glyme (9 ml) was heated at 125–130° for 18 hr. Work-up as described above gave **3**, $R = n\text{-}C_3H_7$.

The urea complex **6** (0.18 g) in diglyme (5 ml) was heated at 125–130° for 2–5 hr. The reaction mixture was cooled somewhat and filtered, and the filtrate was evaporated *in vacuo*. The residue was treated with pentane (10 ml) and filtered, and the filtrate was evaporated to give 0.009 g (5.4%) of **8**, $R = n\text{-}C_3H_7$. The pentane-insoluble solid (0.049 g, 80%) was **4**, $R = n\text{-}C_3H_7$.

Reaction of Diiron Enneacarbonyl with 2-Methyl-2-nitropropane.—A mixture of 2-methyl-2-nitropropane (2.78 g, 27.0 mm) and diiron enneacarbonyl (10.9 g, 30.0 mm) in dry benzene (80 ml) was stirred at room temperature for 26 hr. The solution was filtered, the filtrate was concentrated *in vacuo*, and the residue was dissolved in pentane and chromatographed on Florisil. Elution with pentane gave 0.37 g (4.9%) of the red-orange complex **5**, $R = (CH_3)_3C$, and 0.036 g (0.63%) of **8**. Elution with benzene gave 0.59 g (10%) of **6**, $R = (CH_3)_3C$. See Table II for melting point, analytical, and infrared and mass spectral data concerning these complexes.

Reactions of Complexes 5, 6, and 8 [$R = (CH_3)_3C$] in Diglyme.—The urea complex **6** [$R = (CH_3)_3C$, 0.55 g] in diglyme (10 ml) was heated at 120–130° for 10 hr. Work-up as described for the 2-methyl-2-nitropropane–iron pentacarbonyl reaction gave 0.17 g (82%) of **4**, $R = (CH_3)_3C$, and traces of **3**, $R = (CH_3)_3C$.

The trinuclear complex **5** (0.30 g) in diglyme (7.5 ml) was heated at 120–130° for 5 hr. Work-up as for the corresponding reaction of **5**, $R = n\text{-}C_3H_7$, gave 0.19 g (84%) of **8** [$R = (CH_3)_3C$] and trace quantities of **3** and **4**. Heating **8** in diglyme gave **7** [see Table II]. A mixture of **7** (0.12 g), iron pentacarbonyl (1.1 ml), and diglyme (11 ml) was heated at 120–130° for 10 hr. Work-up as described earlier gave **3**, $R = (CH_3)_3C$.

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Cyclic Amine Complexes of Iron. Electrochemistry, Preparation, and Properties

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The electrochemistry, preparation, and properties of some iron complexes of a macrocyclic tetramine are reported. Compounds containing Fe(III), Fe(II), and a reduction product which appears to be an iron hydride were isolated and characterized. The dependence of the redox potentials of Cu, Ni, Co and Fe macrocyclic tetraamine complexes on electronic properties of the central metal ion is discussed.

Introduction

Transition metal complexes of tetradentate cyclic amines formed by condensing linear amines with ketones in the presence of certain metal salts were first discovered in 1960 by Curtis.[1] A growing interest in these complexes has led to a considerable amount of work on their preparation, properties, and chemistry. An excellent review article by Curtis[2] covering the work up to 1968 has appeared in the literature. More recently, electrochemical studies of a number of the cyclic amine complexes revealed the remarkable ability of these ligands to stabilize unusual oxidation states, *e.g.*, Ni(I) and Ni(III),[3] Co(I),[4] and Cu(III),[5] as well as Cu(I)[5,6] which is rarely found in a square-planar complex. Preparation and isolation of the M(I) and M(III) complexes as perchlorate or tetrafluoroborate salts demonstrated that most of them are surprisingly stable in the absence of oxidizing or reducing agents.

In an extension of our electrochemical investigation of cyclic amine complexes to other metals, we have carried out a study involving Fe. Some work on Fe complexes has already appeared in the literature. Thus, Fe(II) and Fe(III) complexes of the unsaturated cyclic ligand obtained by condensing acetone with ethylenediamine have been reported.[7] The Fe(II) complex of the corresponding saturated amine, L, shown in Figure 1, has also been isolated as the dichloride salt.[8] A recent electrochemical study of these complexes[8] indicated that Fe(II) cyclic amines exhibit a redox chemistry similar to the Cu, Ni, and Co compounds, but none of the oxidation or reduction products were isolated and characterized. We have prepared the new complexes $FeL(BF_4)_2$ and $(CH_3CN)_2FeL(BF_4)_2 \cdot 2CH_3CN$, containing Fe(II) in high- and low-spin states, respectively. Using electrochemical techniques, $(CH_3CN)_2Fe(BF_4)_3$ and what appears to be a hydride, $HFeL(solvent)(BF_4)$, have also been obtained. This report deals with the preparation, electrochemistry, and properties of these iron cyclic amines.

Experimental Section

Polarographic and Voltammetric Measurements.—The electrochemical instrumentation, cells, electrodes, and techniques have been previously described.[3,5,9] The purification of the solvent (acetonitrile) and of the supporting electrolyte (tetraethylammonium perchlorate) can be found in the above references. All measurements were carried out at 25.0 ± 0.05°.

Spectra.—The infrared spectra were measured, using a Beckman IR-5A. An IR-4 was used to locate the Fe–H stretch more accurately. The spectra were obtained in Nujol and Fluorolube mulls as well as KBr pellets.

The visible and ultraviolet spectra were obtained with a Cary 14 automatic spectrophotometer provided with an inert atmosphere. The cell length was varied between 0.1 mm and 1 cm in order to avoid the necessity for dilution of solutions.

Magnetic Measurements.—The magnetic measurements were made by the Gouy method using the solid samples. The balance was calibrated with diamagnetic and paramagnetic standards.

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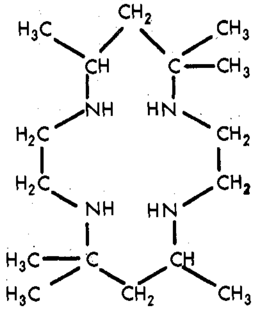

L

Figure 1.—The cyclic amine ligand.

The diamagnetic standard was distilled water and the two paramagnetic standards were ferrous ammonium sulfate and manganese pyrophosphate. The μ_{eff} was calculated from the slope of a Curie curve ($1/\chi_M$ *vs.* T). The temperature range covered was 80-300°K. Diamagnetic corrections for the ligands and anions were calculated from Pascal's constants. The field strength was varied between zero and 9000 G in five steps.

Preparation of Complexes.—The preparation of some of the starting materials can be found in several previous reports.[3-5] Similarly the purification of solvents has been described earlier. All reactions were done in a Vacuum Atmospheres Dri Lab.

$(CH_3CN)_2FeL(BF_4)_2 \cdot 2CH_3CN$ and $FeL(BF_4)_2$.—A solution of 2.2 g of anhydrous cyclic amine and 4.4 g of $Fe(CH_3CN)_6(BF_4)_2$[10] in 200 ml of acetonitrile was refluxed overnight. Purple crystals formed in 1 day at room temperature. They were filtered and dried under vacuum for 0.5 hr. More crystals can be obtained when the solvent is evaporated to 75 ml. The total yield of $(CH_3CN)_2FeL(BF_4)_2 \cdot 2CH_3CN$ was 4.3 g. The acetonitriles can be removed by pumping at $<10^{-5}$ Torr for several hours. A powder blue $FeL(BF_4)_2$ complex is then the product. Infrared spectra of the Fe(II) complexes were consistent with the trans, meso isomer. *Anal.* Calcd for $(CH_3CN)_4FeL(BF_4)_2$: C, 42.6; H, 6.6; N, 16.5. Found (purple compound): C, 42.7; H, 6.4; N, 16.3. Calcd for $FeL(BF_4)_2$: C, 37.4; H, 6.6; N, 10.9 Found (blue compound): C, 37.4; H, 6.8; N, 10.6.

$(CH_3CN)_2FeL(BF_4)_3$.—Four grams of $(CH_3CN)_4FeL(BF_4)_2$ was added to 125 ml of acetonitrile. The complex was only partially soluble. The solution was made 0.2 *M* in Et_4NBF_4 and was oxidized at a Pt foil electrode at +0.75 V. When the current had dropped to 5% of its original value, the electrolysis was stopped. The solvent was evaporated under vacuum to about 25 ml and the solution was filtered. The orange crystals were washed with acetonitrile and were dried for 0.5 hr under vacuum. The yield was 2.8 g. *Anal.* Calcd for $(CH_3CN)_2FeL(BF_4)_3$: C, 35.2; H, 6.2; N, 12.3. Found: C, 35.5; H, 6.3; N, 12.0.

Reduction Product or HFeL(solvent)(BF_4).—The hydride can be prepared either by reduction at a Pt-foil electrode or with Na(Hg). The latter method is described here. A solution of 1.8 g of $(CH_3CN)_4FeL(BF_4)_2$ in 125 ml of acetonitrile was stirred over Na(Hg) (0.25 g of Na in 15 ml of Hg) for 30 min. A color change from purple to green occurs during the first few minutes. The solution was filtered and rapidly stripped to dryness. The solid was extracted into 100 ml of THF to separate it from $NaBF_4$ and the solution was stripped to dryness. The yield was 0.5 g. Some free ligand is usually present, presumably due to some decomposition of the complex during reduction. This can be removed with some loss in yield by washing the sample with small portions of THF. The product contains coordinated CH_3CN and THF.

Thermal Decomposition of HFeL(solvent)(BF_4) and Mass Spectral Analysis of Products.—An 11.0-mg sample of HFeL(solvent)(BF_4) (26 μmol) was heated 30 min in a closed tube under vacuum at 175°. A color change to a lighter green occurred. The infrared spectrum of the green solid was typical of a saturated cyclic amine complex with the exception of an intense band at 2035 cm^{-1}. The following products were found by mass spectroscopy: CH_3CN (10.6 μmol), THF (3.9 μmol), CH_4 (8.5 μmol), H_2 (2.1 μmol), N_2 (0.6 μmol).

When the hydride (~25 μmol) was prepared in CD_3CN (no THF treatment) and decomposed under the same conditions, the following products were formed: (1) CD_3CN, CD_2HCN, CDH_2CN, CH_3CN, all at about the same level (1-5 μmol); (2) 10 μmol of methanes with the distribution 9% CH_4, 20% CH_3D, 13% CH_2D_2, 34% CHD_3, 24% CD_4; (3) H_2, HD, D_2 not determined; (4) the recovered solid which exhibited new bands in the infrared region at 2035 and 2430 cm^{-1}.

Results

Electrochemistry. Fe(II) Complex.—At the dropping mercury electrode (dme), Fe(*trans*-tetramine)$^{2+}$ gave two cathodic waves. The first wave was diffusion controlled and corresponded to the uptake of a single electron. A large maximum which could be diminished but not eliminated by dilution prevented a log analysis (E *vs.* log ($i/i_d - i$)) of the wave. The second wave was irreversible ($E_{1/2} \approx -2.9$ V) and its height was double that expected for a one-electron reduction. The nature of the process giving rise to the second wave is unknown but probably yields Fe metal as a product.

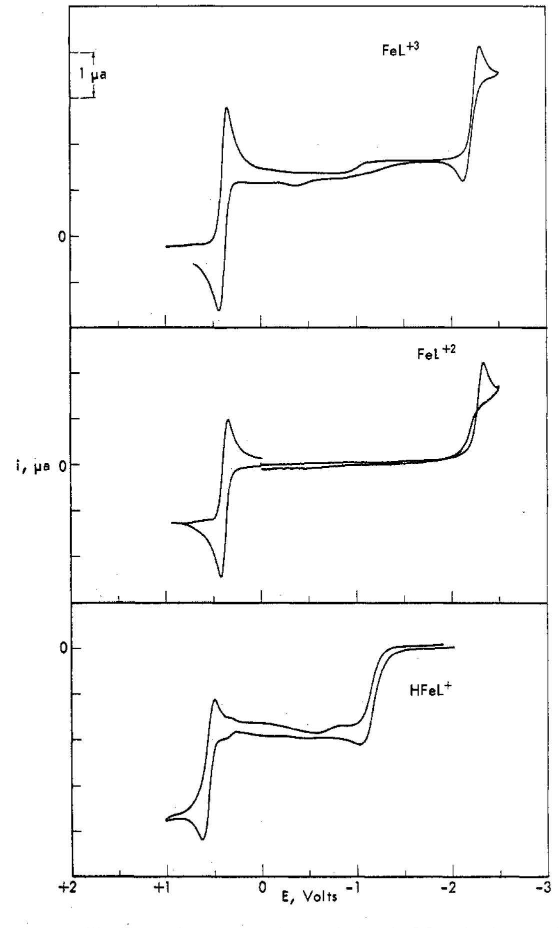

Figure 2.—Cyclic voltammograms of 10^{-3} *M* solutions of the iron-cyclic amine complexes.

On a platinum electrode both an anodic and a cathodic peak were observed as seen in Figure 2. The anodic peak was due to a reversible single-electron process, $FeL^{2+} - e^- \rightarrow FeL^{3+}$, as shown by the separation of the peak potentials of the peaks obtained on the forward and reverse scans during cyclic voltammetry.[11] In addition, the ratio of the heights of the peaks was close to the unity indicating a reversible process with a product stable on the voltammetric time scale.[11] The

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cathodic peak was totally irreversible. No anodic peak due to the electrode product was observed on the reverse sweep. Fe metal was not a product of the reduction since a metal stripping peak was absent. The irreversibility as shown later is due to a following chemical reaction of the FeL^+ formed at the electrode to produce an iron hydride.

Fe(III) Complex.—Constant-potential oxidation of FeL^{2+} in acetonitrile yielded $(CH_3CN)_2FeL(BF_4)_3$. A polarogram of the Fe(III) complex on the dme exhibited three cathodic waves. The first wave was continuous with the anodic limiting current (electrochemical dissolution of mercury) on the dme. The height of the wave corresponded to the uptake of one electron due to the reduction of FeL^{3+} to FeL^{2+}. The remaining two cathodic waves corresponded to the cathodic waves observed for the Fe(II) complex.

On a platinum indicating electrode two cathodic peaks were observed (Figure 2). The first peak was due to a reversible single-electron process as shown by cyclic voltammetry. The second peak occurred in a similar potential region as the cathodic peak of the Fe(II) complex but differed in that an anodic peak was observed on the reverse sweep. The ratio of the peak heights was 0.89 indicating that the Fe(I) species formed as the electrode was undergoing a rapid chemical reaction. The separation of the peaks was 150 mV which is larger than expected for a reversible electrode reaction.

$HFeL^+$.—The totally irreversible cathodic peak obtained with cyclic voltammetry of FeL^{2+} indicated the Fe(I) complex is unstable. This was confirmed by constant-potential electrolysis which yielded what is believed to be a hydride, $HFeL(BF_4)$ (see later in text). A polarogram of $HFeL(solvent)(BF_4)$ on the dme exhibited a single-electron anodic wave. A log plot of the wave gave a slope of 91 mV; a 60-mV slope is expected for a one-electron reversible process. Near the limiting potential in acetonitrile (≈ -3.0 V) a cathodic wave was also observed.

On a platinum electrode, two anodic peaks were obtained (Figure 2). The first peak was totally irreversible giving no cathodic peak on the reverse sweep. The second anodic peak was quasireversible as shown by cyclic voltammetry. The potential at which the second anodic peak of $HFeL(solvent)(BF_4)$ occurred did not correspond to the anodic peak of FeL^{2+} indicating that the product of the oxidation of $HFeL^+$ is not FeL^{2+}. The relevant electrochemical data are assembled in Table I.

Spectra.—Ultraviolet and visible absorption spectra of the Fe complexes were obtained in acetonitrile. The wavelengths and intensities of the peaks are listed in Table II.

Infrared spectra were obtained in Fluorolube mulls. The absorption lines appearing in the regions 3600–1200 cm^{-1} are shown in Figure 3. The rest of the spectra between 625 and 1200 cm^{-1} contain the intense tetrafluoroborate bands and very few others of any interest.

Magnetic Moments.—The magnetic moments of the Fe complexes are given in Table III. All of the compounds gave a linear Curie curve over the temperature range of 80–300°K. The complex $FeL(BF_4)_2$ is paramagnetic with a moment characteristic of four unpaired electrons. The complex $(CH_3CN)_4FeL(BF_4)_2$, on the other hand, is diamagnetic. The Fe(III) compound $(CH_3CN)_2FeL(BF_4)_3$ has a moment characteristics of one unpaired electron. The moment of $HFeL(solvent)(BF_4)$ is discussed in the following section.

TABLE I
ELECTROCHEMICAL DATA

Dme

Electrode reaction	$E_{1/2}$,[a] V	Slope, mV	I_D[b]
$FeL^{2+} + e^- \rightarrow HFeL^+$	-2.1	[c]	2.90
$HFeL^+ - e^- \rightarrow I^d$	-1.455	91	2.20

Pt Electrode

Electrode reaction	$E_{1/2}$,[a,e] V	E_p, V
$FeL^{2+} + e^- \rightarrow FeL^+$		-2.250^f
$FeL^{2+} - e^- \rightarrow FeL^{3+}$	$+0.340$	
$FeL^{3+} + e^- \rightarrow FeL^{2+}$	$+0.328$	
$HFeL^+ - e^- \rightarrow I^d$		-1.02
$I^d - e^- \rightarrow II^d$	$+0.548$	

[a] *Vs.* Ag–0.10 *M* $AgNO_3$ in CH_3CN. [b] $i_d/Cm^{2/3}t^{1/6}$. [c] Maximum prevented log analysis of wave. [d] Product unidentified; see text. [e] E at $i = 0.852i_p$. [f] From second reduction step of FeL^{3+}; see text.

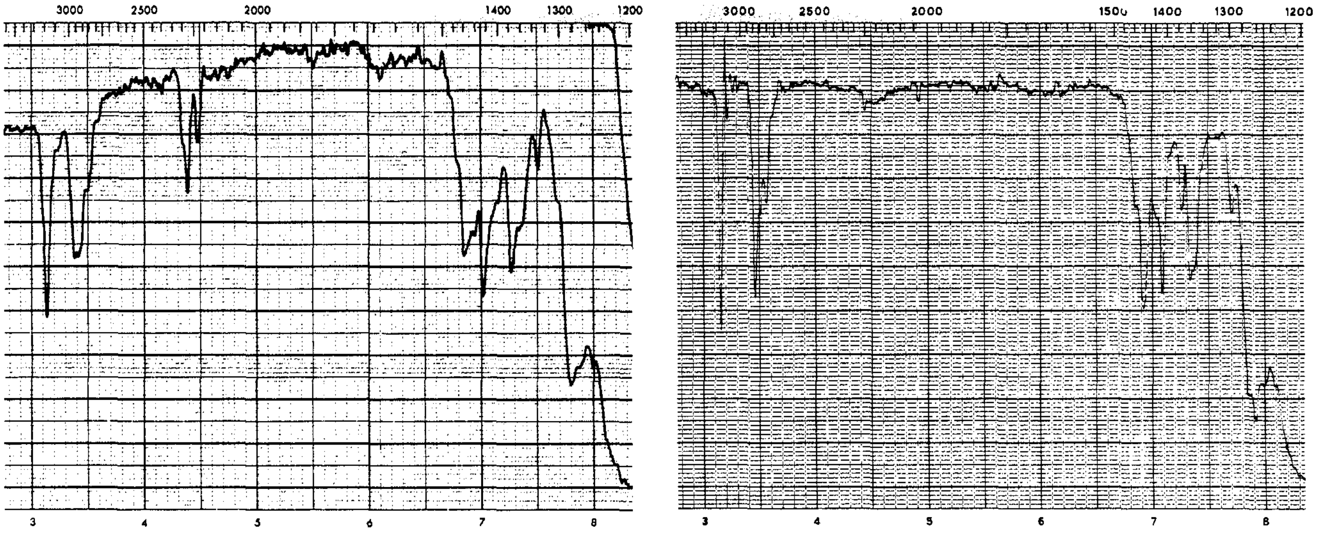
TABLE II
ELECTRONIC SPECTRA IN ACETONITRILE

Complex	λ, mμ	ε, M^{-1} cm^{-1}
$(CH_3CN)_2FeL(BF_4)_2 \cdot 2CH_3CN$	559	41.5
	379	48.4
	266	13,500
$(CH_3CN)_2FeL(BF_4)_3$	525 sh	37
	450 sh	137
	253	11,000
	390	349
$HFeL(solvent)(BF_4)$	643	145
	620	162
	420 sh	111
	310 sh	490
	262 sh	1,800
	223	5,580

TABLE III
MAGNETIC MOMENTS

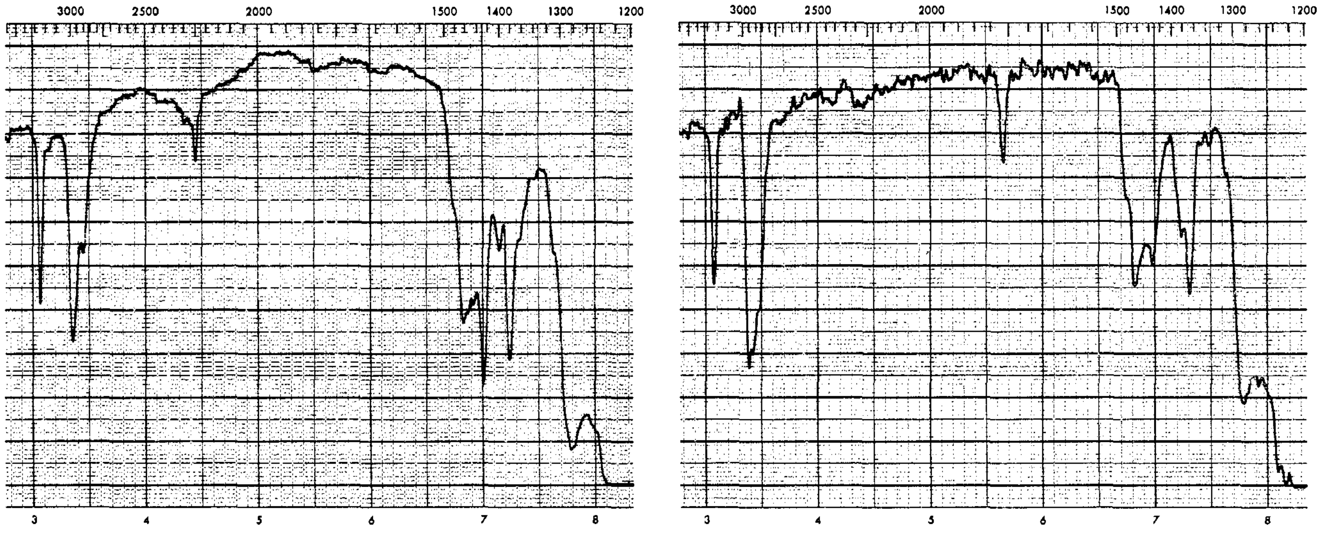
Complex	μ, BM
$(CH_3CN)_2FeL(BF_4)_2 \cdot 2CH_3CN$	Diamag
$FeL(BF_4)_2$	5.47
$(CH_3CN)_2FeL(BF_4)_3$	2.190
$HFeL(solvent)(BF_4)$	3.7

Characterization of the Reduction Product.—Satisfactory elemental analyses were not obtained for the reduction product due to the difficulty of preparing a pure sample. The initial product isolated from the Na(Hg) reduction was contaminated with $NaBF_4$ as well as free ligand resulting from partial decomposition of the complex. While these could be removed for the most part by extraction with THF, coordinated THF as well as CH_3CN remained attached to the complex and could not be completely removed under prolonged vacuum. Thus, one sample prepared in this manner yielded CH_3CN, THF, and CH_4 when heated under vacuum as described in the Experimental Section. Presumably the CH_4 derived from decomposition of CH_3CN by the Fe (see Discussion). Analyses of the products gave 0.73 mol of CH_3CN and 0.15 mol of THF/mol of Fe. On this basis the reduction product appears to contain 1 mol of coordinated solvent. The F content clearly indicated the presence of one BF_4^- anion/mol of complex. The infrared spectrum, while typical of a cyclic amine complex with a BF_4^- anion, exhibited a new band at 1769 cm^{-1} which could be due



$(CH_3CN)_4Fe(trans\text{-}TETRAMINE)(BF_4)_2$

$Fe(trans\text{-}TETRAMINE)(BF_4)_2$



$(CH_3CN)_2Fe(trans\text{-}TETRAMINE)(BF_4)_3$

$HFe(trans\text{-}TETRAMINE)(BF_4)$

Figure 3.—Infrared spectra.

to a hydride. This band disappears on exposure of the compound to air. Two chemical tests often used for metal hydrides are reaction with phenol or carbon tetrachloride. The former produces H_2 while the latter gives chloroform. The compound reacted with phenol as evidenced by a color change but no H_2 was detected by mass spectrometry. However, we have observed that in a few cases known hydrides do not yield H_2 in their reaction with phenol. Reaction occurred rapidly with carbon tetrachloride yielding chloroform in 25% of the stoichiometric amount assuming a monohydride. Nmr measurements on the complex could not be made due to paramagnetism. While not conclusive, the evidence points to a hydride having the formula HFeL(solvent)-(BF_4). The ligand, L, may be a modified cyclic amine as discussed in the following section.

Discussion

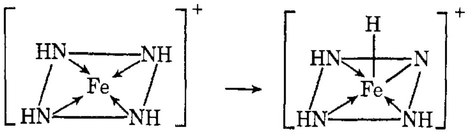
The Fe(II) complex of the trans tetramine (see Figure 1) can be obtained in either a low-spin or a high-spin form. The ligand field strength of the cyclic amine is inadequate to cause spin pairing but pairing does occur when acetonitrile is coordinated in the axial positions. Crystallization of the complex from acetonitrile gives diamagnetic $(CH_3CN)_2FeL(BF_4)_2 \cdot 2CH_3CN$. The acetonitriles can be readily removed under vacuum to give the square-planar high-spin complex having four unpaired electrons.

The pattern of redox behavior and the trend in redox potentials observed with the cyclic amine complexes of Cu, Ni, and Co[3-5] also extends to the Fe complexes. The Fe(II) compound undergoes single-electron oxidation and reduction to the corresponding Fe(III) and Fe(I) complexes. The Fe(III) complex is stable and was isolated as $(CH_3CN)_2FeL(BF_4)_3$. It is low spin with one unpaired electron. The reduction product proved difficult to characterize conclusively. As discussed in the previous section, we believe that the product is a hydride. The evidence for a hydride is a new infrared band at 1769 cm^{-1} which disappears on exposure to air and the products obtained on reaction of the compound with CCl_4 as well as on heating at 175°. Although the 1769-cm^{-1} band occurs 40–100 cm^{-1} lower than the normal region for ν(Fe–H), this may be due to the effect of the cyclic amine ligand. Most previously reported iron hydrides contain tertiary phosphine ligands. Reaction of the compound with CCl_4 produced $CHCl_3$ as expected for a hydride, although only 25% of the theoretical amount. Heating the solid at 175° under vacuum yielded as gaseous products CH_3CN, H_2, and CH_4 and a light green solid which, based on infrared evidence, appeared to be a $FeL(CN)(BF_4)$ complex. Its infrared spectrum contained an intense band at 2035 cm^{-1} in the region characteristic of coordinated CN^- but was otherwise typical of a saturated cyclic amine complex. The formation of H_2 and CH_4 can be rationalized by the following reactions of a hydride, where coordinated acetonitrile is originally present in the complex

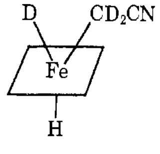
$$2HFeL^+ \longrightarrow 2FeL^+ + H_2 \qquad (1)$$

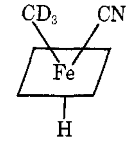
$$HFeL(CH_3CN) \longrightarrow FeL(CN) + CH_4 \qquad (2)$$

The combined H_2 and CH_4 obtained accounted for 0.5 equiv of hydride. The yield of substoichiometric amounts of products expected from a hydride may be due to a mixture of $HFeL^+$ and FeL^+; however, the voltammetric pattern obtained in acetonitrile for the compound indicated the presence of a single species. The formation of a hydride raises the question of the source of the hydrogen. Reduction of $FeL(BF_4)_2$ in deuterioacetonitrile yielded the same product as obtained in acetonitrile demonstrating that hydrogen is not abstracted from the solvent. If hydrogen is abstracted from the ligand, it probably comes from the amine groups. Deprotonation of amines by transition metal ions to form metal amides, $M–NR_2$, has been reported.[12,13] An intermediate in this type of reaction could be a hydride formed by oxidative addition of the amine, *i.e.*, for the iron complex



Oxidative addition of an N–H bond would not be surprising in view of the strong reducing power of the Fe(I) complex. It is interesting that when the iron complex prepared in deuterioacetonitrile is heated to 175°, the full range of CD_xH_yCN and CD_xH_y products is formed. The compound transforms to a solid which exhibits a new infrared band at 2430 cm^{-1} which is in the region expected for ν(N–D). Thus, exchange of hydrogen between acetonitrile and the coordinated cyclic amine appears to occur, which could be accounted for by intermediates such as





The "decyanidation" of acetonitrile is similar to the decarbonylation of ethanol to carbonyl complexes and CH_4 by some metal ions.[14,15] It may also occur slowly in solution at room temperature since the iron compound was observed to decompose slowly in acetonitrile. While identification of the decomposition products was not pursued, free ligand was found, which would be expected if sufficient cyanide was produced to displace the cyclic amine completely. The compound is stable as a solid for at least 1 month.

As pointed out in a previous report,[4] the trend in $E_{1/2}$ values of both the $ML^+ - e^- \rightarrow ML^{2+}$ and $ML^{2+} - e^- \rightarrow ML^{3+}$ couples of the cyclic amine complexes of Cu, Ni, and Co parallels the trend in ionization potentials of the corresponding gaseous metal ions. A linear plot of $E_{1/2}$ *vs.* IP, the ionization potential, is obtained as seen in Figure 4, where the $E_{1/2}$ values of the saturated complexes which give the most reversible electrode processes are used. The $ML^+ - e^- \rightarrow ML^{2+}$ and $ML^{2+} - e^- \rightarrow ML^{3+}$ couples fall on separate parallel lines. In order to determine whether the Fe complexes fit the linear correlation, reversible $E_{1/2}$ values must be available. Cyclic voltammetry of the Fe(II) complex showed that the $FeL^{2+} + e^- \rightarrow FeL^+$ step is totally irreversible since no anodic peak was obtained on the reverse scan (Figure 2). However, when the Fe(III) complex was used as the depolarizer, a peak was obtained on reversing the scan after the $FeL^{2+} + e^- \rightarrow FeL^+$ (Figure 2). The reason for this difference is not known but may be due to some structural or conformational difference in the Fe(III) complex which is retained on reduction to the Fe(I) species and which inhibits the following chemical reaction. Even in this case part of the Fe(I) is consumed by the following chemical reaction during the scan since the Fe(I) peak is not fully developed ($(i_p)_r/(i_p)_f < 1.0$). An estimate

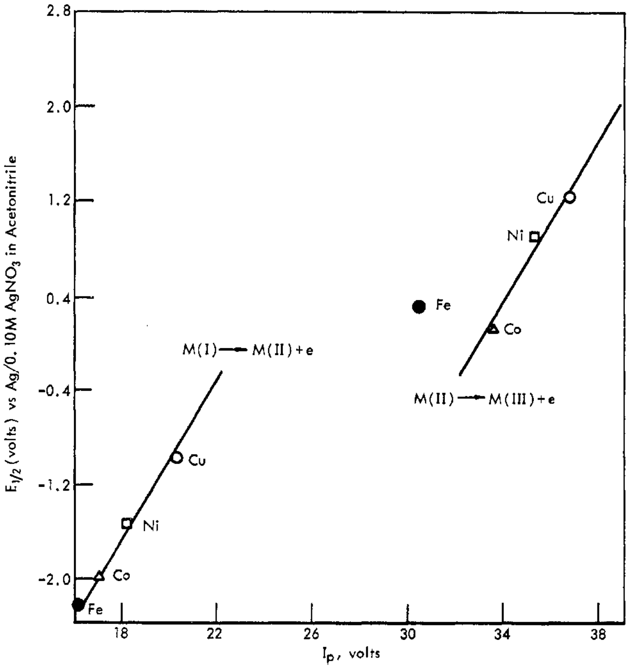


Figure 4.—Relationship between the $E_{1/2}$ values of the redox reactions of the trans-tetramine–metal complexes and the ionization potential, IP, of the corresponding gaseous metal ions.

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of the reversible $E_{1/2}$ of the $FeL^{2+} + e^- \rightarrow FeL^+$ step is taken as the potential midway between the peak potentials of the cathodic and anodic peaks. This $E_{1/2}$ value falls on the appropriate line in Figure 4.

A linear dependence of $E_{1/2}$ on IP was also reported recently for a series of metalloporphyrins and metallophthalocyanines.[16] The linear relationship was observed for the oxidation step, $M(II) - e^- \rightarrow M(III)$, with the metals Ni, Co, and Fe when the third ionization potentials of the metals were used. It is interesting that with the cyclic amines the linear relationship holds for Cu, Ni, and Co but does not extend to Fe. The $E_{1/2}$ for Fe(II) occurs 1.2 V more positive than predicted from the IP. The reason for the failure of Fe(II) to fit the linear relationship is not clear but it is probably due to the participation of a different set of orbitals in the oxidation process of lower energy than those involved with the Cu, Ni, and Co complexes. In a reversible oxidation process an electron is extracted from the highest occupied orbital and $E_{1/2}$ is related to the energy of this orbital. In an octahedral environment (both Co(II) and Fe(II) crystallize with axially coordinated acetonitrile) low-spin Co(II) has one electron in the higher energy e_g set of orbitals. This set of orbitals is empty for Fe(II) and an electron must be extracted from the lower energy t_{2g} orbitals. This would cause a positive shift in the $E_{1/2}$ *vs.* IP line as observed. In support of this argument is the observation that the linear relationship does extend to Fe for the $M(I) - e^- \rightarrow M(II)$ step which would be expected since Fe(I) has an electron in the e_g orbitals. Since the metalloporphyrins and metallophenalocyanins probably maintain essentially a square-planar geometry in the solvents in which the electrochemical measurements were carried out, a discontinuity in the linear $E_{1/2}$ *vs.* IP relationship would not be expected at Fe(II) for these complexes.

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The Oxidation of Hexaaquoiron(II) by Chlorine(III) in Aqueous Solution

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The oxidation of iron(II) by chlorine(III) appears to occur *via* a one-electron-transfer mechanism. The reaction was studied at 10 and 25° under pseudo-first-order conditions with iron(II) being in excess. Chloride ion and phenol were added to the reaction mixtures in order effectively to eliminate complicating side reactions of the intermediate product chlorine(I). The reaction rates are essentially unaffected by chloride ion concentration. The hydrogen ion dependence is appropriate to the rate expression

$$\frac{-d[Fe(II)]}{dt} = k_1[Fe(II)][Cl(III)] + \frac{k_2[Fe(II)][Cl(III)]}{[H^+]}$$

At 25° and 2.0 M ionic strength, $k_1 = (1.89 \pm 0.09) \times 10^3\ M^{-1}\ sec^{-1}$ and $k_2 = 58 \pm 10\ sec^{-1}$. The results are discussed in terms of several possible one-electron-transfer mechanisms.

Introduction

Conocchioli, Hamilton, and Sutin[1] have studied the oxidation of iron(II) by a number of possible two-electron oxidizing agents. They observed that hypochlorous acid and ozone react with iron(II) to produce appreciable amounts of the iron(III) dimer, $[Fe(OH)_2Fe]^{4+}$. The overall second-order kinetics are consistent with the dimer being formed according to eq 1 and 2.

$$Fe(II) + Ox \longrightarrow Fe(IV) + Red \quad \text{(rate determining)} \quad (1)$$

$$Fe(IV) + Fe(II) \xrightarrow{\text{rapid}} [Fe(III)]_2 \quad (2)$$

Those reactions in which little or no dimer is produced are assumed to proceed primarily *via* a one-electron pathway.

Chlorine(III) is known to react with tris(1,10-phenanthroline)iron(II) by a mechanism which is dependent on the dissociation of the complex prior to the oxidation step.[2] In view of the fact that this reaction also appears to involve a two-electron-transfer process, it is of interest to make comparisons with other analogous iron(II) reactions.

In the present study of the iron(II)–chlorine(III) reaction, we have attempted to differentiate between one- and two-electron-transfer mechanisms by a detailed evaluation of the rate law and by observing the formation of the iron(III) dimer.

Experimental Section

Chemicals.—Stock solutions of iron(II) perchlorate were prepared by dissolving reagent grade iron wire in 1 M perchloric acid with gentle heating to increase the rate of dissolution. Iron(II) solutions were stored at 5° and handled under a nitrogen atmosphere by using syringe techniques to transfer the solution. The concentration of iron(II) solutions was determined by titration with primary standard potassium dichromate.

Phenol was purified by fractional distillation at 20 mm.[3] Solutions were prepared gravimetrically by diluting the purified solid to the appropriate volume.

Lithium perchlorate was prepared from the reaction of the carbonate with perchloric acid and was twice recrystallized from water. Stock solutions were adjusted to pH 7 in order that the

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(2) B. Z. Shakhashiri and G. Gordon, *ibid.*, **91**, 1103 (1969); M. Ondrus and G. Gordon, *Inorg. Chem.*, **10**, 474 (1971).

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