

Spectroscopic and Electrochemical Characterization of a Bis-Macrocyclic Diiron Compound

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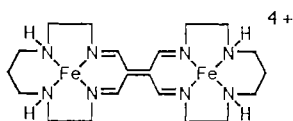
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The properties of the complex $[\text{Fe}_2(\text{C}_{20}\text{H}_{36}\text{N}_8)(\text{CH}_3\text{CN})_4](\text{ClO}_4)_4$ have been extensively investigated by optical and Mössbauer spectroscopy as well as by electrochemistry. The binucleating ligand TIED (tetraaminoethylene dimacrocyclic) is an exceptionally good π acceptor as indicated by the Mössbauer spectrum, which shows a low value for the center shift and a high value for the quadrupole splitting parameter. This behavior is consistent with the unusually high value for the first oxidation potential (1.18 V vs NHE) since Fe^{2+} is a much better π donor than Fe^{3+} . Also, extensive back-bonding from iron to an unoccupied π^* orbital of the ligand may help produce the very short Fe-N(imine) distance of 1.89 Å that was found in the complex. Electrochemical oxidation apparently occurs at the metal centers, since the potential shows a large solvent dependence, which we attribute to axial ligand exchange by coordinating solvent molecules. Electrochemical reduction, while formally occurring at the ligand, shows indications of extensive mixing of ligand and metal orbitals. There is a change from two, well-separated one-electron reductions in CH_3CN to closely overlapping reductions in DMF and H_2O . Another indication of orbital mixing is the fact that substitution of Ni for Fe in the complex causes a large shift of 780 mV in the first ligand reduction potential.

Introduction

The study of multimetallic molecules is important for both practical and fundamental reasons. For example, dicobalt(II) cofacial porphyrin dimers act as efficient electrocatalysts for the four-electron reduction of O_2 to H_2O .¹ Multiple metal systems are common in nature and are often involved in multiple-electron redox reactions.² Consequently, there has been a great deal of work aimed at synthesizing biomimetic multinuclear models which may provide insight into the actual structure of the metalloenzyme or the mechanism of the catalysis. Multimetallic systems are also important to the inorganic chemist for more fundamental studies. These types of investigations include magnetic exchange coupling, extent of mixing of metal and ligand orbitals, and optically induced intrasystem charge transfer.

We recently described³ the structure of a diiron compound $[\text{Fe}_2(\text{C}_{20}\text{H}_{36}\text{N}_8)(\text{CH}_3\text{CN})_4](\text{ClO}_4)_4$



that is unique in that it contains a conjugated bridge between metals in two macrocycles. As isolated from acetonitrile, each low-spin iron(II) has two axial acetonitrile ligands. The $[\text{Fe}_2(\text{TIED})(\text{CH}_3\text{CN})_4]^{4+}$ species (TIED = tetraaminoethylene dimacrocyclic) exhibits several unusual properties, among which is an intense absorption band with $\epsilon = 24\,600\text{ M}^{-1}\text{ cm}^{-1}$ at 874 nm in acetonitrile.

In this report we describe further characterization of the diiron complex with an emphasis on the solvent dependence of its optical

spectrum and of its electrochemical behavior. The Mössbauer spectroscopic data are also included.

Recently, a second example, a dinickel compound, with the same binucleating ligand was reported.⁴ Comparison of the redox properties of the diiron and dinickel complexes is especially interesting. Oxidation of both of these bimetallic systems involves the metal atom, while reduction processes in both compounds are assigned to placing electrons in the conjugated portion of the ligand. What is unusual is the large difference between reduction potentials; the square planar dinickel compound is reduced 780 mV more positive than the diiron compound. This suggests extensive mixing of metal orbitals and ligand orbitals.

Experimental Section

Materials. The 1,4,8,11-Tetraazacyclotetradecane (cyclam) was purchased from Lancaster Synthesis Inc. Iron perchlorate hexahydrate was obtained from Johnson Matthey Electronics. Acetonitrile and dimethylformamide (DMF) were from Burdick-Jackson Chemical. Acetonitrile was distilled once from CaH_2 and twice from P_2O_5 immediately prior to use. Tetrabutylammonium hexafluorophosphate (TBAF) and tetrabutylammonium perchlorate (TBAP) were purchased from Fluka. TBAF was recrystallized from hot absolute ethanol three times and then dried in low vacuum at 60 °C for 2 h. TBAP was purified by 3-fold recrystallization with warm ethyl acetate; the solid was then kept in low vacuum at 60 °C for 2 h. Deionized water was glass-distilled and then passed through a Barnstead NANOPure II system. All other chemicals were reagent grade, and solvents were HPLC grade.

$[\text{Fe}_2(\text{TIED})(\text{CH}_3\text{CN})_4](\text{ClO}_4)_4$. $[\text{Fe}_2(\text{C}_{20}\text{H}_{36}\text{N}_8)(\text{CH}_3\text{CN})_4](\text{ClO}_4)_4 \cdot 2\text{CH}_3\text{CN}$ was prepared by dissolving 5.2 g (14.3 mmol) of $\text{Fe}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ in 125 mL of oxygenated acetonitrile. Then 1.00 g (4.99 mmol) of cyclam was added to the yellow solution. This was stirred for 2 h to give a purple solution, which was then filtered to remove brown hydrous iron oxide. The purple filtrate was put into a loosely-covered beaker, and the solution was allowed to stand. After 2 days, dark green crystals of $[\text{Fe}_2(\text{C}_{20}\text{H}_{36}\text{N}_8)(\text{CH}_3\text{CN})_4](\text{ClO}_4)_4 \cdot 2\text{CH}_3\text{CN}$, referred to as $[\text{Fe}_2(\text{TIED})(\text{CH}_3\text{CN})_4](\text{ClO}_4)_4$, formed on the bottom and sides of the beaker. The supernatant (purple solution) was carefully decanted into a 250-mL beaker. The crystals were then washed with CHCl_3 several times to remove residual mother liquor and hydrous brown iron oxides and then rinsed quickly with 50% CH_3CN -50% CHCl_3 three times. The shiny dark green X-ray-quality crystals were dried under Ar gas. The yield was typically 0.14-

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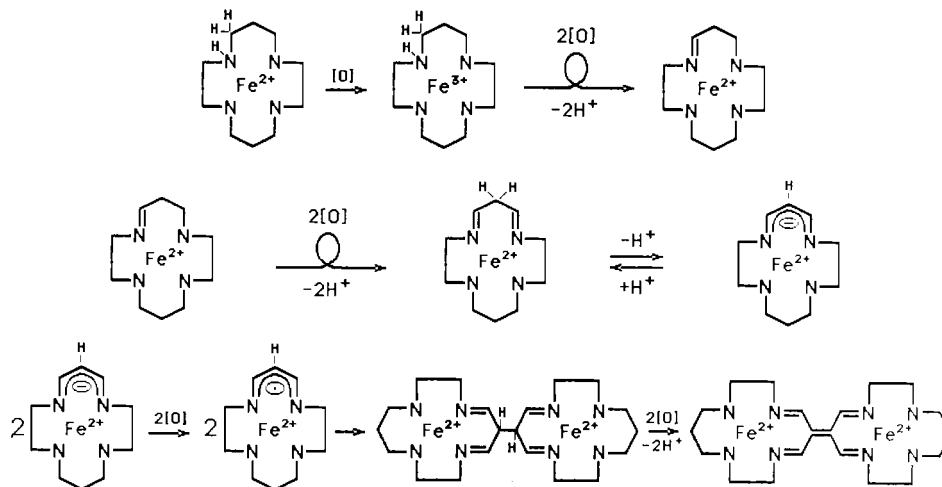


Figure 1. Proposed scheme for the formation of $[\text{Fe}_2(\text{TIED})(\text{CH}_3\text{CN})_4]^{4+}$ from the fully saturated iron(II) complex in oxygenated acetonitrile.

0.16 g. The 125 mL of supernatant solution in a 250-mL beaker was placed in an 800-mL beaker in which there was 20 mL of diethyl ether. This was then covered with plastic film so that the diethyl ether slowly diffused into the purple solution. After 2 days, an additional crop of $[\text{Fe}_2(\text{TIED})(\text{CH}_3\text{CN})_4](\text{ClO}_4)_4$ crystals were separated from the purple solution. Typical yields were 0.05–0.07 g. The total conversion yield was 4%–5% based on the original macrocycle.

Measurements. The electrochemical measurements were performed with an IBM EC 225^{2A} voltammetric analyzer or with a PAR Model 175 potentiostat equipped with a PAR Model 173 controller and a Model 179 digital coulometer. Potentials were measured vs a nonaqueous Ag/Ag^+ (BAS) electrode at room temperature. The potential of the Ag/Ag^+ reference electrode was calibrated versus the ferrocene/ferrocenium couple. Cyclic voltammograms were done in CH_3CN and DMF under Ar with 0.1 M TBAF as the electrolyte. Tetramethylammonium perchlorate (TMAP) was used as the electrolyte in water. To examine further the electron-transfer steps for the reduction process in DMF and water, differential pulse polarography (DPP) was performed. Solutions used for cyclic voltammograms and DPP were of millimolar concentration. Glassy carbon or Pt disk electrodes were used as the working electrode, and Pt wire was used as the counter electrode for both CV and DPP. The $E_{1/2}$ values from cyclic voltammetry were calculated from half the sum of the E_p values for the anodic and cathodic waves.

UV–visible spectra were obtained on a Lambda Array 3840 Perkin-Elmer spectrophotometer with a Model 7500 Professional Computer using 1-cm quartz cells. For the near-IR region, a Lambda 9 Perkin-Elmer spectrophotometer was used.

Mössbauer spectroscopy was done by R. B. F.

Results and Discussion

Synthesis. The sequence of reactions that produces the conjugated bis-macrocyclic is remarkable in itself. The saturated macrocycle 1,4,8,11-tetraazacyclotetradecane (cyclam) is stirred with $\text{Fe}(\text{OH})_2(\text{ClO}_4)_2$ in acetonitrile with oxygen present. A brown precipitate first forms (hydrous iron oxides), but within 30 min a deeply colored purple solution forms. After several days, dark green crystals of $[\text{Fe}_2(\text{TIED})(\text{CH}_3\text{CN})_4](\text{ClO}_4)_4$ form. In this process, a total of four carbon–nitrogen double bonds are formed from single bonds and a new carbon–carbon double bond is formed. Also, a total of 12 protons are released. The characteristic intense near-infrared band can be observed in a diluted aliquot of the reaction solution within 15 min of initiation of the reaction. If oxygen is excluded, the solution remains dark purple but $[\text{Fe}_2(\text{TIED})(\text{CH}_3\text{CN})_4]^{4+}$ does not form.

A reasonable hypothesis about the mechanism of formation of $[\text{Fe}_2(\text{TIED})(\text{CH}_3\text{CN})_4]^{4+}$ can be formulated on the basis of previous work (Figure 1). A number of transition metal ions are known to promote conversion of coordinated amine ligands to imines. For the group VIII metals, Fe and Ru, these oxidative dehydrogenation reactions are often effected by molecular oxygen

under normal conditions of temperature and pressure.⁵ Of particular relevance to the formation of $[\text{Fe}_2(\text{TIED})(\text{CH}_3\text{CN})_4]^{4+}$, Busch and co-workers established^{6,7} that in the presence of oxygen iron promotes the formation of imine bonds in saturated tetraazamacrocycles. The detailed mechanism of most metal-promoted oxidative dehydrogenation reactions remains unclear. In any case formation of $[\text{Fe}_2(\text{TIED})(\text{CH}_3\text{CN})_4]^{4+}$ must involve an intermediate with a C=N double bond in a six-membered chelated ring. It seems reasonable to postulate a second oxidative dehydrogenation reaction to produce a β -diimine.

It is appropriate to note that Busch et al. concluded from their work that an Fe(II) α -diimine system has special stability.⁷ In concurrence with that, chromatography of the mother liquor of the crystals of $[\text{Fe}_2(\text{TIED})(\text{CH}_3\text{CN})_4]^{4+}$ indicates that major iron components are di- and tetraene species with C=N double bonds in the five-membered chelate rings. The next step in the proposed sequence involves loss of a proton to form a resonance stabilized anion. It is well-known that six-membered metal chelates with β double bonds readily do this. Subsequent oxidation would produce a radical; coupling between two radicals would lead to formation of a dimer linked by a single bond. Here again there is precedent in the literature. Several studies have appeared in which single-bond-linked bis-macrocycles have been formed by electrochemical or chemical oxidation of metal tetraazaanullenes.^{8,9} In even more closely related work, Endicott and co-workers found¹⁰ that when a Co(II) β -diimine macrocycle is exposed to oxygen in an acidic medium, a dimeric molecule is formed.

In none of the cases cited above is there clear evidence that further oxidation leads to formation of a carbon–carbon double bond. This is most likely due to steric interaction of the methyl groups that are present on the carbon atoms of the six-membered chelate rings in the previous studies. However, a nickel dimer with 13-membered dimethyl macrocycles with an apparently similar double-bond arrangement to $[\text{Fe}_2(\text{TIED})(\text{CH}_3\text{CN})_4]^{4+}$ has been reported,¹¹ and this species is formed in essentially the same way, i.e., by aerobic oxidation.

In the present case with no methyl groups, the final oxidation leading to a double-bond-linked bis-macrocyclic is obviously facile. This can be ascribed to resonance stabilization of the cross-conjugated, delocalized system. These observations have led us

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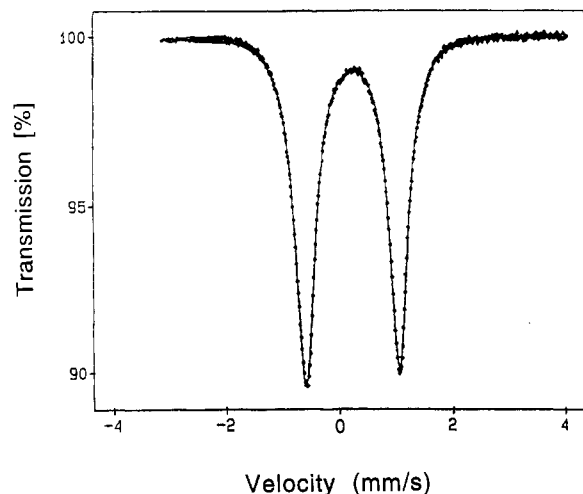


Figure 2. Mössbauer spectrum of $[\text{Fe}_2(\text{TIED})(\text{CH}_3\text{CN})_4](\text{ClO}_4)_4$ at 90 K. Center shift = 0.34 mm/s (relative to stainless steel); quadrupole splitting = 1.63 mm/s.

Table 1. Mössbauer Parameters^a for Tetraazamacrocyclic Iron Complexes

compd ^b	δ , mm/s	ΔE_q , mm/s
$[\text{Fe}_2(\text{TIED})(\text{CH}_3\text{CN})_4]^{4+}$	0.34	1.63
I	0.60	0.55
II	0.51	1.07
III	0.47	1.28
IV	0.44	1.36
V	0.41	1.23
VI	0.39	1.51
VII	0.40	1.86
VIII	0.40	1.41
IX	0.43	1.58
FeTPP(Py) ₂	0.51	1.15
FePc(Py) ₂	0.46	1.89

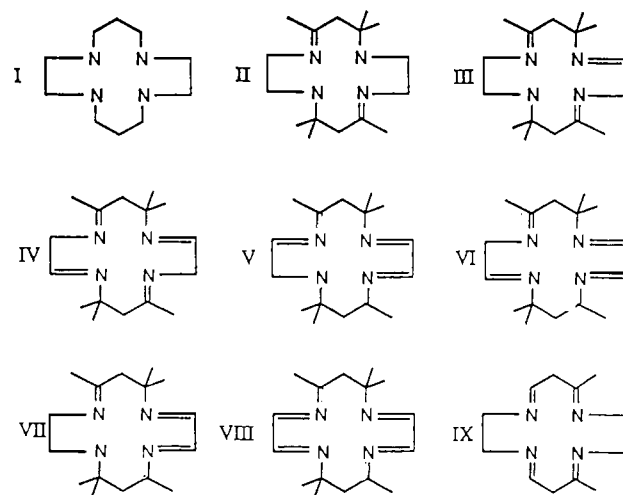
^a Values from ref 13 except for $[\text{Fe}_2(\text{TIED})(\text{CH}_3\text{CN})_4](\text{ClO}_4)_4$. All complexes except for those with TPP and Pc have axial CH_3CN ligands. All have ClO_4^- as a counterion except VI, VII, and VIII, which have PF_6^- .
^b The macrocycles for I–IX are shown in Chart 1.

to duplicate the electrochemical oxidation of nickel tetraazannulenes with no methyl groups present. Observation of this system indicated formation of double-bond-linked dimers.¹²

Mössbauer. The Mössbauer spectrum of $[\text{Fe}_2(\text{TIED})(\text{CH}_3\text{CN})_4](\text{ClO}_4)_4$ at 90 K is shown in Figure 2. The spectrum consists of a quadrupole-split doublet with a center shift, δ , of 0.34 mm/s and a quadrupole splitting, ΔE_q , of 1.63 mm/s. These values can be compared with those in the literature for a number of low-spin, six-coordinate Fe(II) complexes with tetraazamacrocyclic ligands. Since the axial ligands play an important role in the magnitude of the CS and QS values, our comparison is restricted to complexes having axial CH_3CN ligands. Fortunately, Busch and co-workers have done Mössbauer studies¹³ on a number of closely related complexes with axial CH_3CN ligands. Values for a series of 14-membered tetraazamacrocyclic complexes are given in Table 1 (and see Chart 1). Most have perchlorate as the counterion and thus are directly comparable to our values. Also given are values for a porphyrin complex and a phthalocyanin complex with pyridine axial ligands.

The center shift of 0.34 mm/s for $[\text{Fe}_2(\text{TIED})(\text{CH}_3\text{CN})_4]^{4+}$ is at the low end of values for this series of closely related complexes. At the same time, the quadrupole splitting parameter of 1.63 mm/s is high compared to reported values. The center shift is inversely related to the amount of s electron density at the

Chart 1. Macrocycles for I–IX



nucleus.¹⁴ Ligands that are good σ donors lead to increased s electron density at the iron nucleus and hence lower the δ value. Also, d electron density can influence s electron density by screening the s electrons from the nuclear charge. Ligands that are good π -acceptor ligands withdraw electron density from d π orbitals, which leads to increased s density and, therefore, lower center shift values. Busch et al.¹³ comment that increasing the unsaturation in the macrocycle lowers the observed center shift and the most likely reason for this is the increase in π -accepting power of the imine group.

The ΔE_q values obtained¹⁵ for the same series of closely related 14-membered tetraazamacrocyclic complexes can be used for comparison. As noted, the 1.63 mm/s value is on the high side of the ΔE_q values for these low-spin Fe(II) complexes. While σ - and π -bonding properties of ligands are additive in determining the center shift value, the quadrupole splitting measures the difference between these two effects.¹⁶ The presence of good π -acceptor ligands such as CO, CN^- , and PR_3 typically lead to large quadrupole splittings.¹³

Busch and co-workers examined the trends in the center shift and quadrupole splittings of a series of 14-membered tetraazamacrocyclic complexes of low-spin Fe(II), all with trans acetonitrile. They found a negative slope in a plot of ΔE_q vs δ for their series, which implies that π effects predominate. Our complex, which also has iron in this same basic ligand environment, should be directly comparable. The low center shift and high quadrupole splittings of $[\text{Fe}_2(\text{TIED})(\text{CH}_3\text{CN})_4]^{4+}$ clearly indicate that the cross-conjugated β imine groups are excellent π acceptors. This conclusion is consistent with the observed exceptionally short Fe–N(imine) bond lengths (1.89 Å) in the compound.³

Electronic Spectra. The electronic spectrum of $[\text{Fe}_2(\text{TIED})(\text{CH}_3\text{CN})_4]^{4+}$ in acetonitrile is shown in Figure 3. There are maxima at 240, 340, and 874 nm. The most unusual feature of the spectrum is the intense peak ($\epsilon = 24\,600\ \text{M}^{-1}\ \text{cm}^{-1}$) in the near-infrared. Very few transition metal complexes or organic molecules have such intense bands in this region. The high intensity clearly rules out assignment as a d–d transition. The band could be due to an internal π to π^* transition associated with the conjugated part of the bis-macrocyclic ligand or it could arise from a charge-transfer transition (metal to ligand, MLCT,

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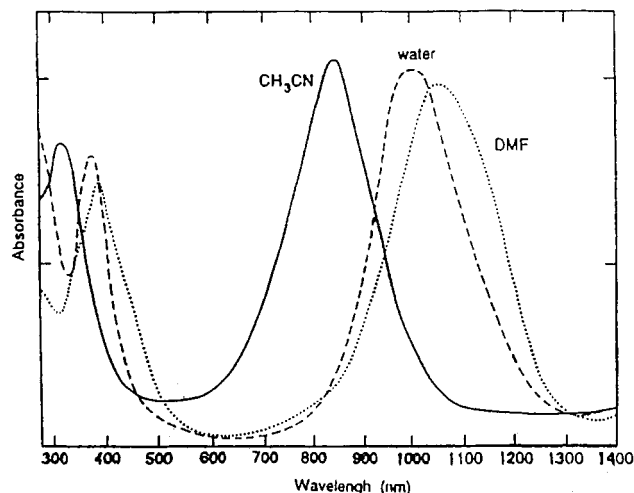


Figure 3. Optical spectra of $\text{Fe}_2(\text{TIED})^{4+}$ in acetonitrile, DMF, and H_2O .

or ligand to metal, LMCT). It is well-known¹⁷ that a number of low-spin Fe(II) complexes with conjugated imine ligands exhibit MLCT bands in the visible region. For example, this type of transition is responsible for the intense red color of iron–bipyridine complexes.

Busch and co-workers have investigated numerous complexes of iron(II) with unsaturated tetraazamacrocycles. All of these di-, tri-, or tetraimine macrocyclic compounds have bands in the 300–550-nm region which they assign to a MLCT transition.^{6,18} Interestingly, the more imine bonds the macrocyclic ligand contains, the lower the energy of the observed MLCT transition. However, none of these reported iron(II) macrocyclic complexes has an intense electronic band anywhere near the low-energy band for $[\text{Fe}_2(\text{TIED})(\text{CH}_3\text{CN})_4]^{4+}$. Evidently the conjugation in the tetraiminoethylene unit fusing the two macrocycles is essential to the near-infrared band.

This conjugated moiety somewhat resembles tetracyanoethylene (TCNE), which is a good electron acceptor and forms numerous charge-transfer complexes. Several complexes have recently been reported¹⁹ with a low-spin $\text{Fe}^{\text{II}}\text{N}_4\text{L}_2$ systems where the trans L ligands are TCNE. These species give long-wavelength (850–950 nm) high-intensity bands which have been assigned as MLCT transitions. Therefore, it seems reasonable to assign the near-infrared band observed in $[\text{Fe}_2(\text{TIED})(\text{CH}_3\text{CN})_4]^{4+}$ to transfer of an electron from filled d_{xz} and d_{yz} orbitals of Fe(II) to a particularly low-lying empty π^* orbital of the tetraiminoethylene moiety.

The energies of the two longest wavelength transitions are extremely sensitive to solvents. Figure 3 shows spectra of $\text{Fe}_2\text{-TIED}^{4+}$ in acetonitrile, dimethylformamide, and water. The latter two solvents were degassed to prevent reaction with oxygen. The near-infrared band changes from 874 nm in acetonitrile to 1075 nm in dimethylformamide, while the UV peak changes from 340 nm in acetonitrile to 390 nm in DMF. The energy of any type of electronic transition that involves a change in dipole moment from the ground to the excited state will exhibit a solvent dependence, and this dependence can often be correlated with some function of the optical dipole moment of the solvent.²⁰ In the present case, however, the shifts are much larger than expected for this type of external solvent interaction and, further, do not

Electrochemistry

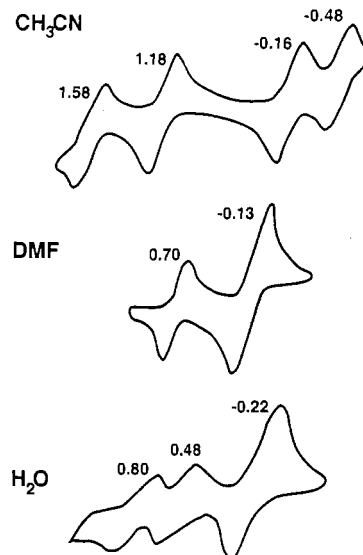


Figure 4. Cyclic voltammograms of $\text{Fe}_2(\text{TIED})^{4+}$ in acetonitrile, DMF, and H_2O . Conditions: Pt disk working electrode; 0.1 M electrolyte; scan rate 200 mV/s; potentials versus NHE.

correlate²¹ with any of the usual functions of optical dipole moment or with Gutman donor numbers.²²

We conclude from these observations that there must be ligand exchange; i.e., the axial acetonitrile ligands in $[\text{Fe}_2(\text{TIED})(\text{CH}_3\text{CN})_4]^{4+}$ can be replaced by coordinating solvent molecules or by other added ligands. Moreover, the consequent changes in the chemical environment of the iron atoms affect not only the position of the near-infrared band but that of the UV band as well.

Electrochemistry. The solvent dependence of the oxidation and reduction potentials of the diiron complex are interesting and are related to the solvent dependence of the electronic spectra. The cyclic voltammograms of the complex in CH_3CN , DMF, and water are given in Figure 4. There are a number of points to be discussed about the value of the potentials and the qualitative and quantitative changes as the solvent is varied.

In rigorously dried acetonitrile there are oxidation waves at 1.18 V (all potentials vs NHE) and 1.68 V and two reductions at -0.16 and -0.48 V. Plots of peak amplitude versus (scan rate)^{1/2} indicate the first oxidation and first reduction steps are quite reversible, while the second oxidation and reduction processes are best classified as quasi-reversible. Our interpretation is that the oxidations involve the iron atoms, while the reduction processes involve placing electrons on the ligands. The complex then exhibits a total of five oxidation levels.

The first oxidation produces a mixed-valence species. In a separate report²³ we have described the characterization of this mixed-valence species as the first low-spin example of a Robin and Day class III delocalized complex ($\text{Fe}^{2.5+}/\text{Fe}^{2.5+}$) which retains this property even to 4.2 K. The second oxidation gives the isoivalent ($\text{Fe}^{3+}/\text{Fe}^{3+}$) ion; however, the appearance of this second oxidation wave is very dependent on the presence of water. If water is added or the solvent not thoroughly dried, anodic current at the higher potential increases significantly and a new cathodic peak appears at +0.2 V. Details of these processes are being investigated.

One notable point is that the first anodic wave at 1.18 V in CH_3CN is quite high for an oxidation of Fe^{2+} to Fe^{3+} . The

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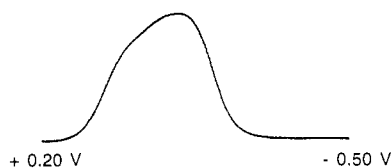


Figure 5. Differential pulse polarogram of $\text{Fe}_2(\text{TIED})^{4+}$ in DMF. Conditions: Glassy-carbon working electrode; 0.1 M TBAF; scan rate 5 mV/s; pulse amplitude 10 μA .

macrocyclic environment with β -imine nitrogens and with axial acetonitrile ligands must stabilize lower oxidation states because Fe(II) is a much better π donor than iron(III). The low-energy MLCT bands as well as the Mössbauer spectrum indicate that the cross-conjugated β -imine coordinating system in $\text{Fe}_2\text{TIED}^{4+}$ is an exceptionally good π -acceptor ligand.

There are several very interesting differences between the electrochemical parameters in CH_3CN and DMF. First, there is a substantial shift in the first oxidation potential, and second, there is a change from two well-separated reduction waves in CH_3CN to a single wave representing a total of two electrons in DMF. The $E^\circ_{1/2}$ value for the oxidation wave shifts from 1.18 V in CH_3CN to 0.70 V in DMF, while the first reduction in CH_3CN and DMF are approximately the same (-0.16 V (CH_3CN); -0.13 V (DMF)). This is quite consistent with the interpretation of the near-infrared electronic band as an MLCT and with the large solvent shifts of this transition. The band shifts to a much lower energy in going from CH_3CN to DMF as DMF molecules replace the axial CH_3CN ligands. This correlates well with the fact that the oxidation of the complex is much easier in DMF.

The cyclic voltammogram shows a change from two one-electron reductions in CH_3CN to a single wave corresponding to two electrons in DMF and water. We have also examined the reduction step in DMF and water by differential pulse polarography which is much better suited to differentiating electron-transfer steps that have similar potentials. The DPP voltammogram for the reduction process in DMF is shown in Figure 5. For DMF the plot is clearly a composite, which shows that the reduction occurs in two one-electron steps although the two peaks are not fully resolved. The DPP technique has frequently been used to obtain $\Delta E = E_2 - E_1$ for subsequent multiple-step electron-transfer reactions. The approach elucidated by Richardson and Taube²⁴ to analyze DPP curves where E_1 and E_2 are close in value has been widely applied. We find a puzzling result when we use their analysis on our data. An important parameter is the width of the peak at half the maximum current. The value from our data is 290 mV. The Richardson and Taube analysis clearly indicates that with such a width, two well-resolved peaks should easily be observed in the DPP. We do not understand this discrepancy.

Another puzzle is why two quite distinct one-electron reduction waves with a separation of 320 mV were found in acetonitrile, while in DMF and water these two reduction steps occur at very nearly the same potential. By comparison, the square-planar dinickel analogue exhibits two distinct reduction waves with separations of about 220 mV in both acetonitrile and water.⁴

One rationalization of these results is that in $[\text{Fe}_2(\text{TIED})(\text{CH}_3\text{CN})_4]^{4+}$ with acetonitrile ligands on the iron atoms there is a large energy separation between the lowest unoccupied molecular orbital (LUMO) and the second lowest unoccupied molecular orbital (SLUMO):



During the reduction steps two electrons are placed sequentially into the LUMO. The potential difference between the first and second reduction steps may be due to the added electrostatic energy necessary to put the second electron into a partially occupied orbital. If this picture is correct, then the square-planar nickel analogue with its two separated reduction waves must also have a similar energy diagram. In contrast, the LUMO and SLUMO orbitals may be much closer in energy when the axial ligands on the iron are DMF or H_2O . In this case the added electrons can go into separate orbitals at nearly the same potential. Evidently the chemical environment of the iron atoms can have a marked effect on the relative energies of the LUMO and SLUMO orbitals.

Another interesting observation is the large difference between the potentials for the first reductions in the diiron and dinickel complexes. Changing the metal should not alter the reduction potential much if the electron is in fact going into a primarily ligand-based orbital. But in acetonitrile the dinickel complex is reduced at $+0.60$ V while the diiron complex is reduced at -0.18 V, a difference of 780 mV. This large dependence on the metal is in contrast to other complexes that also involve ligand-based reductions. For example, the first ligand reductions for $\text{Fe}(\text{bpy})_3^{2+}$, $\text{Ru}(\text{bpy})_2^{2+}$, and $\text{Os}(\text{bpy})_3^{2+}$ are at -1.26 , -1.25 , and -1.19 V, respectively (all in DMF under the same conditions).²⁵ Similarly, metalloporphyrin complexes with metals in the same oxidation state do not show large potential ranges in reductions involving the porphyrin ring. There are not many studies available involving reductions of the bridging ligand in binuclear complexes. However, for $(\text{OC})_4\text{MLM}(\text{CO})_4$, where L is the π -delocalized bichelating ligand 2,5-bis(2-pyridyl)pyrazine, the potential range for the first reduction was 170 mV for the series $\text{M} = \text{Cr}, \text{Mo}, \text{W}$.²⁶ The exceptionally large metal effect on the reduction potential of the binucleating ligand, TIED, probably stems from extensive mixing of metal and ligand orbitals, which would also produce strong coupling between the two metal centers.²³ Efforts are in progress to further probe the electronic nature of this interesting new diiron complex.

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