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July 1995

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Axial Ligand Effects on Redox Properties of a Strongly-Coupled Bis-Macrocyclic Diiron Compound

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July 1995

Abstract

The axial ligands L of the bis-macrocyclic diiron compound, $[Fe_2C_{20}H_{36}N_4)L_4]^{4+}$, play an important role in affecting its redox reactions. Altering the ligands produces not only quantitative effects in reaction rates but also changes the reaction pathways and products. When $L = Cl^-$, dioxygen removes one electron to produce a valence-averaged mixed-valence species. When $L = DMF$ dioxygen attacks the central carbon-carbon double bond to produce two, like, keto β-diimine monomeric species. Oxidation when $L = CH_3CN$ in wet CH_3CN produces oxidative dehydrogenation and gives a new diiron species with two keto β-diimine moieties, one on each end of the bis-macrocyclic ligand. When $L = CH_3CN$, reduction proceeds in two, well-separated, one-electron steps. When $L = Cl^-$, DMF, or H_2O a single broad reduction wave corresponding to two electrons is observed in the cyclic voltammogram.

Key words: bis-macrocyclic, mixed-valence, keto, beta-diimine

1. Introduction

We are investigating the chemistry of unique bimetallic compounds that contain two macrocycles linked by a cross-conjugated π-electron system.
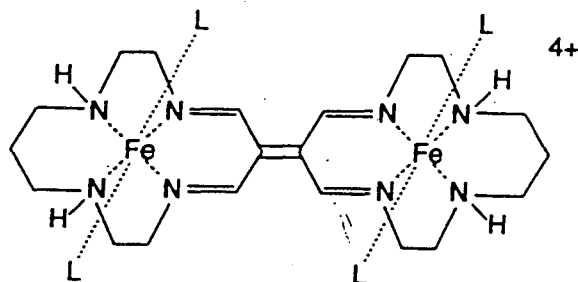
Shortly after our report of an iron complex (1)$Fe_2(C_{20}H_{36}N_8)(CH_3CN)_4](ClO_4)_4$, an independent paper was published (2) describing a square planar nickel analogue $[Ni_2(C_{20}H_{36}N_8)](ClO_4)_4$. We have also described the properties of a ruthenium mixed-valence compound $[Ru_2(C_{20}H_{36}N_8)Cl_4]Cl$ (3). By virtue of their structure, these M_2TIED (TIED = tetraiminoethylenedimacrocycle) complexes exhibit unusual properties, among which are intense electronic transitions in the long wavelength visible and near infrared spectral regions. The macrocyclic metal binding sites promote stability by inhibiting metal dissociation and, at the same time, the cross-conjugated π system permits extensive communication between the metals. A high degree of mixing of metal and ligand orbitals in M_2TIED complexes contributes to the coupling between the metals and to the unusual optical properties. One manifestation of this covalency is the very short M-N(imine) bond lengths; in fact, the iron(II)-N(imine) bond, 1.89 A, is the shortest of its type in the literature (1).

An interesting aspect of the chemistry of the $[Fe_2TIED(L)_4]^{4+}$ series of complexes is the degree to which optical, redox, and reaction properties are dictated by the identity of the axial ligands. The TIED binucleating ligand is an excellent π-acceptor and all the iron complexes are low-spin. However, the characteristic intense NIR band shows extremely large solvatochromic shifts of peak maxima, and there is a correspondingly large solvent

dependence of the Eo values in the cyclic voltammogram (4). These large optical and redox solvent dependencies are due to exchange of axial ligands with coordinating solvent molecules.

Redox reaction rates and products also show a marked dependence on the axial Ligand L. For example, different reaction products are produced as L varies when

$[Fe_2TIEDL_4]^{4+}$ complexes react with oxygen. When L is DMF, dioxygen attacks the central carbon-carbon bond to produce rapidly and with high yield two monomeric keto macrocycles (Scheme 1). On the other hand, when L is Cl⁻, reactions with dioxygen result in a one-electron oxidation that rapidly and quantitatively gives a mixed-valence species $[Fe_2TIEDCl_4]^+$.

The nature of L also has a profound effect on reduction processes. Electrochemical reduction is assumed to be due to placing electrons on the conjugated portion of the ligand. With CH_3CN axial ligands there are two well-separated one-electron reductions, while with Cl⁻ or DMF axial ligands there is one reduction wave in the cyclic voltammogram that corresponds to two electrons. These and other examples of the importance of the axial ligand in determining redox reaction pathways and products of the redox chemistry of $[Fe_2TIEDL_4]$ complexes are discussed in this report.

2. Experimental

2.1. Materials

The 1,4,8,11-tetraazacyclotetradecane (cyclam) was purchased from Lancaster Synthesis, Inc. Acetonitrile and dimethylformamide (DMF) were from Burdick-Jackson Chemical. All other chemicals were purchased from Aldrich and were the highest purity available. Solvents were dried by storage over activated 4-A molecular sieves. Rigorously dried CH_3CN was distilled once from CaH_2 and twice from P_2O_5 immediately prior to use. Tetrabutylammonium hexafluorophosphate (TBAF), tetrabutylammonium perchlorate (TBAP), and tetraethylammonium chloride (TEACl) were purified by literature methods (4).

[Fe(cyclam)(CH_3CN)_2](ClO_4)_3. A quantitative solution of $[Fe(CH_3CN)_6](CF_3SO_3)_2$ was prepared by addition of 10.0 g (66.7 mmols) of CF_3SO_3H to 75 ml of dry and previously-deaerated CH_3CN and then by refluxing with excess (10.0 g) of iron filings. After four hours refluxing the yellow solution was filtered, washed with CH_3CN and diluted to 100 ml in a volumetric flask and stored under argon. Then 15 ml (0.33 M, 5.0 mmol) of the $[Fe(CH_3CN)_6](CF_3SO_3)_2$ solution was combined with 35 ml of previously-degassed CH_3CN and 1.0 gm (5.0 mmol) of cyclam.After refluxing under argon for 30 minutes, 3.4 g (10 mmol) of TBAP was added and the solution was refluxed another 30 minutes. After cooling in an ice bath, 30 ml of diethyl ether was added to complete the precipitation of purple $[Fe(cyclam)(CH_3CN)_2](ClO_4)_2$. Yield 2.4 g, 88%. The air-senstive purple solid should be used immediately to synthesize the ferric cyclam.

[Fe(cyclam)(CH_3CN)_2](ClO_4)_3. $[Fe(cyclam)(CH_3CN)_2](ClO_4)_2$ (2.4 g, 4.5 mmol) was dissolved as a slurry in 100 ml of CH_3CN and 8 ml of concentrated $HClO_4$was added. The purple solution was stirred exposed to air until the color changed to a yellow-orange and a bright yellow solid formed. Then 100 ml of diethyl ether was added and the solution was filtered. The yellow solid was washed with diethyl ether and air dried. Yield 2.5 g, 89%.

CAUTION: PERCHLORATE SALTS ARE KNOWN TO BE EXPLOSIVE. THE YELLOW Fe(III) CYCLAM PERCHLORATE SALT HAS DETONATED WHEN SCRAPED WITH A METAL SPATULA. TO AVOID PROBLEMS, DO NOT USE GLASS FILTERS AND METAL SPATULAS, AIR DRY AFTER ETHER WASHING, AND DO NOT SCRAPE ANY SOLIDS ADHERING TO GLASSWARE.

$[Fe_2(C_{20}H_{36}N_8)(CH_3CN)_4](ClO_4)_4 \cdot 2CH_3CN$
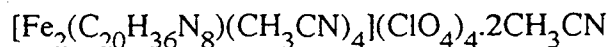
$[Fe_2TIED(CH_3CN)_4](ClO_4)_4$ was prepared by aerobic oxidation of $[Fe(cyclam)(CH_3CN)_2](ClO_4)_3$. A slurry of 2.5 g of $[Fe(cyclam)(CH_3CN)_2](ClO_4)_3$ in 40 ml of CH_3CN with 10 drops of added water was stirred for 5 days in a 250 ml round-bottomed flask. The solution was then filtered and the green powdery solid was washed several times with cold 50% CH_3CN-50% diethyl ether to remove purple imine by-products. Yield 0.600 g, 28%.

$[Fe_2(C_{20}H_{24}N_8O_2)(CH_3CN)_4] (PF_6)_4$
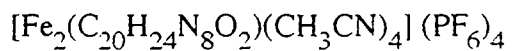
$[Fe_2TIED(CHC_3N)_4](ClO_4)$ (0.200 g, .19 mmol) was dissolved in 100 ml of CH_3CN and excess $Cu(OH_2)_6(ClO_4)_2$ (1.5 g, 4.1 mmol) was added. The green solution was allowed to stand at room temperature for 12 hours. Then 100 ml of diethyl ether was added and the resultant dark blue solution was stored overnight in a refrigerator. The dark blue solid was filtered and then 50 ml of CH_3CN was added. To this slurry a solution of 5 g of NH_4PF_6 in 100 ml of water was added until the ClO_4 salt had dissolved and the PF_6 salt (also blue) had just started to precipitate. The solution was then stored in a refrigerataor to yield 0.15 g of $[Fe_2(C_{20}H_{24}N_8O_2)(CH_3CN)_4](PF_6)_4$. An additional crop of product could be obtained by addition of 100 ml of diethyl ether and cool storage. The second crop of diketone product was contaminated by colorless $[Cu(CH_3CN)_4]ClO_4$ solid.

2.2 Measurements

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.

The electrochemical measurements were performed on an IBM Ec225a 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 non-aqueous $Ag/Ag+$ (BAS) electrode which was calibrated versus the ferrocene/ferrocinium couple. Cyclic voltammograms were done under argon with 0.1 M TBAF as the supporting electrolyte. Glassy carbon or Pt disk electrodes were used as the working electrode with a Pt wire as the counter electrode. The spectroelectrochemical cell has been described previously (4).

3.   Results and Discussion

The rate of replacement of the axial ligands in $[Fe_2TIED(L)_4]$ complexes is fairly rapid. We have not yet completed quantitative measurements, but with addition of an anionic ligand such as Cl- to $[Fe_2TIED(CH_3CN)_4]^{4+}$ in CH_3CN, the solution will reach equilibrium within ten seconds at room temperature. Exchange of neutral ligands such as DMF for CH_3CN takes two or three times longer to reach equilibrium. In the following

discussion we refer to Scheme 1 which gives various redox reactions and products as a function of axial ligand.

3.1. Mixed Valence (A)

Formation Reactions. One-electron oxidation of $[Fe_2TIEDL_4]^{4+}$ species can be accomplished in a number of ways depending on the identity of L. In dry CH_3CN with CH_3CN axial ligands electrochemical oxidation at Pt mesh electrodes with tetrabutylammonium hexafluorophosphate or perchlorate as the supporting electrolyte gives $[Fe_2TIED(CH_3CN)_4]^{5+}$. Similarly, electrochemical oxidation is DMF gives $[Fe_2TIED(DMF)_4]^{5+}$ species. Chemical oxidants such as Cu^{+2}, Ce^{+4} can also effect the oxidation in CH_3CN or DMF.

Reactions with room temperature, atmospheric pressure dioxygen are particularly dependent on L. Over periods of hours no observable reaction takes place with

$[Fe_2TIED(CH_3CN)_4]^{4+}$ in aerated CH_3CN solutions. In atmospheric dioxygen- saturated DMF a reaction occurs in minutes but the products are two, like, monomeric keto macrocycles [Scheme 1 (C)]. In contrast, injection of air into DMF or CH_3CN solutions containing $[Fe_2TIEDCl_4]$ rapidly yields the pink mixed-valence $[Fe_2TIEDCl_4]^+$ ion. The first oxidations of $[Fe_2TIEDCl_4]^o$ and $[Fe_2TIED(DMF)_4]^{4+}$ are at 0.27 V and 0.24 V, respectively, in DMF, measured as half-wave potentials versus the ferrocene/ferrocinium couple. In other words, dioxygen has the thermodynamic capacity to remove one electron from either species, but with DMF axial ligands attack occurs at the linking carbon-carbon double bond while with chloride axial ligands the mixed-valence species is produced. Both reactions are quite rapid and occur with >95% yield. Furthermore, isosbestic points are maintained as aliquots of air are injected into DMF solutions to give the monomeric keto macrocycles and dioxygen does not rapidly attack electrochemically-generated $[Fe_2TIED(DMF)_4]^{5+}$. These results indicate that a mixed-valence species is not

an intermediate in the reaction of dioxygen with the diiron complex with axial DMF ligands.

Properties of Mixed-Valence Species. The binucleating TIED ligand with macrocyclic metal binding sites allows the isolation and study of a series of interesting mixed-valence diiron compounds that differ in the identity of the axial ligands. A $[Fe_2TIED(CH_3CN)_4](ClO_4)_5$ salt was isolated after electrochemical oxidation and characterized by a number of physical techniques (5). The magnetic, optical, electrochemical and Mossbauer studies indicate $[Fe_2TIED(CH_3CN)_4]^{5+}$ is the first example of a Class III low-spin diiron coordination species which remains delocalized even at 4 K. This is a significant result since the only other diiron coordination complex that retains Class III behavior at low temperatures is a high-spin species with the iron bridged by hydroxy groups (6). Our $[Fe_2TIED(CH_3CN)_4]^{5+}$ complex has a 5.3 A distance between the iron centers and the delocalization occurs through seven bonds.

The comproportionation constant for formation of the mixed-valence species from the

$$(2+, 2+) \ + \ (3+, 3+) \ \rightleftharpoons \ 2(2+, 3+)$$
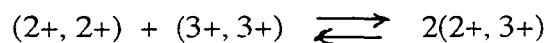
lower and higher isovalent forms gives relative stabilities. The K_{com} as measured by the difference in successive oxidation potentials is larger with Cl- than with CH_3CN axial ligands both measured in CH_3CN solvent (L = CH_3CN, K_{com} = 2.8 x 10^8 ; L = Cl-, K_{com} = 1.7 x 10^{13}).The larger K_{com} presumably results from the fact that the σ–donating Cl- axial ligand leads to a larger resonance stabilization in the mixed-valence form than the π-accepting CH_3CN axial ligands.

Some interesting behavior occurs in the optical spectra of the mixed-valence species compared to their isovalent analogues. The characteristic intense NIR band of the (2, 2+) isovalent dinuclear species has been assigned as an MLCT from filled d_π orbitals of the metal to empty π^* orbitals of the ligand. As mentioned, this transition changes energy

significantly as the axial ligand is replaced: L = CH3CN, λ_{max} = 874 nm; L = DMF, λ_{max} = 985nm. There is also an intense NIR band in all the mixed-valence species. Transition metal mixed-valence species often exhibit intense long wavelength visible or NIR optical transitions due to electron transfer between metals in difference oxidation states. Class III valence-averaged species will not have such an IT band but should exhibit a new transition due to their mixed-valence nature. The intense NIR bands for the $[Fe_2TIEDL_4]^{5+}$ mixed-valence species have not been assigned but their λ_{max} do depend on L but to a different degree and fashion from the isovalent forms: L = CH_3CN, λ_{max} = 940 nm; L = DMF, λ_{max} = 883 nm. There is thus a bathochromic shift from the isovalent to the mixed-valence species with L = CH_3CN, but the shift is in the opposite direction with L = Cl⁻ or DMF. Further studies of the mixed-valence species with L = Cl⁻ or DMF as well as spectral investigations of the origin of the mixed-valence NIR bands are needed before this behavior is understood.

3.1 Diketo Dinuclear (B)

The binuclear TIED complexes are initially formed by metal-promoted oxidative dehydrogenation of the saturated 14-member cyclam (1,4,8,11-tetraazacyclotetradecane) complexes. With iron (and also ruthenium) the oxidizing agent, dioxygen, is at room temperature and atmospheric pressure, and the yield is about 30% based on cyclam. A β-diimine intermediate with two C-N double bonds in a six-membered chelate ring must be present which is then oxidatively coupled and further oxidized to form the M_2TIED complexes. Oxidation of $[Fe_2TIED(CH_3CN)_4]^{4+}$ in the presence of water leads to further oxidative dehydrogenation and to the formation of terminal conjugated keto β-diimine moieties on the ligand. In this unusual reaction the carbonyl oxygens must come from water molecules.

Formation Reactions. There are two one-electron oxidation waves in the cyclic voltammogram in rigorously dry CH_3CN for $[Fe_2TIED(CH_3CN)_4]^{4+}$. The first at 1.18 V (vs NHE) gives the mixed-valence species. The second quasi-reversible wave at 1.68 V

presumably gives the isovalent (Fe^{+3}, Fe^{+3}) ion; however, the appearance of this second 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 dramatically. A new cathodic peak appears at 0.2 V (Figure 1),

Thirty to forty electrons per diiron molecule can be passed during bulk electrolysis at E = 1.75 V in wet CN_3CN solution. Eventually the current drops to lower but non-zero values as a slow irreversible change occurs in the bimetallic species. The products of this bulk oxidative electrolysis are of interest. The central question of possible catalytic oxidation of water is under investrigation and will be described in another report. The final metallic product is blue and its optical spectrum is very similar to that of the original diiron complex in that it retains an intense near-infrared band (834 nm). A blue species with an identical optical spectrum can be synthesized by reaction of a large excess (>20 equivalents) of $[Cu(OH_2)_6](ClO_4)_2$ with CH_3CN solutions of $[Fe_2 TIED(CH_3 CN)_4]^{4+}$. Copper II ion in CH_3CN is a potent oxidizing agent so the overall conditions are similar to the bulk electrolysis, i. e., exhaustive oxidation with water present.

Properties of Diketo Dinuclear Compound. Comparisons of the structural details of the diketo-diiron complex to the original binuclear compound and to keto-β-diimine macrocyclic complexes in the literature are presented in a separate report (7). One important difference between the diketo-diiron complex and the original $[Fe_2TIED(CH_3CN)_4]^{4+}$ and the $[Ni_2TIED]^{4+}$ structures is the length of the carbon-carbon bond linking the two macrocycles. In the diiron and dinickel complexes of the TIED ligand the central carbon-carbon bond length is 1.40 A, intermediate between a double bond and a single bond. In the diketo species the bond length is 1.34 A which is similar to that expected for an isolated carbon-carbon double bond. Our interpretation is that in $[Fe_2TIED(CH_3 CN)_4]^{4+}$ the iron II centers donate electron density into π antibonding orbitals of the ligand, thus increasing the imine and central carbon-carbon bond lengths. In the diketo-diiron complex the axial CH_3CN ligands are the same but the terminal saturated

sigma-donating nitrogens of the TIED binucleating ligand have been converted to a strongly electron withdrawing keto-β-diimine moiety. This decreases the electron donating capacity of the iron II center to the cross-conjugated central portion of the ligand. This interpretation is supported by the observed decrease in the imine carbon-nitrogen bond lengths in the central portion of the ligand: central C=N in diketo-diiron, 1.26 A versus 1.29 A in $[Fe_2TIED(CH_3CN)_4]^{4+}$.

Despite the severe oxidative conditions in which it is produced, the diketo-diiron compound is a diamagnetic low-spin (Fe^{2+}, Fe^{2+}) species. The first oxidation wave in its cyclic voltammogram is at the very positive value of 1.5 V (NHE) in acetonitrile. This remarkable degree of stabilization of the iron +2 oxidation state is due to the strong π acid nature of the ligand. The central cross-conjugated portion of the ligand has previously been recognized as an excellent π acid (4) and the carbonyl oxygen evidently attracts electron density and greatly increases the π acid capabilities of the terminal imine nitrogens. The higher oxidation potential of the diketo species relative to the original diiron compound is also reflected in the differences in the optical spectra. The characteristic low-energy MLCT band at 874 nm of the original binuclear complex in acetonitrile has shifted to 834 nm in the diketo species. This shift to higher energy reflects the lowering of energy of metal d_π orbitals due to the accepting ability of the keto β-diimine moiety at the terminal ends of the ligand.

There are also two broad quasi-reversible reduction waves in the cyclic voltammogram of the diketo species. There are several portions of the ligand that can accommodate added electrons: the central cross-conjugated section and the two keto terminal ends. Preliminary coulometric studies indicate four electrons per diiron complex can be added in the reduction processes. More data are needed to sort out this complicated system.

3.1. Keto Monomers (C)

<u>Formation Reactions.</u> One of our first observations of the $[Fe_2TIED(CH_3CN)_4]^{4+}$ complex was that solid samples of the perchlorate salt underwent a slow reaction if exposed to the atmosphere. A blue surface film forms on green crystals of the diiron complex over periods of weeks and the film can be removed by rapid washing with acetonitrile. If the solid is finely divided, the reaction with atmospheric dixoygen proceeds more rapidly. The spectrum of the blue product in acetonitrile solution has a visible peak at 650 nm. A similar blue species is also formed in CH_3CN solution by reaction of $[Fe_2TIED(CH_3CN)_4]^{4+}$ and dilute solution of potential oxo atom transfer agents such as OCl^- or H_2O_2. The reaction with H_2O_2 occurs with no appreciable build-up of intermediates as evidenced by an isosbestic point in successive optical spectra. The blue species is also formed by reaction between the bimetallic complex and room temperature, atmospheric pressure dioxygen. Interestingly, the rate of this reaction is strongly solvent-dependent. In oxygen-saturated acetonitrile solutions, the reaction to form keto monomers has a half-life of over a week. In oxygen-saturated DMF the half-life for formation of the keto-monomer is less than a minute. This is greater than a factor of 10^4 increase in reaction rate and is due to replacement of axial CH_3CN ligands with DMF

The attack of molecular oxygen on the bridging carbon-carbon double bond produces a very high percentage yield (>95%) of the keto monomeric product (L = DMF). The high yield and the fact that the reaction also occurs in the solid state suggests that a dioxetane intermediate is involved. Dioxetane species are known to produce high yields of ketones (8)

$$\begin{array}{c} O-O \\ | \quad | \\ {\searrow}C - C{\swarrow} \end{array}$$
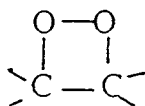
and a concerted cleavage to form two keto-monomeric molecules can reasonably be expected to occur in solids. The formation of keto monomers is independent of light so singlet oxygen is probably not involved in the reaction. We are not aware of any examples

in the organic literature of facile reactions in the dark of room temperature, atmospheric pressure dioxygen with conjugated olefins. Thus, it appears that the iron centers in $[Fe_2TIEDL_4]^{4+}$ are important and are directly involved. A plausible mechanism for formation of the dioxetane intermediate involves an initial transfer of one electron from the π-system to a dioxygen molecule. This produces a peroxide radical with concomitant formation of a radical in the other six-membered chelate ring. The total spin can be
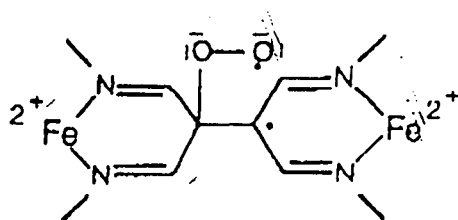
conserved in this step. The presence of d_π electrons on the iron center can act to stabilize the radical in the six-membered ring and facilitate triplet-to-singlet intersystem conversion. Direct combination of a singlet radical peroxide and the radical chelate will form a dioxetane intermediate. Any modification of the iron center, i.e., change of axial ligands, which will favor more π-backbonding will favor formation of the dioxetane intermediate. Available iron d_π electrron density will be much greater with DMF than with CH_3CN axial ligands. This may be a major factor in the large accelration of over 10^4 of the rate of formation of the keto monomer in DMF versus CH_3CN.

With Cl- axial ligands a simple one-electron oxidation takes place with dioxygen rather than attack at the linking carbon-carbon bond. Subtle variations between $[Fe_2TIEDCl_4]^0$ and $[Fe_2TIED(DMF)_4]^{4+}$ could be responsible for the different reaction pathways since there are stringent electronic and steric requirements for formation of the four-membered dioxetane ring.

Properties of Keto Monomer. The monomeric nature of the keto species was established by electrospray mass spectral studies. IR and optical spectroscopic data were

also useful in its characterization. The conformaton of the keto macrocycle is fixed on the NMR time scale and all ten non-equivalent protons in the complex can be unambiguously assigned (9). In rigid cyclic systems the equatorial proton is consistently downfield relative to the axial proton on the same carbon atom. This is the situation for the keto-macrocycle complex but the differences in chemical shifts of the equatorial and axial protons range from 0.52 to 0.82 ppm compared to the usual 0.1 to 0.5 ppm range.

The axial ligands in the keto macrocycle complex are readily exchanged and like $[Fe_2TIEDL_4]^{4+}$ species, the optical and electrochemical properties vary widely with the nature of the ligand. The visible spectra are dominated by metal d_{xz}, d_{yz} electron transfer to a π^* orbital of the ligand. Acetonitrile solutions are blue (λ_{max} = 650 nm) while the addition of Cl- leads to yellow-green solution (λ_{max} = 810 nm). The simplest explanation is that the energies of the metal d_π orbitals increase as the axial ligand changes from CH_3CN to Cl-, bringing the metal orbitals closer in energy to the lowest unoccupied ligand orbital. This interpretation is consistent with the observed shift from 0.93 V to 0.27 V in the first oxidation potential when Cl- is added to the acetonitrile solution of the keto-macrocycle (V vs Fc/Fc+).

The keto functional groups may be useful as a route to other binuclear or linked donor-acceptor complexes. We have established (10) that the keto group can be selectively reduced to a yellow β-diimine macrocycle that is then very easily oxidatively coupled by dioxygen to form the original cross-conjugated diiron complex. We will continue to explore synthetic possibilities with the keto macrocycle.

3.4. Singly-Reduced Species (D)

The $[Fe_2TIED(CH_3CN)_4]^{4+}$ complex in CH_3CN exhibits two well-separated reversible reduction waves in the cyclic voltammogram. These waves appear at -0.16 V and -0.48 V versus NHE. It is unlikely that reduction to Fe(I) occurs and the reduction processes are assumed to be due to placement of electrons in π^* ligand orbitals. In contrast, $[Fe_2TIEDL_4]^{4+}$ complexes with axial ligands other than nitriles exhibit a single

reversible reduction wave in their cyclic voltammogram that corresponds to two electrons. The square planar [Ni$_2$TIED]$^{4+}$ compound also has two separated reduction waves. The blue [Ni$_2$TIED]$^{4+}$ radical species has been examined by ESR and optical spectroscopies. (2) The ESR spectrum shows a slightly broadened g = 2 signal with no discernible indication of metal hyperfine interaction. The optical spectrum for the [Ni$_2$TIED]$^{3+}$ radical has a prominent band at 724 nm with ε = 13,000 M-1 cm-1 compared to a broader band at 524 nm (ε = 6,500 M-1cm-1) for the [Ni$_2$TIED]$^{4+}$ species. The electronic transition at 724 nm for the radical species has been assigned as an LMCT.

Formation Reactions. Singly reduced species can be generated by electrochemical reduction product at potentials just negative of the first reduction potential in nitrile-based solvents (acetonitrile, propionitrile, benzonitrile, chloroacetonitrile). The single-electron reduced products are all very sensitive to oxidation by dioxygen and we have not succeeded in isolating any of the species.

Properties. Spectroelectrochemistry has been done on the single electron reduction product of [Fe$_2$TIED(CH$_3$CN)$_4$]$^{4+}$ in CH$_3$CN solutions (Figure 2). The 874 nm band disappears and a new NIR band with diminished intensity (ε =10^{4}M-1cm-1) appears at 960 nm for the [Fe$_2$ TIED(CH$_3$CN)$_4$]$^{3+}$ radical. The original [Fe$_2$TIED(CH$_3$CN)$_4$]$^{4+}$ species can only be partially regenerated (85-95%) by electrochemical oxidation at 0.0 V. Furthermore, isosbestic points are not maintained during the spectroelectrochemical reduction or re-oxidation processes. These observations indicate several species are present, which complicates characterization by ESR. The new NIR band at 960 nm is, however, very likely due to the radical [Fe$_2$ TIED(CH$_3$CN$_4$)]$^{3+}$ ion. It seems unlikely that the 960 nm band is still due to a metal-to-ligand charge transfer transition since the presence of an added electron in a ligand orbital should not cause a shift to lower energy. One possibility is that the transition is ligand-based, i.e., π^* to another higher energy π^*. The presence of higher energy empty ligand orbitals is indicated by the shifts in energy of a UV band in addition to the energy shifts of theNIR band in

$[Fe_2TIEDL_4]^{4+}$ complexes as the axial ligands change. (4) Another possibility is that after an electron has been added to a ligand orbital, a ligand-to-metal charge transfer can occur. Such an MLCT would presumably have to involve electron transfer from a π^* ligand orbital to an empty $d_{x^2-y^2}$ or d_{z^2} metal orbital. The symmetries of these orbitals, however, do not allow overlap. Isolation of pure samples of radical $[Fe_2TIEDL_4]^{3+}$ species and more physical data are needed to assign the optical spectra and to characterize the singly reduced species.

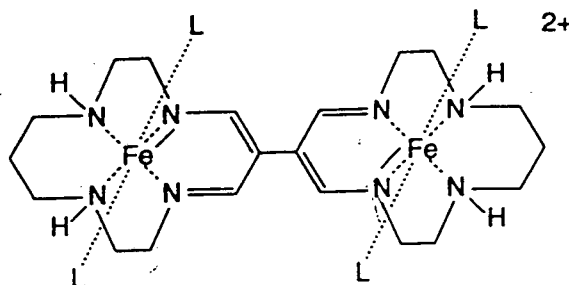### 3.5 Doubly-Reduced (E)

Formation Reactions. With other axial ligands such as Cl^-, DMF, or H_2O, $[Fe_2TIEDL_4]^{4+}$ compounds have a single, two-electron reduction wave in their cyclic voltammograms. This contrasts with the two, well-separated one-electron reduction waves with the nitrile type axial ligands. Differential pulse polarography (DPP) is much better suited to differentiating electron transfer steps that have similar potentials. In DMF and H_2O the DPP voltammogram is a composite which indicates that the reduction occurs in two, one-electron steps although the two steps are not fully resolved.

Bulk electrolytic reduction in DMF or in CH_3CN solutions containing Cl^- with Pt mesh electrodes will produce solutions of doubly-reduced species. Also, reductions in CH_3CN solution at potentials negative of the second reduction wave yield a doubly-reduced species. Chemical reduction with sodium amalgam under the same conditions also produces doubly-reduced species.

Properties. Spectroelectrochemical reduction experiments with $[Fe_2TIEDCl_4]^0$ have been performed in acetonitrile. The yellow isovalent $|Fe_2TIEDCl_4|^0$ molecule has λ_{max} at 985 nm and 375 nm; upon reduction a brown species is formed with a broad, low intensity maximum and a featureless slope into the UV region (Figure 3). The two-electron reduction is probably ligand-centered since an (Fe^+, Fe^+) species would be unprecedented. The added electron on the ligand makes an MLCT transition impossible and no evidence of low-energy LMCT bands are observed.

There are two six-membered chelate rings that can accommodate one added electron each in $[Fe_2TIEDL_4]^{2+}$ species. If one electron is then added to each chelate ring from the bridging double bond, a six π-electron quasi "aromatic" ring structure can be formed.

Such a structure was postulated for the doubly-reduced species $[Ni_2 TIED]^{2+}$.

The electrochemical two-electron reduction of $[Fe_{2+}TIEDCl_4]^0$ is not clean since an isosbestic point is not maintained and re-oxidation only gives about 80-85% return to the original chromophore. The doubly-reduced $[Fe_2TIEDCl_4]^{2-}$ species is very reactive to dioxygen and products other than the original isovalent (Fe^{2+}, Fe^{2+}) species are formed. A number of techniques such as ^{13}C and ^{1}H NMR, IR, and Mossbauer spectroscopy can be applied to characterize the doubly-reduced species if pure samples can be obtained. We will do electrochemical and chemical reductions in different solvents with different axial ligands to find conditions under which doubly-reduced compounds can be isolated. .

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Scheme 1

A. (1) **Electrochemical oxidation**

Solvent, dry CH_3CN; $L = CH_3CN$

(2) **Oxidation with O_2**

Solvent, CH_3CN; $L = Cl^-$.

B. (1) **Electrochemical oxidative electrolysis**

Solvent, CH_3CN with 0.5% H_2O; $L = CH_3CN$

(2) **Oxidation with excess $Cu(OH_2)_6(ClO_4)_2$**

Solvent, CH_3CN; $L = CH_3CN$

C. (1) **Reaction with O_2**

Solvent, DMF; $L = DMF$

(2) **Reaction with H_2O_2**

Solvent, CH_3CN; $L = CH_3CN$

D. (1) **Electrochemical reduction**

Solvent, CH_3CN; $L = CH_3CN$

(2) **Electrochemical reduction**

Solvent, C_6H_5CN; $L = C_6H_5CN$

E. (1) **Electrochemical reduction**

Solvent, CH_3CN; $L = Cl^-$

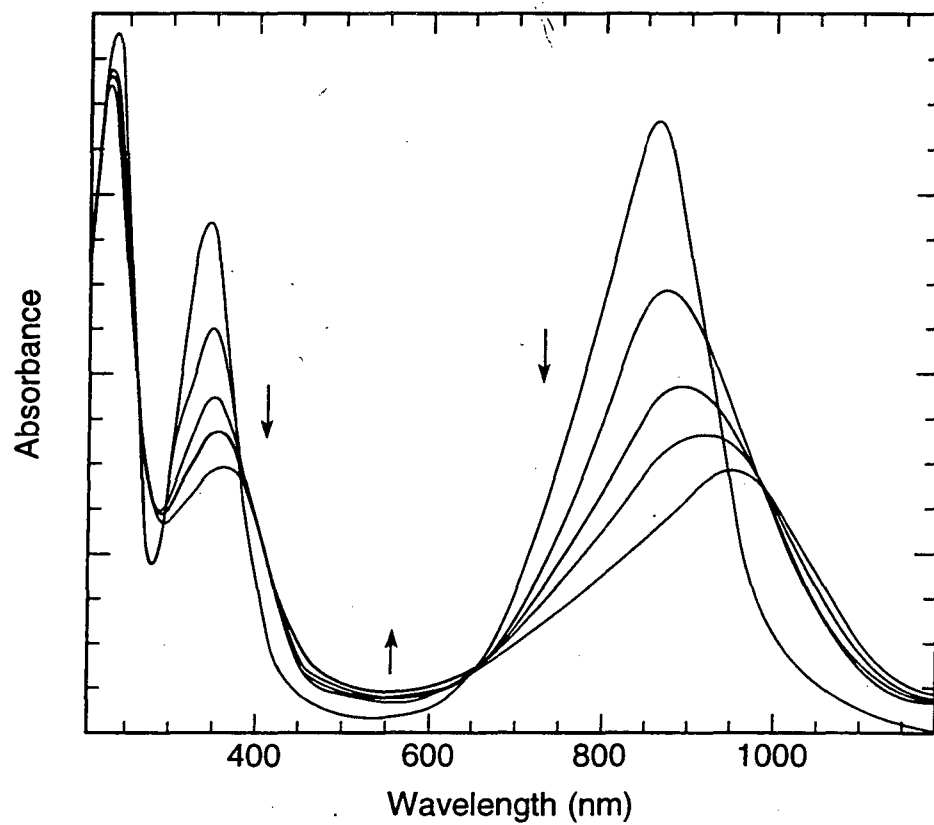(2) **Reduction with Na/Hg**

Solvent, DMF; $L = DMF$

Scheme 1

Figure 1

2.5   2.0   1.5   1.0   0.5   0.0   -0.5   -1.0
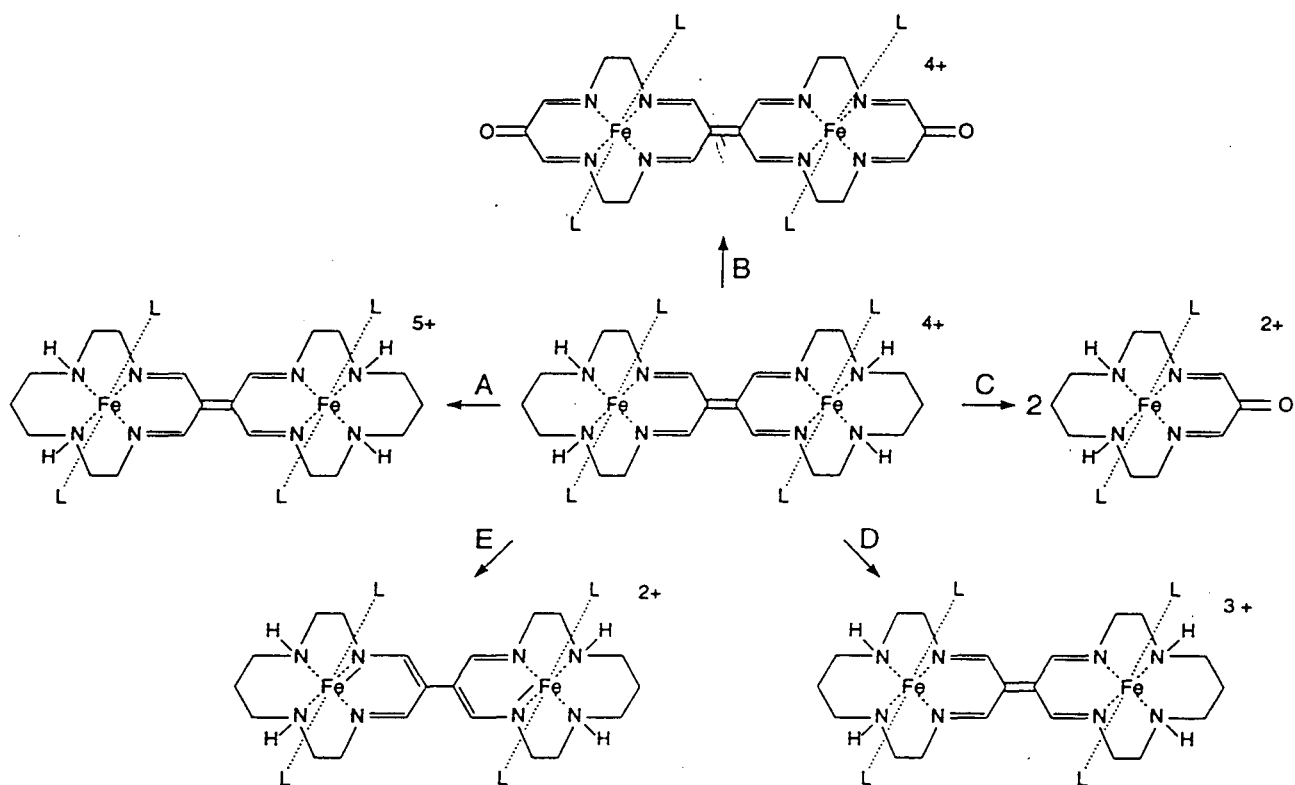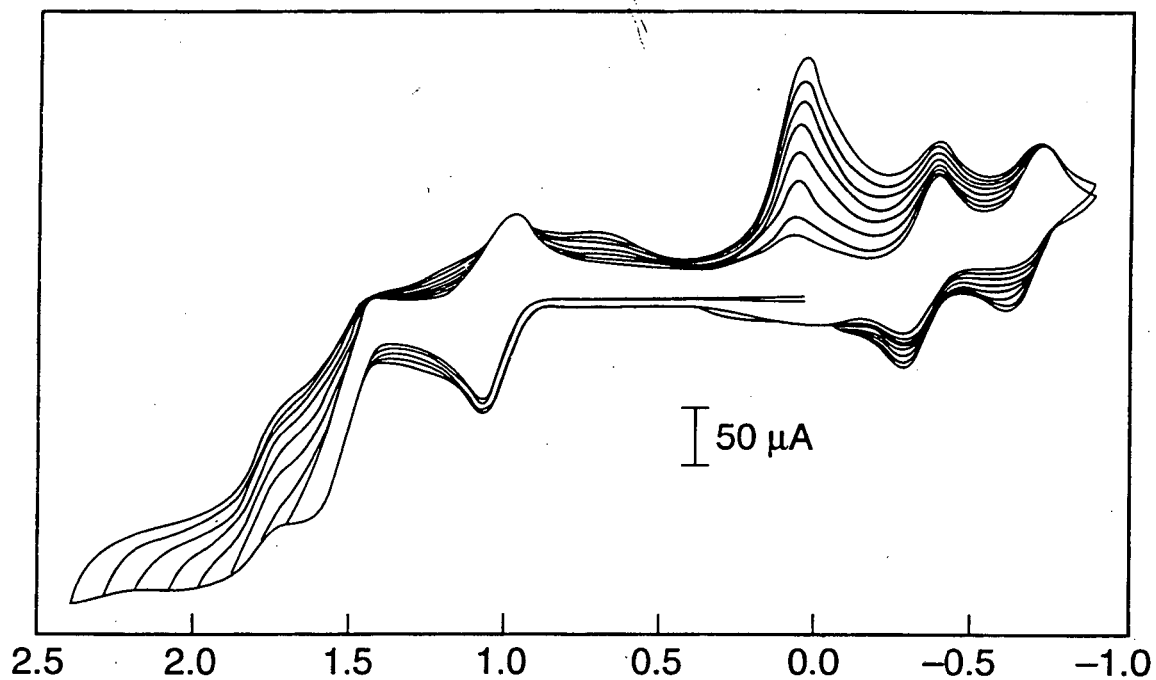
Cyclic voltammograms of $[Fe_2TIED(CH_3CN)_4]^{4+}$ in CH_3CN with 0.5%
H_2O by volume. The positive potential is increased by 50 mV on
each successive sweep. Conditions: 0.1 $\underline{M}$ TBAH; Pt disc working
and Pt wire counter electrode; Ag+/Ag reference; sweep rate 100 mV/
sec.

Figure 2   22

One-electron spectroelectrochemical reduction of $[Fe_2TIED(CH_3CN)_4]^{4+}$ in CH_3CN. Reduction at -0.42 V vs At^+/Ag reference electrode; 0.1 $\underline{M}$ TBAH.

XBD 9507-03368.ILR

Figure 3
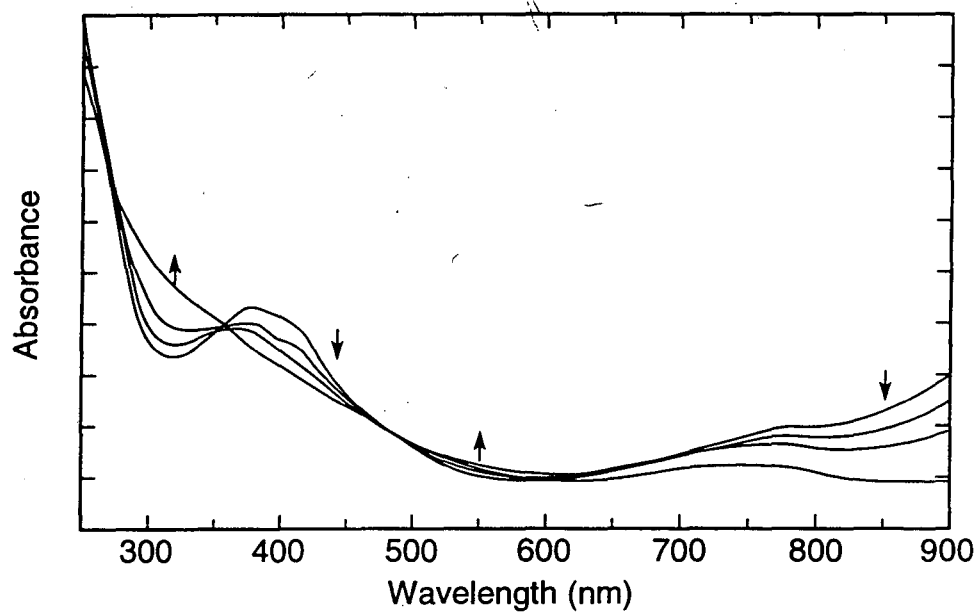
Two-electron spectroelectrochemical reduction of $[Fe_2TIEDCl_4]^o$ in CH_3CN. Reduction at -0.50 V vs Ag^+/Ag reference electrode; 0.1 $\underline{M}$ TBAH.