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Spectrophotometric and Electrochemical Investigations of [Tetrakis(1-methylpyridinium-4-yl)porphine]iron(III) Ion in Aqueous Solution

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The equilibria among the species of [tetrakis(1-methylpyridinium-4-yl)porphine]iron(III) ion (Fe(III)-TMPyP) in aqueous solution and the redox reactions of their central metals were investigated by means of spectrophotometric, electrochemical and spectroelectrochemical methods. Two acid-dissociation equilibria involving three monomeric species of Fe(III)-TMPyP were found: one with a pK_a of 5.5 and the other with a pK_a of *ca.* 12. After electrochemical reduction, an equilibrium between two monomeric species of Fe(II)-TMPyP with a pK_a of 11 was observed. In the Fe(III)-TMPyP solution at relatively high concentration, two additional different species, probably dimeric, were found in the pH regions of 5—8 and 9—13, respectively. The consistency of specification of the species with the scheme of redox reactions is discussed.

Since water-soluble metalloporphyrins were synthesized by introducing hydrophilic groups into the meso-positions of porphine rings, they have attracted the increasing interest of many chemists and biochemists as model substances for studies on biological processes.[1] Considerable information that is attractive to chemists has become available: *e.g.* the reaction mechanisms of complex formation,[2,3] the specification of species,[4-8] the substitution of axial ligands[9-12] and the mechanisms of redox reactions.[13,14]

Among water-soluble porphyrins, [tetrakis(1-methyl pyridinium-4-yl)porphine]iron(III) ion (Fe(III)-TMPyP) has often been studied because of its stability and relatively high solubility over a wide pH region. Nevertheless, the specification of species is very complicated and has not yet been clarified completely, owing to simultaneous acid-dissociation and dimerization equilibria depending on pH and/or concentration.

Therefore, this work was undertaken in order to specify the species of Fe(III)-TMPyP in aqueous solution and to clarify the mechanism of electrochemical redox reaction of the central metal of each species. In the course of the work, a paper concerning the same subject was published by Forshey and Kuwana.[15] However, our spectrophotometric, electrochemical and spectroelectrochemical investigations gave results which were significantly different from those reported,[15] especially in the pH region of 5—10. In addition, at pH 11 we newly confirmed monomeric iron(II) and iron(III) species. In this paper, we provide an overall scheme for the acid-dissociation equilibria among the Fe(III)-TMPyP species in aqueous solution at pH 1—13 and for the redox reactions of the species involved.

Experimental

Materials and Sample Solutions. Fe(III)-TMPyP perchlorate was prepared according to the method of Hambright and Fleischer[2] with a slight modification and stored in aqueous solution because of its explosiveness. The concentration of the Fe(III)-TMPyP stock solution was determined spectrophotometrically at 403 nm by the use of a molar absorption coefficient of 1.02×10^5 mol^{-1} dm^3 cm^{-1} at pH 2 and at an ionic strength of 0.1 mol dm^{-3}.[7] All other chemicals of guaranteed reagent grade were used without further purification.

Sample solutions were prepared by diluting the stock solution appropriately with deionized-distilled water. The pH values of the sample solutions were adjusted with sulfuric acid or sodium hydroxide solution and the ionic strength with sodium sulfate solution at 0.1 mol dm^{-3}, except for the highly acidic (pH$\leqslant$1) and basic (pH$\geqslant$13) solutions. In case buffered solutions were required, the following buffers were used: acetate buffer at pH 3—6, phosphate at pH 4.5—7.2, and phosphate-borate at 5.8—9.

Spectrophotometric, Electrochemical, and Spectroelectrochemical Measurements. A Shimadzu UV-300 and a Hitachi 100-30 spectrophotometer were used for the spectrophotometric investigation over a wide pH range. The pH values of the solutions were measured with a TOA HM-5B pH meter.

The cyclic voltammograms of Fe(III)-TMPyP in the same pH region were obtained by means of an NF FG-121B function generator and a Yanaco P8-CV potentiostat equipped with a conventional three-electrode system. A glassy carbon rod (GC-30, Tokai Carbon) plugged into a Teflon tube was used as the working electrode. The carbon surface exposed to a solution was a circle 0.196 cm^2 in area. The electrode surface was polished with diamond lapping paste (6×10^4 meshes) until a mirrorlike finish was obtained. Then it was wiped with a chamois skin dampened with carbon tetrachloride and rinsed with methanol and then with water. A platinum plate ($0.1 \times 5 \times 5$ mm^3) and a saturated calomel electrode (SCE) were employed as the counter and reference electrodes, respectively. Prior to both the electrochemical and spectroelectrochemical measurements, the sample solution was deoxygenated by bubbling a high-purity nitrogen gas through the solution for about 15 min, and the measurements were carried out under an atmosphere of nitrogen.

The spectroelectrochemical examination was achieved with an optically transparent thin layer electrode (OTTLE)[16] constructed with a gold minigrid (500 wires per inch, Buckbee Mears) which was sandwiched between two micro-slide glasses. The distance between two plates was controlled with Teflon spacers (*ca.* 0.1 mm thick, Delectrix DF-1200). The assembled OTTLE system had a thickness of an absorbing medium of *ca.* 0.22 mm and a transmittance of *ca.* 53%. While the Soret-band spectra of Fe(III)- and/or Fe(II)-TMPyP were measured with a Hitachi 100-30 spectrophotometer, the potential at the gold minigrid as the working electrode was controlled by a Yanaco P8-DP potentiostat using an SCE both as the counter and as the reference electrode.

All the measurements were performed at 25 °C.

Results and Discussion

Spectrophotometry. Figure 1 shows the typical UV- and visible spectra of Fe(III)–TMPyP aqueous solutions at various pH values. Since the spectra at pH above 10 changed gradually, they were obtained within 0.5 h after the preparation of each sample solution, except for spectrum e′. Three different species, corresponding to spectra a, c, and e in Fig. 1, were observed in turn with two sets of isosbestic points with increasing pH of the solution.

Insofar as we know, spectrum e at pH above 13 was observed for the first time, although spectra a and c were in fair agreement with those in the literature.[6,8] The e spectrum faded out depending on the time after the preparation of the sample solution and then altered to spectrum e′ after 48 h. This suggests that decomposition and/or transformation of species e to other formes should occur in such a strongly basic solution.

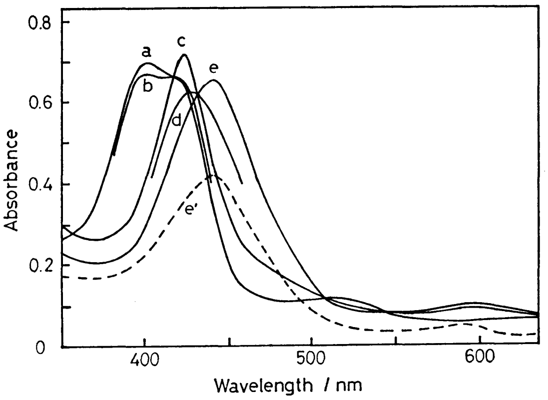


Fig. 1. Absorption spectra of Fe(III)-TMPy Paqueous solution at various pH.
Concentration: 7.06×10^{-6} mol dm^{-3}; pH of solutions: a 1.4, b 4.2, c 7.6, d 11.9, e 13.1, e′ 13.1 after 48 h.

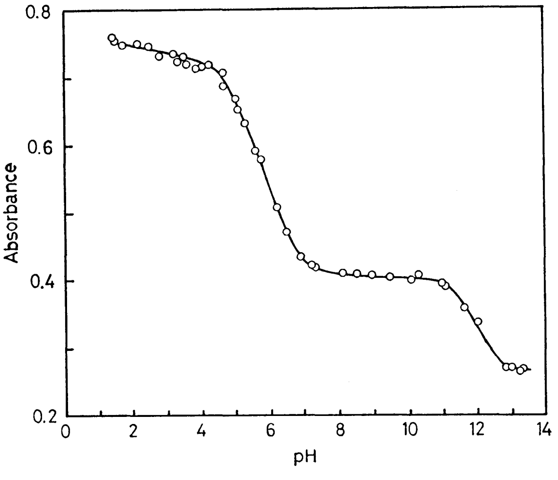


Fig. 2. Spectrophotometric pH titration curve of Fe(III)-TMPyP solution.
Concentration: 7.08×10^{-6} mol dm^{-3}; λ: 403 nm.

In order to examine the equilibria involving the new species e, spectrophotometric pH titrations were performed at the wavelengths of absorption maxima in spectra a, c, and e (403, 424, 440, and 596 nm). In the region of pH above 10, the absorbance at the time immediately after preparation was employed to remove any effect due to the decomposition and/or transformation of the species included. Figure 2 shows the pH titration curve obtained with 7.6×10^{-6} mol dm^{-3} Fe(III)–TMPyP solution at 403 nm. Since the phosphate buffer appreciably depressed the absorbance at pH below 6, the acetate buffer was used in that pH region.

A set of two inflection points was observed in each instance, and their positions were the same irrespective of the wavelength examined. This indicates the existence of two equilibria accompanying proton transfer: the one at pH 4—8 includes species a and c, and the other at pH 11—13 includes species c and e. We also examined the relationship between the absorbance and the concentration of Fe(III)–TMPyP solutions (Beer's law test) over the concentration range of 2.5×10^{-7}—1×10^{-5} and 5×10^{-7}—1×10^{-5} mol dm^{-3} at pH 2 and 13.6, respectively, at the wavelengths of absorption maxima (403 and 440 nm). The absorbance immediately after the preparation of sample solutions was employed at pH 13.6. The excellent proportionality obtained in the Beer's law test gave no evidence for any dimeric species in concentrations lower than 1×10^{-5} mol dm^{-3}. Therefore, at least species a and e should be monomeric, and the former in acidic solution is probably [Fe(III)–TMPyP(H_2O)]$^{5+}$ as proposed in the literature,[7,15] or diaqua-monomer.

Consequently, the equilibrium between species a and c may be represented by one of the following equations:

$$\text{Monomer} \rightleftharpoons \text{Monomer}' + n\,\text{H}^+, \qquad (1)$$

$$2\ \text{Monomer} \rightleftharpoons \text{Dimer} + n\,\text{H}^+ . \qquad (2)$$

The number of transferred protons, n, and the equilibrium constant, K_a, were evaluated from the data of the pH titration experiments according to Eqs. 1 and 2 (Table 1). As can be seen in Table 1, the equilibrium in the region of pH 4—8 should include the reaction accompanying one proton transfer between different monomers under the experimental conditions employed, because the n and pK_a values according to Eq. 1 are close to an integer and to the pH value corresponding to the inflection point, respectively.

Table 1. The number of transferred protons (n) and the equilibrium constant (K_a) obtained from pH titration curves

pH	λ / nm	M⇌M′ n	M⇌M′ pK_a	2M⇌D n	2M⇌D pK_a
4—8	403	0.9	5.1	1.4	2.9
	424	0.9	5.3	1.2	2.2
	596	1.0	5.9	1.8	5.5
10—14	424	1.0	11.4	1.5	16.6
	440	1.1	13.2	1.6	13.9

M: Monomer, M′: monomer′, D: dimer.

This fact leads to the specification of species c to be $[Fe(III)\text{-}TMPyP(H_2O)(OH)]^{4+}$. Similary, species e can also be specified to be $[Fe(III)\text{-}TMPyP(OH)_2]^{3+}$ from the values of n and pK_a in Table 1. Only one equilibrium with a pK_a of 5.5 in the region of pH 4—8 is inconsistent with the two equilibria with pK_a values of 4.7 and 6.5 reported by Pasternack *et al.*[7] However, the specification of the three monomeric species is well consistent with the results obtained by the present electrochemical and spectroelectrochemical investigations, as described in the last section.

Electrochemistry. Figure 3 illustrates typical cyclic voltammograms of 1.4×10^{-4} mol dm^{-3} Fe(III)-TMPyP solutions at different pH values obtained at a scan rate of 0.1 V s^{-1}. Peak A accompanied by a corresponding oxidation wave was assigned to the reduction peak of monomeric species. The potential of peak A was independent of the pH of the solution, in acidic solution at pH below 5.5. On the other hand, at pH above 5.5 peak A shifted to become more negative with increasing pH and an additional reduction peak B appeared at a more negative potential than that of peak A with no corresponding oxidation wave. Multicycle or slow (0.01 V s^{-1}) scanning diminished peak B. The number of transferred electrons in the redox reactions was confirmed to be unity from the results of electrochemical and spectroelectrochemical measurements. These phenomena are fundamentally similar to those reported already.[15]

However, we found that in the region of pH 5.5—9 the reduction potential, $(E_p)_R$, of peak A in buffered solutions differs significantly from that in solutions free from the buffer, as shown in Fig. 4. In order to clarify the reason, nonbuffered sample solutions in the neutral pH region were reduced in an H-shaped cell which was separated into two compartments by a sintered glass. The pH of the solution in the compartment in which the working electrode was immersed increased beyond 9 as the electrolytic reduction progressed, indicating that the reduction of Fe(III)-TMPyP consumes hydrogen ions. This fact suggests that near the surface of the working electrode the pH value of the nonbuffered solutions in the pH range of 5.5—9 varied to higher pH than that of the bulk during the cathodic potential scanning.

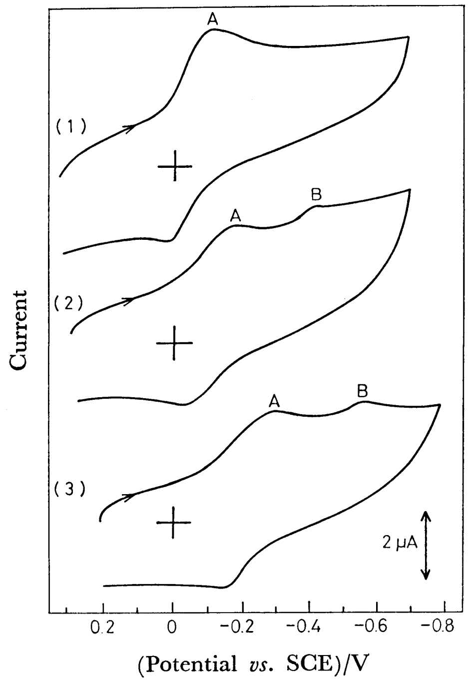


Fig. 3. Cyclic voltammograms of Fe(III)-TMPyP solution.
Concentration: 1.4×10^{-4} mol dm^{-3}; scan rate: 0.1 V s^{-1}; pH: (1) 4.6, (2) 6.5, (3) 9.4.

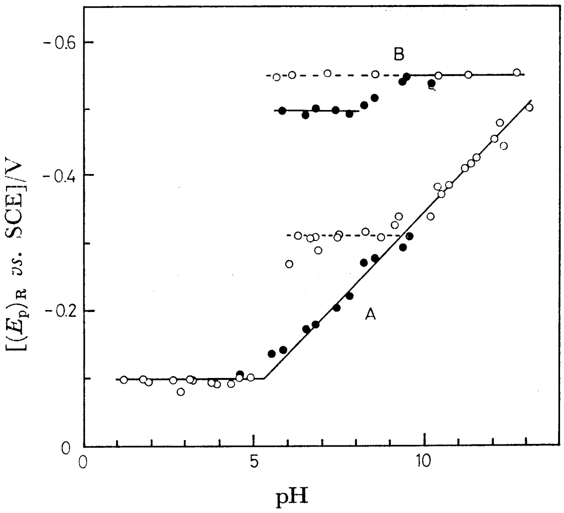


Fig. 4. Plot of $(E_p)_R$ vs. pH for Fe(III)-TMPyP solution.
○: In nonbuffered solution, ●: in buffered solution. Others are the same as in Fig. 3. $(E_p)_R$: see text.

As can be seen in Fig. 4, $(E_p)_R$ of peak A shifts by *ca.* −60 mV/pH at pH higher than 5.5, while it is independent of pH below 5.5. This finding indicates that the reduction yielding peak A accompanies only one-electron transfer in the region of pH below 5.5, and both one-electron and one-proton additions in the region of pH above 5.5.

Peak B may be assigned to that arising from the reduction of dimeric species as proposed by Forshey and Kuwana.[15] There is a probability of dimerization, because the electrochemical data were obtained on a concentrated solution, 10^{-4} mol dm^{-3}. In preliminary experiments, the value of the peak-current ratio of B to A increased with increasing the concentration beyond 10^{-5} mol dm^{-3}. The $(E_p)_R$ value of peak B in the buffered solution was appreciably different from that in the nonbuffered solution over the pH range of 5.5—9. This may also be ascribed to the variation in pH due to the reduction which consumes hydrogen ions.

The decomposition and/or transformation of the monomeric species at very high pH, mentioned in the preceding section, was investigated by following the time-course of I—E curves of peak A by means of linear sweep voltammetry. The reduction current of peak A decreased with an increase in time at pH above 11.5. Figure 5 demonstrates a typical example of the time dependence of the I—E curve at pH 12.5. In Fig. 6 is shown the time-dependent variation of

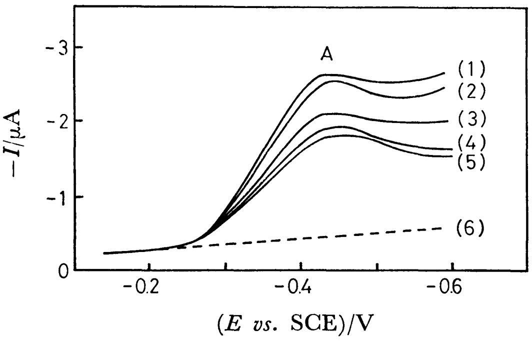


Fig. 5. $I-E$ curves of Fe(III)-TMPyP solution at various time after sample preparation.
Concentration: 1.0×10^{-4} mol dm^{-3}; pH: 12.5; time: (1) 0.5 h, (2) 2 h, (3) 7 h, (4) 24 h, (5) 7 d; (6): base line.

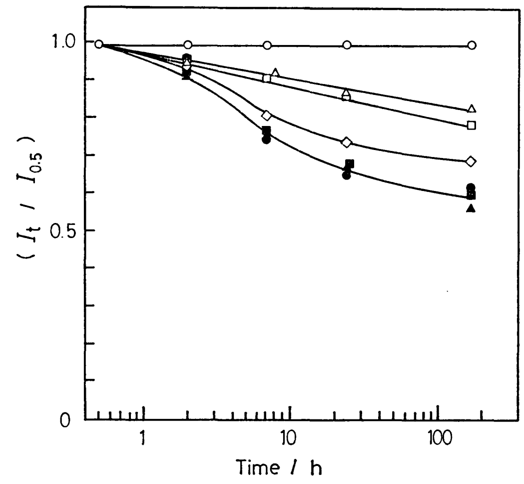


Fig. 6. $(I_t/I_{0.5})$ vs. time after sample preparation.
pH: ○ 11.30, △ 11.50, □ 11.80, ◇ 12.15, ● 12.49, ▲ 12.79, ■ 13.25.

$(I_t/I_{0.5})$ values, which are the ratios of the reduction currents of peak A at various times after the sample preparation to that obtained within 0.5 h. The $(I_t/I_{0.5})$ value decreases with increasing time after preparation at different rates depending on the pH of the solution, and finally it seems to approach a limiting value. This phenomenon corresponds well with the fade-out of spectrum e at pH 13.1, suggesting the fact that the monomeric species in highly basic solution transformes gradually into other forms which are inert to both the spectrophotometric and electrochemical detection.

Spectroelectrochemistry. The Soret-band spectra of 1.7×10^{-4} mol dm^{-3} Fe(III)-TMPyP aqueous solutions at various pH values were obtained before and after the electrochemical reduction by the use of an OTTLE. Figure 7 shows the wavelengths of Soret-band maxima, λ_{max}, of both iron(II) and iron(III) species plotted as a function of pH. The spectra before reduction, of course, were identical with those obtained at corresponding pH values in.

Spectrophotometry. The variation in Soret-band spectrum during incremental charge addition at pH below 10.5 was the same as that reported by Forshey and Kuwana.[15] At pH above 10.5, a new spectrum with an absorption maximum of 456 nm was observed as an iron(II) species. The λ_{max} values of iron(II) species in nonbuffered solutions at pH 6—10.5 were also different from those in buffered solutions, owing to the cause mentioned in *Electrochemistry*.

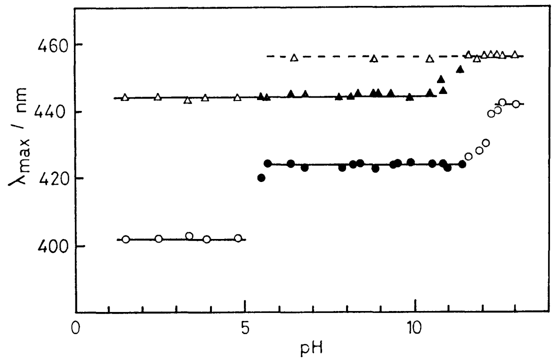
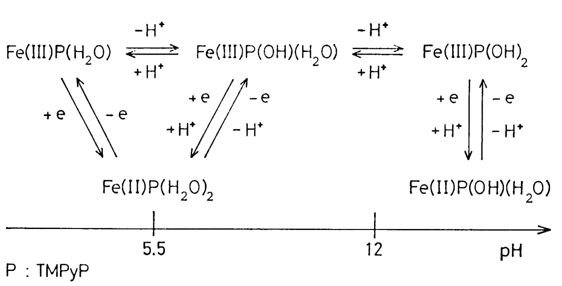


Fig. 7. Wavelength of Soret-band maxima (λ_{max}) vs. pH of Fe(III)-TMPyP solution before and after the reduction on OTTLE.
Concentration: 1.7×10^{-4} mol dm^{-3}. ○,●: Before the reduction in non-buffered and buffered solutions; △,▲: after the reduction in nonbuffered and buffered solutions, respectively.

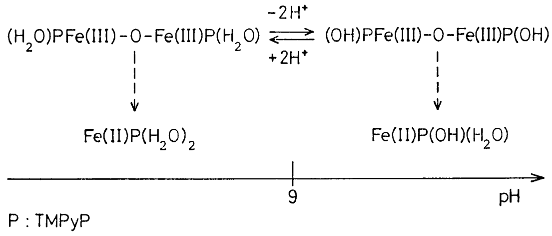
Consequently, three iron(III) species were observed predominantly in respective pH regions before the reduction. After the reduction, however, only two iron(II) species were recognized as the predominants in the regions of pH above and below 11, although Forshey and Kuwana proposed two different iron(II) species at pH values below 11.[15]

Equilibria among Species and Schemes of Their Redox Reactions. The spectrophotometric investigation revealed two acid-dissociation equilibria with pK_a values of 5.5 and 12 in dilute Fe(III)-TMPyP solutions over the pH range of 1—13. The equilibria involve three monomeric species which were specified to be those given in Scheme 1. Each equilibrium undergoes the transfer process of one proton. After the reduction with the OTTLE, an equilibrium with a pK_a of *ca.* 11 was found between two iron(II) species, probably both monomeric, which were also assigned to be those in Scheme 1 according to the results of this work. Cyclic voltammetric examination showed that the reduction of the monomeric species accompanies additions of only one electron at pH below 5.5, and of both one electron and one proton at pH above 5.5. At pH above 11.5, the monomeric species transforms gradually into other forms, inert for the detection methods employed in this study.

Preliminary ESR experiments provided additional information for the specification of the monomeric species. Namely, only a high-spin signal with a *g*-value of 5.5[4] was observed in acidic solution, and the signal height decreased with increasing pH. At pH values above 11 low-spin signals appeared with *g*-values of 1.9, 2.1, and 2.5;[4] these signals grew markedly with increasing pH. This phenomenon suggests the successive replacement of the axial ligands from a water molecule to a hydroxide ion, as shown in Scheme 1.



Scheme 1.



Scheme 2.

Two different dimeric species, probably μ-oxo-iron(III) dimer,[7,15] were found over the pH range of 5.5—9 and 9—13 in the electrochemical experiments. The reduction peaks of the dimeric species were not accompanied by any corresponding oxidation wave and diminished by the repetition of a cyclic potential sweep regardless of the pH range. These phenomena probably mean that the reduction of dimer gives iron(II) monomers and the dimerization of iron(III) monomers is a very slow process. These results lead to Scheme 2, which indicates that the reduction of both two iron(III) dimers results in formation of the iron(II) monomers with different combinations of the axial ligands depending on the pH of the solution. The specification of the dimeric species and the investigation of their reduction mechanism are in progress.

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References

1) K. M. Smith, "Porphyrins and Metalloporphyrins," Elsevier Sci. Pub. Co., Amsterdam (1975).

2) P. Hambright and E. B. Fleischer, *Inorg. Chem.*, **9**, 1757 (1970).

3) P. Hambright and P. B. Chock, *J. Am. Chem. Soc.*, **96**, 3123 (1974).

4) E. B. Fleischer, J. M. Palmer, T. S. Srivastava, and A. Chatterjee, *J. Am. Chem. Soc.*, **93**, 3162 (1971).

5) H. Baker, P. Hambright, and L. Wagner, *J. Am. Chem. Soc.*, **95**, 5942 (1973).

6) R. F. Pasternack, L. Francesconi, D. Raff, and E. Spiro, *Inorg. Chem.*, **12**, 2606 (1973).

7) R. F. Pasternack, H. Lee, P. Malek, and C. Spencer, *J. Inorg. Nucl. Chem.*, **39**, 1865 (1977).

8) F. L. Harris and D. L. Toppen, *Inorg. Chem.*, **17**, 71 (1978).

9) E. B. Fleischer, S. Jacobs, and L. Mestichelli, *J. Am. Chem. Soc.*, **90**, 2527 (1968).

10) E. B. Fleischer and M. Krishnamurthy, *J. Coord. Chem.*, **2**, 89 (1972).

11) R. F. Pasternack and M. A. Cobb, *J. Inorg. Nucl. Chem.*, **35**, 4327 (1973).

12) F. L. Harris and D. L. Toppen, *Inorg. Chem.*, **17**, 74 (1978).

13) R. F. Pasternack and N. Sutin, *Inorg. Chem.*, **13**, 1956 (1974).

14) R. F. Pasternack, M. A. Cobb, and N. Sutin, *Inorg. Chem.*, **14**, 866 (1975).

15) P. A. Forshey and T. Kuwana, *Inorg. Chem.*, **20**, 693 (1981).

16) R. W. Murray, W. R. Heineman, and G. W. O'Dom, *Anal. Chem.*, **39**, 1666 (1967).