(13) Meyer, F. K.; Merbach, A. E. *J. Phys. E* **1979**, *12*, 185–6.
(14) Swift, T. J.; Connick, R. E. *J. Chem. Phys.* **1962**, *37*, 307–20.
(15) Luz, Z.; Meiboom, S. *J. Chem. Phys.* **1964**, *40*, 2686–92.
(16) Matwiyoff, N. A. *Inorg. Chem.* **1966**, *5*, 788–95.
(17) West, R. J.; Lincoln, S. F. *Inorg. Chem.* **1972**, *11*, 1688–91.
(18) Babiec, J. S.; Langford, C. H.; Stengle, T. R. *Inorg. Chem.* **1966**, *5*, 1362–4.
(19) Frankel, L. S. *Inorg. Chem.* **1971**, *10*, 2360–1.
(20) Matwiyoff, N. A.; Hooker, S. V. *Inorg. Chem.* **1967**, *6*, 1127–33.
(21) Langford, C. H.; Gray, H. B. "Ligand Substitution Processes"; W. A. Benjamin: New York, 1966; Chapter 1.
(22) (a) Eigen, M.; Wilkins, R. G. *Adv. Chem. Ser.* **1965**, *No. 49*, 55. (b) Wilkins, R. G. *Acc. Chem. Res.* **1970**, *3*, 408–16.
(23) Bennetto, H. P.; Caldin, E. F. *J. Chem. Soc. A* **1971**, 2191–8.
(24) Caldin, E. F.; Bennetto, H. P. *J. Solution Chem.* **1973**, *2*, 217–38.
(25) Frank, H. S.; Wen, W-Y. *Discuss. Faraday Soc.* **1957**, *24*, 133.

(26) Coetzee, J. F. "Solute-Solvent Interactions"; Coetzee, J. F., Ritchie, C. D., Eds.; Marcel Dekker: New York, 1967; Vol. 2, Chapter 14.
(27) Frankel, L. S. *Inorg. Chem.* **1971**, *10*, 814–7.
(28) McGlashan, M. L. *J. Chem. Educ.* **1966**, *43*, 226–32.
(29) Reference 7b, p 313.
(30) Kohnstam, G. *Prog. React. Kinet.* **1970**, *5*, 335–408.
(31) Reference 7b, p 329.
(32) Gutmann, V. ; Schmid, R. *Monatsh. Chem.* **1971**, *102*, 1217–25.
(33) Hoffmann, H.; Janjic, T.; Sperati, R. *Ber. Bunsenges. Phys. Chem.* **1974**, *78*, 223–8.
(34) Funahashi, S.; Jordan, R. B. *Inorg. Chem.* **1977**, *16*, 1301–6.
(35) Rusnak, L. L.; Yang, E. S.; Jordan, R. B. *Inorg. Chem.* **1978**, *17*, 1810–3.
(36) Tanaka, M. *Inorg. Chem.* **1976**, *15*, 2325–7.
(37) (a) Basolo, F.; Pearson, R. G. "Mechanisms of Inorganic Reactions", 2nd ed.; Wiley: New York, 1967; Chapters 2 and 3. (b) Companion, A. L. *J. Phys. Chem.* **1969**, *73*, 739–41.

Systematic Variation of the Redox Potential of the Fe^{2+}/Fe^{3+} Couple in Iron(II) Complexes of 2,3,9,10-Tetrasubstituted-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene Ligands[1]

RAM G. GOEL,* PATRICK M. HENRY, and P. CALDEIRA POLYZOU

Fe(II) complexes of 2,3,9,10-tetrasubstituted-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene ligands have been synthesized and characterized by elemental analysis and by spectral (infrared, UV–visible, and ^1H NMR) measurements. The dependence of the half-wave oxidation potentials of the Fe^{2+}/Fe^{3+} couple upon the electronic properties of substituents on the macrocyclic ligand has been investigated. A linear relationship between the half-wave potentials for the Fe^{2+}/Fe^{3+} couple and the σ_P constants for the substituents on the macrocycle ring has been observed.

Recent work on iron complexes of synthetic macrocyclic ligands[2-4] has greatly increased our understanding of the mode of binding of molecular oxygen in naturally occurring oxygen carriers, hemoglobin and myoglobin. As an aid in understanding the catalytic role of heme proteins in various redox reactions, the redox properties of iron, cobalt, and nickel complexes of a variety of tetraaza tetradentate macrocycles have been investigated by Busch and co-workers.[5,6] In Ni(II) complexes the potential for the Ni^{2+}/Ni^{3+} couple has been found to be sensitive to the electron withdrawing or releasing ability of the substituents on the macrocyclic ring[5] but no such correlations have been reported for iron complexes. Iron complexes of the macrocyclic ligand 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene (TIM), complex V, Figure 1, have been studied recently[7] and crystallographic study[8] of the complex $[Fe^{II}TIM(CH_3CN)_2]^{2+}$ has shown that the Fe(II) and the four nitrogen donor atoms of the macrocyclic ligand in the complex are coplanar. Very recently it has been reported that the Fe^{II}–TIM complex catalyzes the oxidation of methanol in the presence of sunlight.[9] In order to study the effects of ring substituents on the potentials for the Fe^{2+}/Fe^{3+} couple in the iron complex of TIM type macrocycle framework, we have synthesized complexes in which the methyl groups of TIM have been replaced by C_6H_5, p-$CH_3C_6H_4$, and p-$CH_3OC_6H_4$ substituents.

Results and Discussion

Complexes I–IV were obtained in good yield from the reaction of 1,3-diaminopropane and the appropriate diketone in the presence of Fe(II) ions. Like $Fe^{II}TIM$,[7] these compounds are intensely colored, air-stable, diamagnetic solids. They are fairly soluble in donor solvents such as acetonitrile, pyridine, and dimethyl sulfoxide and sparingly soluble in dichloromethane. The ionic constitution of the complexes was

established by conductance measurements in acetonitrile (data in Table I).

Infrared Spectra. The important infrared bands observed for the reported compounds are listed in Table II. The infrared spectra of all four compounds (I to IV) do not contain any bands that could be assigned to the C=O or NH_2 groups.[10] For each complex, an infrared band is observed in the 1245–1270-cm^{-1} region, which is similar to the 1210-cm^{-1} band observed for the Fe^{II}–TIM[7] complex V. Characteristic infrared bands due to the phenyl or substituted phenyl groups are present in the spectra of all the four compounds in the 700–770-cm^{-1} region. The infrared spectrum of $Fe^{II}Ph$–TIM (complex I) like that of $Fe^{II}TIM$ does not show any band at 1600 cm^{-1}, which could be assigned to the C=N stretching vibrations.[7,11] However, a weak band at ca. 1620 cm^{-1} is present in the spectra for the complexes II, III, and IV. The infrared spectra for all the four compounds show two very weak bands in the 2340- and 2380-cm^{-1} region due to the C≡N stretching vibrations of the axial acetonitrile ligands[7,12] and strong bands at 845 and 560 cm^{-1} due to the PF_6^- anion.[13]

Proton Magnetic Resonance Spectra. The ^1H NMR data for the complexes are listed in Table III. The resonance signals due to the phenyl, methyl, and the α-CH_2 hydrogens as well as the hydrogens of the substituent groups on the phenyl rings can be assigned unambiguously although the resonance peaks due to the β-CH_2 groups for all the complexes are masked by the acetonitrile peak. In the case of complex IV, the broad resonance signal at 2.16 ppm ($J = 2$ Hz) could be in part due to the methyl protons of one isomer, which are coupled with the homoallylic protons, and in part due to the β-CH_2 protons. The neighboring acetonitrile peak prevents an exact integration of this part of the spectrum. The existence of two isomers of IV (cis and trans) is also supported by the observed broadness of the phenyl and α-CH_2 peaks. The lower

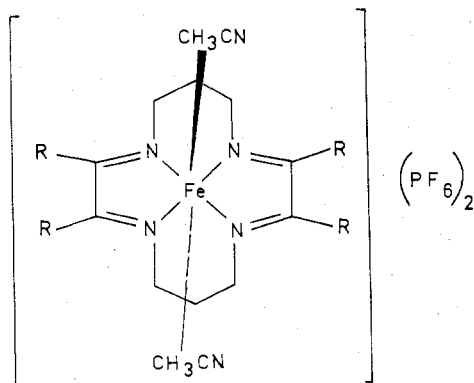**Table I.** Analytical Data, Molar Conductances,[a] and Electronic Spectra[b] for the Complexes

com-plex	color	%C calcd	%C found	%H calcd	%H found	%N calcd	%N found	% yield[c]	Λ_m	electronic spectra, cm⁻¹ × 10³
I	violet	49.31	49.14	4.12	4.09	9.10	9.10	22	242	17.18 (11633), 18.38 (7827), ~20.08 sh, 36.10 (9553)
II	blue-violet	51.55	51.44	4.72	4.58	8.57	8.39	20	234	17.12 (21454), 18.41 (9454), ~20.04 sh, 35.09 (13018)
III	blue-violet	48.29	48.03	4.43	4.28	8.04	8.03	42	215	17.06 (4524), 18.38 (3114), ~19.92 sh, 36.90 (27144)
IV	dark violet	41.50	42.10	4.19	4.47	10.37	10.28	48	229	17.70 (6032), 18.94 (4327), ~20.70 sh, 36.90 (22295)

[a] 10⁻³ M acetonitrile solutions, values in Ω^{-1} cm² mol⁻¹. [b] In deaerated acetonitrile, molar extinction coefficients in M⁻¹ cm⁻¹ given in parentheses. [c] Based on [Fe²⁺].

Table II. Infrared Spectral Bands for the Complexes[a]

com-plex	PF₆⁻	macrocyclic ligand	axial CH₃CN
I	560 s, 845 s	710 s, 750 w, 770 m, 1080 w, 1115 w, 1165 w, 1270 m, 1320 m, 1340 m	1030 w, 2340 w, 2360 w
II	560 s, 845 s	740 b, 765 m, 1000 m, 1080 w, 1115 m, 1130 m, 1200 s, 1225 m, 1270 s, 1320 s, 1330 s, 1550 w, 1570 w, 1620 wb	1030, 2380 wb
III	560 s, 845 s	745 b, 1120 w, 1180 s, 1260 s, 1300 m, 1310 m, 1330 w, 1515 s, 1575 w, 1615 m	1045 s, 2370 wb
IV	560 s, 845 s	710 s, 750 w, 770 m, 1085 w, 1170 wb, 1245 m, 1330 b, 1615 wb	1035 w, 2340 w, 2360 w

[a] Nujol mulls, values in cm⁻¹; w = weak, s = strong, b = broad, m = medium.

R = C₆H₅   I
p-CH₃C₆H₄   II
p-CH₃OC₆H₄   III
2 R's = CH₃ , C₆H₅   IV
R = CH₃   V

Figure 1. Structures of complexes I–V.

Table III. ¹H NMR Data for the Complexes[a,b]

com-plex	Ph	α-CH₂	p-CH₃O	p-CH₃	CH₃
I	7.00–7.65 m (20)	4.11 t[c] (8)			
II	6.97–7.50 m (16)	4.07 t[c] (7.9)		2.34 s (12)	
III	6.60–7.63 m (16)	4.12 t[c] + 3.80 s (20.3)			
IV	6.60–8.40 b, m (10)	4.02 b, m (7.2)			2.42 b, s (4.2) 2.16 b

[a] Chemical shifts are in ppm downfield from Me₄Si at ambient temperature; solvent is CD₃CN. The number of protons is given in parentheses. Key: s = singlet, d = doublet, m = multiplet, t = triplet, b = broad. [b] The axial bonded CH₃CN undergoes exchange with the solvent in the time span of the measurements giving rise to a multiplet at 1.95 ppm. [c] Coupling constant J = 5 Hz.

Table IV. Half-Wave Potentials of Fe²⁺/Fe³⁺ for the Complexes and Hammett's Constants σ_p and $\Sigma\sigma_p$ for substituents, R, on the Macrocyclic Ligands (Figure 1)

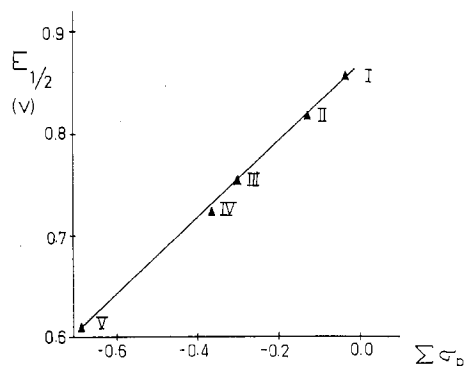| com-plex	$E_{1/2}$ oxid, V	Δp,[a] mV	R	σ_p	$\Sigma\sigma_p$
I	0.86	70	C₆H₅	−0.007[b]	−0.03
II	0.82	70	p-CH₃C₆H₄	−0.03[b]	−0.12
III	0.76	65	p-CH₃OC₆H₄	−0.076[b]	−0.30
IV	0.73	70	2R's = CH₃ 2R's = C₆H₅		−0.36
V	0.61	70	CH₃	−0.17[c]	−0.68

[a] $\Delta p = E_{p,a} - E_{p,c}$. [b] Calculated from the pK values in ref 17. [c] From ref 18.

be determined accurately but it is approximately half that of the 1.800-μm⁻¹ band. The higher energy bands at 3.600–3.690 μm⁻¹ are assigned to $\pi \rightarrow \pi^*$ transitions of the ligand.[15,16] This band is absent in the spectrum of the TIM complex (complex V) but for the Ph–TIM and substituted Ph–TIM ligands this transition is shifted toward lower energies due to the additional moderate conjugation present in these systems.

Redox Potentials. Busch and co-workers[5,6] have correlated the substituent effect and $E_{1/2}$ for Ni²⁺/Ni³⁺ in Ni(II) complexes. The half-wave potentials for the Fe²⁺/Fe³⁺ couple for the complexes I to V are given in Table IV. The data in Table IV clearly show that the electronic effect of the substituents on the α-diimine system is transmitted to the central iron atom. Moreover, by comparison of the $E_{1/2}$ for the complexes I, II, and III, it is evident that the electronic effect of the electron-donating para substituents CH₃ and CH₃O on the phenyl ring is also transmitted to the iron atom.

The observed variations in the $E_{1/2}$ for the complexes clearly show that the Fe(III) oxidation state is stabilized with increasing σ-donor strength of the macrocyclic ligands and the Fe(II) oxidation state is stabilized with increasing π-acceptor ability of the ligands.

The σ_p values for R = p-XC₆H₄ (X = CH₃, CH₃O, or H) were calculated from their pK_a values[17] and are listed together with σ_p constants for R = CH₃ in Table IV. In Figure 2 the

than theoretical number of protons at 2.42 ppm supports the suggestion of the existence of cis and trans isomers.

Electronic Absorption Spectra. The observed absorption bands in the visible and ultraviolet region are listed in Table I. The intense absorption bands ($\epsilon \sim$ 20000–4500) near 1.700 and 1.800 μm⁻¹ observed for all the Ph–TIM complexes (Table I) can be attributed to a metal-to-ligand charge transfer (MTLCT), which is characteristic for all iron–α-diimine complexes.[11,14,15] The band near 2.000 μm⁻¹ observed for all four complexes (I–IV) is possibly also a MTLCT band, because its intensity is too strong for a d–d transition band. However, the overlap and mixing of the metal d orbitals with the ligand orbitals could enhance the intensity of this band, making it an intermediate between a pure d–d transition and a CT band. The extinction coefficient of this band could not

Figure 2. Half-wave oxidation potentials for complexes I–V vs. $\sum \sigma_p$ for the substituents R on the macrocyclic ligand.
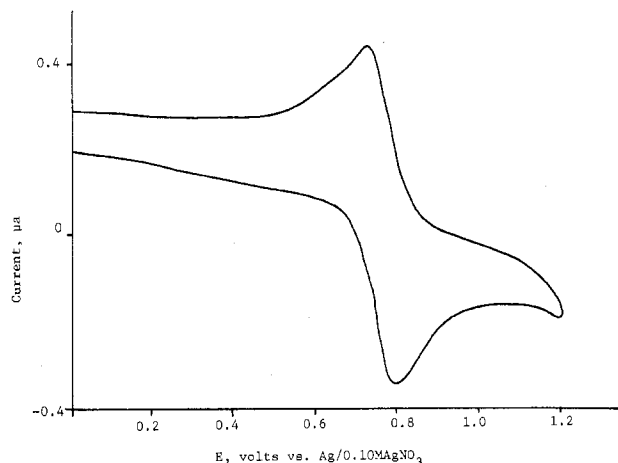
Figure 3. Cyclic voltammogram of 10^{-3} M $[Fe(2,3,9,10-\{p\text{-}CH_3OC_6H_4\}_4[14]1,3,8,10\text{-tetraeneN}_4)(CH_3CN)_2](PF_6)_2$ (III) in acetonitrile.

sum of the σ_p constants for the R's in the complexes I, II, III, IV, and V are plotted against their $E_{1/2}$ values. The correlation coefficient is 0.999 and the slope $\rho = 0.38$. The straight line in Figure 2 obeys the following equation:

$$E_{1/2} = 0.87 + 0.38\sum \sigma_p$$

Dreiding molecular models show that steric interference between substituents at the 2, 3 and 9, 10 positions would prevent the phenyl rings from being coplanar with the tetraimine system. Therefore, the Ph substituent cannot be fully conjugated with the planar system containing the four C=N bonds. However, the ρ of 0.38 indicates a significant transmission of the electron-releasing ability of the para substituents on the phenyl ring to the central iron atom. This transmission is accomplished mainly by electrostatic induction rather than by resonance.[18] Similar effects were observed for the nickel(II) tetraphenylporphyrins.[19]

A typical cyclic voltammogram is shown in Figure 3. The reversibility of the redox process is evident from the separation of the peak potentials and the ratio of the heights of the peaks, which is close to unity.

Experimental Section

Materials. 1,3-Diaminopropane, benzil, 4,4′-dimethylbenzil, 4,4′-dimethoxybenzil, and 1-phenyl-1,2-propanedione were obtained from Aldrich Chemical Co. Other chemicals were reagent grade. Tetraethylammonium perchlorate was recrystallized twice from water and dried for several hours under vacuum at 70 °C. Acetonitrile used for electrochemical measurements was distilled twice over KMnO₄ and P₂O₅. Other solvents were spectral grade and were used without further purification. Solution of ferrous chloride in methanol was prepared under nitrogen following the method of Reichgott and Rose[9]

by using anhydrous ferric chloride, excess iron powder, and small amounts of stannous chloride.

Physical Measurements. Elemental analyses were performed by M.H.W. Laboratories, Phoenix, Ariz. Infrared spectra were recorded on a Beckman IR-12 double-beam spectrophotometer. The samples were prepared as mulls in Nujol. Proton magnetic resonance spectra were recorded on either a Varian A-60A or a Bruker WP60 spectrometer. The UV–visible spectra were measured with a Cary 118 spectrophotometer using quartz cells. Redox potentials for the Fe^{2+}/Fe^{3+} couples were determined in acetonitrile by cyclic voltammetry measurements by using a Princeton Applied Research 170 polarograph. The electrode system consisted of a Ag/0.1 M AgNO₃ reference electrode, a stationary platinum electrode, and a platinum foil, functioning as the third electrode. Measurements were made at room temperature in a closed glass cell, which was flushed with nitrogen. Contact of the solution with the reference electrode was made through a glass tube with a medium glass frit and through a VIGOR "thirsty" glass tube 13-mm long. The compounds were dissolved in purified and deaerated acetonitrile containing 0.1 M tetraethylammonium perchlorate as supporting electrolyte. The concentration of the complexes was 2×10^{-3} or 1×10^{-3} M. The scanning voltage was 200 or 500 mV/s and the current range 1 or 2 μA. Conductances were measured in acetonitrile ($\sim 10^{-3}$ M solutions) at 25 °C by using a Yellow Springs Instrument conductivity bridge and a conductivity cell with platinized platinum electrodes.

Preparation of the Complexes. Complexes I–V were prepared following a modified method of Reichgott and Rose.[9] Monoprotonated 1,3-diaminopropane, appropriate α-diketone and freshly prepared ferrous chloride were allowed to react for 48 h instead of 24 h. The analytical data, yields, molar conductances, and the electronic spectral data for the new complexes are given in Table I.

References and Notes

(1) Presented in part at the National Meeting of the American Chemical Society, Miami, Fla., Sept 1978.
(2) J. P. Collman, R. R. Gagne, C. A. Reed, T. R. Halbert, G. Lang, and W. T. Robinson, *J. Am. Chem. Soc.*, **97**, 1427 (1975), and references cited therein.
(3) J. E. Baldwin and J. Huff, *J. Am. Chem. Soc.*, **95**, 5757 (1973).
(4) R. G. Little, J. A. Ibers, and J. E. Baldwin, *J. Am. Chem. Soc.*, **97**, 7049 (1975).
(5) D. G. Pillsbury and D. H. Busch, *J. Am. Chem. Soc.*, **98**, 7836 (1976).
(6) D. H. Busch, D. G. Pillsbury, F. V. Lovecchio, A. M. Tait, Y. Hung, S. Jackels, M. C. Rakowski, W. P. Schammel, and L. Y. Martin, *ACS Symp. Ser.*, No. 38, 32 (1977), and references cited therein.
(7) D. A. Baldwin, R. M. Pfeiffer, D. W. Reichgott, and N. J. Rose, *J. Am. Chem. Soc.*, **95**, 5152 (1973), and references cited therein.
(8) H. W. Smith, G. W. Svetich, and E. C. Lingafelter, Abstracts of the American Crystallographic Association Meeting, 1973, series 2, Vol. 1, No. M5, p 174.
(9) D. W. Reichgott and N. J. Rose, *J. Am. Chem. Soc.*, **99**, 1813 (1977).
(10) N. B. Colthup, L. H. Daly, and S. E. Wiberley, "Introduction to Infrared and Raman Spectroscopy", Academic Press, New York, 1964.
(11) D. H. Busch and J. C. Bailar, *J. Am. Chem. Soc.*, **78**, 1137 (1956).
(12) (a) F. W. Parker, A. H. Nielson, and W. H. Fletcher, *J. Mol. Spectrosc.*, **1**, 107 (1957); (b) R. E. Clarke and P. C. Ford, *Inorg. Chem.*, **9**, 227 (1970).
(13) N. J. Rose, M. S. Elder, and D. H. Busch, *Inorg. Chem.*, **6**, 1924, (1967).
(14) P. Krumholz, *Struct. Bonding (Berlin)*, **9**, 147 (1971).
(15) T. Ito, N. Tanada, I. Hanazaki, and S. Nagakura, *Bull. Chem. Soc. Jpn.*, **41**, 365 (1968).
(16) O. Wandiga, J. E. Sarneski, and F. L. Urbach, *Inorg. Chem.*, **11**, 1349 (1972).
(17) E. Berliner and E. A. Blommers, *J. Am. Chem. Soc.*, **73**, 2479 (1951).
(18) D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, **23**, 420 (1958).
(19) F. A. Walker, E. Hui, and J. M. Walker, *J. Am. Chem. Soc.*, **97**, 2390 (1975).