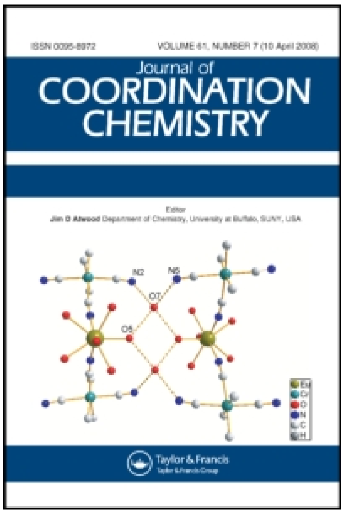

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THE TRINUCLEAR COMPLEX *BIS*-μ-PYRAZINE-*TRANS*-TETRAAMMINERUTHENIUM (II) *BIS* [PENTACYANOFERRATE (II)]

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THE TRINUCLEAR COMPLEX *BIS*-μ-PYRAZINE-*TRANS*-TETRAAMMINERUTHENIUM (II) *BIS* [PENTACYANOFERRATE (II)]

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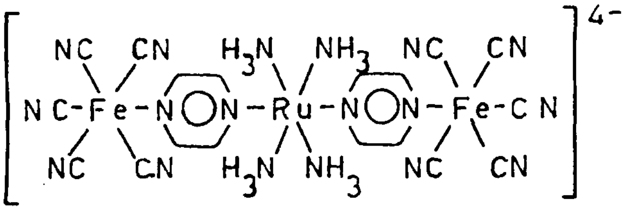
Reported are the properties and reactivity of the linear, trinuclear complex *trans*-$Ru(NH_3)_4[pzFe(CN)_5]_2{}^{4-}$ (pz = pyrazine) in aqueous solution. Consecutive kinetics of formation and dissociation of the trinuclear and of the intermediate binuclear complexes were investigated at their isosbestic points, 545 nm and 504 nm, respectively. The mixed valence chemistry of the trinuclear complex is discussed based on electronic and cyclic voltammetry data.

Key words: trinuclear ion, ruthenium-pyrazine-iron, mixed valence complex.

INTRODUCTION

For its novelty and interest in the chemistry of mixed valence complexes[1–12] the linear trinuclear ion *bis*-μ-pyrazine-*trans*-tetraammineruthenium(II)-bis[pentacyanoferrate(II)] was synthesized in the present work.



The kinetics and mechanisms of formation and dissociation of the trinuclear complex and of the intermediate binuclear complex were studied. Electronic spectroscopy and cyclic voltammetry were used to obtain evidence of extended interactions in this system.

EXPERIMENTAL SECTION

Materials

trans$[(NH_3)_4Ru(pz)_2](C_7H_7SO_3)_2$ was prepared from *trans*$[(NH_3)_4RuCl_2]Cl$[13] as described by Anson et al,[14] but using silver p-toluenesulfonate and lithium p-toluenesulfonate instead of silver trifluoroacetate and sodium perchlorate, respectively. *Anal.* Calcd: C, 40.0; N, 16.3; H, 5.4. *Found:* C, 39.4; N, 16.6; H, 5.1.

$Na_3[Fe(CN)_5NH_3]\cdot 3H_2O$ was prepared for sodium nitroprusside according to the conventional procedure.[15] *Anal.* Calcd: C, 18.4; N, 25.7; H, 2.76. *Found:* C, 18.3; N, 25.5; H, 2.6.

$Na_4[$*trans*-$Ru(NH_3)_4\ pzFe(CN)_5\ {}_2]\cdot nH_2O$ was prepared according to the following procedure: 0.21 mmol of sodium amminopentacyanoferrate(II) was dissolved in *ca.* 20 ml of argon saturated water and treated with 0.10 mmol of the *trans*-tetraamine-bis(pyrazine)ruthenium(II) complex. A deep blue solution was immediately formed. After 20 minutes, 10 g of sodium iodide were added to facilitate the precipitation of the trimeric salt with ethanol. The black-violet solid was purified twice by reprecipitating in water-ethanol mixtures, in the presence of sodium iodide. *Anal.* Calcd. assuming 10 molecules of water per mol of the complex: C, 22.2; N, 25.8; H, 4.14. *Found:* C, 22.5; N, 25.6; H, 4.4. The presence of a large amount of water was also detected in the infrared spectra of the compound.

Spectra Near infrared, visible and ultraviolet spectra were recorded on a Cary 17 Spectrophotometer in aqueous solution or in D_2O.

Cyclic voltammetry A Princeton Applied Research Co. system, consisting of a Model 173 Potentiostat and a Model 175 Universal Programmer was employed in the cyclic voltammetry measurements. Platinum wires were used as auxiliary and working electrodes, with saturated calomel as the reference electrode.

Kinetics measurements The rates of substitution in the aquopentacyanoferrate(II) ion were measured with a Durrum Instrument Co., Model D-110 stopped-flow spectrophotometer, equipped with a Kel-F flow system. A Cary 14 spectrophotometer was used in the slow substitution kinetics of the trinuclear complex with dimethyl sulfoxide.

RESULTS AND DISCUSSION

Kinetics studies The visible absorption spectrum, recorded during the titration of the *trans*-tetraamminebis(pyrazine)ruthenium(II) complex with the aquopentacyanoferrate(II), is shown in Figure 1. The independent isobestic points at 504 and 545 nm are consistent with two consecutive equilibria, associated to the formation of the binuclear and trinuclear complexes, $(NH_3)_4pzRupzFe(CN)_5^-$ and $(NH_3)_4Ru[pzFe(CN)_5]_2^{4-}$, respectively.

$$pzRu(NH_3)_4pz^{2+} + Fe(CN)_5H_2O^{3-} \rightleftharpoons pzRu(NH_3)_4pzFe(CN)_5^- + H_2O$$

$$pzRu(NH_3)_4pzFe(CN)_5^- + Fe(CN)_5H_2O^{3-} \rightleftharpoons (CN)_5FepzRu(NH_3)_4pzFe(CN)_5^{4-} + H_2O$$

Formation of the intermediate binuclear complex can be conveniently studied at 545 nm, by the stopped-flow technique. At this wavelength both the complexes have the same absorptivity, and the kinetics become typically of first order. Analogously, the study of formation of the trinuclear complex can be carried out at 505 nm, where the mononuclear and binuclear complexes absorb to the same extent. An induction period, necessary to form the intermediate binuclear complex, was observed at this wavelength.

The aquopentacyanoferrate(II) ion at 10^{-4} –

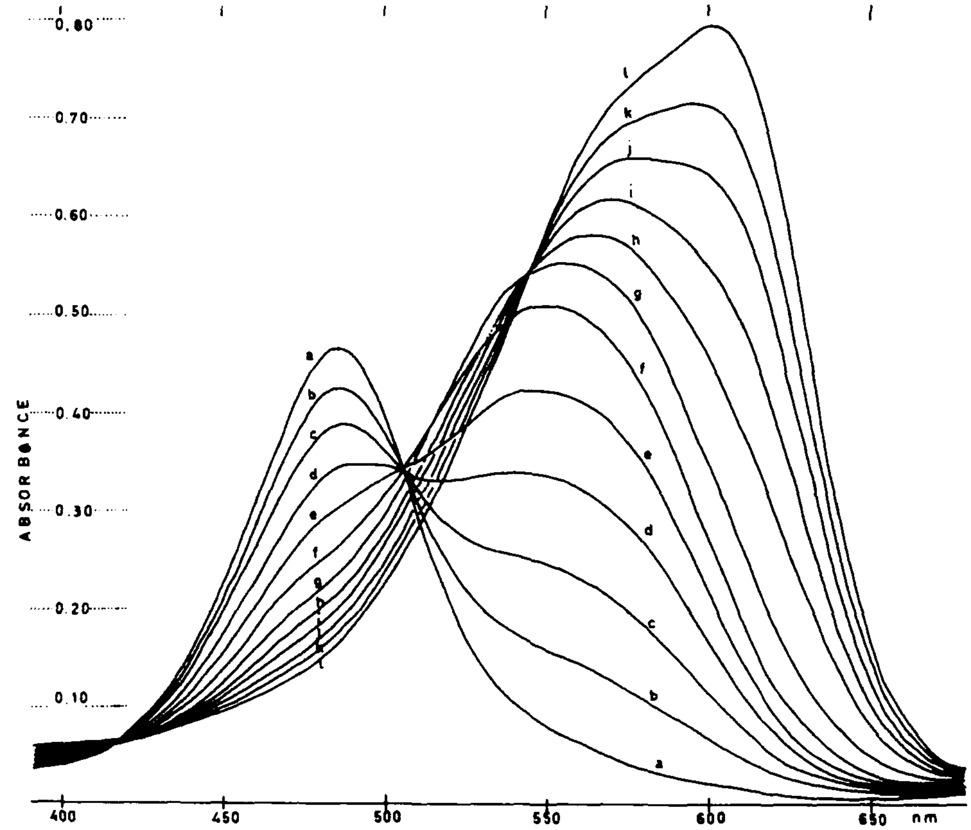


FIGURE 1 Spectrophotometric titration of *trans*-$Ru(NH_3)_4(pz)_2^{2+}$ ($2.2 \times 10^{-5} M$) with $Fe(CN)_5H_2O^{3-}$. Spectra b–k refer to successive additions of 5×10^{-6} *M* amounts of aquopentacyanoferrate(II). In spectrum *l*, this ion is present in large excess.

TABLE I
Rate constants[a] for the reaction $\mathrm{Fe(CN)_5H_2O^{3-}} + \mathrm{Ru(NH_3)_4(pz)_2{}^{2+}}$

T (± 0.2°C)	μ[b] (*M*)	$[\mathrm{Fe(CN)_5H_2O^{3-}}]$ (x 10^4 *M*)	k_{obsd}^{545} (s^{-1}	k_{obsd}^{504} (s^{-1})	k_2^{545} (x $10^{-3}M^{-1}s^{-1}$)	k_2^{504}
15.0	0.100	1.04	0.32_8	0.076	3.1_5	0.73
20.0	0.100	1.04	0.50	0.120	4.8	1.15
25.0	0.100	0.30	0.200	0.050	6.7	1.67
25.0	0.100	0.51	0.346	0.083	6.8	1.63
25.0	0.100	0.70	0.47	0.118	6.7	1.68
25.0	0.100	1.09	0.77	0.180	7.0	1.65
25.0	0.100	1.52	1.05	0.260	6.9	1.71
25.0	0.015	1.09	2.20	0.222	20.2	2.03
25.0	0.200	1.09	0.34_7	0.130	3.1_8	1.19
30.0	0.100	1.04	1.22	0.265	11.7	2.52
Activation Parameters:	$\Delta H^‡$ (± 0.5 kcal.mol^{-1})				+15.1	+14.3
	$\Delta S^‡$ (± 2 cal.deg^{-1}mol^{-1})				+10	+4

[a] formation of the binuclear and trinuclear complexes (10^{-6} *M*) was monitored at 545 nm and at 504 nm, respectively.

[b] ionic strength adjusted with lithium perchlorate, in the presence of acetate buffer, 10^{-3} *M*.

10^{-5} *M*, was generated from the amminopentacyanoferrate(II) complex, in the presence of acetate buffer (10^{-3} *M*) under argon atmosphere.[16] Due to ageing processes[16] associated with this ion, only freshly prepared solutions were employed in this work.

A summary of the results of the dependence of the observed rate constants on the temperature, ionic strength and the concentration of the reactants, is shown in Table I.

Under the conditions of this work, formation of the intermediate binuclear complex occurs with a rate at least four times faster than that at which the trinuclear complex is formed. This ratio increases at low ionic strengths, as a consequence of a more pronounced medium effect on the first reaction. Both reactions are first order with respect to the aquopentacyanoferrate(II) complex.

Typical S_N1 dissociative mechanisms have been postulated for substitution in the aquopentacyanoferrate(II) ion by neutral ligands.[17-18] The activation parameters reported[17,19] for substitution with a series of neutral and monocharged ligands are typically in the range of $\Delta H^‡$ from 15 to 18 kcal.mol^{-1} and $\Delta S^‡$ from 4 to 11 cal.mol^{-1}.deg^{-1}.

Another related mechanism, which seems more likely for substitution in the aquopentacyanoferrate(II) complex by cationic ligands, is the ion-pair S_N1 mechanism of Eigen.[20] Both mechanisms can be visualized in the following scheme:

$$\begin{tikzcd}
(1)\ \mathrm{Fe(CN)_5H_2O^{3-}} \arrow[r, shift left, "+L^{n+}"] \arrow[d, shift right, "-H_2O"'] & \mathrm{Fe(CN)_5H_2O^{3-}\cdot L^{n+}}\ (3) \arrow[l, shift left, "-L^{n+}"] \arrow[d, shift right, "-H_2O"'] \\
(2)\ \mathrm{Fe(CN)_5{}^{3-}} \arrow[r, shift left, "+L^{n+}"] \arrow[u, shift right, "+H_2O"'] & \mathrm{Fe(CN)_5L^{n-3}}\ (4) \arrow[l, shift left, "-L^{n+}"] \arrow[u, shift right, "+H_2O"']
\end{tikzcd}$$

In the pathway, 1–3–4 the rate determining step, 3–4 is preceded by ion pair formation (step 1–3), which is known to depend on the ionic strength.[21,22] This pathway seems more reasonable for the mechanism of formation of the binuclear intermediate, $\mathrm{pzRu(NH_3)_4pzFe(CN)_5{}^-}$, since ion pairing is favored by the opposite charges of the reacting ions, $\mathrm{Fe(CN)_5H_2O^{3-}}$ and $\mathrm{Ru(NH_3)_4(pz)_2{}^{2+}}$.

Under the conditions of this work, the observed rate constant in the ion pair mechanism can be expressed by a product of two terms:

$$k_{obsd} = k_{34} \cdot K_{13}$$

According to Eigen's equation,[21] the calculated (K_{13}) constants for association of dipositive and trinegative ions, separated by *ca* 9 Å, are 14, 22 and 64 M^{-1} at μ = 0.20 *M*, 0.10 *M* and 0.015 *M*, respectively. Although these values are only approximate, it is remarkable that very similar ratios result for K_{13} and k_{obsd} at the several ionic strengths.

This is consistent to the proposed mechanism, where the removal of the coordinated water in the aquopentacyanoferrate(II) ion is not expected to be ionic strength dependent.

The influence of the ionic strength is expected to be relatively less important for the pathway 1–2–4, since the rate determing steps (1–2) precedes the association of charged species. This pathway is more likely for the reaction of $Fe(CN)_5H_2O^{3-}$ with the binuclear ion $Fe(CN)_5pzRu(NH_3)_4pz^-$, where the negative charges in both the species preclude the formation of stable ion pairs.

The activation parameters, $\Delta H^{\ddagger} = 14.3$ kcal.mol^{-1} and $\Delta S^{\ddagger} = 4$ cal.mol^{-1}.deg^{-1} do not differ appreciably from those reported for substitution in the aquopentacyanoferrate(II) ion. In agreement to this mechanism, the rates of formation of the trinuclear complex are only slightly dependent on the ionic strength. Minor interactions with the supporting electrolytes may be responsible for this small dependence.

Dissociation of the trinuclear and binuclear complexes was investigated using dimethyl sulfoxide (dmso) as scavenger for the aquopentacyanoferrate(II) ion.[23] The isosbestic points at 504 and 545 nm were chosen for monitoring the stepwise dissociation of the trimer. Typical first order behavior was observed at 504 nm. For the decay of the binuclear complex, at 545 nm, the kinetics are preceded by an induction period, corresponding to the first reaction.

The observed rate constants for the dissociation reactions at several temperatures, ionic strengths and concentrations of the reactants, are collected in Table II.

Based on the principle of microscopic reversibility, inverse mechanisms to those postulated for the formation reaction, can be proposed for the dissociation process. Now, the rate determing step is the dissociation of the pentacyanoferrate(II) moiety from the ruthenium(II)-pyrazine bridged complex, e.g.,

$$(CN)_5FepzRu(NH_3)_4pzFe(CN)_5{}^{4-} \xrightarrow{k_{504\ nm}} (CN)_5FepzRu(NH_3)_4pz^- + Fe(CN)_5{}^{3-}$$

or

$$(CN)_5FepzRu(NH_3)_4pz^- \xrightarrow{k_{545\ nm}} (CN)_5Fe^{3-} + pzRu(NH_3)_4pz^{2+}$$

Dissociation of the ruthenium(II)-pyrazine bond is neglegible since the final products were spectrophotometrically identified as $Fe(CN)_5dmso^{3-}$ and *trans*-$Ru(NH_3)_4(pz)_2{}^{2+}$. Substitution in *trans*-$Ru(NH_3)_4(pz)_2{}^{2+}$ with dmso was observed to occur, but on a longer time scale.

As for a limiting dissociative mechanism[23-25] the rates of dissociation of the binuclear and trinuclear complexes were independent on the concentrations of dmso, in the range employed (0.44–0.044 *M*). Only the rates of dissociation of the

TABLE II
Rate constants[a] for the dissociation of $(NH_3)_4Ru[pzFe(CN)_5]_2{}^{4-}$

T (± 0.2°C)	μ[b] (*M*)	dmso (*M*)	k_{obsd}^{545} (x 10^4 s^{-1})	k_{obsd}^{504} (x 10^4 s^{-1})
20.0	0.100	0.132	2.21	0.51
25.0	0.100	0.044	5.7	1.37
25.0	0.100	0.132	5.7	1.31
25.0	0.100	0.440	5.6	1.32
25.0	0.015	0.440	5.7	0.92
25.0	0.200	0.440	5.6	1.57
30.0	0.100	0.132	11.3	3.27
35.0	0.100	0.132	25.1	6.5
Activation Parameters: $\Delta H^{\ddagger}$ (± 1 kcal.mol^{-1})			+28.6	+29.6
$\Delta S^{\ddagger}$ (± 4 cal.deg.$^{-1}$mol^{-1})			+22	+27

[a] dissociation of the binuclear and trinuclear complexes (10^{-5} *M*) monitored at 545 nm and at 504 nm, respectively.

[b] adjusted with lithium perchlorate.

trinuclear complex have some dependence on the ionic strength. This is probably caused by interactions with the supporting electrolytes, frequently reported[26-28] in the chemistry of cyano-iron complexes.

The positive entropies of activation (Table II) are also consistent to the dissociative mechanism proposed in this article. The activation parameters, compared to those reported for the $Fe(CN)_5pz^{3-}$ complex (e.g. 26.4 kcal.mol^{-1} for $\Delta H^{\ddagger}$)[24] are somewhat higher in *ca.* 2–3 kcal.mol^{-1}. This suggest the presence of stronger chemical bonds in the binuclear and trinuclear complexes, as a consequence of a more extended electronic delocalization.

From the kinetics data in Table I and II, the following equilibrium constants and thermodynamic parameters were calculated: $K = 1.23 \times 10^7$ M^{-1}, $\Delta H = -13.5$ kcal.mol^{-1}, $\Delta S = -12$ cal.deg^{-1}.mol^{-1} and $K = 1.26 \times 10^6$ M^{-1}, $\Delta H = -15.3$ kcal.mol^{-1}, $\Delta S = -23$ cal.deg.$^{-1}$mol^{-1} for the formation of the binuclear and trinuclear complexes, respectively.

Electronic Spectra and Mixed Valence Chemistry

The electronic spectra of the trinuclear ion in the near infrared, visible and ultraviolet region are shown in Figure 2. As with many related systems,[5,24] the very intense absorption band in the visible ($\epsilon = 3.7 \times 10^4$ M^{-1}cm^{-1}) can be assigned to a charge transfer transition. Simple gaussian analysis of this band indicates the presence of a strong absorption centered at 605 nm (16.5 kK) followed by another at 552 nm (18.1 kK) of relative intensity 0.7. An expanded view of this band was shown in Figure 1. A third, weak band, can be visualized at *ca.* 450 nm as a shoulder on the tail of the charge transfer band. Since it has also been observed in many pentacyanoferrates,[29] a d–d transition is suggested.

The ultraviolet spectra of the trimer are dominated by the $\pi\rightarrow\pi^*$ absorptions in the heterocyclic ligand (260 nm or 38.4 kK) and the metal-to-cyanide charge transfer transitions (<220 nm or > 45 kK).

No near infrared absorption was observed using up to 10^{-3} *M* solutions of the trimer, in D_2O. However, after the addition of bromine, a weak near infrared absorption appeared at 7 kK, moving up to 9.5 kK with increasing bromine concentrations. Spectra *b* and *c* in Figure 2 illustrate this for independent, 2×10^{-5} *M* solutions of the trinuclear

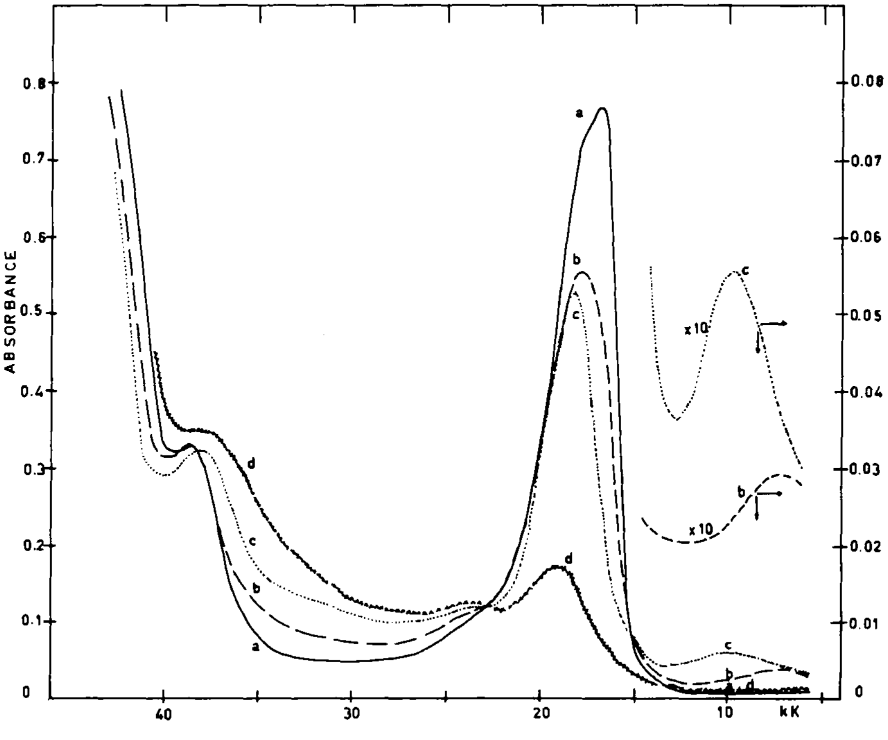


FIGURE 2 Absorption spectra of the trinuclear complex *trans*-$Ru(NH_3)_4[pzFe(CN)_5]_2^{4-}$ (a) and of the products of oxidation with one (b), and two (c) and four (d) equivalent amounts of bromine, in D_2O.

complex, in the presence of one and two equivalent amounts of bromine, respectively.

Complete disappearance of the absorption bands in the visible and near infrared region requires a large excess of bromine. Presumably, a high oxidation potential is involved in the last step. The oxidation process at this stage seems to be poorly reversible; reductants like ascorbic acid, thiosulfate and ferrocyanide do not generate the original spectrum.

In more concentrated solutions $(> 10^{-4}\ M)$ the partial oxidation of the trinuclear complex produces a fine, black precipitate. Even at $10^{-5}\ M$, although precipitation has not been observed, the visible-near infrared spectra of the partially oxidized complex exhibit clear evidence of slow decomposition. This is not totally unexpected, since most ruthenium(II) and iron(II) complexes of unsaturated ligands is known to be less stable in the oxidized form. Due to decomposition, only freshly prepared solutions of the oxidized complexes have been used for the spectral measurements.

Based on the model proposed by Zwickel and Creutz for the *trans*-tetraammine*bis*(pyrazine)-ruthenium(II),[30] a simplified π-MO scheme (Figure 3) can be devised for the trinuclear complex. In this model, a D_{2h} symmetry was assumed and only the d_{xy} orbital of the metal and the lowest unoccupied π-orbital of pyrazine were considered. The orbitals of symmetry associated to the MO scheme of Figure 3 are illustrated in Figure 4. They have been deduced with the aid of projection operators in group theory.[31]

In the FepzRupzFe^{4-} complex, the low lying b_{1g}, b_{2u} and b_{1g} orbitals are occupied. Therefore, if one excludes the highest energy transitions to the unoccupied b_{1g} orbital (expected to occur in the UV region), only two Laporte allowed transitions are possible. They are the transitions from the A_g, $(b_{1g})^2(b_{2u})^2(b_{1g})^2$ ground state to the B_{3u}, $(b_{1g})^2(b_{2u})^2(b_{1g})(b_{2u})$ and $(b_{1g})(b_{2u})^2(b_{1g})^2(b_{2u})$ excited states, respectively. Since only two bands have been observed in the visible spectrum of the trinuclear complex, one may associate them to these Laporte allowed transitions.

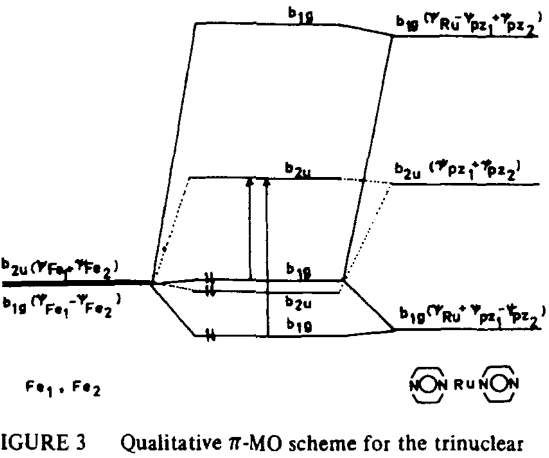


FIGURE 3 Qualitative π-MO scheme for the trinuclear complex, *trans*-$Ru(NH_3)_4[pzFe(CN)_5]_2^{4-}$.

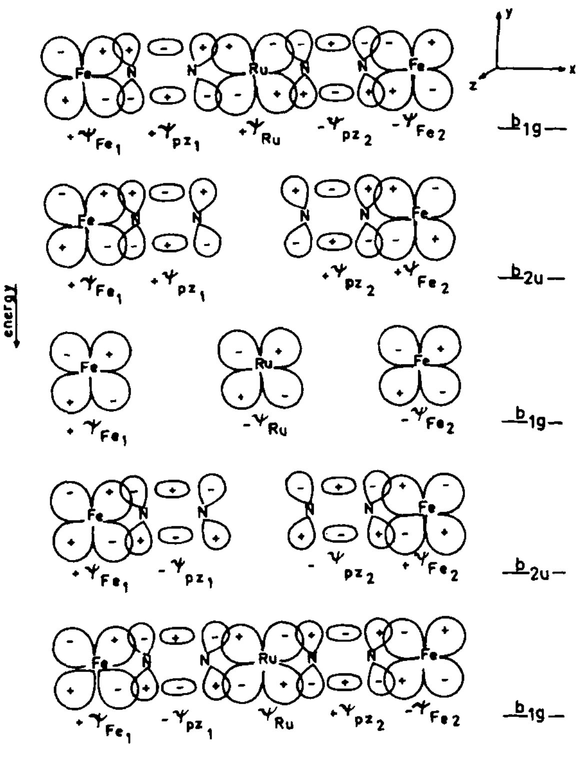


FIGURE 4 Orbitals of symmetry for the trinuclear complex, *trans*-$Ru(NH_3)_4[pzFe(CN)_5]_2^{4-}$.

Spectrum *c* of Figure 2, which refers to the twice oxidized form of the trimer, exhibits only one charge transfer band in the visible, with practically the same energy of the highest $A_g \rightarrow B_{3u}$ transition in the original complex. The occurrence of a single band agrees with the MO scheme, since now, the middle b_{1g} level is unoccupied. The near infrared band appearing at 9.5 kK might be assigned to the symmetry forbidden transition from the A_g, $(b_{1g})^2(b_{2u})^2$ ground state, to the A_g, $(b_{1g})(b_{2u})^2(b_{1g})$ excited state. This assignment is consistent to the relatively small intensity of the near infrared band, in comparison to those of the totally allowed transitions in the visible region.

Spectrum *b* which refers to the monooxidized form of the trimer, exhibits a probably composite band at

17.8 kK and a near infrared band at *ca.* 7 kK. We propose a similar assignment to that for spectra *a* and *c*.

Conproportionation equilibrium of the type FepzRupzFe^{3-} ⇋ FepzRupzFe^{4-} + FepzRupzFe^{2-} cannot be neglected, especially in the case of spectrum *b*. To investigate this point, and to evaluate the formal potentials for the complex, some cyclic voltammetry measurements were carried out. Typical cyclic voltammograms for the trinuclear complex are shown in Figure 5. Only two waves have been observed in the 0.2–1.2 V range (vs. NHE); at 0.65 V and 0.95 V, respectively.

It was previously reported that an excess of bromine ($E^\circ = 1.08$ V) is required for the complete oxidation of the trinuclear complex. This is evidence for a high oxidation potential associated with the FrepzRupzFe^{2-} complex, presumably near 1 V. Based on this fact, the wave at *ca.* 0.95 V *vs.* NHE was assigned to the final stage of oxidation (3 electrons) of the trinuclear complex. As consequence, for the first and second steps, the waves must be superimposed, yielding the broad wave at 0.65 V.

Using a localized approach for the valence description in the trinuclear complex, the observed waves at 0.65 V and 0.95 V may be assigned to the oxidation of the iron(II) and ruthenium(II) centers, respectively. These values are consistent with those reported for the pentacyano(pyrazine)ferrate(II) (0.55 V)[24] and the *trans*-tetraammine(pyrazine)-ruthenium(II) (0.78 V)[14] complexes.

The similar potentials for the oxidation of the iron(II) centers greatly support the occurrence of the conproportionation equilibrium above. However, the low stability of the oxidized products and the somewhat irreversible nature of the cyclic voltammetry waves, preclude a quantitative study on this subject.

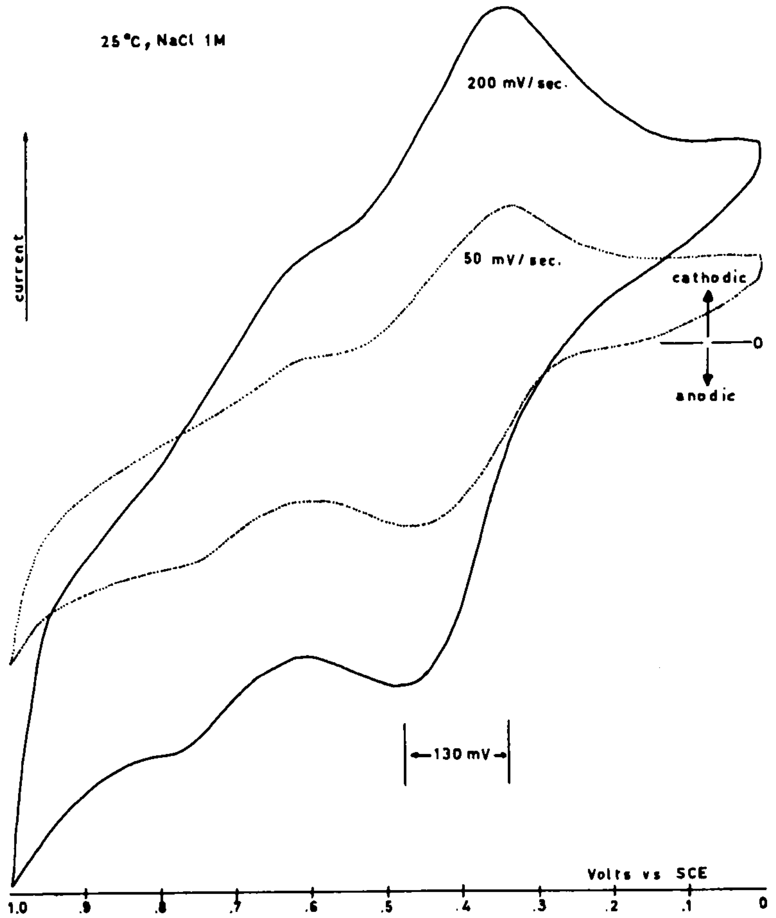


FIGURE 5 Cyclic voltammograms of the trinuclear complex, *trans*-$Ru(NH_3)_4[pzFe(CN)_5]_2^{4-}$.

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