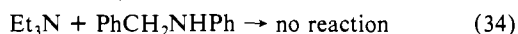


transalkylation in anhydrous alcoholic media. However, in aqueous media the reaction does proceed but not in the absence of benzaniline or benzaldehyde.



$\text{Fe}(\text{CO})_5$  does not catalyze C for H exchange on aliphatic amines.<sup>49</sup> Consequently, in (35) benzaldehyde must activate the catalyst and/or the amine to promote transalkylation perhaps by electron transfer. We have independently noted that we can promote transalkylation and reaction (35) by using *ruthenium catalysts and water* with mononuclear ruthenium catalysts.<sup>49</sup> Deuteration and product selectivity studies reveal an additional and different transalkylation mechanism that can be promoted in the presence of  $\text{H}_2\text{O}$ . This mechanism appears to be quite different from the mechanism described here, which works best

(49) Blum, Y.; Wilson, R. B.; Laine, R. M.; Shvo, Y., unpublished results.

in the *absence of water* (see Figure 4) and under CO.

We will report on the second mechanism together with some anomalies noted in the above studies at a later date.<sup>49</sup>

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**Registry No.**  $\text{Ru}_3(\text{CO})_{12}$ , 15243-33-1;  $\text{Fe}(\text{CO})_5$ , 13463-40-6;  $\text{Me}_3\text{N}$ , 75-50-3;  $\text{Et}_3\text{N}$ , 121-44-8;  $\text{Pr}_3\text{N}$ , 102-69-2;  $N,N,N',N'$ -tetramethylethylenediamine, 110-18-9;  $N,N$ -dimethylpiperazine, 106-58-1;  $N,N,N',N'$ -tetraethylethylenediamine, 150-77-6;  $N,N,N',N',N''$ -pentaethyldiethylenetriamine, 24426-21-9;  $N,N,N',N',N'',N'''$ -hexaethyldiethylenetetramine, 24426-32-2; perethyltetraethylenepentamine, 93783-07-4.

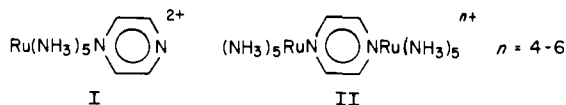
## Aqueous Solution Chemistry of $\mu$ -Pyrazinepentaammineruthenium(II,III) Pentacyanoferrate(II,III): Formation, Redox Reactions, and Intervalence Properties<sup>1</sup>

Andrew Yeh and Albert Haim\*

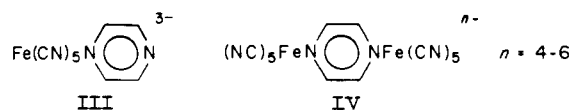
Contribution from the Department of Chemistry, State University of New York, Stony Brook, New York 11794-3400. Received July 3, 1984

**Abstract:** Several pyrazine (pz) bridged binuclear complexes of the general formula  $(\text{NC})_5\text{MpzM}'(\text{NH}_3)_5^n$  were prepared in aqueous solution via the substitution reactions  $\text{M}(\text{CN})_5\text{OH}_2^{n-} + \text{M}'(\text{NH}_3)_5\text{pz}^{n+} = (\text{NC})_5\text{MpzM}'(\text{NH}_3)_5^n$ , where  $\text{M} = \text{Fe}(\text{II,III})$  or  $\text{Co}(\text{II,III})$  and  $\text{M}' = \text{Ru}(\text{II,III})$  or  $\text{Rh}(\text{III})$ . All the complexes containing Fe(II) and/or Ru(II) are intensely colored substances, displaying a metal-to-ligand charge-transfer band in the 500–600-nm region. Rate constants for the formation and dissociation of the binuclear complexes with  $\text{M} = \text{Fe}(\text{II})$  were measured. Selected redox reactions of two of the binuclear complexes, namely,  $(\text{NC})_5\text{FepzRu}(\text{NH}_3)_5^n$  ( $V$ ) ( $n = 1-, 0$ ), were studied in some detail. Cyclic voltammetry of  $V$  ( $n = 1-$ ) shows that its oxidation proceeds in two one-electron steps at 0.72 and 0.49 V, respectively. Chemical oxidation of  $V$  ( $n = 1-$ ) with peroxydisulfate (second-order reaction with rate constant  $(3.79 \pm 0.04) \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$  at 25 °C, pH 4.28, and ionic strength 0.10 M) yields  $V$  ( $n = 0$ ). The latter complex exhibits its metal-to-ligand charge-transfer band at 590 nm with molar absorbance  $\sim 10^4 \text{ M}^{-1} \text{ cm}^{-1}$  and an intervalence band (in  $\text{D}_2\text{O}$ ) at 1650 nm with molar absorbance  $1.55 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$  and half-width  $0.43 \mu\text{m}^{-1}$ . Spectroscopic, electrochemical, and kinetic data on  $V$  ( $n = 0$ ) are interpreted on the basis of a trapped valence formulation containing the localized oxidation states Fe(II) and Ru(III). The stability of the mixed valence state  $V$  ( $n = 0$ ) with respect to electronic isomerization ( $V$  with  $n = 0$  but with localized valences Fe(III) and Ru(II)) and with respect to disproportionation to form the isoivalent states  $V$  ( $n = 1-$ ) and  $V$  ( $n = 1+$ ) is discussed in some detail.

The feature that dominates the chemistry of the pentaammine-ruthenium(II) moiety is its ability to enter into  $\pi$ -bonding interactions with appropriate ligands, e.g., dinitrogen,<sup>2</sup> pyridines,<sup>3</sup> and nitriles.<sup>4</sup> One of the consequences of the  $\pi$ -donating ability of  $\text{Ru}(\text{NH}_3)_5^{2+}$  is the increased basicity<sup>2</sup> of the remote nitrogen atom in I. This led to the syntheses<sup>5</sup> of the binuclear complexes



II. Since then a great deal of work has been devoted to this system, in particular to the mixed valence ion with  $n = 5$ .<sup>6</sup> The nitrogen heterocyclic chemistry<sup>3</sup> of  $\text{Ru}(\text{NH}_3)_5^{2+}$  has been duplicated<sup>7</sup> with the isoelectronic moiety  $\text{Fe}(\text{CN})_5^{3-}$ . In particular, the basicity of the remote nitrogen in III was noted,<sup>7</sup> and the syntheses of the binuclear complexes IV were reported.<sup>8</sup>



In the work referenced above, the primary concerns have been synthetic and structural.<sup>6</sup> In particular, the electronic structures of the mixed valence ions have been the subject of much work.<sup>6</sup> In view of our long standing interest in the dynamic solution

(1) This work was supported by Grants CHE 79709253 and CHE 8203887 from the National Science Foundation.

(2) Harrison, D. F.; Weissberger, E.; Taube, H. *Science (Washington, D. C.)* **1968**, *159*, 320.

(3) Ford, P. C.; Rudd, D. F. P.; Gaunder, R. G.; Taube, H. *J. Am. Chem. Soc.* **1968**, *90*, 1187.

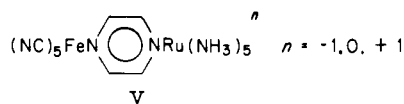
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(7) Toma, H. E.; Malin, J. M. *Inorg. Chem.* **1973**, *12*, 1039

behavior of heterobinuclear complexes,<sup>9</sup> we began a mechanistic study centered on complexes V. In the present paper we report



studies on the formation, dissociation, and some redox reactions of complexes V, with emphasis being placed on the characterization of the mixed valence molecule V with  $n = 0$ . Analogues of V where Fe is replaced by Co or Ru by Rh have also been prepared and characterized. Similar studies, but using 4,4'-bipyridine as a bridging ligand, have also been carried out. In some instances, the compounds are too insoluble to permit solution studies. The solid-state work in this class of compounds was reported earlier.<sup>10</sup>

### Experimental Section

**Materials.** Sodium aminopentacyanoferrate(II) trihydrate and sodium aminopentacyanoferrate(III) monohydrate were prepared by following standard procedures.<sup>11</sup> The former compound was purified as described earlier.<sup>12</sup> The preparation of solutions containing  $\sim 2 \times 10^{-4}$  M  $\text{Fe}(\text{CN})_5\text{OH}_2^{2-}$  followed the literature method.<sup>13</sup> The syntheses of mononuclear ruthenium and rhodium complexes were as reported earlier.<sup>10</sup> Solutions of  $(\text{NC})_5\text{Fe}^{\text{II}}\text{pzRu}^{\text{III}}(\text{NH}_3)_5^-$  were obtained by mixing a solution of  $\text{Fe}(\text{CN})_5\text{OH}_2^{2-}$  ( $< 1 \times 10^{-4}$  M) with a solution containing a 2-fold excess of  $\text{Ru}(\text{NH}_3)_5\text{pz}^{2+}$ . The resulting solution was passed through a column of Sephadex CM 25 cation-exchange resin. All the operations were carried out at 10 °C and in the absence of light and oxygen. Solutions of  $(\text{NC})_5\text{Co}^{\text{III}}\text{pzRu}^{\text{II}}(\text{NH}_3)_5$  were obtained by reaction ( $\sim 8$  h) of  $\text{Co}(\text{CN})_5\text{OH}_2^{2-}$  ( $\sim 2 \times 10^{-3}$  M, prepared by aqution of  $\text{Co}(\text{CN})_5\text{Cl}^{3-14}$ ) with an equimolar amount of  $\text{Ru}(\text{NH}_3)_5\text{pz}^{2+}$  at 56 °C under argon. The purifications of the water, argon, and lithium perchlorate were described previously.<sup>15</sup> All other materials were of reagent grade and used as received.

**Kinetic Measurements.** Rates of formation of the binuclear complexes  $(\text{NC})_5\text{Fe}^{\text{II}}\text{LRu}^{\text{III}}(\text{NH}_3)_5^-$  (L = pyrazine or 4,4'-bipyridine) and  $(\text{NC})_5\text{Fe}^{\text{II}}\text{pzRh}^{\text{III}}(\text{NH}_3)_5$  were measured by mixing freshly prepared solutions of  $\text{Fe}(\text{CN})_5\text{OH}_2^{2-}$  with an excess of  $\text{Ru}^{\text{II}}(\text{NH}_3)_5\text{L}^{2+}$  or  $\text{Rh}(\text{NH}_3)_5\text{pz}^{2+}$  in a Durrum D-110 stopped-flow instrument interfaced to an IBM 1800 computer. The measurements were carried out by following the absorbance increase near or at the maximum wavelength for the binuclear complex. Rates of oxidation of the ruthenium(II) complexes were measured by mixing the desired complex with an excess of peroxydisulfate in the stopped-flow apparatus. The measurements were carried out by following the absorbance decrease at the maximum wavelength for the ruthenium complex. Rates of dissociation of the binuclear complexes were measured by adding an excess of pyridine to a solution of the complex and following the slow, subsequent absorbance decrease at the maximum wavelength for the complex. The measurements were carried out in a Cary 17 or 118 recording spectrophotometer equipped with a thermostated cell compartment modified as described previously.<sup>16</sup> All the kinetic measurements were carried out at 25 °C and ionic strength 0.10 M (lithium perchlorate). Observed rate constants were calculated by least-squares fitting of  $\ln(A_t - A_\infty)$  to time.  $A_t$  and  $A_\infty$  are the absorbances at time  $t$  and at the completion of the reaction.

**Electrochemical Measurements.** A Princeton Applied Research Corp. Model 170 electrochemistry system was employed in the cyclic voltammetry measurements. Cyclic voltammograms were obtained at sweep rates varying from 20 to 200 mV/s, using platinum wires as counter-electrode and working electrode and a saturated calomel electrode as the reference. Solutions were kept at 25 °C in a PAR cell Type 9300 and were  $(1-5) \times 10^{-4}$  M in the electroactive species and 0.10 M in lithium perchlorate.

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(15) Szecsy, A. P.; Haim, A. *J. Am. Chem. Soc.* **1981**, *103*, 1679.

(16) Miralles, A. J.; Armstrong, R. E.; Haim, A. *J. Am. Chem. Soc.* **1977**, *99*, 1416.

**Table I.** Absorption Spectra of Iron(II) and Ruthenium(II) Pyrazine (pz) and 4,4'-Bipyridine Complexes (bpy)

complex	$\lambda_{\text{max}}$		log $\epsilon$		ref
	pz	bpy	pz	bpy	
$\text{Fe}^{\text{II}}(\text{CN})_5\text{L}^{3-}$	452	437	3.70	3.75	a
$\text{Fe}^{\text{II}}(\text{CN})_5\text{LH}^{2-}$	$\sim 625$	$\sim 505$			b, c
$\text{Ru}^{\text{II}}(\text{NH}_3)_5\text{L}^{2+}$	474	482	4.26	4.08	d, e
$\text{Ru}^{\text{II}}(\text{NH}_3)_5\text{LH}^{3+}$	528	563	4.11	4.14	d, e
$(\text{NC})_5\text{Fe}^{\text{II}}\text{LRu}^{\text{III}}(\text{NH}_3)_5^-$	522	497	4.36	4.26	this work
$(\text{NC})_5\text{Fe}^{\text{II}}\text{LRu}^{\text{III}}(\text{NH}_3)_5$	$\sim 590$	505 <sup>f</sup>	4		this work
$(\text{NC})_5\text{Fe}^{\text{II}}\text{LRh}^{\text{III}}(\text{NH}_3)_5$	576 <sup>g</sup>	515 <sup>f</sup>	4.03 <sup>g</sup>		this work
$(\text{NC})_5\text{Co}^{\text{III}}\text{LRu}^{\text{II}}(\text{NH}_3)_5$	520	532 <sup>f</sup>	4.24		this work

<sup>a</sup> Reference 7. <sup>b</sup> Johnson, C. R.; Shepherd, R. E. *Inorg. Chem.* **1983**, *22*, 1117. <sup>c</sup> Gaswick, D. E.; Haim, A. *J. Am. Chem. Soc.* **1974**, *95*, 7845. <sup>d</sup> Reference 20. <sup>e</sup> Fleischer, E. B.; Lavallee, D. K. *J. Am. Chem. Soc.* **1972**, *94*, 2599. <sup>f</sup> Solid-state spectrum, ref 10. <sup>g</sup> Compare with  $\lambda_{\text{max}} = 572$  nm and log  $\epsilon = 3.97$ , ref 27.

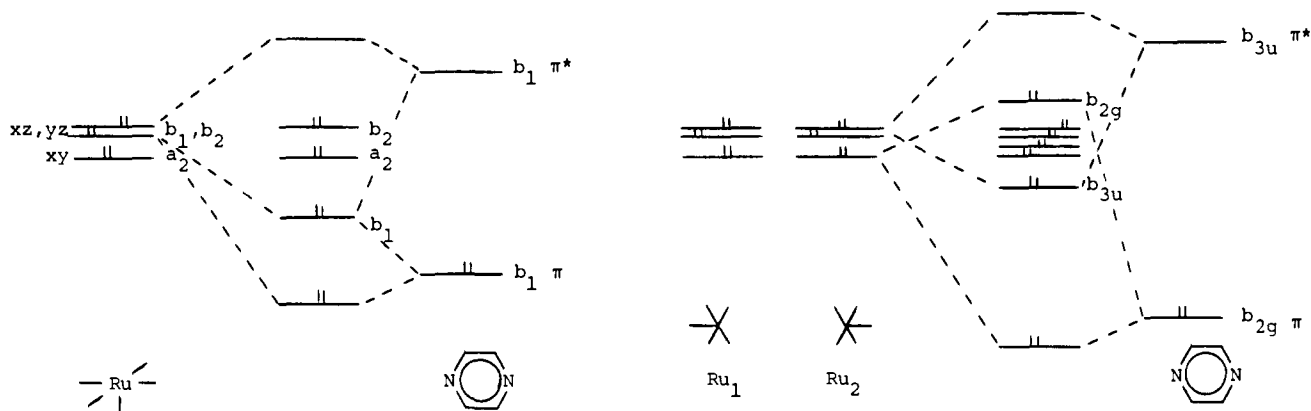
### Results and Discussion

At the outset it is necessary to state the conditions chosen to handle the solutions utilized in the present work. Cyanoferrate(II) and aminoruthenium(III) complexes with nitrogen heterocycles have different pH regions of stability. Below pH 4, the iron complexes begin to protonate and are susceptible to oxidation by dioxygen. Above pH 6, the ruthenium(III) complexes generate ruthenium(II) via poorly understood disproportionation reactions. Many if not all of the complexes are photosensitive. Therefore, as a matter of routine, solutions were handled under an atmosphere of argon, in subdued light and in the pH range 4-6.

**Absorption Spectra and the Electronic Structure of  $(\text{NC})_5\text{Fe}^{\text{II}}\text{pzRu}^{\text{III}}(\text{NH}_3)_5$ .** All the ruthenium(II) and iron(II) complexes with nitrogen heterocycles utilized in the present work exhibit characteristic MLCT bands in the visible region with molar absorbances of several thousands inverse molar inverse centimeters. The bands are sensitive to substituent effects<sup>3,7</sup> and disappear upon oxidation. In Table I we list the spectral features of interest in the present work. It will be seen that the addition of an electron withdrawing substituent to the remote nitrogen of the mononuclear pyrazine or 4,4'-bipyridine complexes results in shifts of the MLCT bands toward lower energies, the effect being considerably more pronounced for the iron(II) than for the ruthenium(II) complexes.<sup>10</sup> Except for complex V ( $n = 0$ ) and for the analogue of V ( $n = 0$ ) where pyrazine is replaced by 4,4'-bipyridine, the oxidation states of the metal centers in the binuclear complexes listed in Table I can be assigned with confidence. Since oxidation states other than +3 for the metal centers in the pentaammine-ruthenium and pentacyanocobaltate moieties are thermodynamically unstable, the oxidation states of iron and ruthenium in  $(\text{NC})_5\text{Fe}^{\text{II}}\text{pzRh}^{\text{III}}(\text{NH}_3)_5$  and in  $(\text{NC})_5\text{Co}^{\text{III}}\text{pzRu}^{\text{II}}(\text{NH}_3)_5$  are as indicated.

There is uncertainty in the assignment of the oxidation states of iron and ruthenium for complex V ( $n = 0$ ), e.g., a delocalized situation or trapped valences such as  $\text{Fe}(\text{II})\text{-Ru}(\text{III})$  or  $\text{Fe}(\text{II})\text{-Ru}(\text{II})$  could obtain. In trying to distinguish between the alternative formulations, it is instructive to consider first the shifts in the MLCT bands that occur in systems with well-defined oxidation states. The 452-nm band of  $\text{Fe}^{\text{II}}(\text{CN})_5\text{pz}^{3-}$  is shifted to 576 nm upon coordination of the exposed nitrogen to  $\text{Rh}^{\text{III}}(\text{NH}_3)_5\text{L}^{3+}$ . Similarly, the 474-nm band of  $\text{Ru}^{\text{II}}(\text{NH}_3)_5\text{pz}^{2+}$  is shifted to 520 nm when the remote nitrogen is bound to  $\text{Co}^{\text{III}}(\text{CN})_5^{2-}$ . Taking the values 576 nm and 520 nm as representing  $\text{Fe}^{\text{II}}\text{pz}$  and  $\text{Ru}^{\text{II}}\text{pz}$  MLCT bands shifted by coordination of the remote nitrogen to a non- $\pi$ -bonding, electropositive +3 metal center, the observed value of  $\sim 590$  nm for complex V ( $n = 0$ ) is taken to indicate the presence of  $\text{Fe}(\text{II})$  and  $\text{Ru}(\text{III})$  oxidation states. The somewhat larger shift for  $\text{Ru}(\text{III})$  as compared to  $\text{Rh}(\text{III})$  is consistent with the  $\pi$ -acceptor properties of the former.<sup>17</sup> The infrared spectral measurements of solid samples<sup>10</sup> of  $(\text{NC})_5\text{Fe}^{\text{II}}\text{pzRu}^{\text{III}}(\text{NH}_3)_5$  in the cyanide stretching and symmetric ammonia deformation regions also confirm the above assignment

(17) Elias, J. H.; Drago, R. *Inorg. Chem.* **1972**, *11*, 415.

Chart I. Molecular Orbital Diagram for  $\text{Ru}(\text{NH}_3)_5\text{pz}^{2+}$  and  $(\text{NH}_3)_5\text{RupzRu}(\text{NH}_3)_5^{4+}$ Table II. Reduction Potentials of Iron(III) and Ruthenium(III) Complexes<sup>a</sup>

couple	$E_{1/2}$ , V	
	pz	bpy
$\text{Fe}^{3\text{II}/\text{I}}(\text{CN})_5\text{L}^{2-/3-}$	0.55, <sup>b</sup> 0.66 <sup>c</sup>	0.46, <sup>d</sup> 0.51 <sup>c</sup>
$\text{Ru}^{3\text{II}/\text{I}}(\text{NH}_3)_5\text{L}^{3+/2+}$	0.52, 0.49 <sup>e</sup>	0.34, <sup>f</sup> 0.33 <sup>c</sup>
$(\text{NC})_5\text{Fe}^{\text{II}/\text{I}}\text{LRu}^{\text{III}}(\text{NH}_3)_5^{1+/0}$	0.72	0.64 <sup>g,h</sup>
$(\text{NC})_5\text{Fe}^{\text{II}}\text{LRu}^{\text{III}/\text{II}}(\text{NH}_3)_5^{0/1-}$	0.49	0.31 <sup>g</sup>
$(\text{NC})_5\text{Fe}^{\text{III}/\text{II}}\text{LRh}^{\text{III}}(\text{NH}_3)_5^{1+/0}$	0.71, 0.71 <sup>c</sup>	0.52 <sup>c</sup>
$(\text{NC})_5\text{Co}^{\text{III}}\text{LRu}^{\text{III}/\text{II}}(\text{NH}_3)_5^{1+/0}$	0.64	

<sup>a</sup>At 25 °C, 0.10 M ionic strength ( $\text{LiClO}_4$ ), and pH 4.28 (acetate buffer). Separation between anodic and cathodic peak potentials = 60–80 mV. <sup>b</sup>From ref 7. <sup>c</sup>In 1 M KCl, ref 19. <sup>d</sup>Phillips, J.; Haim, A. *Inorg. Chem.* **1980**, *19*, 1616. <sup>e</sup>In 1 M NaCl; Lim, H. S.; Barclay, D. J.; Anson, F. C. *Inorg. Chem.* **1972**, *11*, 1460. <sup>f</sup>Phillips, J.; Haim, A. *Inorg. Chem.* **1980**, *19*, 76. <sup>g</sup>At pH 6.16 (phosphate buffer). <sup>h</sup>No cathodic wave observed; value estimated from  $E_{p,c} + \Delta E_p$ , with  $\Delta E_p = 60$  mV.

of oxidation states and moreover serve to rule out the delocalized formulation.<sup>18</sup> Entirely analogous arguments can be brought forth to support the assignment of +2 and +3 oxidation states to iron and ruthenium, respectively, in  $(\text{NC})_5\text{Fe}^{\text{II}}\text{bpyRu}^{\text{III}}(\text{NH}_3)_5$ .

Additional evidence in favor of a localized formulation featuring Fe(II) and Ru(III) in complex V ( $n = 0$ ) comes from a consideration of the reduction potentials of the various couples. The relevant values are listed in Table II. It will be seen that the reduction potentials of  $(\text{NC})_5\text{Fe}^{\text{II}}\text{pzRh}^{\text{III}}(\text{NH}_3)_5^{19}$  and of  $(\text{NC})_5\text{Co}^{\text{III}}\text{pzRu}^{\text{III}}(\text{NH}_3)_5$  are 0.71 and 0.64 V, respectively. Since the reductions of Co(III) or Rh(III) require much more negative potentials, the observed values are taken to be a measure of the oxidizing abilities of the  $\text{Fe}^{\text{II}}(\text{CN})_5\text{pz}^{3-}$  and  $\text{Ru}^{\text{III}}(\text{NH}_3)_5\text{pz}^{3+}$  moieties with the remote pyrazine nitrogen coordinated to a tripositive electron withdrawing tripositive metal center,  $\text{Rh}^{\text{III}}(\text{NH}_3)_5^{3+}$  or  $\text{Co}^{\text{III}}(\text{CN})_5^{2-}$ , respectively. The observed value for the one-electron reduction of  $(\text{NC})_5\text{Fe}^{\text{II}}\text{pzRu}^{\text{III}}(\text{NH}_3)_5^{19}$ , 0.72 V, is almost identical with the value for the Fe(III)–Rh(III) complex where reduction occurs at the Fe(III) center. The comparison indicates that the electroactive metal center in  $(\text{NC})_5\text{Fe}^{\text{II}}\text{pzRu}^{\text{III}}(\text{NH}_3)_5^{19}$  is Fe(III) as well, and, therefore, we infer that complex V ( $n = 0$ ) features trapped Fe(II) and Ru(III) valences.<sup>20,21</sup>

(18) It is noteworthy that the MLCT bands of  $(\text{NC})_5\text{Fe}^{\text{II}}\text{pzRu}^{\text{III}}(\text{NH}_3)_5^{19}$  and  $(\text{NC})_5\text{Co}^{\text{III}}\text{pzRu}^{\text{III}}(\text{NH}_3)_5$  occur at virtually the same energy (522 and 520 nm, respectively). Since the orbitals utilized in  $\pi$  bonding by iron(II) are 3d whereas those utilized by ruthenium(II) are 4d and, in addition, in view of the strong  $\pi$ -accepting ability of the cyanide ligands, it is expected that the competition between Fe(II) and Ru(II) for  $\pi$  bonding to the pyrazine bridge will be strongly in favor of Ru(II). Under these circumstances, the pentacyanoferrate moiety acts just as a  $\sigma$  acid, in the same way as the non- $\pi$ -bonding pentacyanocobaltate moiety. Thus, although for complex V ( $n = -1$ ), where the molecular orbital treatment presented by Lauher (Lauher, *J. Inorg. Chim. Acta* **1980**, *39*, 119) would be applicable, the localized formulation represents a good approximation.

(19) Moore, K. J.; Lee, L.; Mabbott, G. A.; Petersen, J. D. *Inorg. Chem.* **1983**, *22*, 1108.

Table III. Reduction Potentials of  $\text{Ru}^{\text{III}}(\text{NH}_3)_5\text{L}$  and  $\text{Ru}^{\text{III}}(\text{EDTA})\text{L}$  Complexes<sup>a</sup>

	$\text{Ru}^{\text{III}}(\text{NH}_3)_5\text{L}^b$		$\text{Ru}^{\text{III}}(\text{EDTA})\text{L}^c$	
	L	$E^\circ$	L	$E^\circ$
pz		0.52	pz	0.24
$\text{pzCH}_3^+$		0.87	$\text{pzCH}_3^+$	0.50
$\text{pzH}^+$		0.69	$\text{pzRh}^{\text{III}}(\text{NH}_3)_5^{3+}$	0.37
$\text{pzRh}^{\text{III}}(\text{NH}_3)_5^{3+}$		0.71	$\text{pzRh}^{\text{III}}(\text{EDTA})^-$	0.28
$\text{pzRh}^{\text{III}}(\text{EDTA})^-$		0.67	$\text{pzRu}^{\text{III}}(\text{EDTA})^-$	0.32
$\text{pzCo}^{\text{III}}(\text{CN})_5^{2-}$		0.67	$\text{pzRu}^{\text{II}}(\text{EDTA})^{2-}$	0.18
$\text{pzRu}^{\text{III}}(\text{EDTA})^-$		0.56		
$\text{pzRu}^{\text{III}}(\text{NH}_3)_5^{3+}$		0.74		
$\text{pzRu}^{\text{II}}(\text{NH}_3)_5^{2+}$		0.35		
$\text{pzFe}^{\text{II}}(\text{CN})_5^{3-}$		0.49		

<sup>a</sup>At 25 °C and ionic strength 0.10 or 0.20 M. <sup>b</sup>From ref 20 or present work. <sup>c</sup>Creutz, C.; Kroger, P.; Matsubara, T.; Netzel, T. L.; Sutin, N. *J. Am. Chem. Soc.* **1979**, *101*, 5442.

Additional comparisons, relevant to the electronic structure of complex V ( $n = 0$ ), relate to its reduction potential which, in the trapped valence formulation given above, corresponds to reduction of Ru(III) to Ru(II). The pertinent data is presented in Table III. It will be seen that, in general, addition of a Lewis acid to the remote N of  $\text{Ru}^{\text{III}}(\text{NH}_3)_5\text{pz}^{3+}$  or  $\text{Ru}^{\text{III}}(\text{EDTA})\text{pz}^-$  results in an increase in the reduction potential of the complex. The lowering of the ligand  $\pi^*$  orbital by the electron withdrawing substituent is accompanied by stabilization of the +2 oxidation state via d  $\pi$ -to-ligand  $\pi^*$  bonding.<sup>22</sup> It will be seen that this trend applies to all the substituents except for  $\text{Fe}^{\text{II}}(\text{CN})_5^{3-}$  and  $\text{Ru}^{\text{II}}(\text{NH}_3)_5^{2+}$  on  $\text{Ru}^{\text{III}}(\text{NH}_3)_5\text{pz}^{3+}$  and for  $\text{Ru}^{\text{II}}(\text{EDTA})^{2-}$  on  $\text{Ru}^{\text{III}}(\text{EDTA})\text{pz}^-$ . Coordination of the remote pyrazine nitrogen in  $\text{Ru}^{\text{III}}(\text{NH}_3)_5\text{pz}^{3+}$  to  $\text{Fe}^{\text{II}}(\text{CN})_5^{3-}$  or  $\text{Ru}^{\text{II}}(\text{NH}_3)_5^{2+}$  results in a decrease in the reduction potential, the effect being larger for ruthenium(II) than for iron(II). Similarly, coordination of the remote N in  $\text{Ru}^{\text{III}}(\text{EDTA})\text{pz}^-$  to  $\text{Ru}^{\text{II}}(\text{EDTA})^{2-}$  decreases the potential.<sup>23</sup> These substituents are acting as Lewis acids and remove electron density through the  $\sigma$  framework (just like all the other substituents in Table III) but return electron density via the  $\pi$  framework. Since the  $\text{Ru}^{\text{II}}(\text{NH}_3)_5^{2+}$  moiety is a stronger  $\pi$  base than  $\text{Fe}^{\text{II}}(\text{CN})_5^{3-}$ ,<sup>7</sup> the decrease in reduction potential is more pronounced for the former than for the latter. Note that the order is opposite to that predicted on the basis of simple electrostatic charge effects.<sup>19</sup> An alternate, but equivalent way of viewing this effect was discussed by Sutton and Taube<sup>21</sup> in their enumeration of the factors that account for the stability of the mixed valence state  $(\text{NH}_3)_5\text{Ru}^{\text{II}}\text{pzRu}^{\text{III}}(\text{NH}_3)_5^{3+}$  compared to the corresponding isoivalent states. They recognized that in making  $(\text{NH}_3)_5\text{Ru}^{\text{II}}\text{pzRu}^{\text{III}}(\text{NH}_3)_5^{4+}$  from two  $\text{Ru}^{\text{II}}(\text{NH}_3)_5^{2+}$  and pyrazine,

(20) Creutz, C.; Taube, H. *J. Am. Chem. Soc.* **1973**, *95*, 1086.

(21) Sutton, J. E.; Taube, H. *Inorg. Chem.* **1981**, *20*, 3125.

(22) Zwickel, A. M.; Creutz, C. *Inorg. Chem.* **1971**, *10*, 2395.

(23) Evidently we are not dealing with a mere charge effect<sup>19</sup> since positive or negative substituents increase and decrease the reduction potential of the  $\text{Ru}^{\text{III}}(\text{NH}_3)_5^{3+}$  center.

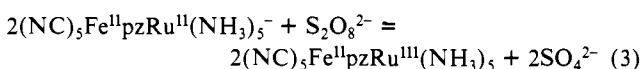
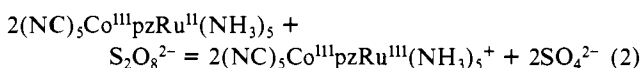
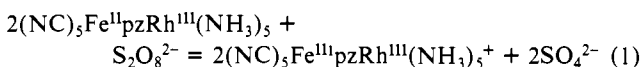
**Table IV.** Oxidation of Ru(II) and Fe(II) Complexes by Peroxydisulfate at 25 °C, pH 4.28 (acetate buffer), and Ionic Strength 0.10 M (LiClO<sub>4</sub>)

complex	<i>k</i> , M <sup>-1</sup> s <sup>-1</sup>
Ru <sup>II</sup> (NH <sub>3</sub> ) <sub>5</sub> pz <sup>2+</sup>	(3.05 ± 0.06) × 10 <sup>3</sup> <sup>a</sup>
(NC) <sub>5</sub> Co <sup>III</sup> pzRu <sup>II</sup> (NH <sub>3</sub> ) <sub>5</sub>	(1.40 ± 0.06) × 10 <sup>2</sup> <sup>b</sup>
(NC) <sub>5</sub> Fe <sup>II</sup> pzRu <sup>II</sup> (NH <sub>3</sub> ) <sub>5</sub> <sup>-</sup>	(3.79 ± 0.14) × 10 <sup>3</sup> <sup>c</sup>
(NC) <sub>5</sub> Fe <sup>II</sup> pzRh <sup>III</sup> (NH <sub>3</sub> ) <sub>5</sub>	~1.5
Fe <sup>II</sup> (CN) <sub>5</sub> pz <sup>3-</sup>	~2.5

<sup>a</sup> [Ru<sup>II</sup>] = 1.35 × 10<sup>-5</sup> M, [S<sub>2</sub>O<sub>8</sub><sup>2-</sup>] = (1.67–5.25) × 10<sup>-4</sup> M. <sup>b</sup> [Ru<sup>II</sup>] = 1.77 × 10<sup>-5</sup> M, [S<sub>2</sub>O<sub>8</sub><sup>2-</sup>] = (2.36–7.10) × 10<sup>-4</sup> M. <sup>c</sup> [Ru<sup>II</sup>] = 1.80 × 10<sup>-5</sup> M, [S<sub>2</sub>O<sub>8</sub><sup>2-</sup>] = (1.47–3.66) × 10<sup>-4</sup> M.

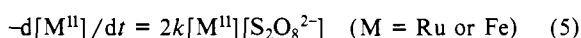
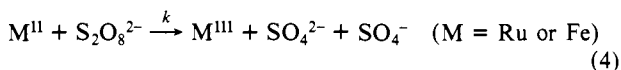
the addition of the second Ru<sup>II</sup>(NH<sub>3</sub>)<sub>5</sub><sup>2+</sup> does not result in as much π-backbonding stabilization as the first, and they suggested that there is an inherent electronic instability in the isovalent II, II complex. To be sure, this instability makes (NH<sub>3</sub>)<sub>5</sub>Ru<sup>II</sup>pzRu<sup>II</sup>(NH<sub>3</sub>)<sub>5</sub><sup>4+</sup> a better reducing agent and, conversely, (NH<sub>3</sub>)<sub>5</sub>Ru<sup>III</sup>pzRu<sup>II</sup>(NH<sub>3</sub>)<sub>5</sub><sup>5+</sup> a poorer oxidant than if Ru(NH<sub>3</sub>)<sub>5</sub><sup>2+</sup> was not a π base. It is also instructive to make the comparison on the basis of the molecular orbital diagram in Chart I.<sup>18</sup> Although in discussing redox potentials it is necessary to consider the MO diagrams for reduced and oxidized forms of the couple, it is noteworthy that for the parent compound Ru<sup>II</sup>(NH<sub>3</sub>)<sub>5</sub>pz<sup>2+</sup> and for the complexes where the substituent is acting solely as a Lewis acid, the diagram on the left is applicable, and it will be seen that the electron removed from Ru(II) comes from a nonbonding orbital. For (NH<sub>3</sub>)<sub>5</sub>Ru<sup>II</sup>pzRu<sup>II</sup>(NH<sub>3</sub>)<sub>5</sub><sup>4+</sup> the diagram on the right is obtained, and it is noteworthy that the electron removed comes from an antibonding orbital.

**Oxidation of Ruthenium(II) and Iron(II) Pyrazine Complexes.** Peroxydisulfate was used as the oxidant in all oxidation experiments because of its stability at pH 5 and because of the possibility of detecting two-electron reactions. However, in all cases, the reaction stoichiometries corresponded to one-electron reactions, eq 1–3. The 2:1 stoichiometry in eq 1 and 2 is, to be sure, not



surprising but very noteworthy for eq 3. As discussed below, the product of eq 3, complex V (*n* = 0), does not undergo further oxidation but a decomposition reaction.

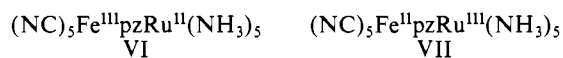
The reactions of the Ru(II) complexes follow mixed second-order kinetics—first order in peroxydisulfate and first order in Ru(II)—quite accurately. Second-order rate constants defined by eq 4 and 5 are listed in column 2 of Table IV. The oxidations



of the Fe(II) complexes were found to be quite slow, and the least-squares fits of ln(*A<sub>t</sub>* - *A<sub>∞</sub>*) vs. time were not as good as those for the Ru(II) complexes. The deviations in the fits are probably caused by competition of dissociation with oxidation. For example, with [Fe<sup>II</sup>(CN)<sub>5</sub>pz<sup>3-</sup>] = 3.77 × 10<sup>-5</sup> M, [S<sub>2</sub>O<sub>8</sub><sup>2-</sup>] = 7.38 × 10<sup>-4</sup> M, and at 25 °C μ = 0.10 M, pH 4.28, the observed rate constant for disappearance of Fe(II) is ~2 × 10<sup>-3</sup> s<sup>-1</sup>, compared with 4.2 × 10<sup>-4</sup> s<sup>-1</sup> for dissociation of Fe(CN)<sub>5</sub>pz<sup>3-</sup> into Fe(CN)<sub>5</sub>OH<sub>2</sub><sup>3-</sup> and pyrazine.<sup>7</sup> Approximate value of the second-order rate constants defined by eq 4 and 5 are listed in column 2 of Table IV.

For the mononuclear complexes listed in Table IV, the oxidation reactions refer to bringing up the oxidation state of the central metal ion from +2 to +3. For the binuclear complexes (NC)<sub>5</sub>Co<sup>III</sup>pzRu<sup>II</sup>(NH<sub>3</sub>)<sub>5</sub> and (NC)<sub>5</sub>Fe<sup>II</sup>pzRh<sup>III</sup>(NH<sub>3</sub>)<sub>5</sub>, the sites

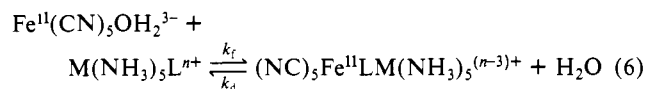
of oxidation are undoubtedly the Ru(II) and Fe(II) centers, respectively, since higher oxidation states of Co(III) and Rh(III) are not readily accessible, if at all. For the binuclear complex (NC)<sub>5</sub>Fe<sup>II</sup>pzRu<sup>II</sup>(NH<sub>3</sub>)<sub>5</sub><sup>-</sup>, however, the question arises as to whether the Fe(II) or the Ru(II) center (or both, in competition with each other) is oxidized. In other words, is isomer VI or isomer VII (or an isomeric mixture) of complex V (*n* = 0) formed as the primary reaction product? In this context it must be noted that



the discussion presented above strongly suggested that VII is the thermodynamically stable isomer. Therefore, the question raised above can be rephrased as follows. Is VII the kinetic (as well as thermodynamic) product, or is VI formed first and then, in a subsequent intramolecular electron transfer, VII is produced? In order to answer this question, the following criterion is proposed. The rate constants for oxidation of Fe<sup>II</sup>(CN)<sub>5</sub>pz<sup>3-</sup> and of the (NC)<sub>5</sub>Fe<sup>II</sup>pzRh<sup>III</sup>(NH<sub>3</sub>)<sub>5</sub> model compound are taken to be characteristic of oxidation of Fe(II) to Fe(III) in these types of compounds. It will be seen that the constants fall in the range 1–3 M<sup>-1</sup> s<sup>-1</sup>. Similarly, the rate constants for oxidation of Ru<sup>II</sup>(NH<sub>3</sub>)<sub>5</sub>pz<sup>2+</sup> and of the (NC)<sub>5</sub>Co<sup>III</sup>pzRu<sup>II</sup>(NH<sub>3</sub>)<sub>5</sub> model compound are indicative of oxidation of Ru(II) to Ru(III), the range of rate constants covered being 10<sup>2</sup>–10<sup>3</sup> M<sup>-1</sup> s<sup>-1</sup>. On this basis the observed value 3.79 × 10<sup>3</sup> M<sup>-1</sup> s<sup>-1</sup> for (NC)<sub>5</sub>Fe<sup>II</sup>pzRu<sup>II</sup>(NH<sub>3</sub>)<sub>5</sub><sup>-</sup> is taken to indicate oxidation of Ru<sup>(II)</sup> to Ru<sup>(III)</sup>, and, therefore, the kinetic, as well as thermodynamic, product is isomer VII. Additional support for the suggestion that in the oxidation of (NC)<sub>5</sub>Fe<sup>II</sup>pzRu<sup>II</sup>(NH<sub>3</sub>)<sub>5</sub><sup>-</sup> the electron is transferred from an orbital primarily ruthenium in character comes from a comparison of the rate constants for oxidation of Ru<sup>II</sup>(NH<sub>3</sub>)<sub>5</sub>pz<sup>2+</sup>, (NC)<sub>5</sub>Co<sup>III</sup>pzRu<sup>II</sup>(NH<sub>3</sub>)<sub>5</sub>, and (NC)<sub>5</sub>Fe<sup>II</sup>pzRu<sup>II</sup>(NH<sub>3</sub>)<sub>5</sub><sup>-</sup>. For outer-sphere oxidation of a series of related complexes by the same reagent, variation in rates are explicable on the basis of electrostatic, thermodynamic, and self-exchange considerations. Taking ion pair formation constants as a measure of the electrostatic factors and the Marcus relationship to estimate the thermodynamic contribution, we calculate that the reactivity ratio for the complexes in the same order as given above is 1:0.045:0.5 to be compared with the observed values 1:0.046:1.24. Considering the approximations involved in estimating ion pair formation constants, the agreement between experimental and calculated reactivity ratios is taken to be excellent. Since electrostatic and thermodynamic factors are sufficient to account for the reactivity differences, we infer that the rate constants for self-exchange in the three complexes are equal. The equality of the rate constants of self-exchange for Ru(NH<sub>3</sub>)<sub>5</sub>pz<sup>3+/2+</sup> and for (NC)<sub>5</sub>Co<sup>III</sup>pzRu<sup>II</sup>(NH<sub>3</sub>)<sub>5</sub><sup>+0</sup> is not unexpected since it has been shown<sup>24</sup> that self-exchange rate constants for Ru(NH<sub>3</sub>)<sub>5</sub>L<sup>3+/2+</sup> (L = substituted pyridine) are rather insensitive to the identity of L. This may be rationalized by recognizing that the electron transferred from Ru(II) is in a nonbonding orbital<sup>18</sup> (b<sub>2</sub>) which is metal in character (4d<sub>xz</sub>) and somewhat unaffected by the detailed nature of the pyridine ligand. It is noteworthy that the equality of self-exchange rates appears to extend to (NC)<sub>5</sub>Fe<sup>II</sup>pzRu<sup>II</sup>(NH<sub>3</sub>)<sub>5</sub><sup>0/-</sup>. In this complex, the electron that is transferred is in an antibonding orbital (b<sub>2g</sub>) which is mostly the x<sub>z</sub> + xz<sub>2</sub> combination<sup>18</sup> of iron and ruthenium orbitals. The equality of the rate of self-exchange is taken to indicate that there is little mixing of the iron orbital and that the electron that is transferred is in an orbital with predominantly ruthenium character. This suggestion is consistent with the spectroscopic evidence.<sup>18</sup>

**Rates of Formation and Dissociation of Pentacyanoferrate(II) Binuclear Complexes.** Rate constants for the forward and reverse reactions in eq 6 (M = Ru<sup>(II)</sup> or Rh<sup>(III)</sup>) and L = pz or bpy) were measured spectrophotometrically. The forward reactions with M = Ru<sup>(II)</sup> were followed at 550 nm to avoid the broad absorption

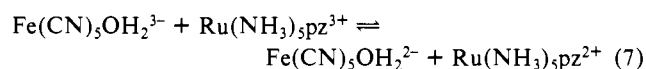
(24) Brown, G. M.; Krentzien, H. J.; Abe, M.; Taube, H. *Inorg. Chem.* 1979, 18, 3374.



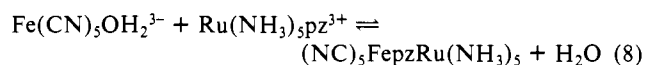
by the  $\text{Ru}(\text{NH}_3)_5\text{L}^{2+}$  reactants at the maxima of the binuclear complexes. Since  $\text{Rh}(\text{NH}_3)_5\text{pz}^{3+}$  has no absorption in the visible, the reaction was followed at 576 nm, the maximum for the product. The reactions were found to be first order in  $\text{Fe}(\text{CN})_5\text{OH}_2^{3-}$  and first order in  $\text{M}(\text{NH}_3)_5\text{L}^{n+}$ . The corresponding second-order rate constants are listed in column 2 of Table V. For the measurements of the reverse reaction, pyridine was used as a scavenger.<sup>7</sup> The stability constant of  $\text{Fe}(\text{CN})_5\text{py}^{3-}$  is very high,<sup>7</sup> and therefore in the presence of excess pyridine, the reverse of reaction 6 proceeds to completion and the absorbance measurements yield first-order rate constants (independent of the pyridine concentration) identified as  $k_d$ . The quantitative formation of  $\text{Fe}(\text{CN})_5\text{py}^{3-}$  and  $\text{M}(\text{NH}_3)_5\text{L}^{n+}$  in the dissociation experiments was verified by spectrophotometric examination of the product solutions. Values of  $k_d$  are listed in column 3 of Table V.

The results obtained conform to and provide additional support for the mechanistic patterns discerned previously.<sup>7,25-27</sup> Undoubtedly, the replacement of water in  $\text{Fe}(\text{CN})_5\text{OH}_2^{3-}$  by various ligands proceeds by a dissociative mechanism, with values of  $k_f$  for neutral ligands falling in the range 200–400  $\text{M}^{-1}\text{s}^{-1}$ .<sup>25</sup> As the positive charge of the incoming ligand increases, values of  $k_f$  also increase and have values of  $\sim 500$ ,  $\sim 3 \times 10^3$ , and  $\sim 6 \times 10^3$  for +1, +2, and +3 charges, respectively.<sup>12,15,27,28</sup>

**Formation, Dissociation, and Decomposition of  $(\text{NC})_5\text{Fe}^{\text{II}}\text{pzRu}^{\text{III}}(\text{NH}_3)_5$ .** Included in Table V are values of  $k_f$  and  $k_d$  for the reaction between  $\text{Fe}(\text{CN})_5\text{OH}_2^{3-}$  and  $\text{Ru}(\text{NH}_3)_5\text{pz}^{3+}$ . These values were not obtained, as was the case for the other entries in the table, by direct measurements of the forward and reverse reactions. When solutions of  $\text{Fe}(\text{CN})_5\text{OH}_2^{3-}$  and  $\text{Ru}(\text{NH}_3)_5\text{pz}^{3+}$  are mixed, the 474-nm absorption of  $\text{Ru}(\text{NH}_3)_5\text{pz}^{2+}$  develops very rapidly. This suggests that the first reaction that takes place between  $\text{Ru}(\text{NH}_3)_5\text{pz}^{3+}$  ( $\sim 10^{-4}$  M) and  $\text{Fe}(\text{CN})_5\text{OH}_2^{3-}$  ( $\sim 10^{-5}$  M) is the rapid, outer-sphere electron-transfer reaction, eq 7. The equilibrium and rate constants for



eq 7 are 157 (calculated from  $E^\circ$  values of 0.39<sup>29</sup> and 0.52 V for  $\text{Fe}(\text{CN})_5\text{OH}_2^{2-/3-}$  and  $\text{Ru}(\text{NH}_3)_5\text{pz}^{3+/2+}$ , respectively) and  $1.5 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$  (estimated from the values  $1.9 \times 10^4$  and  $1.1 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$  for the self-exchange rate constants for iron<sup>30</sup> and ruthenium<sup>24</sup> complexes, respectively, utilizing the Marcus cross relation corrected<sup>16</sup> for electrostatic effects). Evidently, the inner-sphere reaction given by eq 8 with an estimated rate constant of  $\sim 6 \times 10^3 \text{ M}^{-1}\text{s}^{-1}$  (by analogy with the corresponding reactions of tripositive complexes<sup>31</sup>) cannot compete with the outer-sphere reaction given by eq 7. Following the rapid equilibration ac-



ording to eq 7, subsequent slow changes are observed. The 474-nm absorption of  $\text{Ru}(\text{NH}_3)_5\text{pz}^{2+}$  shows a shift toward longer wavelengths, and, depending on the initial  $\text{Ru}(\text{NH}_3)_5\text{pz}^{3+}$  and  $\text{Fe}(\text{CN})_5\text{OH}_2^{3-}$  concentrations, maxima in the 540–570-nm region develop after  $\sim 10$  min. Evidently, following the very fast outer-sphere reaction, the binuclear complex  $(\text{NC})_5\text{Fe}^{\text{II}}\text{pzRu}^{\text{III}}(\text{NH}_3)_5$  is formed. Since equilibration according to eq 7 is faster than reaction according to eq 8, in principle it is possible to start with either  $\text{Fe}(\text{CN})_5\text{OH}_2^{3-}-\text{Ru}(\text{NH}_3)_5\text{pz}^{3+}$  or  $\text{Fe}(\text{CN})_5\text{OH}_2^{2-}-\text{Ru}$

**Table V.** Kinetics of Formation and Dissociation of Pentacyanoferrate(II) Binuclear Complexes<sup>a</sup>

L	$\text{Fe}^{\text{II}}(\text{CN})_5\text{OH}_2^{3-} + \text{L}^{n+} \xrightleftharpoons[k_d]{k_f} (\text{NC})_5\text{Fe}^{\text{II}}\text{L}^{(n-3)+} + \text{H}_2\text{O}$		
	$10^{-3}k_f$ , $\text{M}^{-1}\text{s}^{-1}$	$10^4k_d$ , $\text{s}^{-1}$ <sup>b</sup>	$10^6K$ , $\text{M}^{-1}$ <sup>c</sup>
$\text{Ru}^{\text{II}}(\text{NH}_3)_5\text{pz}^{2+}$ <sup>d</sup>	$3.7 \pm 0.1$	$7.2 \pm 0.1$	$5.1 \pm 0.3$
$\text{Ru}^{\text{II}}(\text{NH}_3)_5\text{bpy}^{2+}$ <sup>e</sup>	$1.6 \pm 0.1$	$24.7 \pm 4.0$	$0.64 \pm 0.20$
$\text{Rh}^{\text{III}}(\text{NH}_3)_5\text{pz}^{3+}$ <sup>d,f</sup>	$8.8 \pm 0.3$	$11.1 \pm 0.1$	$7.9 \pm 0$
$\text{Ru}^{\text{III}}(\text{NH}_3)_5\text{pz}^{3+}$	$5.5 \pm 0.5$	$29 \pm 20$ <sup>g</sup>	$16 \pm 11$ <sup>h</sup>

<sup>a</sup> At 25 °C, ionic strength 0.10 M ( $\text{LiClO}_4$ ),  $[\text{Fe}(\text{CN})_5\text{OH}_2^{3-}] = (1-3) \times 10^{-5}$  M,  $[\text{L}] = (1-3) \times 10^{-4}$  M,  $[\text{Fe}(\text{CN})_5\text{L}] = (2-5) \times 10^{-5}$  M. <sup>b</sup>  $[\text{Pyridine}] = 0.05-0.20$  M. <sup>c</sup> Calculated from  $k_f/k_d$ . <sup>d</sup> pH 6.06,  $[\text{ascorbic acid}] = 1.0 \times 10^{-4}$  M. <sup>e</sup> pH 8.03,  $[\text{ascorbic acid}] = 1.0 \times 10^{-4}$  M. <sup>f</sup> Compare with  $k_f = 2.6 \times 10^3 \text{ M}^{-1}\text{s}^{-1}$  and  $k_d = 7.4 \times 10^{-4} \text{ s}^{-1}$  at ionic strength 0.50 M, ref 27. <sup>g</sup> Calculated from  $K/k_f$ . <sup>h</sup> Indirect estimate; see text.

$(\text{NH}_3)_5\text{pz}^{2+}$  mixtures in order to measure the rate constant for eq 8. In practice we found it more convenient to start with the latter mixtures (using an excess of iron) and we followed the absorbance increase at 560 nm. Under these circumstances, the mechanism of formation of  $(\text{NC})_5\text{FepzRu}(\text{NH}_3)_5$  proceeds via the reverse of eq 7 followed by eq 8, and the rate constant  $k_f$  for eq 8 was obtained from the slope of  $Y(t)$  vs. time, eq 9.  $[\text{Fe}(\text{CN})_5\text{OH}_2^{2-}]_0$  is the initial concentration of  $\text{Fe}(\text{CN})_5\text{OH}_2^{2-}$  (present in at least 10-fold excess over  $\text{Ru}(\text{NH}_3)_5\text{pz}^{2+}$ ),  $k_f$  and  $K$  are the rate and equilibrium constants for eq 8 and 7, respectively, and  $Y(t)$  is defined in eq 10.<sup>32</sup> Six experiments were

$$Y(t) = -k_f[\text{Fe}(\text{CN})_5\text{OH}_2^{2-}]_0 t / 2K + C \quad (9)$$

$Y(t) = \ln(y-1) - 1/(y-1)$

$$y = (1+x)^{1/2}$$

$$x = (4K/[\text{Fe}(\text{CN})_5\text{OH}_2^{2-}]_0)([\text{Ru}(\text{NH}_3)_5\text{pz}^{2+}]_0 + [\text{V}(n=0)]_t) \quad (10)$$

carried out with  $[\text{Fe}(\text{CN})_5\text{OH}_2^{2-}]_0 = (4.62-7.07) \times 10^{-4}$  M,  $[\text{Ru}(\text{NH}_3)_5\text{pz}^{2+}]_0 = (3.23-7.13) \times 10^{-5}$  M,  $t = 25$  °C,  $\mu = 0.10$  M ( $\text{LiClO}_4$ ), and pH 4.28 (acetate). From the slopes of eq 9 (plots were linear for at least 80% reaction) and  $K = 158$ , values of  $k_f$  were found to be in the range  $(4.8-6.0) \times 10^3 \text{ M}^{-1}\text{s}^{-1}$ . The average value  $(5.5 \pm 0.5) \times 10^3 \text{ M}^{-1}\text{s}^{-1}$  falls nicely near the range of rate constants for the reactions of  $\text{Fe}(\text{CN})_5\text{OH}_2^{3-}$  with other tripositive pyrazine complexes, such as  $\text{Rh}(\text{NH}_3)_5\text{pz}^{3+}$  ( $k_f = 8.8 \times 10^3 \text{ M}^{-1}\text{s}^{-1}$ ) and  $\text{Co}(\text{NH}_3)_5\text{pz}^{3+}$  ( $k_f = 7.0 \times 10^3 \text{ M}^{-1}\text{s}^{-1}$ ).<sup>33</sup>

The rate constant  $k_d$  for dissociation of  $\text{V}(n=0)$  could not be measured by the pyridine scavenging method. When pyridine is added to  $\text{V}(n=0)$  prepared by reaction of  $\text{Fe}(\text{CN})_5\text{OH}_2^{2-}$  with  $\text{Ru}(\text{NH}_3)_5\text{pz}^{2+}$ , the 590-nm absorption of  $\text{V}(n=0)$  disappears with a rate constant of  $(4.4 \pm 0.3) \times 10^{-4} \text{ s}^{-1}$  (average of two experiments at 25 °C,  $\mu = 0.10$  M,  $[\text{pyridine}] = 0.10$  M,  $[\text{Ru}(\text{NH}_3)_5\text{pz}^{2+}] = (4-7) \times 10^{-5}$  M, and  $[\text{Fe}(\text{CN})_5\text{OH}_2^{3-}] = (4-7) \times 10^{-4}$  M). However, the observed rate constant cannot be assigned to the reverse of reaction 8 because spectrophotometric examination of the product solutions revealed the presence of both  $\text{Ru}(\text{NH}_3)_5\text{py}^{2+}$  and  $\text{Ru}(\text{NH}_3)_5\text{pz}^{2+}$ . For example, when  $\text{V}(n=0)$  was prepared by reaction of  $4.01 \times 10^{-4}$  M  $\text{Fe}(\text{CN})_5\text{OH}_2^{2-}$  with  $3.96 \times 10^{-5}$  M  $\text{Ru}(\text{NH}_3)_5\text{pz}^{2+}$  and then treated with pyridine, the product solution was found to contain  $2.63 \times 10^{-5}$  M  $\text{Ru}(\text{NH}_3)_5\text{py}^{2+}$  and  $1.37 \times 10^{-5}$  M  $\text{Ru}(\text{NH}_3)_5\text{pz}^{2+}$ . Evidently, any  $\text{Ru}(\text{III})$  complex present initially is reduced by an unspecified base-dependent process. Perhaps in the unbuffered pyridine medium, disproportionation of  $\text{Ru}(\text{III})$  to  $\text{Ru}(\text{II})$  and  $\text{Ru}(\text{IV})$  is obtained and is followed by rapid loss of pyrazine from  $\text{Ru}(\text{IV})$  and eventual reduction to  $\text{Ru}(\text{II})$ .

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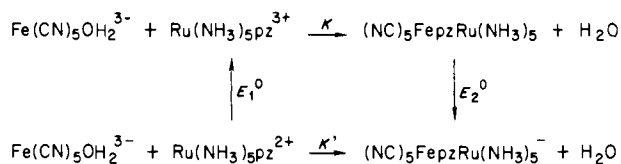
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An estimate of the value of  $k_d$  was obtained from a study of the decomposition of  $V$  ( $n = 0$ ) in the absence of excess mononuclear iron or ruthenium complexes. As indicated above, solutions of  $V$  ( $n = 0$ ) can be prepared cleanly by oxidation of  $V$  ( $n = -1$ ) (purified by ion exchange) with 1 equiv of peroxydisulfate. Such solutions are initially blue and display a maximum at 590 nm. However, this absorption shifts with time, and, after about 20 min, a fairly stable solution is obtained which exhibits a maximum at  $\sim 490$  nm and a shoulder at 570 nm. We suggest that the observed spectral changes of  $(\text{NC})_5\text{FepzRu}(\text{NH}_3)_5$  are initiated by its dissociation via the reverse of eq 8, and this is followed by the fast outer-sphere redox reaction according to eq 7, until equilibrium between  $V$  ( $n = 0$ ),  $\text{Fe}(\text{CN})_5\text{OH}_2^{2-}$ ,  $\text{Ru}(\text{NH}_3)_5\text{pz}^{2+}$ ,  $\text{Fe}(\text{CN})_5\text{OH}_2^{3-}$ , and  $\text{Ru}(\text{NH}_3)_5\text{pz}^{3+}$  is reached. This proposed reaction sequence is supported by three experimental pieces of information. First, the spectra of solutions obtained by mixing equimolar solutions of  $\text{Fe}(\text{CN})_5\text{OH}_2^{3-}$  and  $\text{Ru}(\text{NH}_3)_5\text{pz}^{3+}$  are, after about 15 min, essentially identical with those obtained after the decomposition of  $(\text{NC})_5\text{FepzRu}(\text{NH}_3)_5$  has proceeded to equilibrium. Both sets of equilibrium solutions display the characteristic absorption maximum of  $\text{Ru}(\text{NH}_3)_5\text{pz}^{2+}$  near 490 nm as well as a shoulder at 570 nm assigned to  $V$  ( $n = 0$ ). Second, when the equilibrium solutions are treated with ascorbic acid,  $(\text{NC})_5\text{FepzRu}(\text{NH}_3)_5$  is produced in more than 90% yield. This observation indicates that in the sequence of reactions that lead to the equilibrium mixture, at no time is the Ru-pz bond broken.<sup>34</sup> Additional confirmation of this inference comes from the observation of quantitative production of equimolar amounts of  $\text{Fe}(\text{CN})_5\text{py}^{3-}$  and  $\text{Ru}(\text{NH}_3)_5\text{pz}^{2+}$  when the equilibrium product solutions from the decomposition of  $V$  ( $n = 0$ ) are treated with pyridine and ascorbic acid. By measuring the decrease in the 590-nm absorption of  $(\text{NC})_5\text{FepzRu}(\text{NH}_3)_5$ , we obtained a nice fit to an exponential decay with a rate constant of  $(1.6 \pm 0.1) \times 10^{-3} \text{ s}^{-1}$  at 25 °C, pH 4.0, and  $\mu = 0.10 \text{ M}$  (average of two measurements). In the interpretation suggested above, this rate constant represents a measure of the rate constant for approach to equilibrium, and we estimate that  $k_d \sim 1 \times 10^{-3} \text{ s}^{-1}$ .<sup>35</sup> Support for the interpretation and the reliability of the estimated value of  $k_d$  comes from a comparison of the equilibrium constant for eq 8 calculated from the ratio  $k_f/k_d = 5.5 \times 10^3/1.0 \times 10^{-3} = 5.5 \times 10^6 \text{ M}^{-1}$  with the value estimated from the following cycle.<sup>29</sup>  $E_1^\circ$ ,  $E_2^\circ$ , and  $K'$  have been measured in the present work (0.52, 0.49 V, Table II, 5.1  $\times 10^6 \text{ M}^{-1}$ , Table V) and therefore  $K = 1.6 \times 10^7 \text{ M}^{-1}$ . The agreement between this value and the value 5.5



$\times 10^6 \text{ M}^{-1}$  estimated above is not spectacular. However, it must be recognized that errors of 0.01 V in the values of  $E_1^\circ$  and  $E_2^\circ$  change the calculated value of  $K$  by a factor of 2, and, thus, considering the approximations and experimental errors, the agreement between the two values of  $K$  is considered acceptable

(34) If the Ru-pz bond had been broken in the decomposition process,  $(\text{NC})_5\text{FepzRu}(\text{NH}_3)_5$  would not have been produced rapidly and quantitatively. Note that substitution of  $\text{H}_2\text{O}$  in  $\text{Ru}(\text{NH}_3)_5\text{OH}_2^{2+}$  by pz or  $\text{Fe}(\text{CN})_5\text{pz}^{2+}$  is a relatively slow process. Moreover, the reaction of  $\text{Fe}(\text{CN})_5\text{pz}^{2+}$  with  $\text{Ru}(\text{NH}_3)_5\text{OH}_2^{2+}$  produces, in part, a cyanide-bridged binuclear complex (Ludi, A., private communication, 1976). No such complex was observed in our system.

(35) The differential equations corresponding to the scheme reverse of reaction 8 followed by eq 7 were solved utilizing the Runge-Kutta approximation and values of  $k_d = 1 \times 10^{-3} \text{ s}^{-1}$ ,  $k_f = 5 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ ,  $k_7 = 2 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ ,  $k_{-7} = 1 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ , and  $[\text{V}]_0 = 2 \times 10^{-5} \text{ M}$ . Absorbance vs. time at 570 nm was calculated from the concentrations and known molar absorbances, and the absorbance values were fitted to the equation  $A_t = A_0 + (A_\infty - A_0) \exp(-kt)$  by a nonlinear least-squares program. The exponential dependence was strictly obeyed for more than five half-lives, and the resulting values of  $k$  was  $1.58 \times 10^{-3} \text{ s}^{-1}$ . Since the conditions in the simulation duplicate quite closely the experimental conditions, we infer that the observed value  $(1.6 \pm 0.1) \times 10^{-3} \text{ s}^{-1}$  corresponds to a  $k_1$  value of  $\sim 1 \times 10^{-3} \text{ s}^{-1}$ .

and reinforces the interpretation of the kinetic measurements of the decomposition of  $V$  ( $n = 0$ ).

**Intervalence Absorption and Intramolecular Electron Transfer in  $(\text{NC})_5\text{Fe}^{\text{II}}\text{pzRu}^{\text{III}}(\text{NH}_3)_5$ .** Mixed valence binuclear complexes are characterized by a metal-to-metal charge-transfer absorption (intervalence band) which provides information about the extent of coupling between the metal centers and the rate of electron transfer from one metal center to the other.<sup>6</sup> Freshly prepared solutions of  $V$  ( $n = 0$ ) in  $\text{D}_2\text{O}$  (obtained by oxidation of  $\sim 1 \times 10^{-4} \text{ M}$  solution of  $V$  ( $n = -1$ ) with  $\text{S}_2\text{O}_8^{2-}$ ) exhibit an intervalence band at 1650 nm ( $6.06 \times 10^3 \text{ cm}^{-1}$ ) with molar absorbance  $1.55 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$  and bandwidth  $0.43 \mu\text{m}^{-1}$ .

Theoretical treatments<sup>6</sup> of intervalence absorption provide useful relationships for the bandwidth  $\nu_{1/2}$ , which in the high temperature limit is given by eq 11, and for the oscillator strength  $f$ , eq 12.

$$\Delta\bar{\nu}_{1/2} = (2310 \bar{\nu}_{\text{max}})^{1/2} \quad (11)$$

$$f = 4.6 \times 10^{-9} \epsilon_{\text{max}} \Delta\bar{\nu}_{1/2} \quad (12)$$

The oscillator strength can also be expressed by eq 13, which when combined with eq 12 yields eq 14.  $\bar{\nu}_{\text{max}}$  and  $\epsilon_{\text{max}}$  are the wave-

$$f = 1.085 \times 10^{-5} \bar{\nu}_{\text{max}} (\alpha d)^2 \quad (13)$$

number and molar absorbance, respectively, of the intervalence absorption, and  $d$  is the distance between the metal centers.  $\alpha^2$

$$\alpha^2 = 4.24 \times 10^{-4} \epsilon_{\text{max}} \Delta\bar{\nu}_{1/2} / \bar{\nu}_{\text{max}} d^2 \quad (14)$$

is a measure of the delocalization in the ground state and is related to the electronic coupling  $H_{\text{AB}}$  between the metal centers by eq 15. Values of  $\Delta\bar{\nu}_{1/2}$ ,  $\alpha^2$ , and  $H_{\text{AB}}$  calculated from eq 11, 14, and

$$H_{\text{AB}} = \bar{\nu}_{\text{max}} \alpha \quad (15)$$

15 for the intervalence band in  $V$  ( $n = 0$ ) are  $0.37 \mu\text{m}^{-1}$ ,  $9.8 \times 10^{-3}$ , and  $600 \text{ cm}^{-1}$ , respectively. The small magnitude of the latter two values indicates that there is little (<1%) electron delocalization in  $V$  ( $n = 0$ ). Additional evidence for this conclusion comes from a comparison between observed and calculated values of the bandwidth, an important diagnostic to assess the extent of delocalization. The observed bandwidth ( $0.43 \mu\text{m}^{-1}$ ) being larger than that calculated from eq 11, it is inferred<sup>6</sup> that  $V$  ( $n = 0$ ) is a valence-trapped species. The inferences drawn from the intervalence absorption further corroborate those reached above based on MLCT spectroscopic and electrochemical considerations, namely that  $V$  ( $n = 0$ ) is to be formulated as a trapped valence species featuring localized Fe(II) and Ru(III) oxidation states.

It is noteworthy that, except for the Creutz and Taube ion,  $(\text{NH}_3)_5\text{RupzRu}(\text{NH}_3)_5^{3+}$ , all other reported ruthenium pyrazine-bridged mixed valence binuclear complexes<sup>6</sup> belong to Robin and Day's class II; e.g., a trapped valence formulation represents the most adequate description of the electronic structure of these compounds. In this respect, complex  $V$  ( $n = 0$ ) conforms to this generalization, but there is one unusual observation for  $V$  ( $n = 0$ ). It has been noted<sup>6</sup> that asymmetric mixed valence binuclear complexes display the intervalence band at energies higher than the average of the energies of the parent symmetric complexes. However, for the asymmetric complex  $V$  ( $n = 0$ ) the opposite situation prevails, e.g., its intervalence band occurs at  $6.06 \times 10^3 \text{ cm}^{-1}$  compared to  $8.30 \times 10^3$  and  $6.40 \times 10^3 \text{ cm}^{-1}$  for  $(\text{NC})_5\text{FepzFe}(\text{CN})_5^{5-}$  and  $(\text{NH}_3)_5\text{RupzRu}(\text{NH}_3)_5^{5+}$ .<sup>8,5,36</sup> Now, the relationship  $\bar{\nu}_{\text{max}}^{\text{ab}} > (\bar{\nu}_{\text{max}}^{\text{aa}} + \bar{\nu}_{\text{max}}^{\text{bb}})/2$  is applicable under the assumption that the inner-shell and solvent reorganization energies of each moiety in the asymmetric complex are equal to the values in the corresponding symmetric complexes, e.g., each mononuclear center is not affected by the presence of the other. Although this assumption may be applicable to the inner-shell contribution, it might not be correct for the solvent contribution in the case of

(36) It may be argued that this comparison is not applicable to  $V$  since one moiety belongs to class II and the other (probably) to class III. However, based on the dependence of  $\bar{\nu}_{\text{max}}$  upon the distance between the metal centers, we estimate that a hypothetical class II Creutz and Taube ion would exhibit the intervalence band at  $\sim 8 \times 10^3 \text{ cm}^{-1}$ .

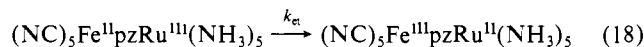
a complex such as V ( $n = 0$ ) where the two moieties have equal and opposite charges. Undoubtedly, the extent of solvation of  $(\text{NC})_5\text{FepzRu}(\text{NH}_3)_5$  is considerably less than that of  $(\text{NC})_5\text{FepzFe}(\text{CN})_5^{5-}$  or  $(\text{NH}_3)_5\text{RupzRu}(\text{NH}_3)_5^{5+}$ . If the decreased solvation of V ( $n = 0$ ) compared to the parent symmetrical complexes also implies a decrease in solvent reorganization energy,<sup>37</sup> then the relationship  $\bar{\nu}_{\text{max}}^{\text{ab}} < (\bar{\nu}_{\text{max}}^{\text{aa}} + \bar{\nu}_{\text{max}}^{\text{bb}})/2$  would be obeyed, provided that the difference in energy between the two electronic isomers of the asymmetric complex is small (for the reaction VII  $\rightleftharpoons$  VI, the free energy difference is 0.07 V; see below). Another example that brings out the importance of the signs of the electric charges in determining the position of  $\bar{\nu}_{\text{max}}$  is found in  $(\text{NH}_3)_5\text{Ru}^{\text{II}}\text{pzRu}^{\text{III}}(\text{EDTA})^+$ .  $\bar{\nu}_{\text{max}}$  for the latter is  $9.80 \times 10^3 \text{ cm}^{-1}$  compared to  $1.03 \times 10^4$  and  $6.40 \times 10^3 \text{ cm}^{-1}$  for  $(\text{EDTA})\text{RupzRu}(\text{EDTA})^{3-}$  and  $(\text{NH}_3)_5\text{RupzRu}(\text{NH}_3)_5^{5+}$ .<sup>38,39</sup> When the value of  $\bar{\nu}_{\text{max}}$  for the asymmetric complex is corrected for the endoergonicity of the reaction  $(\text{NH}_3)_5\text{Ru}^{\text{II}}\text{pzRu}^{\text{III}}(\text{EDTA})^+ \rightarrow (\text{NH}_3)_5\text{Ru}^{\text{III}}\text{pzRu}^{\text{II}}(\text{EDTA})^+ (-0.3 \text{ V})$ , we obtain  $7.4 \times 10^3 \text{ cm}^{-1}$  compared to the average  $8.4 \times 10^3 \text{ cm}^{-1}$  for the corresponding symmetric complexes. As was the case for V ( $n = 0$ ), the opposite charges in the asymmetric complex  $(\text{NH}_3)_5\text{RupzRu}(\text{EDTA})^+$  result in considerably less solvation than in the parent symmetrical complexes  $(\text{EDTA})\text{RupzRu}(\text{EDTA})^{3-}$  and  $(\text{NH}_3)_5\text{RupzRu}(\text{NH}_3)_5^{5+}$ . We suggest that the decrease in solvation is accompanied by a decrease in solvent reorganization, and therefore the value for  $\bar{\nu}_{\text{max}}$  for the asymmetric complex is, after correction for endoergonicity, higher than the average of the values for the parent symmetric complexes.

By utilization of the experimental results and eq 16–17 where

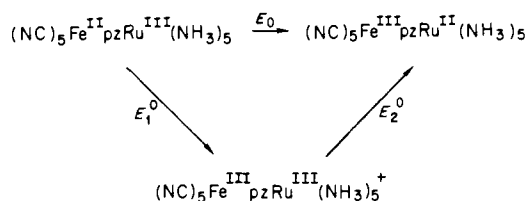
$$E_{\text{th}} = [E_{\text{op}}^2 / [4(E_{\text{op}} - E_0)] - H_{\text{AB}}] \quad (16)$$

$$k_{\text{el}} = \nu_{\text{el}} \exp(-E_{\text{th}}/RT) \quad (17)$$

$E_{\text{th}}$  and  $E_{\text{op}}$  are the thermal and optical electron transfer barriers,  $E_0$  and  $k_{\text{el}}$  are the energy change and rate constant for intramolecular electron transfer according to eq 18, and  $\nu_{\text{el}}$  is an electron



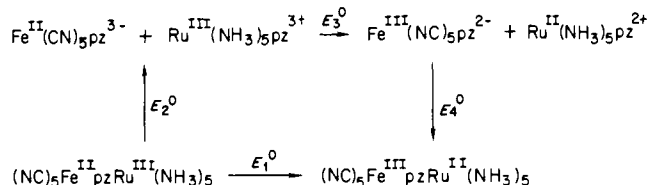
hopping frequency taken to be  $5 \times 10^{12} \text{ s}^{-1}$ ,<sup>6</sup> we calculate  $E_{\text{th}} = 3.12 \text{ kcal}$  and  $k_{\text{el}} = 2.7 \times 10^{10} \text{ s}^{-1}$ . The value of  $E_0$  was obtained from the following cycle:  $E_1^\circ$  was measured in the present work



( $-0.72 \text{ V}$ ) and  $E_2^\circ$  was taken as  $0.64 \text{ V}$ , the value for reduction of  $(\text{NC})_5\text{Co}^{\text{III}}\text{pzRu}^{\text{III}}(\text{NH}_3)_5$  to the corresponding ruthenium(II) complex. It is instructive to compare the value of  $k_{\text{el}}$  calculated above for reaction 18 with the calculated value for the reaction of the analogous asymmetric complex  $(\text{EDTA})\text{Ru}^{\text{II}}\text{pzRu}^{\text{III}}(\text{NH}_3)_5^+$  ( $1 \times 10^{11} \text{ s}^{-1}$ )<sup>6</sup> and with the measured values for the corresponding reactions of the cobalt(III) complexes  $(\text{NC})_5\text{Fe}^{\text{II}}\text{pzCo}^{\text{III}}(\text{NH}_3)_5$  ( $5.5 \times 10^{-2} \text{ s}^{-1}$ )<sup>9</sup> and  $(\text{EDTA})\text{Ru}^{\text{II}}\text{pzCo}^{\text{III}}(\text{NH}_3)_5$  ( $21 \text{ s}^{-1}$ ).<sup>9</sup> In making the comparisons, the quantities of interest are the reactivity ratios of  $\text{Ru}^{\text{II}}(\text{EDTA})^{2-}$  and  $\text{Fe}^{\text{II}}(\text{CN})_5^{3-}$  toward the common oxidants  $\text{Ru}^{\text{III}}(\text{NH}_3)_5\text{pz}^{3+}$  and  $\text{Co}^{\text{III}}(\text{NH}_3)_5\text{pz}^{3+}$ , 4 and  $\sim 4 \times 10^2$ , respectively, and the reactivity ratios of  $\text{Ru}(\text{NH}_3)_5\text{pz}^{3+}$  and  $\text{Co}(\text{NH}_3)_5\text{pz}^{3+}$  toward the common reductants  $\text{Ru}(\text{EDTA})^{2-}$  and  $\text{Fe}(\text{CN})_5^{3-}$ ,  $\sim 5 \times 10^9$  and  $\sim 5 \times 10^{11}$ , respectively. These reactivity ratios bring out two notable features. First, as noted previously by Creutz<sup>6</sup> for other systems, the rate constants calculated from intervalence absorption

data are rather insensitive to the identity of the metal centers and their coordination sphere ( $k_{\text{el}}$  for  $(\text{EDTA})\text{Ru}^{\text{II}}\text{pzRu}^{\text{III}}(\text{NH}_3)_5^+/k_{\text{el}}$  for  $(\text{NC})_5\text{Fe}^{\text{II}}\text{pzRu}^{\text{III}}(\text{NH}_3)_5^+ \sim 4$ ), whereas rate constants for the same systems calculated from thermal reactions measured experimentally display a higher discrimination ( $k_{\text{el}}$  for  $(\text{EDTA})\text{Ru}^{\text{II}}\text{pzCo}^{\text{III}}(\text{NH}_3)_5^+/k_{\text{el}}$  for  $(\text{NC})_5\text{Fe}^{\text{II}}\text{pzCo}^{\text{III}}(\text{NH}_3)_5$ , 400). Second, the reactivity ratio of  $\text{Ru}(\text{NH}_3)_5\text{pz}^{3+}$  vs.  $\text{Co}(\text{NH}_3)_5\text{pz}^{3+}$  calculated from intervalence data for Ru and from thermal data for Co is  $5 \times 10^{10}$ , whereas the ratio is  $5 \times 10^5$  when both Ru and Co are compared in thermal reactions.<sup>16</sup> As noted before,<sup>37</sup> values of  $k_{\text{el}}$  estimated from intervalence bands may be overestimated. A similar discrepancy is found when comparing the thermally measured and spectroscopically calculated rate constants for intramolecular electron transfer in the ion pair  $\text{Fe}(\text{CN})_6^{4-}$  and  $\text{Ru}(\text{NH}_3)_5\text{pz}^{3+}$ ,  $\sim 10^3$  and  $\sim 10^6 \text{ s}^{-1}$ , respectively.<sup>16,40</sup> All these comparisons are not encouraging regarding the validity of calculated rate constants for electron transfer from the properties of intervalence bands, and clearly additional work is called for in this area.

**Stability of the Mixed Valence Complex  $(\text{NC})_5\text{Fe}^{\text{II}}\text{pzRu}^{\text{III}}(\text{NH}_3)_5$ .** The electron-transfer isomerization reaction (eq 18) that produces the unstable electronic isomer of V ( $n = 0$ ) is, as shown above, unfavorable by 0.08 V. It is important to elucidate the factors that stabilize one or the other electronic isomer, and, for this purpose, it is instructive to consider the following quasi-thermodynamic cycle. Since the two electronic isomers differ



in the charges of the respective moieties (3+ and 3- and 2+ and 2-), the cycle includes as two of the steps the electrostatic contributions of disassembling ( $E_2^\circ$ ) or assembling ( $E_4^\circ$ ) the stable or unstable binuclear isomers into or from the parent mononuclear complexes. These values were estimated from the relevant equations for ion pair formation constants<sup>16</sup> by taking radii of  $3.6 \times 10^{-8}$  and  $4.1 \times 10^{-8} \text{ cm}$  for cation and anion, respectively (these are the radii of the spheres of equal volume). The ion pair constants yield the values  $E_2^\circ = -0.12 \text{ V}$  and  $E_4^\circ = 0.06 \text{ V}$ . The value of  $E_3^\circ$  (from Table II) is  $-0.03 \text{ V}$ , and the value of  $E_1^\circ$  estimated above is  $-0.08 \text{ V}$  to be compared with the value  $-0.09 \text{ V}$  calculated from  $E_2^\circ + E_3^\circ + E_4^\circ$ . The excellent agreement between the value of  $E_1^\circ$  estimated from redox potentials and the value of  $E_1^\circ$  calculated from the cycle justifies the validity of the approximations used in the proposed cycle. According to the cycle the value of  $E_1^\circ$  is determined by two factors. First, an "intrinsic" relative stability of  $\text{Fe}(\text{III})/\text{Fe}(\text{II})$  vs.  $\text{Ru}(\text{III})/\text{Ru}(\text{II})$  is measured by  $E_3^\circ$ , the difference in oxidation potentials between the mononuclear units. This factor favors Ru(III) and Fe(II) over Ru(II) and Fe(III) by 0.03 V. Second, an electrostatic factor is measured by  $E_2^\circ + E_4^\circ$ , the difference in the stability of the two isomeric binuclear complexes associated with the electrostatic attraction between the two pairs of moieties. This term also favors the Ru(III)–Fe(II) pair over the Ru(II)–Fe(III) pair, this time by 0.06 V. It will be seen from the above analysis that the increased stability of the binuclear complex containing Ru(III) and Fe(II) vs. the one containing Ru(II) and Fe(III) as compared to the corresponding mononuclear units is entirely rationalized on the basis of the more favorable electrostatics of the Ru(III)–Fe(II) combination (+3, -3) vs. the Ru(II)–Fe(III) combination (+2, -2). An alternate way of assessing the increased stability of  $(\text{NC})_5\text{Fe}^{\text{II}}\text{pzRu}^{\text{III}}(\text{NH}_3)_5$  vs.  $(\text{NC})_5\text{Fe}^{\text{III}}\text{pzRu}^{\text{II}}(\text{NH}_3)_5$  as compared to the mononuclear complexes is to determine the increased stability of Fe(II) attending coordination of the remote N in  $\text{Fe}^{\text{II}}(\text{CN})_5\text{pz}^{3-}$  by  $\text{Ru}^{\text{III}}(\text{NH}_3)_5\text{pz}^{3+}$  and the increased stability of Ru(II) attending coordination of the remote N in  $\text{Ru}^{\text{II}}(\text{NH}_3)_5\text{pz}^{2+}$

(37) It must be noted that the theoretical equations utilized to calculate the solvent reorganization energy are independent of the charge: Cannon, R. D. *Adv. Inorg. Chem. Radiochem.* **1978**, *21*, 179.

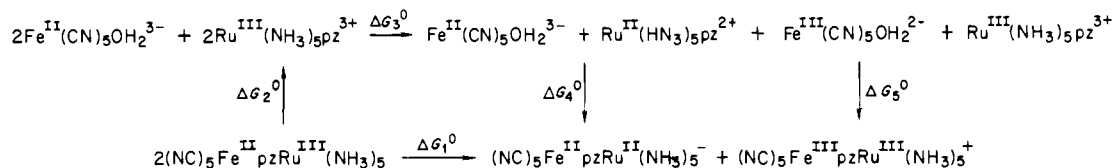
(38) Footnote c of Table III.

(39) Oliveira, L. A. A.; Haim, A. *J. Am. Chem. Soc.* **1982**, *104*, 3363.

(40) Curtis, J. C.; Meyer, T. J. *Inorg. Chem.* **1982**, *21*, 1562.

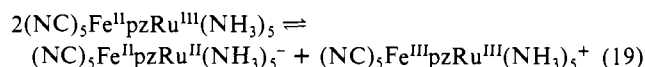


## Scheme I



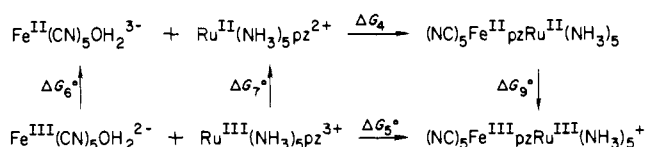
by  $\text{Fe}^{\text{III}}(\text{CN})_5^{3-}$ . The stabilization amounts to 0.17 V in the former case ( $E^\circ$  for  $(\text{NC})_5\text{Fe}^{\text{III}}\text{pzRu}^{\text{III}}(\text{NH}_3)_5^{1+/0}$  is 0.72 V vs. 0.55 V for  $\text{Fe}^{\text{III/II}}(\text{CN})_5\text{pz}^{2-/3-}$ ) and to 0.12 V in the latter ( $E^\circ$  for  $(\text{NC})_5\text{Co}^{\text{III}}\text{pzRu}^{\text{III/II}}(\text{NH}_3)_5^{1+/0}$  is 0.64 V vs. 0.52 V for  $\text{Ru}^{\text{III/II}}(\text{NH}_3)_5\text{pz}^{3+/2+}$ ). According to this analysis, the increased stability of the binuclear complex containing Fe(II)–Ru(III) vs. the one with Fe(III)–Ru(II) compared to the corresponding mononuclear units is 0.05 V, in remarkably good agreement with the value 0.06 V estimated from the electrostatic terms ( $E_2^\circ + E_3^\circ$ ).

Finally, we inquire into the stability of the mixed valence compound with respect to the isovalent states, eq 19. The



equilibrium constant for eq 19 calculated from the appropriate reduction potentials (Table II) is  $1.3 \times 10^{-4}$ , and therefore the additional stability of V ( $n = 0$ ) as compared to V ( $n = -1$ ) and V ( $n = +1$ ) is 2.6 kcal/mol. An excellent analysis of the factors that contribute to the stability has been presented,<sup>41,42</sup> and we make use of this analysis in the present system. The stability associated with electronic delocalization ( $\alpha^2\bar{\nu}_{\text{max}}$ ) is 0.17 kcal/mol. Since the system is best described as possessing trapped valences, it is not surprising that the resonance stabilization energy is quite small. The electrostatic factor, in contrast, is quite sizeable. The mixed valence state (2 mol) contains +3 and -3 moieties (for an electrostatic attraction of  $3 \times 3 \times 2 = 18$ ) whereas the isovalent states contain +2, -3 and +3, -2 moieties (for an electrostatic attraction of  $2 \times 3 + 3 \times 2 = 12$ ). The electrostatic contribution was calculated from the appropriate ion pair formation constants and is 0.9 kcal/mol. It is noteworthy that the electrostatic contribution of V ( $n = 0$ ), a complex made up of moieties of opposite electric charge, is considerably larger than for binuclear complexes of similar size but having moieties with charges of the same sign.<sup>21,41</sup> The third factor, again a very important one, has to do with  $d\pi-\pi^*$  back-bonding. In the isovalent II, II state, the metal centers acting as  $\pi$  bases compete for the  $\pi$  acidity of the bridging ligand. In contrast, in the mixed valence II, III state, the inductive effect

of the M(III) metal center coordinated to the pyrazine increases its  $\pi$  acidity and thus stabilizes the M(II)–pzM(III) interaction.<sup>21</sup> The very large shift in the MLCT band of  $\text{Fe}(\text{CN})_5\text{pz}^{3-}$  upon coordination of the remote N to  $\text{Ru}(\text{NH}_3)_5^{3+}$  (452 to 590 nm) suggests that the enhanced  $\pi$  acidity of pyrazine contributes appreciably to the stability of the mixed valence ion, perhaps the full 1.4 kcal/mol not accounted for by electron delocalization and the electrostatic factor. From a purely thermodynamic viewpoint, the stability of V ( $n = 0$ ) compared to the isovalent states can be assessed by considering Scheme I. Values of  $\Delta G_1^\circ$ ,  $\Delta G_2^\circ$ ,  $\Delta G_3^\circ$ , and  $\Delta G_4^\circ$  can be calculated from equilibrium constants and reduction potentials listed in Tables II and V. The value of  $\Delta G_5^\circ$  can be obtained from the following cycle. Values of  $\Delta G_6^\circ$ ,  $\Delta G_7^\circ$ , and  $\Delta G_9^\circ$ , calculated from  $E^\circ$  values given in Table II,



are -8.99, -11.99, and 27.90 kcal, respectively.  $\Delta G_4^\circ$  (from  $K$  in Table V) is -9.12 kcal. Therefore,  $\Delta G_5^\circ = -2.20$  kcal ( $K_{\text{eq}} = 41 \text{ M}^{-1}$ ).<sup>43</sup> Values of  $\Delta G_1^\circ$ ,  $\Delta G_2^\circ$ , and  $\Delta G_3^\circ$  are 5.29, -19.59, and -3.00 kcal, respectively. Evidently, the most important factor in determining the stability of the mixed valence ion as compared to the isovalent states resides in the contrasting affinities of the  $\text{Fe}^{\text{III}}(\text{CN})_5^{2-}$  and  $\text{Fe}^{\text{II}}(\text{CN})_5^{3-}$  moieties for the remote N in  $\text{Ru}^{\text{III}}(\text{NH}_3)_5\text{pz}^{3+}$ . The strong affinity exhibited by  $\text{Fe}^{\text{II}}(\text{CN})_5^{3-}$  (9.12 kcal,  $5.1 \times 10^6 \text{ M}^{-1}$ ) is, to be sure, a consequence of its strong back-bonding ability. In contrast, the decreased  $\sigma$  basicity of the pyrazine N caused by the inductive effect of the  $\text{Ru}^{\text{III}}(\text{NH}_3)_5^{3+}$  center and the absence of  $\pi$  basicity for  $\text{Fe}^{\text{III}}(\text{CN})_5^{2-}$  combine to give a low stability to the  $\text{Fe}^{\text{III}}(\text{CN})_5^{3-}$ -pyrazine bond.

**Acknowledgment.** One of the authors (A. H.) benefited from many illuminating discussions with Prof. Joseph Lauher and with Dr. Urs Fürholz.

(41) Richardson, D. E.; Taube, H. *J. Am. Chem. Soc.* **1983**, *105*, 40.

(42) For a +3, +2 mixed valence state the electrostatic term is  $3 \times 2 \times 2 = 12$  compared to  $3 \times 3 + 2 \times 2 = 13$  for the isovalent states.

(43) A similar calculation of the equilibrium constant at 25 °C for  $\text{Fe}^{\text{III}}(\text{CN})_5\text{OH}_2^{2-} + \text{Rh}(\text{NH}_3)_5\text{pz}^{3+} \rightleftharpoons (\text{NC})_5\text{Fe}^{\text{III}}\text{pzRh}^{\text{III}}(\text{NH}_3)_5^+ + \text{H}_2\text{O}$  yields  $31 \text{ M}^{-1}$  ( $\mu = 0.10 \text{ M}$ ) to be compared with the value  $6.7 \text{ M}^{-1}$  ( $\mu = 0.50 \text{ M}$ ) reported previously.<sup>19</sup>