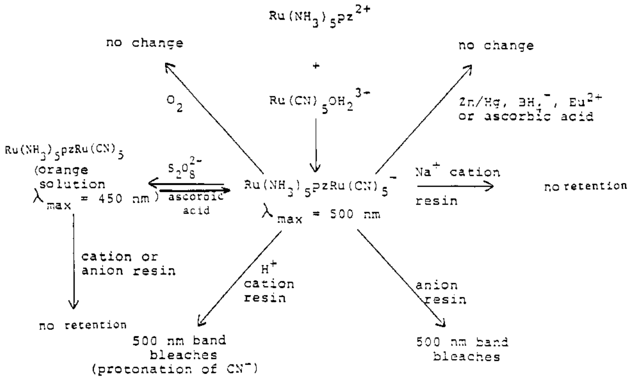
[a] $Fe(CN)_5^{3-}$ complexes from ref 18. [b] Values reported by Haim, Ludi, et al.[34]

crease in the intensity at 500 nm, shows the presence of both the CN^- and NH_3 frequencies. These are enumerated with assignments in Table I along with data for the $(NH_3)_5Ru(pz)Fe(CN)_5^{0/-}$ binuclear complexes as reported by Toma and Santos[18] and by Haim, Ludi, et al.[34] Changes in oxidation state or in the identity of the second metal center do not significantly alter the IR frequencies. The symmetric ammonia deformation frequencies for pentaammineruthenium(II) and -ruthenium(III) fall in the ranges 1260–1290 and 1330–1360 cm^{-1}, respectively.[34] Less difference is observed for the $(NH_3)_5Ru(pz)Ru(CN)_5^{0/-}$ pair (Δ of 18 cm^{-1}) than for the $(NH_3)_5Ru(pz)Fe(CN)_5^{0/-}$ pair (Δ of 30[18] and 50 cm^{-1} [34]). The cyanide stretching frequency in both $(NH_3)_5Ru(pz)Ru(CN)_5^-$ and $(NH_3)_5Ru(pz)Ru(CN)_5^0$ at 2055 cm^{-1} and at 2065 and 2050 cm^{-1}, respectively, are very close to the value for $K_4Ru(CN)_6$ of 2048 cm^{-1}.[35] Therefore, the infrared data support a Ru(II) oxidation state for the $Ru(CN)_5$ moiety in both solids of the pyrazine-bridged binuclear complexes because an increase in oxidation state in metal cyanide complexes from II to III usually causes an increase of about 70 cm^{-1} in ν_{CN}.[35]

An attempt was made to synthesize the mixed-metal binuclear ion $Ru(CN)_5(pz)Fe(CN)_5^{6-}$ by two methods; both were unsuccessful. The addition of a $Fe(CN)_5OH_2^{3-}$ solution to one of $Ru(CN)_5(pz)^{3-}$ occurred with no short-term change in the visible spectrum. When $Ru(CN)_5OH_2^{3-}$ and $Fe(CN)_5(pz)^{3-}$ were mixed, the 452-nm band of the iron(II)–pyrazine complex bleached and the 368-nm band of the ruthenium(II)–pyrazine complex[17] grew in. The reaction continued for several days without the formation of an isosbestic point. Presumably this lack of an isosbestic point was caused by further polymerization of $Fe(CN)_5OH_2^{3-}$ detected at 420 nm. The rate of formation of $(CN)_5Ru(pz)^{3-}$ was faster than anticipated for dissociation of pyrazine from $(CN)_5Fe(pz)^{3-}$ followed by substitution of free pyrazine on the $(CN)_5RuOH_2^{3-}$ complex. Thus it appears that $(CN)_5Ru(pz)Fe(CN)_5^{6-}$ forms as an intermediate at low concentration, followed by Fe(II)–pyrazine bond rupture to complete the inner-sphere transfer of the ligand to Ru(II).

The results of the $Ru(CN)_5^{3-}$–pyrazine–$Fe(CN)_5^{3-}$ system expose the importance of π back-bonding in the stabilization of pyrazine complexes. The pyrazine is a poor σ or π donor and requires strong π-acceptor interaction with the metal. The 4d ruthenium ion, with the same ligand set, is a better π base than the 3d iron.[17] The observations of Toma[18] and of Haim et al.[34] show that $(NH_3)_5Ru(pz)Fe(CN)_5^-$ is a moderately stable entity while our data show that $(CN)_5Ru(pz)Fe(CN)_5^{6-}$ dissociates to produce $(CN)_5Ru(pz)^{3-}$. Coordination to $Ru(CN)_5^{3-}$ results in a slight net decrease in the basicity of pyrazine (pK_a(complex) = 0.30).[17] Even though the Ru(II)–pyrazine π bonding appears to be much less than that for the $(NH_3)_5Ru^{2+}$ complex, the presence of $Ru(CN)_5^{3-}$ appears to make pyrazine unable to accept enough π density from the iron to offset electrostatic repulsion. Part of the driving force may be the formation of the cyano-bridged iron complexes, which prevents a true equilibrium among $(CN)_5FeH_2O^{3-}$, $(CN)_5Fe(pz)^{3-}$, $(CN)_5RuOH_2^{3-}$, and $(CN)_5Ru(pz)^{3-}$ from being achieved.

Scheme I



Reactivity of the $Ru^{II}Ru^{II}$ Complex. The behavior of the $Ru^{II}Ru^{II}$ title complex under various conditions is shown in Scheme I. No further chemical reduction is achieved with Zn/Hg, Eu^{2+}, BH_4^-, or ascorbic acid. This is consistent with the oxidation state assignment of $Ru^{II}Ru^{II}$ for the ion that absorbs at 500 nm. This binuclear anion is unaffected and was not bound by cation-exchange resin in the Na^+ form, but exposure to the high activity of H^+ in the resin phase of a cation resin reduces the intensity of the 500-nm band. Protonation at CN^- is suggested as shown by the related broadening and loss of intensity by the spectrum of the $(CN)_5Ru(pz)^{3-}$ monomer species at high-[acid] conditions.[17] Oxidation of the $(NH_3)_5Ru(pz)Ru(CN)_5^-$ complex does not occur on exposure to O_2. However stronger oxidants (Br_2, Ce(IV),

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Table II. MLCT Absorption Bands of Binuclear Ions and Monomer Components

complex	λ_{max}, nm	ref
$Ru(NH_3)_5(pz)Ru(CN)_5^-$	500	this work
$Ru(NH_3)_5(pz)Ru(CN)_5^0$	450	this work
$[Ru(NH_3)_5]_2(pz)^{4+}$	547	1
$[Ru(NH_3)_5]_2(pz)^{5+}$	565, 1570	1
$[Ru(NH_3)_5]_2(pz)^{6+}$	352	1
$[Ru(NH_3)_5(pz)Fe(CN)_5]^-$	535	34[a]
$[Ru(NH_3)_5(pz)Fe(CN)_5]^0$	567	34[a]
$[Fe(CN)_5]_2(pz)^{6-}$	505	24
$[Fe(CN)_5]_2(pz)^{5-}$	458, 1170	24
$Ru(NH_3)_5(pz)^{2+}$	472	1
$Ru(NH_3)_5(pz)^{3+}$	330 sh	1
$Ru(CN)_5(pz)^{3-}$	368	17
$Fe(CN)_5(pz)^{3-}$	452	25
$Fe(CN)_5(pzH)^{2-}$	610	25
$Ru(CN)_5(pzH)^{2-}$	420	17
$Ru(NH_3)_5(pzH)^{3+}$	527	1

[a] Toma and Santos[18] report 523 nm for $[Ru^{II},Fe^{II}]$ and 523 and 1330 nm for $[Ru^{III},Fe^{II}]$; the purity of the $[Ru^{III},Fe^{II}]$ and the authenticity of the 1330-nm band are questioned by Haim, Ludi, et al.[34]

$S_2O_8^{2-}$) cause a change in the solution color from reddish purple to orange.

The orange species has its maximum in the visible region at 450 nm, $\epsilon \simeq (5.83 \pm 0.41) \times 10^3$ M^{-1} cm^{-1} (Figure 2). Subsequent data show the species absorbing at 450 nm to be the $Ru^{II}Ru^{III}$ mixed-valence complex, $(NH_3)_5Ru(pz)Ru(CN)_5$. The same $Ru^{II}Ru^{III}$ complex may be generated by the substitution reaction (eq 4) of $(NH_3)_5Ru(pz)^{3+}$ on $(CN)_5RuOH_2^{3-}$. The

$$(NH_3)_5Ru(pz)^{3+} + (CN)_5RuOH_2^{3-} \rightarrow (NH_3)_5Ru(pz)Ru(CN)_5 + H_2O \quad (4)$$

absorbance maximum for the product of the substitution reaction is also 450 nm. Addition of ascorbic acid reduces the $Ru^{II}Ru^{III}$ binuclear complex to the $Ru^{II}Ru^{II}$ complex (λ_{max} = 500 nm) as prepared via eq 1. The value of the calculated extinction coefficient exceeds those of ion-pair type OSCT transitions found for $[Ru^{II}(CN)_6^{4-},(NH_3)_5Ru^{III}L]$ species by a factor of 10^2.[21] Ion-exchange behavior, described below, also supports the ligand-bridged formulation as opposed to simple ion pairing. The positions of the long-wavelength maxima for binuclear ions and monomer components are given in Table II.

The visible absorption band in $Ru(NH_3)_5L^{2+}$ spectra is assigned to a metal π_d to ligand π^* charge transfer (MLCT). The transition in $Ru(NH_3)_5(pz)Ru(CN)_5^-$ at 500 nm is consistent with the trend stated by Creutz and Taube,[1] if one also considers the π back-donation into the pyrazine ring from the pentacyanoruthenium moiety. Positive charge stabilizes the excited state, causing a bathochromic shift in λ_{max} (nm) [H^+, 529; $Rh^{III}(NH_3)_5^{3+}$, 528; CH_3^+, 538], but π back-donation from a second metal partially negates the change by raising π^* [$Fe^{II}(CN)_5^{3-}$, 523,[18] 535;[34] $Ru^{II}(CN)_5^{3-}$, 500].

When the (II,II) ion is oxidized, one would expect $Ru(CN)_5$, which is more able to stabilize the Ru(II) state via π back-bonding to the cyanide ligands, to retain its oxidation state. This is consistent with the charge-transfer band of the (II,III) ion. If the $Ru(NH_3)_5^{2+}$ moiety were formally Ru(II), charge withdrawal by $Ru(CN)_5$ without π back-bonding possible from Ru(III) would shift the MLCT to lower energy. (Cf. Table II for the influence of H^+ on the monomer MLCT spectra.) The actual wavelength is 450 nm—higher in energy than the 472-nm maximum of $Ru(NH_3)_5(pz)^{2+}$ but lower in energy than the 368-nm maximum of $Ru(CN)_5(pz)^{3-}$. This indicates the oxidized site is at the $(NH_3)_5Ru$ moiety.

Specific Effects of Oxidants on $Ru^{II}Ru^{II}$. A titration of $(CN)_5Ru(pz)Ru(NH_3)_5^-$, (II,II), was started with $S_2O_8^{2-}$ as the oxidant (Figure 3).

Two moles of (II,II) is consumed per mole of $S_2O_8^{2-}$, yielding the same species (λ_{max} = 450 nm) as formed via eq 4. Therefore, the product of the $S_2O_8^{2-}$ oxidation is the mixed-oxidation-state ion (II,III). Addition of excess $S_2O_8^{2-}$ produced a reduction in the intensity of the 450-nm band by further oxidation.

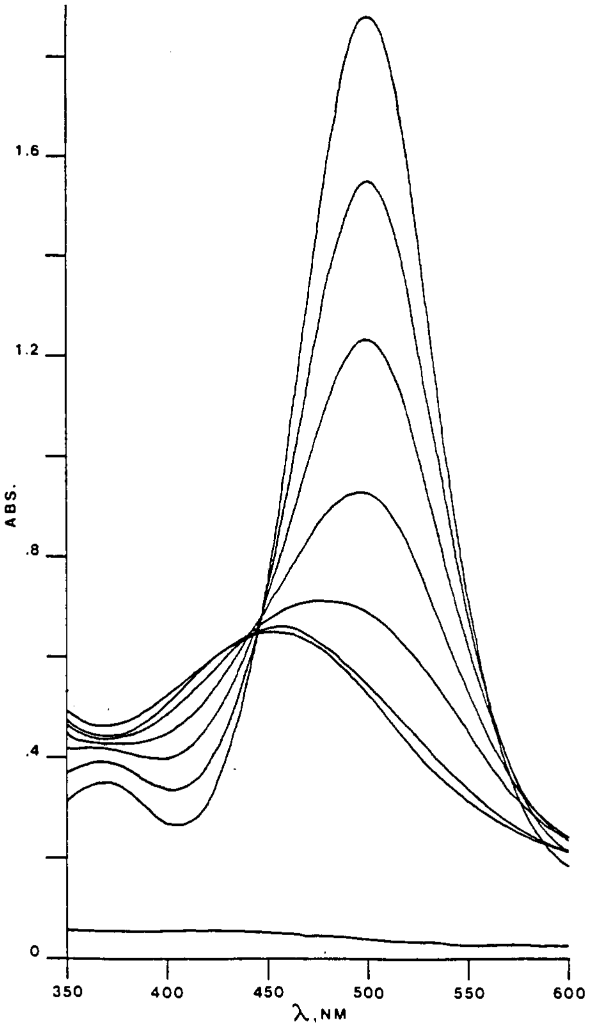

Figure 3. Titration of (II,II) with $S_2O_8^{2-}$. Descending curves: 0 equiv, 0.10 equiv, 0.20 equiv, 0.30 equiv, 0.40 equiv, 0.50 equiv (complete conversion to (II,III)), 1.00 equiv ($S_2O_8^{2-}$ in excess, no change), blank. $[II,II]_i = 1.09 \times 10^{-4}$ M; $[II,III]_f = 1.09 \times 10^{-4}$ M; $\epsilon_{450}(II,III) = 5.42 \times 10^3$ M^{-1} cm^{-1}.

Previous work has shown that the Ru^{III} complexes of $(CN)_5RuL^{2-}$ are labile.[17,30] Additional oxidation by excess $S_2O_8^{2-}$ will be accompanied by rupture of the binuclear complex. Therefore no attempts were made to characterize or isolate a (III,III) binuclear species. (II,II) is also oxidized by PbO_2 to (II,III), but acidic conditions are necessary to promote the heterogeneous phase oxidation.

Use of Br_2 as an oxidant produces changes that are not yet completely understood. One mole of Br_2 per mole of (II,II) is the observed stoichiometry (1.00:1.00) rather than 0.50:1.00. The product of the oxidation also appears to have a maximum near 450 nm. Elemental analysis (Galbraith) of the solid isolated after oxidation of (II,II) with Br_2 gives a composition closest to $(NH_3)_4(H_2O)Ru(pz)Ru(CN)_5 \cdot 2H_2O$ contaminated with some of the triammine analogue. Thus it appears that Br_2 oxidation proceeds by an unknown mechanism with aquation of NH_3 from the $(NH_3)_5Ru$ site of (II,II). Additional evidence exists for a relatively labile coordination site on the (II,III) ion produced by Br_2 oxidation of (II,II). When 4-methylpyrazole is added to this (II,III) solution, the spectrum shifts back toward 500 nm with loss of intensity compared to that of the original (II,II) solution. There is no change in the spectrum of the (II,III) solution produced via $S_2O_8^{2-}$ oxidation of (II,II) upon addition of 4-methylpyrazole. Pentaammineruthenium(III) complexes of pyrazoles, imidazoles, and disubstituted aminopyridines exhibit LMCT transitions in the 400–500-nm region.[26] If 4-methylpyrazole were to displace H_2O of $(NH_3)_4(H_2O)Ru(pz)Ru(CN)_5$, a new band toward lower energy would be anticipated. Therefore, it appears that $S_2O_8^{2-}$ oxidizes (II,II) with retention of the five NH_3 donors while Br_2 oxidizes (II,II) with labilization of at least one NH_3 position. A pentaammine or tetraammine aquo environment at the Ru^{III} site is not sufficiently different to change the band position of the MLCT transition of the $(CN)_5Ru(pz)M^{III}$ chromophore, which is dominated by the Ru^{II}–CN bonding and electrostatics provided by any suitable tripositive charge on the acceptor pyrazine ring.

Studies of Related Ion Pairs. A number of experiments were performed to establish that the species formed in reactions 1 and 4 were not merely ion pairs of $(NH_3)_5Ru(pz)^{2+}$ and $(NH_3)_5Ru(pz)^{3+}$ with $(CN)_5RuOH_2^{3-}$, similar to the $[(NH_3)_5RuL^{3+},Ru(CN)_6^{4-}]^-$ ion pairs described by Curtis and Meyer.[21] In particular the ion described in this paper as (II,III), which exhibits its λ_{max} at 450 nm, would be anticipated to have an OSCT band at a position of about 700 ± 10 nm ($\epsilon \simeq 39 \pm 5$ M^{-1} cm^{-1}) on the basis of the values given by Curtis and Meyer for the ion pair with L = 3,5-dimethylpyrazine. The $E_{1/2}$ values for $Ru(CN)_6^{4-/3-}$ vs. $Ru(CN)_5OH_2^{3-/2-}$ differ by only 94 mV,[33] with $Ru(CN)_5OH_2^{3-}$ being slightly easier to oxidize than $Ru(CN)_6^{4-}$. Thus an ion pair of the type $[(NH_3)_5RuL^{3+},(CN)_5RuOH_2^{3-}]$ should exhibit its OSCT at either the same or slightly longer wavelength as that of the related ion pairs using $Ru(CN)_6^{4-}$ as the reductant site. Even though the above predictions are possible, we attempted to observe the ion pair of $(NH_3)_5Ru(pz)^{3+}$ with $Ru(CN)_6^{4-}$ directly. $Ru(CN)_6^{4-}$ was chosen as the test species to prevent inner-sphere substitution by pyrazine of $(NH_3)_5Ru(pz)^{3+}$ (forming a bridged ion). In addition, the extent of ion pairing with $(NH_3)_5Ru(pz)^{3+}$ will be greater for $Ru(CN)_6^{4-}$ than for $(CN)_5RuOH_2^{3-}$ due to its greater charge product; thus ion pairs with $Ru(CN)_6^{4-}$ will be more fully formed in solution. $Ru(CN)_6^{4-}$ has the added advantage over $Ru(CN)_5OH_2^{3-}$ that, at the concentrations required to observe ion pairs of low ϵ's (20–50 M^{-1} cm^{-1}), $Ru(CN)_6^{4-}$ will not polymerize. $(CN)_5RuOH_2^{3-}$ can rapidly form cyano-bridged $Ru^{II}Ru^{III}$ and $Ru^{II}Ru^{II}$ species as noted previously in other accounts.[21,27] Finally, both $Ru(CN)_6^{4-}$ and $Ru(CN)_5OH_2^{3-}$ are transparent in the visible and near-IR regions of the spectrum,[27] so that $Ru(CN)_6^{4-}$ is the stand-in of choice for $Ru(CN)_5OH_2^{3-}$ in ion-pairing studies. Curtis and Meyer had found that, with L = various N-heterocyclic ligands in the $[(NH_3)_5RuL^{3+},Ru(CN)_6^{4-}]^-$ ion pairs, the pairs were fully formed at concentrations of each component greater than 1×10^{-3} M but that insolubility problems restricted concentrations below 6×10^{-3} M. In our study with L = pyrazine, precipitation was immediate even at 1.0×10^{-3} M concentrations in $(NH_3)_5Ru(pz)^{3+}$ and $Ru(CN)_6^{4-}$ for each. At 2×10^{-4} M the species remain in solution, but no distinct features related to an ion pair were observed.

When $(NH_3)_5Ru(pz)^{3+}$ and $Ru(CN)_6^{4-}$ were combined at 1.00×10^{-3} M, precipitation of an insoluble solid and the appearance of a pale orange-pink solution were observed. The solution had a spectrum typical of $(NH_3)_5Ru(pz)^{2+}$. On the basis of the known ϵ of $(NH_3)_5Ru(pz)^{2+}$ at 472 nm, the amount of $(NH_3)_5Ru(pz)^{2+}$ was shown to be only 2% of the initial 1×10^{-3} M. Addition of ascorbic acid immediately reduced $(NH_3)_5Ru(pz)^{3+}$, which was also present, but only 5.8% of the initial $(NH_3)_5Ru(pz)^{3+}$ was found as Ru(III) in solution. Therefore, 92% had been removed by precipitation. The amount of $(NH_3)_5Ru(pz)^{2+}$ present after precipitation was found to be a function of the stoichiometry of the initial $(NH_3)_5Ru(pz)^{3+}$ and $Ru(CN)_6^{4-}$, increasing ca. 15% with 15% excess $Ru(CN)_6^{4-}$. The presence of $(NH_3)_5Ru(pz)^{2+}$ after mixing is explained by the thermodynamically unfavorable redox equilibrium

$$(NH_3)_5Ru(pz)^{3+} + Ru(CN)_6^{4-} \rightleftarrows (NH_3)_5Ru(pz)^{2+} + Ru(CN)_6^{3-} \quad (5)$$

which is driven to the right by the subsequent precipitation reactions. It was noted that precipitation occurs at even concentrations of 2×10^{-4} M each in $(NH_3)_5Ru(pz)^{2+}$ and $Ru(CN)_6^{4-}$. We examined the solution phase of both the solutions prepared at 2×10^{-4} M in $(NH_3)_5Ru(pz)^{3+}$ and $Ru(CN)_6^{4-}$ and the filtrate which was generated from mixing 1.0×10^{-3} M in each. No new species were identified at concentrations of 2×10^{-4} M in reagents. The solution phase of the combination of the 1×10^{-3} M reagents was examined after filtration by taking aliquots for anion or cation exchange. The $(NH_3)_5Ru(pz)^{2+}$ species, or its ion pair with $Ru(CN)_6^{4-}$ in solution, which exhibited a λ_{max} near 476 nm, was bound by Dowex 50W-X8 cation-exchange resin in Na^+ form. The trace product $(NH_3)_5RuL^{2+}$ was then eluted with NaCl solution and its spectrum confirmed as that of $(NH_3)_5Ru(pz)^{2+}$. The orange solution was also passed through AG-4X anion-exchange resin in the Cl^- form. The $(NH_3)_5Ru(pz)^{2+}$ species passed through the column, and a green species was observed that was either present in solution at low concentration and had a low extinction coefficient or formed during concentration of the $Ru(CN)_6^{4-}$ (or its derivatives) in the resin phase. The green anion was eluted with nearly saturated NaCl, and its spectrum showed maxima at 675 and 375 nm with ϵ's in a ratio of about 1:2. The green solution of the isolated green anion was not changed by the addition of ascorbic acid for over 1 h; since reduction of $(NH_3)_5Ru(pz)^{3+}$ is immediate with ascorbic acid, the isolated green ion could not be the ion pair of $[(NH_3)_5Ru(pz)^{3+},Ru(CN)_6^{4-}]^-$ nor is it the species formed by reactions 1 and 4. Its high charge suggests the species is a Ru(II)–cyano polymer.

Table III. Differential-Pulse Peak Potentials at 25.0 °C

		$E_{1/2}$(species) vs. NHE, V			
[NaCl]	$\mu^{1/2}$	$(NH_3)_5$-$Ru(pz)^{3+/2+}$	$(CN)_5$-$Ru(pz)^{2-/3-}$	$(II,II)^{0/-}$	$(II,III)^{+/0}$
0.100[a]	0.316	0.540	0.957	0.529	0.972
0.200	0.447	0.527	0.972	0.529	0.978
0.500	0.707	0.514	0.993	0.526	0.983
0.800	0.894	0.508	1.001	0.527	0.992
1.000	1.00	0.507	1.008	0.529	1.013
0.100[b]	0.316	0.538	0.913	0.505	0.968

[a] 25.0 °C; [monomer complex] = 1.0×10^{-3} M; [binuclear ion] = 1.0×10^{-4} M. [b] 20.0 °C; other conditions are the same.

No species having a λ_{max} near 450 or 500 nm with extinction coefficients of those of the products of reactions 4 and 1 were ever obtained by combining $(NH_3)_5Ru(pz)^{3+}$ and $Ru(CN)_6^{4-}$. The difference in the behavior of $(NH_3)_5Ru(pz)^{3+}$ with $(NH_3)_5Ru(3,5\text{-dimethylpyrazine})^{3+}$ would appear to be the lattice energy difference of the $[(NH_3)_5RuL^{2+}]_2[Ru(CN)_6^{4-}]$ or $[(NH_3)_5RuL^{2+}]_3[Ru(CN)_6^{3-}]_2$ salts that drives reaction 5 to the right and that prevents the presence of any appreciable concentration of the $[(NH_3)_5Ru(pz)^{3+},Ru(CN)_6^{4-}]^-$ ion pair in solution. Thus, the best estimate of the wavelength position and ϵ rests with the literature value of the ion pair with L = 3,5-dimethylpyrazine. Clearly the species formed by reaction 4 (λ_{max} = 450 nm) and its reduced form prepared via ascorbic acid reduction (λ_{max} = 500 nm) are not outer-sphere ion pairs. In addition (II,II) and (II,III) exhibit their own ion-exchange behavior that is different from mixtures where $(NH_3)_5Ru(pz)^{2+}$ or $(NH_3)_5Ru(pz)^{3+}$ is restricted to an outer-sphere role.

Electrochemical Studies. The differential-pulse voltammetry method was used to determine $E_{1/2}$ values for $(NH_3)_5Ru(pz)^{3+/2+}$, $(CN)_5Ru(pz)^{2-/3-}$, $(CN)_5Ru(pz)Ru(NH_3)_5^{0/-}$, and $(CN)_5Ru(pz)Ru(NH_3)_5^{+/0}$ in NaCl electrolyte solutions between 0.10 and 1.00 M. The data at 25.0 °C are reported in Table III. Plots of $E_{1/2}$ vs. $\mu^{-1/2}$ are linear. In the case of the cationic monomer complexes, $(NH_3)_5Ru(pz)^{3+/2+}$, the slope and intercept are found to be $+(1.552 \pm 0.046) \times 10^{-2}$ and 0.491 ± 0.009 V. The slope is negative for the anionic monomer complexes, $(CN)_5Ru(pz)^{2-/3-}$. The slope is found to be $-(2.310 \pm 0.195) \times 10^{-2}$, and the intercept is 1.027 ± 0.004 V. The intercepts of these plots represent the values of $E_{1/2}$ for these couples at high electrolyte concentration. For the binuclear complexes, $E(1)_{1/2}$ for (II,II) is found to be independent of $\mu^{-1/2}$, within experimental error, (slope $(7.44 \pm 7.91) \times 10^{-4}$, intercept 0.527 ± 0.002 V). The second one-electron potential, $E(2)_{1/2}$, for $(II,III)^{+/0}$ exhibits a slope of $-(1.426 \pm 0.597) \times 10^{-2}$ with an intercept of 1.013 ± 0.012 V. Note that $E(2)_{1/2}$ for $(II,III)^{+/0}$ behaves like that of an overall anionic complex as a function of $\mu^{-1/2}$. This suggests that substantial amounts of an ion pair formed with Cl^- exist in the range 0.10–1.00 M NaCl. The (II,III) complex should possess a large dipole moment since it has isolated 3+ and 3− components at a distance of about 6.9 Å. Such an ion could easily attract counterions at either end in a selective fashion.

The major observation from Table III is that $E(1)_{1/2}$ for the binuclear ion is nearly the same as $E_{1/2}$ for $(NH_3)_5Ru(pz)^{3+/2+}$. Again, $E(2)_{1/2}$ for the binuclear system is very close to the $E_{1/2}$ value for the $(CN)_5Ru(pz)^{2-/3-}$ couple. Considering the effect of electrolyte concentration on $E_{1/2}$ values, it appears that the presence of a second metal ion site across the pyrazine bridge influences the $E_{1/2}$ values very little. The implication from these results is that the metal centers are very weakly interactive, if at all (cf. ref 15). The same conclusion may be drawn from the absence of an IT band in the near-IR visible region of the spectrum of (II,III).

Note that $E(1)_{1/2}$ is 0.022 V higher than the $(NH_3)_5Ru(pz)^{3+/2+}$ couple at 1.00 M NaCl, but 0.011 V lower at 0.10 M as a consequence of a potential nearly independent of ionic strength for $(II,II)^{0/-}$ but a decreasing potential dependence for the $(NH_3)_5Ru(pz)^{3+/2+}$ couple. Arguments such as those brought forward by Meyer et al.[15] to account for a raised potential for $E_{1/2}$ of the $(NH_3)_5Ru(pz)RuCl(bpy)_2^{4+/3+}$ system would not seem appropriate here in that significantly different charge types are involved. Overall, there is a strong similarity in the electrochemical behavior of Meyer's ion[15] and the one of this report, leading to oxidation state assignments of $(NH_3)_5Ru^{III}(pz)Ru^{II}(CN)_5$ and $(NH_3)_5Ru^{III}(pz)Ru^{II}Cl(bpy)_2^{4+}$ for the mixed-valence species in each case.

Discussion

The position of the MLCT transition at 450 nm, the infrared data, and the electrochemical data support the $(NH_3)_5Ru$ site as the one that is oxidized for the mixed-valence $(NH_3)_5Ru^{III}(pz)Ru^{II}(CN)_5$ species. In this regard the present system is similar to Meyer's $(NH_3)_5Ru^{III}(pz)Ru^{II}Cl(bpy)_2^{4+}$ ion. However, no detectable intervalent transition appears in the near-IR region of the spectrum for $(NH_3)_5Ru^{III}(pz)Ru^{II}(CN)_5$, in contrast to Meyer's ion. It may be concluded that coupling between the Ru(II) and Ru(III) sites is very weak on this basis. As a result of the weak coupling, the $(NH_3)_5Ru(pz)Ru(CN)_5$ complex behaves in a spectral sense like the very weakly coupled $(NH_3)_5RuLRu(NH_3)_5^{5+}$ ions with L = 1,6-dicyanonaphthalene or 2,7-dicyanonaphthalene where very weak coupling prevents detection of the IT band and the interaction energy is below 50 cm^{-1}.[14]

It should be noted that Haim, Ludi, et al. reported that the $Fe^{II}(CN)_5$ analogue of (II,III) described in this report did not exhibit a near-IR band in freshly prepared samples other than a band at 1370 nm, which was attributed to sample decomposition.[34] Even for $Rh^{III}(NH_3)_5$ bridged to pyrazine and 4,4′-bipyridine complexes of $Fe(CN)_5^{3-}$, the binuclear ions exhibit the 1370-nm band in the Haim–Ludi study.[34] As the spectra were taken in KBr pellets, no estimate of the lower limit for ϵ of a near-IR transition with $(NH_3)_5Ru(pz)Fe(CN)_5$ could be made. In the case of $(NH_3)_5Ru(pz)Ru(CN)_5$ of this present report, we examined the near-IR region out to 1500 nm. No transition with an ϵ of greater than 50 M^{-1} cm^{-1} beyond 800 nm can be accommodated by the base lines in comparing the (II,III) and (II,II) spectra.

If data at T = 25.0 °C and μ = 0.10 are compared for $(NH_3)_5Ru(pz)Ru(CN)_5$ and $(NH_3)_5Ru(pz)RuCl(bpy)_2^{4+/3+}$, the values of $E(1)_{1/2}$ are reasonably similar: 0.529 vs. 0.61 V.[15] This is also true of the $E(2)_{1/2}$ oxidations: 0.972 vs. 1.03 V,[15] respectively. As pointed out by Hush, the energy of an intervalent transition for an unsymmetrical ion will equal the sum of the Franck–Condon energy (E_{FC}) and the difference in internal energy between the thermally equilibrated ion and its redox isomer (E_0). The complexes under consideration will be $(NH_3)_5Ru^{III}(pz)Ru^{II}(CN)_5$ and its redox isomer $(NH_3)_5Ru^{II}(pz)Ru^{III}(CN)_5$ in the present case. $E°$ will be about 0.3 V, following the arguments of Meyer[15] concerning the $(NH_3)_5Ru^{III}(pz)Ru^{II}Cl(bpy)_2^{4+}$ system and the similar electrochemical potentials for $(NH_3)_5Ru(pz)Ru(CN)_5^{0/-}$ and Meyer's ion. For the sake of discussion, first assume that the value of E_{FC} is probably similar for the cyanide and bipyridine systems. One may conclude that **if an IT band were to be observed** for the $(NH_3)_5Ru(pz)Ru(CN)_5$ complex, the band would appear near the 940-nm value of Meyer's ion. The absence of a band in this region emphasizes the weaker coupling for $(NH_3)_5Ru^{III}(pz)Ru^{II}(CN)_5$ relative to that for $(NH_3)_5Ru^{III}(pz)Ru^{II}Cl(bpy)_2^{4+}$ and the substantially weaker coupling of the title ion relative to that of $(NH_3)_5Ru(pz)Ru(NH_3)_5^{5+}$.

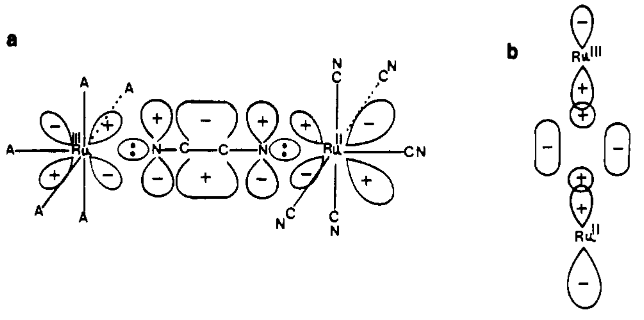

Figure 4. Pictorial representation of the molecular orbitals in $(NH_3)_5Ru^{III}(pz)Ru^{II}(CN)_5$: (a) side view; (b) top view.

The OSCT transitions for $Ru^{II}(CN)_6^{4-}$ ions paired with $(NH_3)_5Ru^{III}Cl^{2+}$ and $(NH_3)_5Ru(pz)^{3+}$ cations occur at 510 and 700 nm, respectively, with extinction coefficients of 20–50 M^{-1} cm^{-1}. Curtis and Meyer have argued rather convincingly that the OSCT excitation occurs across the ammine face of $(NH_3)_5RuL^{3+}$ over a distance of about 8.5 Å (K_{OS} = 2700 ± 300).[21,22] The interaction energy is found to be ca. 100–200 cm^{-1} with a detectable OSCT band. It is rather curious that, with the bridging pyrazine ring actually penetrating to the Ru^{II} center in $Ru(CN)_5$ of $(NH_3)_5Ru^{III}(pz)Ru^{II}(CN)_5$ giving a separation of ca. 6.9 Å, even less coupling to the $(NH_3)_5Ru^{III}$ occurs than is found for the related $[(NH_3)_5Ru^{III}(py)^{3+},Ru(CN)_6^{4-}]$ ion pair. This in turn suggests that the bridging pyrazine participates very unequally in its donation to the $(NH_3)_5Ru^{III}$ and $(CN)_5Ru^{II}$ sites of $(NH_3)_5Ru(pz)Ru(CN)_5$. Thus a shorter metal–metal distance will not necessarily produce a complex having an IT band. The extent of metal–metal interactions is expected to be controlled by both the bridging and nonbridging ligands that surround the ruthenium centers.[14c,15] In this case the interaction energy must have dropped from 3200 cm^{-1} in $(NH_3)_5Ru(pz)Ru(NH_3)_5^{5+}$ to well below 50 cm^{-1} in $(NH_3)_5Ru(pz)Ru(CN)_5$.

A reasonable explanation for the existence of IT bands for $(NH_3)_5Ru(pz)Ru(NH_3)_5^{5+}$ and $(NH_3)_5Ru(pz)RuCl(bpy)_2^{4+}$ and the OSCT bands for $[(NH_3)_5RuL^{3+},Ru(CN)_6^{4-}]$ ion pairs while $(NH_3)_5Ru(pz)Ru(CN)_5$ exhibits no apparent IT band is possible considering the degree of metal–metal orbital overlap in the various cases. Johnson and Shepherd showed that the percent ligand character in the ground-state Ru–pyrazine bond is about 22% for $(NH_3)_5Ru(pz)^{2+}$ and small (<10%) for $(CN)_5Ru(pz)^{3-}$.[17] The cyanide ligands compete very favorably with pyrazine, which makes d_π donation to the pyrazine small in $(CN)_5Ru(pz)^{3-}$; thus, the five CN^- ligands serve as withdrawing groups for the Ru^{II} d_π density. If the $(CN)_5Ru^{II}(pz)^{3-}$ unit is added to $(NH_3)_5Ru^{III}$, the relative metal orbital density along the axis bridged by pyrazine will be as shown pictorially in Figure 4a with the t_{2g} orbitals of the $Ru^{II}(CN)_5^{3-}$ site drawn back toward the cyanides and less available for π mixing with the pyrazine π^* level. The ring is viewed edge-on in Figure 4a, with the antibonding acceptor orbital of the pyrazine shown above and below the plane of the ring. The top view of the signs of the contributing 2p orbitals of the pyrazine ring atoms and d_{xz} orbitals of the Ru centers are shown in Figure 4b; each Ru is attached to one of the N's of the pyrazine ring by the in-plane σ-bonding electron pairs. The lobes of the t_{2g}^6 set of orbitals of the $Ru^{II}(CN)_5$ site in the direction of the pyrazine ring are diminished in size but still of proper sign for positive overlap with the π^* orbital of the bridging pyrazine. This is confirmed by the existence of the MLCT band at 450 nm. However, the reduced magnitude of the radial extension of the

t_{2g}^6 set of $Ru^{II}(CN)_5^{3-}$ in the direction along the bridging axis will allow less Ru^{II}–Ru^{III} through-space overlap of the metal orbitals than for $(NH_3)_5Ru(pz)Ru(NH_3)_5^{5+}$, which has its IT band at 1530 nm ($\epsilon \simeq 5000$ M^{-1} cm^{-1}). Meyer's ion, $(NH_3)_5Ru^{III}(pz)Ru^{II}Cl(bpy)_2^{4+}$, appears intermediate in the degree to which competition for $d_\pi \rightarrow pz$ or $d_\pi \rightarrow bpy$ back-donation can occur relative to that in $(NH_3)_5Ru(pz)Ru(NH_3)_5^{5+}$ and $(NH_3)_5Ru(pz)Ru(CN)_5$. In that pyrazine and bipyridine are closer as π acceptors than pyrazine and cyanide as ligands,[28] the intermediate nature as to how the t_{2g}^6 density is drawn away from the Ru^{II} center relative to NH_3 or CN^- is as one would anticipate.[29] Thus an IT band at 960 nm with a reduced ϵ of 530 M^{-1} cm^{-1} is consistent with less effective orbital contraction along the bridging direction for bpy at the Ru^{II} site than for CN^-, yet the influence of bpy as a withdrawing group vs. NH_3 is already detectable as lowering the metal–metal orbital contact.[29] In the extreme case of CN^- as the withdrawing group, the through-space Ru^{III} orbital–Ru^{II} orbital interaction should decrease below that of Meyer's ion. Thus the extinction coefficient as a measure of the extent of mixing approaches zero for $(NH_3)_5Ru(pz)Ru(CN)_5$. An interesting study by Cloninger and Callahan[32] has shown that, with the symmetrical binuclear ions using substituted phenanthroline ligands to replace the NH_3's and bpy's of Meyer's ion, no discernible decrease in the comproportionation constant (or its free energy) is observed if substituents of the phenanthroline change from $-NO_2$ to $-H$ to $-CH_3$. Yet a decrease in extinction coefficient for the IT band is observed: $-NO_2$, 458 M^{-1} cm^{-1}; $-H$, 650 M^{-1} cm^{-1}; $-CH_3$, 735 M^{-1} cm^{-1}. These results suggest that the influence of CN^- as a withdrawing ligand in $(NH_3)_5Ru(pz)Ru(CN)_5$ is much greater than a substituent effect found for substituted N-heterocyclic nonbridging ligands.

It is intriguing that no near-IR band attributed to the intervalent transition is observed for either $(NH_3)_5Ru(pz)Ru(CN)_5$ or $(NH_3)_5Ru(pz)Fe(CN)_5$. We cannot rule out completely the possibility that an IT band might be shifted to very high energy relative to those of $(NH_3)_5Ru(pz)Ru(NH_3)_5^{5+}$ and $(NH_3)_5Ru(pz)RuCl(bpy)_2^{4+}$ and remain hidden for $(NH_3)_5Ru(pz)Ru(CN)_5$ under the MLCT band near 450 nm. The MLCT band of (II,III) has an ϵ of 5.8×10^3 M^{-1} cm^{-1}, which would bury an IT band of $\epsilon \lesssim 50$ M^{-1}, assuming at least another order of magnitude reduction in ϵ relative to that of Meyer's ion due to poorer orbital interaction. As assumed previously, the energy of this transition is probably near that of Meyer's ion on the basis of similar $E_{1/2}$ values and even approximately equal values for Franck–Condon barriers. The difference between a IT band at 960 nm for Meyer's ion and a "buried IT" band at 600 nm under the low-energy tail of the 450-nm MLCT transition would infer a difference to be made up by *additional* Franck–Condon factors of ca. 17 kcal/mol for CN^- vs. bpy. This seems unrealistically high as inner-sphere reorganization (λ_i) is about 10–16 kcal/mol for Creutz–Taube or Meyer type systems previously studied.[29] Outer-sphere reorganizations (λ_o) frequently range between 6 and 10 kcal/mol. Thus the total barrier, λ, is usually near 24 kcal/mol. Ion pairs such as $[(NH_3)_5RuL^{3+},Ru(CN)_6^{4-}]^-$ exhibit OSCT bands that have been shown to indicate similar λ values[21] (18.4 kcal/mol, L = py). Ion pairs of this type have charge distributions similar to that of $(NH_3)_5Ru(pz)Ru(CN)_5$. It is reasonable to assume that these ion pairs should have a reasonable approximation to the environmental factors that establish solvation and ion association for the ground-state $(NH_3)_5Ru(pz)Ru(CN)_5$ complex. The value of λ_o (12.5 kcal/mol for L = py) in the ion pair should give an approximate value valid for $(NH_3)_5Ru(pz)Ru(CN)_5$. The values found for λ_i with an additional spin–orbit barrier account for another 6 kcal/mol barrier. Thus λ, λ_o, and λ_i for the ion pairs are comparable in magnitude and not significantly larger than those reported for the pyrazine-bridged mixed-valence ions, and it would not appear likely that an additional 17 kcal/mol or more could be found in Franck–Condon factors. The absence of a detectable band is more likely due to an even lower value of ϵ, which infers very poor coupling of the Ru^{II} and Ru^{III} centers for $(NH_3)_5Ru(pz)Ru(CN)_5$.

The existence of OSCT bands for $[(NH_3)_5RuL^{3+},Ru(CN)_6^{4-}]$ ion pairs in the region 600–700 nm[21] might at first appear to be a problem concerning its apparent absence in $(NH_3)_5Ru(pz)Ru(CN)_5$. In the binuclear ion the Ru–Ru distance (ca. 6.9 Å) will be less than in the ion pairs, bound across the ammine and cyanide faces of $(NH_3)_5RuL^{3+}$ and $(CN)_6Ru^{4-}$ components (ca. 9 Å).[21] Again the result is consistent if one adopts an orbital overlap view of these ion pairs vs. the one for $(NH_3)_5Ru(pz)Ru(CN)_5$ in Figure 4a. In the ion pair the $Ru(CN)_6^{4-}$ site has its t_{2g}^6 density symmetrically placed. Thus *on formation of the ion pair, the radial extension of the filled d_π orbital pointing toward the Ru^{III} acceptor will actually be larger than for the analogous $Ru(CN)_5^{3-}$ site of $(NH_3)_5Ru(pz)Ru(CN)_5$.* Therefore, the statement that the distance between sites may be shorter than for $[(NH_3)_5RuL^{3+},Ru(CN)_6^{4-}]$ with no IT band detected for $(NH_3)_5Ru(pz)Ru(CN)_5$ is not at odds with the great body of previous work on Creutz–Taube type ions. It amplifies the fact that direct metal orbital–metal orbital interaction is an important component leading to the existence of intervalent transitions in such molecules and that the extent of this overlap is the primary factor, not the distance of separation.[31] Of course in most cases the degree of overlap will be enhanced by the shortest distance between metal centers except in cases where the "spectator ligands" so polarize the electron density to severely alter the radial extension of the d_π density in a specific direction.

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Registry No. $(NH_3)_5Ru(pz)^{2+}$, 19471-65-9; $(CN)_5RuOH_2^{3-}$, 74009-27-1; $(NH_3)_5Ru(pz)Ru(CN)_5^-$, 96455-65-1; $(CN)_5Ru(pz)^{3-}$, 96455-66-2; $(NH_3)_5RuOH_2^{2+}$, 21393-88-4; $Ru(CN)_5(pz)Fe(CN)_5^{6-}$, 96481-46-8; $(NH_3)_5Ru(pz)Ru(CN)_5$, 96455-67-3; $(NH_3)_5Ru(pz)^{3+}$, 38139-16-1; $S_2O_8^{2-}$, 15092-81-6; PbO_2, 1309-60-0; Br_2, 7726-95-6; $(NH_3)_4(H_2O)Ru(pz)Ru(CN)_5$, 96455-68-4; $(CN)_5Ru(pz)^{2-}$, 96455-69-5; $(CN)_5Ru(pz)Ru(NH_3)_5^+$, 96455-70-8.