Notes

Intramolecular Electron-Transfer Assistance in the Redox Reaction of (μ-Cyano)pentaammineruthenium(III) Pentacyanoferrate(II). Role of the Electronic Isomer and of the Specific Donor−Acceptor Interactions

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Introduction

As a part of the emerging interest in the redox reactions of mixed-valence binuclear complexes, particular attention has been given to the reactions of complexes of the $[(NC)_5Fe-L-Ru(NH_3)_5]^n$ series with peroxydisulfate as oxidant.[1] Addressing the question of which metal center is kinetically active in the route to the fully oxidized complex highlighted the role of the electronic isomer having a $[Fe^{III}-Ru^{II}]$ distribution. This was done for L = μ-1,2-bis(4-pyridyl)ethane (bpa),[2] a noncommunicating bridging ligand, as well as for L = imidazolato (Im^-)[3] and cyanopyridine (Cnpy),[4] which provide a weak coupling between the metal centers. By performance of a mechanistic analysis, conclusions were drawn on the ineffectiveness of the direct attack of peroxydisulfate on the Fe^{II} center, supported by previous measurements of the rates of reaction of different $Fe^{II}(CN)_5L^{n-}$ complexes with peroxydisulfate.[2−5] These rates were significantly slower than the ones for the corresponding $Ru^{II}(NH_3)_5L^{n+}$ complexes by about 2−3 orders of magnitude.[1−4]

Recently, a Marcus LFE relationship was found to hold for the redox reactions of the cyanoferrate complexes with peroxydisulfate;[6] this is complementary of a similar behavior found for the ruthenium−pentaammine systems.[3] As a result, the rationalization of mechanisms dealing either with the direct attack at Fe^{II} or with the relevance of electronic isomerization routes can be put on a more quantitative basis. In this work, we present a kinetic and mechanistic study with the cyanide-bridged mixed-valence complex, for which a moderate electronic coupling between metal centers is operative.[7]

Experimental Section

Potassium hexacyanoferrate(II) and potassium peroxydisulfate (both from Merck) were recrystallized from water. The first one was dried at 100 °C for complete dehydration. $[Ru(NH_3)_5(OSO_2CF_3)](CF_3SO_3)_2$ was prepared as described in the literature.[8] The mixed-valence binuclear complex was prepared by reaction of equimolar solutions of $Fe(CN)_6^{4-}$ and $[Ru(NH_3)_5(H_2O)]^{3+}$ (pH 4.75) under an argon atmosphere. The latter ion was obtained through aquation of the ruthenium−triflate compound.[7]

The kinetic experiments for the oxidation reactions of the mixed-valence complex (*ca.* 5×10^{-5} M), as well as for mononuclear $Fe(CN)_6^{4-}$ with peroxydisulfate, were performed under pseudo-first-order conditions (excess of peroxydisulfate, range $(1.5-15) \times 10^{-3}$ M), at $I = 0.1$ M ($NaClO_4$), pH 4.75, $T = 25.0$ °C, with a stopped-flow mixing device (Applied Photophysics RX 1000) interfaced with a Hewlett-Packard HP 8452A diode-array instrument. Alternatively, a Hitech PQ/SF-53 stopped-flow spectrophotometer was used for the complete set of experiments with the binuclear complex. The reaction of $Fe(CN)_6^{4-}$ was followed by measuring the formation of $Fe(CN)_6^{3-}$ at 420 nm. Either the formation of product (420 and 530 nm) or the disappearance of the reactant (800 nm) was used for the reaction of the binuclear complex.

The square-wave voltammograms were measured with a PAR 273 A instrument, by using a conventional three-electrode cell with vitreous carbon as the working electrode, a platinum net as the counterelectrode, and a Ag/AgCl electrode as a reference, at $I = 0.1$ M (KNO_3). Successive runs were obtained with different solutions, starting with mononuclear $Fe(CN)_6^{4-}$ (ca. 5×10^{-3} M) and adding aliquots of $Ru(NH_3)_5H_2O^{3+}$, up to an equimolar composition. The values of the potentials are referred to the NHE scale.

Results and Discussion

Upon mixing of the mixed-valence reactant with peroxydisulfate, the absorption of the intervalence band at 980 nm[7] decreases and new bands appear at 420 and 530 nm (Supporting Information, Figure S1). The stoichiometry is described by eq 1.

$$2[(NC)_5Fe^{II}CNRu^{III}(NH_3)_5]^- + S_2O_8^{2-} \rightarrow 2[(NC)_5Fe^{III}CNRu^{III}(NH_3)_5] + 2SO_4^{2-} \quad (1)$$

The 420 nm absorption corresponds to a LMCT transition from cyanides to Fe^{III}, as in $Fe(CN)_6^{3-}$, while the 530 nm band suggests a similar transition from the bridging cyanide to the Ru^{III} center.

The rate-law for eq 1 was $-d[Fe^{II}Ru^{III}]/dt = k_{obs}[Fe^{II}Ru^{III}]$ and was well-behaved up to 3 half-lives, independently of the selected wavelength. By the plotting of k_{obs} against $[S_2O_8^{2-}]$, a linear behavior was obtained, with a zero intercept. From the slope, the second-order rate constant was calculated, $k_1 = 4.0 \pm 0.4$ M^{-1} s^{-1} (25 °C), according to $k_{obs} = k_1[S_2O_8^{2-}]$.

At a first glance, the value of k_1 appears to be consistent with a direct attack of peroxydisulfate on the Fe^{II} center, as suggested by previous results on the oxidation of $Fe^{II}(CN)_5L^{n-}$ complexes with peroxydisulfate, showing values around 1 M^{-1} s^{-1}.[2−5] However, recent work[6] showed that the rate constants for oxidation within the latter series of complexes are dependent on the redox potentials at the iron center, displaying a Marcus type LFE behavior. Figure 1 shows the linear correlation between ln k_{Fe} and E_{Fe} for a series of $Fe^{II}(CN)_5L^{n-}$ complexes. For the rate of oxidation of mononuclear $Fe(CN)_6^{4-}$ with peroxydisulfate, under similar conditions as in the oxidation of the binuclear complex, the rate constant was 0.14 ± 0.02 M^{-1}

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(1) Haim, A. In *Electron Transfer Reactions: Inorganic, Organometallic, and Biological Applications*; Isied, S. S., Ed.; Advances in Chemistry Series No. 253; American Chemical Society: Washington, DC, 1997.

(2) Olabe, J. A.; Haim, A. *Inorg. Chem.* **1989**, *28*, 3278.

(3) Parise, A. C.; Baraldo, L. M.; Olabe, J. A. *Inorg. Chem.* **1996**, *35*, 5080.

(4) Almaraz, A. E.; Gentil, L. A.; Baraldo, L. M.; Olabe, J. A. *Inorg. Chem.* **1996**, *35*, 7718.

(5) (a) Yeh, A.; Haim, A. *J. Am. Chem. Soc.* **1985**, *107*, 369. (b) Sulfab, Y. *Inorg. Chim. Acta* **1977**, *22*, 35.

(6) Chen, M. H.; Lee, S.; Liu, S.; Yeh, A. *Inorg. Chem.* **1996**, *35*, 2627.

(7) Burewicz, A.; Haim, A. *Inorg. Chem.* **1988**, *27*, 1611.

(8) Dixon, N. E.; Lawrance, G. A.; Lay, P. A.; Sargeson, A. M. *Inorg. Chem.* **1984**, *23*, 2940.

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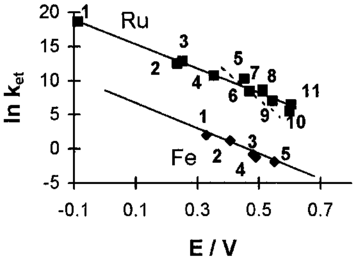

Figure 1. Plots of ln k_{et} *vs* $E°_M$ (M = Fe, Ru) for "intramolecular" electron transfer in the ion pairs $[X_5M-L-Ru^{II}(NH_3)_5]^n \,||\, S_2O_8^{2-}$. Top line, X_5M-L: **1**, $(NC)_5Fe^{III}-Im^{3-}$; **2**, $(NC)_5Fe^{II}-bpa^{3-}$; **3**, $(NC)_5Fe^{III}-bpa^{2-}$; **4**, $(edta)Ru^{II}-pz^{2-}$; **5**, $(NC)_5Fe^{II}-pz^{3-}$; **6**, $(NC)_5Fe^{III}-CN^{4-}$; **7**, $(NC)_5Fe^{II}-3pyCN^{3-}$; **8**, $(NC)_5Fe^{II}-4pyCN^{3-}$; **9**, $(NC)_5Fe^{III}-3pyCN^{2-}$; **10**, $(NC)_5Co^{III}-pz^{2-}$; **11**, $(NC)_5Fe^{III}-4pyCN^{2-}$; taken from ref 3. Bottom line, similar relation for the ion pairs $[Fe^{II}(CN)_5L]^n \,||\, S_2O_8^{2-}$,L: **1**, 4-ampy; **2**, py; **3**, pz; **4**, 4,4′-bpy; **5**, CN^-; taken from ref 6. The values of k_{et} are in s^{-1}, and $E°_M$ are in V *vs* NHE (both corrected for ion-pairing; *cf.* ref 3).

s^{-1} (25 °C), in agreement with previously measured values.[9] After correction for electrostatic effects, this value fitted quite well in the correlation, as seen in Figure 1, considering $E°_{Fe} = 0.42$ V.[10] Now, for predicting the value of k_{Fe} in the binuclear complex, we need the redox potential, which was not measured earlier. From the voltammograms of solutions containing $Fe(CN)_6^{4-}$ and $Ru(NH_3)_5H_2O^{3+}$ it can be seen that the peaks associated with the mononuclear Fe (0.42 V) and Ru (0.04 V) complexes shift to 0.65 and −0.06 V, respectively, upon mixing the reactants. The shifts associated with the formation of the binuclear $[Fe^{II}Ru^{III}]$ complex are associated with the electronic coupling induced by the cyanide bridging ligand. A discussion on this subject can be found elsewhere.[3−5] By entering into the linear correlation in Figure 1 with $E°_{Fe(corr)} = 0.62$ V, we predict a value of $k_{Fe} = 0.03$ M^{-1} s^{-1}, which is 2 orders of magnitude lower than the one measured in the present work. Thus, we could in principle rule out the direct attack on Fe^{II}.

Consider the mechanism displayed by eqs 2−4′, which was proposed to hold for some related binuclear complexes with L = bpa, Im^-, and CNpy.[2−4]

$$[Fe^{II}-Ru^{III}]^- \rightleftarrows [Fe^{III}-Ru^{II}]^- \qquad K_{et} = k_{et}/k_{-et} \qquad (2)$$

$$[Fe^{II}-Ru^{III}]^- + S_2O_8^{2-} \rightarrow [Fe^{III}-Ru^{III}] + SO_4^- + SO_4^{2-} \qquad k_3 \quad (3)$$

$$[Fe^{II}-Ru^{III}]^- + SO_4^- \rightarrow [Fe^{III}-Ru^{III}] + SO_4^{2-} \qquad \text{fast} \quad (3')$$

$$[Fe^{III}-Ru^{II}]^- + S_2O_8^{2-} \rightarrow [Fe^{III}-Ru^{III}] + SO_4^- + SO_4^{2-} \qquad k_{Ru} \quad (4)$$

$$[Fe^{III}-Ru^{II}]^- + SO_4^- \rightarrow [Fe^{III}-Ru^{III}] + SO_4^{2-} \qquad \text{fast} \quad (4')$$

From the mechanism in eqs 2−4′, we obtain $k_1 = 2K_{et}k_{Ru} + 2k_3$ (cf. ref 3). If we assume that $2k_3$ is negligible, the second-order rate constant for oxidation of the binuclear complex, k_1, should be related to the equilibrium constant for electronic isomerization, K_{et}, times k_{Ru}, which involves a direct attack on the Ru^{II} center (eq 4). An estimation of K_{et} can be obtained with the following thermodynamic cycle:

$$\begin{tikzcd}
 & {[Fe^{III}–Ru^{III}]} \arrow[dl, shift right, "E°_1 = 0.65\ V"'] \arrow[dr, shift left, "E°_3 = 0.5\ V"] & \\
{[Fe^{II}–Ru^{III}]} \arrow[ur, shift right] \arrow[rr, shift left, "\Delta E°_{et}"] & & {[Fe^{III}–Ru^{II}]} \arrow[ll, shift left] \arrow[ul, shift left]
\end{tikzcd}$$

Here $E°_1$ corresponds to the measured value for the iron couple and $E°_3$ was estimated by comparison with related nitrile-bound ruthenium complexes.[4,11] Thus, $\Delta E°_{et} = -0.15$ V and $K_{et} = 2.9 \times 10^{-3}$. With K_{et} and the experimental value for k_1, we calculate a value for $k_{Ru} = 665$ M^{-1} s^{-1}. To check if this value has any significance, we enter the linear correlation for the $[Ru(NH_3)_5L]^n$ series corrected for ion-pairing effects,[3] also shown in Figure 1. We find, for $E°_{Ru,\ corr} = 0.47$ V, that the value of ln $k_{Ru,\ corr}$, 8.4, fits very well indeed.

As a conclusion, the mechanism involving the fast reaction of the unstable electronic isomer has been validated again. Two points should be stressed: First, the fact that the Ru^{II} center is kinetically active in the present study is predictable, because K_{et} presents a moderately high value, similar to the one found for L = bpa;[2] note that this path was operative even with the imidazolato-bridged complex, with $K_{et} = 1.2 \times 10^{-6}$. Second, the values of k_{Ru} and k_{Fe} in Figure 1 have been corrected for electrostatic interactions, associated with the ion-pair formation between $S_2O_8^{2-}$ and the corresponding binuclear complexes.[3,12] As the intrinsic reactivities for the $Fe(CN)_5L^{n-}$ and $[Ru(NH_3)_5L]^{n+}$ ions seem to be very similar (given the similar electron exchange rates),[6,13] the two lines for the iron and ruthenium complexes in Figure 1 should, in fact, collapse into a single line. In contrast to the generally accepted mechanism,[12] in which eq 5 considers only ion-pair interactions (K_{ip}), we now

$$[Fe^{III}-Ru^{II}]^- + S_2O_8^{2-} \rightleftarrows [Fe^{III}-Ru^{II}]^- \,||\, S_2O_8^{2-} \qquad K_{pc}, \text{fast} \quad (5)$$

$$[Fe^{III}-Ru^{II}]^- \,||\, S_2O_8^{2-} \rightarrow [Fe^{III}-Ru^{III}] \,||\, SO_4^-,SO_4^{2-} \qquad k_{et}, \text{slow} \quad (6)$$

$$[Fe^{III}-Ru^{III}] \,||\, SO_4^-,SO_4^{2-} \rightarrow \text{products} \qquad (7)$$

define K_{pc},[14] corresponding to the formation of a precursor complex which takes into account also the specific interactions between the reactants.

As $k_{et} = k_{Ru}/K_{pc}$, the upward shift in k_{et} for the ruthenium line in Figure 1 corresponds to an energy difference associated with K_{pc} and K_{ip} values, which amounts to *ca.* 5 kcal/mol. The explanation agrees with the closely similar behavior of bound ammines through their interactions with donor solvents.[15] In contrast, donor cyanides show specific interactions with acceptor

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(9) López, C.; Rodríguez, A.; Gómez-Herrera, H.; Sánchez, F.; Moyá, M. L. *J. Chem. Soc., Faraday Trans.* **1992**, *88*, 2701.

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

(11) Matsubara, T.; Ford, P. C. *Inorg. Chem.* **1976**, *15*, 1107. This estimation is crucial, because it affects both $\Delta E°_{et}$ and k_{Ru} values. It is known that cyanide interacts strongly with $[Ru(NH_3)_5]$ when binding through the N(nitrile) atom. An average value was taken, 0.5 V, considering the *E* values measured for L = Cnpy,[4] AcN, and other nitrile-binding ligands. The dotted line in Figure 1 highlights the calculated values for $E'_{Ru}° = E_{Ru}° \pm 0.1$ V, showing that the uncertainties do not shift significantly the k_{Ru} values.

(12) Haim, A. *Comments Inorg. Chem.* **1985**, *4*, 113.

(13) Creutz, C. *Prog. Inorg. Chem.* **1983**, *30*, 1.

(14) The chemical process related to K_{pc} involves two energetic contributions associated with electrostatic and specific interactions. Consequently, $K_{pc} = K_{si}K_{ip}$, where $K_{si} = 4.6 \times 10^3$ M^{-1} (−5 kcal/mol; see text) and $K_{ip} = 0.14$ M^{-1} for $[Fe^{III}-Ru^{II}]^- \,||\, S_2O_8^{2-}$ (see ref 12 for detailed calculation); then, $K_{pc} = 630$ M^{-1}.

(15) Curtis, J. C.; Sullivan, B. P.; Meyer, T. J. *Inorg. Chem.* **1983**, *22*, 224.

solvents[16] and, thus, should not be preferentially involved in the interactions with the peroxydisulfate reactant.

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Supporting Information Available: Successive UV−visible spectra in the reaction of $[(NC)_5Fe^{II}CNRu^{III}(NH_3)_5]^-$ with an excess of $S_2O_8^{2-}$, Figure S1, and kinetic data for the latter reaction, Figure S2 (3 pages). Ordering information is given on any current masthead page.

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(16) (a) Toma, H. E.; Takasugi. *J. Solution Chem.* **1983**, *12*, 547. (b) Toma, H. E.; Takasugi. **1989**, *18*, 575.