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Characterization of a Delocalized Mixed-Valence Bis-Macrocyclic Diiron Compound

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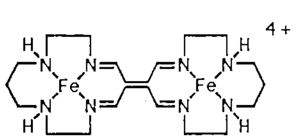
A mixed-valence Fe^{II}/Fe^{III} compound has been obtained by electrochemical oxidation of a bis-macrocyclic Fe^{II}/Fe^{II} complex. The binucleating ligand provides a delocalized π system that facilitates electronic interaction between the metals. The Mössbauer spectrum of the mixed-valence compound consists of a single quadrupole-split doublet down to 4 K which establishes the equivalency of the two iron atoms. The cyclic voltammogram of the Fe^{II}/Fe^{II} species in rigorously dried acetonitrile shows two reversible oxidations with $\Delta E_{1/2} = 500$ mV. This corresponds to a comproportionation constant for the mixed-valence compound of 10^{11}. This large value also indicates the mixed-valence species is valence-averaged class III and is stabilized by delocalization. The mixed-valence compound has an intense near-infrared band ($\lambda_{max} = 940$ nm, $\epsilon = 27\,000$ M^{-1} cm^{-1}). Analysis of this band using Hush's equations for an intervalence transition also indicates the system is delocalized.

We recently described the structure of a new bis-macrocyclic dinuclear iron complex[2] shown as follows:



The dark green low-spin (Fe^{2+}/Fe^{2+}) complex has two axial acetonitrile ligands on each iron. The binucleating ligand provides a delocalized π-system that facilitates electronic interaction between the metals, and the tetraazamacrocyclic binding sites inhibit metal dissociation. This new complex thus offers many interesting areas of study. Specifically, its structure suggested the possibility of generation of a stable mixed-valence complex. This expectation has been realized, and this paper describes magnetic, spectroscopic, and electrochemical results which support characterization of the mixed-valence compound as a delocalized ($Fe^{2.5+}$,$Fe^{2,5+}$) species. To our knowledge this is the first example of a Robin and Day[3] class III nonorganometallic, low-spin, mixed-valence iron compound.

Experimental Section

Materials. 1,4,8,11-Tetraazacyclotetradecane (cyclam) was purchased from Lancaster Synthesis, Inc. Iron perchlorate hexahydrate was obtained from Johnson Mathey Electronics. Acetonitrile (Burdick-Jackson Chemical) was refluxed for 24 h over CaH_2 and then distilled twice from P_2O_5 and stored over 4A molecular sieves. Tetrabutylammonium perchlorate (TBAP) (Fluka) was purified by 3-fold recrystallization from boiling ethyl acetate and dried under vacuum at 60 °C.

$[Fe_2(C_{20}H_{36}N_8)(CH_3CN)_4](ClO_4)_4 2CH_3CN$ ($[(Fe_2(TIED)(CH_3CN)_4](ClO_4)_4$ (TIED = Tetraaminoethylene Dimacrocycle)). Iron(II) perchlorate hexahydrate (5.2 g, 14.3 mmol) was dissolved in 125 mL of acetonitrile; then 1.0 g (5.0 mmol) of cyclam was added. The solution was stirred for 2 h to give a purple solution, which was then filtered to remove brown hydrous iron oxides. The purple filtrate was loosely covered and set aside for several days during which time dark green crystals of $[Fe_2(TIED)(CH_3CN)_4](ClO_4)_4{\cdot}2CH_3CN$ formed. The purple supernatant was carefully decanted and treated with ether to yield a second crop of crystals. The crystals were then rinsed several times with $CHCl_3$ to remove residual mother liquor and hydrous brown iron oxides. Typical yields were 0.14–0.20 g.

Oxidation Product of $[Fe_2(TIED)(CH_3CN)_4](ClO_4)_4$. A green solution of $[Fe_2(TIED)(CH_3CN)_4]^{4+}$ in acetonitrile with 0.1 M TBAP was oxidized at +1.25 V vs a Ag^+/Ag reference electrode. The working electrode was Pt mesh and was separated from the counter electrode (Pt foil) compartment by a medium glass frit. The electrolysis was continued until the current dropped to a low constant value, and completion of the oxidation was checked by UV–vis spectroscopy. The yellow solution containing the oxidized product was transferred under argon to a round-bottom flask. The solvent was then removed under vacuum to yield a yellow solid. The TBAP electrolyte was then removed by washing with $CHCl_3$. After drying in low vacuum at room temperature, the yellow solid was stored under Ar gas.

Equipment. UV–vis–near-IR spectra were taken on a Perkin-Elmer Lambda 9 spectrophotometer. Electrochemical studies were done with an IBM EC 225^{2A} voltammetric analyzer or a PAR 173 potentiostat and PAR 175 programmer equipped with a Model 179 digital coulometer. The spectroelectrochemical cell has been described previously.[8] Bulk magnetic susceptibility measurements were made using a precalibrated Teflon sample holder on a Quantum Design MPMS SQUID magnetometer. Mössbauer spectra were taken by R.B.F. and G.C.P. ESR measurements were made on a Varian E9 Spectrophotometer equipped with an Air Products He dewar.

Results and Discussion

The cyclic voltamogram of the (Fe^{2+},Fe^{2+}) species in CH_3CN has a reversible oxidation at 0.95 V (Ag^+/Ag reference electrode). The perchlorate salt of the mixed-valence compound was obtained by bulk electrolysis at 1.25 V in CH_3CN at a Pt mesh electrode. After removal of the solvent, the TBAP electrolyte was dissolved in $CHCl_3$, leaving the yellow green solid as a pure compound. Bulk magnetic susceptibility measurements of this compound were made from 5 to 100 K. Curie behavior was observed with a magnetic moment of 1.82 μ_B. This establishes an $S = {}^1/_2$ ground state and is consistent with low-spin formally Fe^{II} and Fe^{III} centers. An $S = {}^1/_2$ ground state could also arise from strongly antiferromagnetically coupled high-spin Fe^{II} and Fe^{III} sites. This

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(1) (a) University of the Pacific. (b) University of California. (c) California Polytechnic State University. (d) Massachusetts Institute of Technology.

(2) Mountford, H. S.; Spreer, L. O.; Otvos, J. W.; Calvin, M.; Brewer, K. J.; Richter, M.; Scott, B. *Inorg. Chem.* **1992**, *31*, 717. Note: A mistake was made on ϵ for the 874-nm band; it is 24 600 and not 14 000 M^{-1} cm^{-1}.

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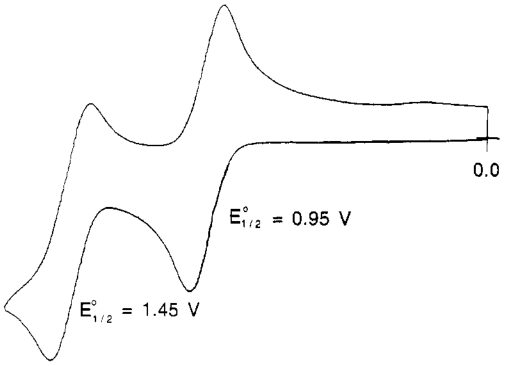

Figure 1. Cyclic voltammogram of the Fe^{II}/Fe^{II} complex from 0.00 to 1.75 V relative to Ag^+/Ag. Conditions: 0.1 M TBAP in CH_3CN; 200 mV/s; Pt disk.

is unlikely since the (Fe^{2+},Fe^{2+}) parent complex is low-spin due to the strong ligand field generated by the tetraazamacrocycles.

A property of mixed-valence compounds which is frequently used to help classify complexes as valence-averaged or valence-trapped is the value of the comproportionation constant, K_{com}, for the equilibrium

$$(II–II) + (III–III) = 2(II–III)$$

The value of K_{com} can be determined by the difference in potentials ($\Delta E_{1/2}$) for oxidation to the (II–III) and (III–III) levels. The cyclic voltammogram for the oxidation of the (Fe^{2+},Fe^{2+}) compound in rigorously dried CH_3CN from 0.0 to 1.65 V (relative to Ag^+/Ag) is shown in Figure 1. Two reversible oxidations were observed in acetonitrile that had been refluxed over CaH_2 and distilled twice from P_2O_5 ($E^0_{1/2}(1) = +0.95$ V; $E^0_{1/2}(2) = 1.45$ V). The higher potential wave is extremely sensitive to the amount of water present, and this chemistry is under investigation. For the present discussion, we assume the second wave is due to oxidation to the (Fe^{3+},Fe^{3+}) level with an estimated $\Delta E_{1/2}$ of 1.45 V. This gives a lower limit for the value of K_{com} of 10^{11}. This very large value is consistent with a class III, valence-averaged, complex.

The $\Delta E_{1/2}$ of mixed-valence complexes is influenced by four factors:[4,6] (1) statistical contributions, (2) electrostatics, (3) difference in solvation energies, and (4) electron delocalization. The dinickel complex of the fully saturated bis(cyclam) binucleating ligand has been studied[7] and is a good analogue to our compound. For the nickel species, the $\Delta E_{1/2}$ value is 75 mV in CH_3CN. Delocalization cannot contribute to the stability of the mixed-valence state for the saturated dinickel complex. Furthermore, the first three factors contributing to $\Delta E_{1/2}$ for the saturated nickel complex and our compound are probably very similar because the charges are the same. The lower limit of $\Delta E_{1/2}$ for the diiron complex is 500 mV of which less than 100 mV can reasonably be assigned to nonelectronic factors. Thus the high degree by which the mixed-valence form is favored over the two isovalent species is largely due to delocalization or resonance stabilization.

One of the most interesting properties of transition metal mixed-valence species is that they often exhibit an optical transition in the visible or near-infrared region due to electron transfer between the different oxidation states. Hush[8] developed a now widely-used analysis of the properties of these intervalence transfer (IT) bands. The (Fe^{2+},Fe^{2+}) dinuclear complex was oxidized in a spectroelectrochemical cell,[9] and spectra as a function of time are presented in Figure 2. The characteristic intense near-infrared band of the (Fe^{2+},Fe^{2+}) compound (λ_{max} = 874 nm, ϵ = 24 000 M^{-1} cm^{-1}) disappears, and a new band grows with a λ_{max} at 940 nm and an extinction coefficient of about 27 000 M^{-1} cm^{-1}. No evidence was found for other electronic bands, either in the (Fe^{2+},Fe^{2+}) parent or in the mixed-valence compound in the range from 1000 to 2400 nm.

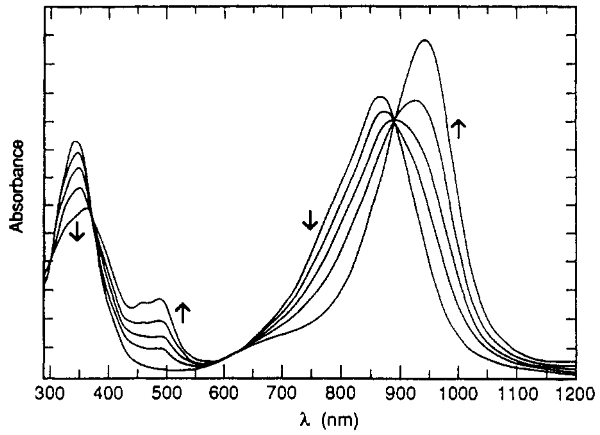

Figure 2. Spectral changes accompanying oxidation of the original Fe^{II}/Fe^{II} binuclear compound in 0.1 M TBAP/CH_3CN. Conditions: Pt mesh working electrode; Pt wire counter electrode; E = 1.25 V vs Ag^+/Ag.

Hush's equations related to the properties of IT bands apply strictly only to moderately coupled class II mixed-valence compounds. It is interesting to assume that the band at 940 nm in the mixed-valence compound is an IT band and then to apply Hush's equation for estimating $\Delta\omega_{1/2}$, the width at half-maximum. The predicted $\Delta\omega_{1/2}$ from Hush's equation is 5000 cm^{-1} whereas the observed width is only 1824 cm^{-1}. Similar results[5] are found for the class III Creutz–Taube ion $[(H_3N)_5Ru)_5(pyrazine)]^{5+}$, i.e., a more narrow IT band than predicted. Also Hush's equations relating λ_{max} and $\Delta\omega_{1/2}$ to the degree of electronic coupling, H_{AB}, between the metals can be applied to the 940-nm band. The value of H_{AB} is 2335 cm^{-1} from this analysis. This is very large compared to the values for a series of class II (valence-trapped) Fe and Ru complexes and is in the range found for class III complexes.[5] As noted above, if the mixed-valence ion is delocalized, the Hush analysis used to estimate H_{AB} does not apply. For class III compounds, a better estimate for H_{AB} is $1/(2\lambda_{max})$ for the intervalence transition; thus H_{AB} is 5320 cm^{-1} if the 940-nm band is an IT band.

The optical analysis is interesting and does point to class III behavior but is subject to some criticism because it is based on our assumption that the 940-nm band is an IT transition. Fortunately, Mössbauer spectroscopy can be applied to the diiron mixed-valence compound and is especially revealing.

The Mössbauer spectrum of the one-electron oxidation product of the Fe^{II}/Fe^{II} parent complex at 90 K is shown in Figure 3. The spectrum consists of a single, quadrupole-split doublet, indicating that on the Mössbauer time scale ($<10^{-7}$ s) the two iron atoms are equivalent. The center shift is 0.20 mm/s and the quadrupole splitting is 2.77 mm/s. The corresponding parameters of the parent Fe^{II}/Fe^{II} species are as follows:[10] center shift, 0.34 mm/s; quadrupole splitting, 1.63 mm/s. The shift in the values is in the direction expected for oxidation of the iron centers.

While the Mössbauer spectrum consists of two lines, they are not identical. There is asymmetry in the intensity, the right peak being more intense. This asymmetry is not due to sample orientation since it also appears when the sample is crushed and

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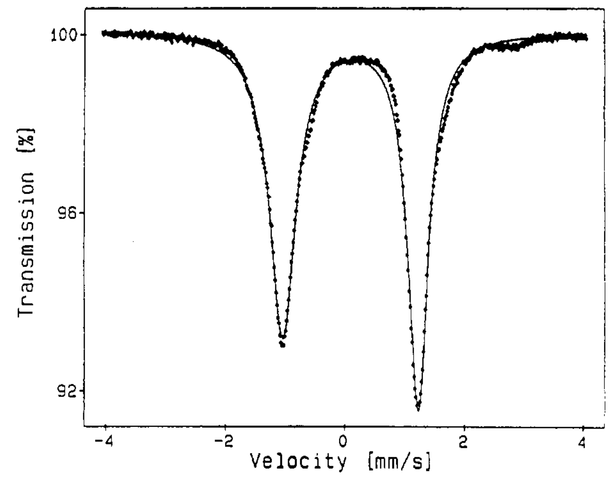

Figure 3. Mössbauer spectrum of the perchlorate salt of the mixed-valence compound at 90 K. CS = 0.21 mm/s (relative to SS at ambient), QS = 2.77 mm/s, Γ = 0.53 mm/s.

diluted into BN. The broadness of the left peak results, at least in part, from a superimposed peak due to an impurity. Mössbauer spectra were obtained on three independently prepared samples, and all exhibited asymmetry although to different degrees. No detectable impurities were observed in the UV–vis spectrum and cyclic voltammogram of the Mössbauer samples. Another possible reason for this asymmetry is a Karyagin effect.[11] That is, there is a difference in probabilities of the Mössbauer transitions to the $m \pm {}^3/_2$ and $\pm {}^1/_2$ states due to anisotropy in the mean-square amplitudes.[12] This type of behavior is not uncommon, particularly for iron complexes with a large degree of tetragonal character such as our compound has.

The essential point to be deduced from the Mössbauer spectra is that the iron atoms are equivalent on the Mossbauer time scale at 90 K. Another sample was analyzed at 80 and 4.2 K. No difference was observed at the lower temperature. Thus, in the ground vibrational state of the mixed-valence complex there is no significant barrier to electron transfer.

Preliminary electron spin resonance spectra have been taken. The electron spin resonance spectrum of the mixed-valence species in acetonitrile (8 K, 2 × 10^{-3} M) is given in Figure 4a. The spectrum is quite unusual for low-spin iron complexes, and accordingly we were concerned about the purity of the sample and whether the spectrum was due to the $[Fe_2(TIED)(CH_3CN)_4]^{5+}$ ion. The mixed-valence complex that gave the spectrum in Figure 4a was generated by electrochemical oxidation using tetrabutylammonium hexafluorophosphate as the electrolyte. The isovalent (Fe^{2+},Fe^{2+}) and mixed-valence (Fe^{2+},Fe^{3+}) compounds can be interconverted quantitatively in spectroelectrochemical experiments. Changing the cation and/or the anion of the electrolyte had no effect on the ESR spectrum. Also the same spectrum was obtained when the mixed-valence compound was generated by chemical oxidation (Ce^{4+} or Cu^{2+}).

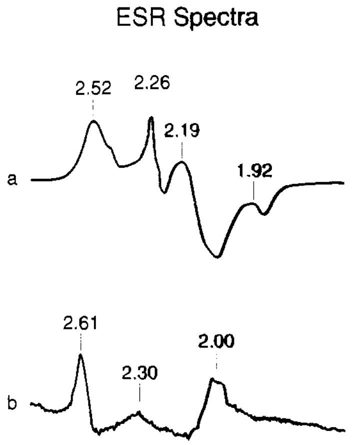

Figure 4. (a) ESR spectrum in acetonitrile (8 K, 2 × 10^{-3} M). Instrument settings: scan range, 2 × 10^3 G; field set, 3100 G; microwave power, 5 mW; modulation amplitude, 20 G; receiver gain, 8 × 10^3. (b) ESR spectrum in acetonitrile (8 K, 2 × 10^{-4} M) with the same instrument settings as (a) except a receiver gain of 4 × 10^4.

The spectrum in Figure 4a does, therefore, represent the true spectrum of the mixed-valence species at 2 × 10^{-3} M concentration in acetonitrile.[13] However, during these verification experiments we noted a concentration dependence of the spectrum. Figure 4b shows the spectrum after a 10-fold dilution with 0.1 M TBAH in acetonitrile. There is a marked change in the spectrum, and we interpret this to mean that the mixed-valence species with axial acetonitrile ligands aggregates in solution and the spectrum in Figure 4a results from at least two interacting magnetic dipoles. The ESR spectrum for interacting magnetic dipoles should show a nonallowed transition at $\Delta m = 2$, the so-called half-field transition.[14] The intensity of this $\Delta m = 2$ transition is expected to be less than 2% of the allowed transition. We examined this region in our spectrum, but the results were ambiguous due to a relatively large residual cavity signal at this exact field.

Summary

The available data, optical, Mössbauer, and electrochemical, indicate that the mixed-valence compound is a delocalized $Fe^{2.5+}/Fe^{2.5+}$ species. Another way of stating the case is that the rate of electron transfer is much faster than 10^7 s^{-1} (the reciprocal of the lifetime of the excited state of the ^{57}Fe nucleus) because there is no evidence of any line broadening beyond lifetime broadening in the Mössbauer spectrum. Additional experiments are needed to determine whether this complex represents a case of valence-detrapping[15] (transitions between Fe^{II} and Fe^{III} which are fast on the Mössbauer time scale but slow on the vibrational time scale) or actual valence delocalization. Further examination of the electrochemical properties and optical, Mössbauer, and ESR spectra of various mixed-valence $[Fe_2(TIED)L_4]^{5+}$ species with different axial ligands is in progress.

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