dppe[AuSglucose(OAc)$_4$]$_2$ (**6**).[2] The X-ray crystal structure determination of several pseudopolymorphic forms of **5** suggests that there is freedom of rotation about the ethane bridge, allowing the molecule to adopt a range of conformations.[27] A similar situation should exist for **2**, and indeed the X-ray crystal structure determination of **2** shows two distinct forms arising from rotation about the Fe axis. Nevertheless, despite the apparent conformational flexibility and the presence of the two labile chloride ligands, **2** has considerably less antitumor activity than **5**. This loss of activity could be due to the size of the ferrocene spacer that connects the (phosphine)gold moieties. Indeed, the intramolecular Au-Au distance of **2** has been shown to be greater than that of dppe(AuCl)$_2$ (**5**).[27]

Spacers larger than ethane have been observed to result in loss of activity.[1] Lastly, it has been argued that the cytostatic properties of ferrocene derivatives are due not to the ferrocene moiety itself but rather to the organic residues attached to the rings.[4] The antitumor activity of ferrocenium salts has been ascribed to their dual lipophilic and hydrophilic properties, which allows for ready distribution of the complexes into the aqueous compartments of the affected organisms.[4] The complex **2** does not have saltlike character and is not water soluble. Together, with the larger spatial separation of the phosphines compared to **5**, these structural and physical property differences may account for the low antitumor activity of **2** in the assays in which it has been tested.

Acknowledgment. We thank Edie Reich of the Physical and Structural Chemistry Department and Priscilla Offen of the Analytical Chemistry Department of Smith Kline & French Laboratories (SKF) for the elemental analysis and ^{31}P NMR spectra, respectively. We also thank Dr. Judith Hempel of SKF for helpful discussion. This work was supported in part by a grant from the Solid State Chemistry Program of the National Science Foundation (NSF Solid State Chemistry Grant No. DMR 8313710) to the Department of Chemistry, Northeastern University.

Registry No. **1**, 12150-46-8; **2**, 122092-52-8; **4**, 1663-45-2; **5**, 18024-34-5; **6**, 15663-27-1; ^{197}Au, 7440-57-5; ^{57}Fe, 14762-69-7; thiodiglycol, 111-48-8; chlorauric acid, 16903-35-8.

Supplementary Material Available: Tables SI-SIII, containing general and anisotropic parameter expressions, bond distances, bond angles, and positional parameters (11 pages); Table SIV, lisiting observed and calculated structure factors (68 pages). Ordering information is given on any current masthead page.

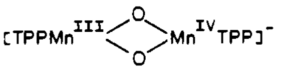
Contribution from the Laboratoire de Chimie Bioorganique et Bioinorganique, URA CNRS 1384,
Institut de Chimie Moléculaire d'Orsay, Université Paris-Sud, 91405 Orsay, France, Laboratoire de Chimie Inorganique,
URA CNRS 420, Institut de Chimie Moléculaire d'Orsay, Université Paris-Sud,
91405 Orsay, France, Laboratorie de Biochimie, Hôpital Raymond Poincaré, 92380 Garches, France,
and Laboratoire de Pharmacochimie, UER de Médecine et de Pharmacie, 76800 Saint-Etienne du Rouvray, France

Voltamperometric and Spectroscopic Studies of the Behavior of Manganese(II) and Manganese(III) Porphyrins with Dioxygen and Superoxide. Evidence for the Formation of a Mixed-Valence Dimeric Manganese Porphyrin

M. Perrée-Fauvet,[*,†] A. Gaudemer,[†] J. Bonvoisin,[‡] J. J. Girerd,[‡] C. Boucly-Goester,[§] and P. Boucly[‖]

Received December 31, 1988

The reactions of superoxide ion with Mn^{II}TPP(py) and Mn^{III}TPP$^+$ have been studied by linear voltammetry, visible spectroscopy, and EPR spectroscopy. Depending on the concentration of superoxide ion, two complexes of very comparable thermodynamic stabilities are generated. The first one, presumably [MnTPPO$_2$]$^-$, results from the stoichiometric 1/1 addition of O$_2$$^{\bullet-}$ to Mn^{II}TPP(py). It can undergo a one-electron reduction at a very negative potential and is EPR silent. The second one, which can be reduced by two electrons at the same potential, is obtained by adding 0.5 equiv of O$_2$$^{\bullet-}$ to Mn^{II}TPP(py) or by addition of an excess of O$_2$$^{\bullet-}$ to Mn^{III}TPP$^+$. It exhibits a 16-line EPR spectrum, which is typical of a mixed-valence dimeric manganese complex. Hyperfine constants of 81 and 163 G were obtained by simulation. Magnetic susceptibility measurements and EPR analysis are in agreement with a strongly antiferromagnetically coupled Mn(III)/Mn(IV) dimer. To take into account the reducing conditions under which it is generated and the very low reduction potential value, we propose the following anionic structure:



Introduction

Manganese porphyrins have proved to be efficient catalysts in the oxidation of olefins with single oxygen atom donors such as iodosylbenzene,[1] alkyl hydroperoxides,[2] amine *N*-oxides,[3] hypochlorites,[4] hydrogen peroxide,[5] periodate,[6] and persulfate.[7] An oxomanganese(V) porphyrin has been postulated as the intermediate active species. The oxidation reactions by molecular dioxygen catalyzed by manganese porphyrins are less efficient, because they require the presence of a reducing agent: borohydride,[8] H$_2$/Pt,[9] ascorbate,[10] *N*-methyldihydronicotinamide,[11] Zn,[12] or electrochemical reduction.[13]

We have recently found,[14] that the systems manganese(III) porphyrin/reducing agent/dioxygen and manganese(III) porphyrin/superoxide ion both catalyze the oxidation of 2,4,6-tri-*tert*-butylphenol and lead to the same oxidation products, whereas

---

[†] Laboratoire de Chimie Bioorganique et Bioinorganique, Université Paris-Sud.

[‡] Laboratoire de Chimie Inorganique, Université Paris-Sud.

[§] Hôpital Raymond Poincaré.

[‖] UER de Médecine et de Pharmacie.

(1) (a) Groves, J. T.; Kruper, W. J.; Haushalter, R. C. *J. Am. Chem. Soc.* **1980**, *102*, 6375. (b) Hill, C. L.; Schardt, B. C. *Ibid.* **1980**, *102*, 6374. (c) Smegal, J. A.; Hill, C. L. *J. Am. Chem. Soc.* **1983**, *105*, 2920. (d) Mansuy, D.; Leclaire, J.; Fontecave, M.; Dansette, P. *Tetrahedron* **1984**, *40*, 2847. (e) Lindsay Smith, J. R.; Mortimer, D. N. *J. Chem. Soc., Perkin Trans. 2* **1986**, 1743.

(2) (a) Mansuy, D.; Battioni, P.; Renaud, J. P. *J. Chem. Soc., Chem. Commun.* **1984**, 1255. (b) Balasubramanian, P. N.; Sinha, A.; Bruice, T. C. *J. Am. Chem. Soc.* **1987**, *109*, 1456.

(3) (a) Powell, M. F.; Pai, E. F.; Bruice, T. C. *J. Am. Chem. Soc.* **1984**, *106*, 3277. (b) Wong, W. H.; Ostovic, D.; Bruice, T. C. *J. Am. Chem. Soc.* **1987**, *109*, 3428.

(4) (a) Meunier, B.; Guilmet, E.; De Carvalho, M. E.; Poilblanc, R. *J. Am. Chem. Soc.* **1984**, *106*, 6668. (b) De Poorter, B.; Meunier, B. *J. Chem. Soc., Perkin Trans. 2* **1985**, 1735. (c) Razenberg, J. A. S. J.; Nolte, R. J. M.; Drenth, W. *Tetrahedron Lett.* **1984**, *25*, 789; *J. Chem. Soc., Chem. Commun.* **1986**, 277.

(5) Renaud, J. P.; Battioni, P.; Bartoli, J. F.; Mansuy, D. *J. Chem. Soc., Chem. Commun.* **1985**, 888.

(6) Takata, T.; Ando, W. *Tetrahedron Lett.* **1983**, *24*, 3631.

0020-1669/89/1328-3533$01.50/0

superoxide ion alone gives different oxygenated products.

The mechanism of the manganese porphyrin catalyzed oxidation reactions by molecular dioxygen and the structure of the active oxygen–manganese complexes have not been elucidated. By contrast with manganese(II) phthalocyanines, which are known to bind dioxygen, providing exceptionally stable complexes formulated as superoxo- and (μ-oxo)manganese(III) dimers,[15] few oxygenated manganese porphyrins have been isolated. Basolo et al. have shown, on the basis of low-temperature EPR spectra, that dioxygen reacts with (tetraphenylporphinato)manganese(II), $Mn^{II}TPP$, to form an adduct formulated as a peroxomanganese(IV) complex.[16] The formation of an adduct between dioxygen and $Mn^{II}TPP$ has been observed electrochemically by Murray et al.[17] Superoxide ion has been shown to reduce $Mn^{III}TPP^+$ to $Mn^{II}TPP$, but addition of 2 equiv of superoxide ion to the same manganese(III) porphyrin generated a new species $[MnTPPO_2]^-$.[18] On the basis of its visible spectrum and of a ^2H NMR study,[19] it was first believed to be a manganese(II) superoxo complex. However, it was recently reported that this species, in the solid state, has the structure of a manganese(III) peroxide.[20] This complex is also postulated as an intermediate in the electrocatalytic epoxidation of olefins by dioxygen.[13]

The formation of dimeric (μ-oxo)manganese porphyrins from the reaction of (tetraphenylporphinato)manganese(III) derivatives with iodosylbenzene has been reported,[21] and very recently, $Mn^{II}TPP$ has been shown to react with air to give a dimeric (μ-oxo)- or (μ-peroxo)manganese porphyrin.[22]

In order to detect the existence, in solution, of reaction products between O_2 or $O_2^{\bullet -}$ and manganese porphyrins, which may be intermediates in the oxidation reactions, we carried out a voltamperometric and spectroscopic study of the behavior of manganese(II) and manganese(III) tetraphenylporphine in the presence of dioxygen and potassium superoxide.

Experimental Section

Materials. $ClMn^{III}TPP$ was prepared by the DMF refluxing method.[23] $Mn^{II}TPP$ was prepared by reduction with tetrabutylammonium borohydride, under argon, of a pyridine solution of $ClMn^{III}TPP$ and isolated as purple crystals on addition of distilled water. Potassium superoxide (in powder) and dibenzo-18-crown-6 were purchased from Fluka and used without further purification. Tetrabutylammonium perchlorate was of analytical grade and was recrystallized from distilled water and dried under vacuum. Dichloromethane (CH_2Cl_2) was dried over $CaCl_2$ and distilled prior to use. Toluene and tetrahydrofuran (THF) were distilled from sodium benzophenone. Dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) were of spectrochemical grade. DMSO was distilled under vacuum from CaH_2. All solvents were purged with argon and stored over activated molecular sieves in brown bottles.

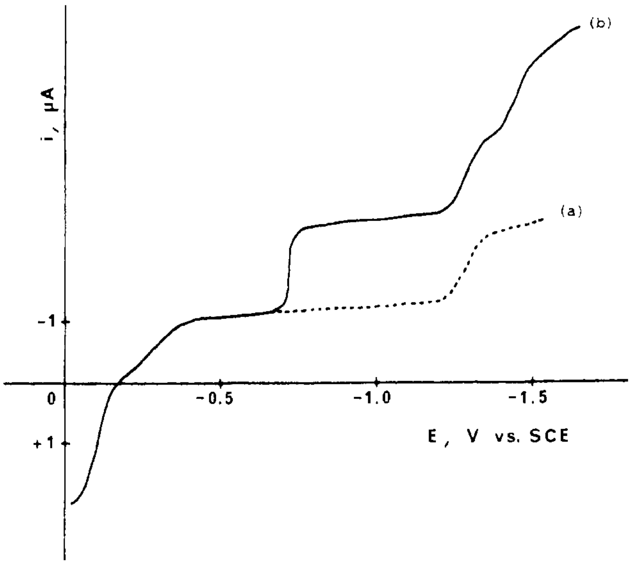


Figure 1. Linear voltammograms at a DME: (a) 3.5 × 10^{-4} M $ClMn^{III}TPP$ in DMSO, under inert atmosphere; (b) initial solution + molecular dioxygen.

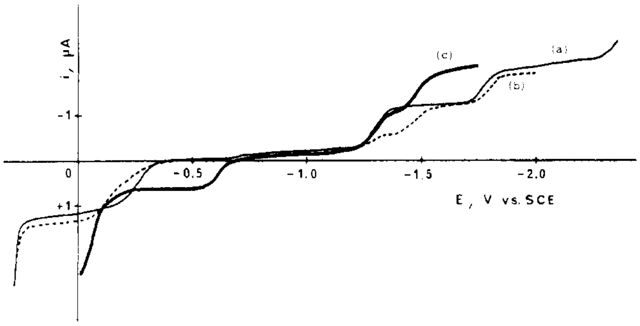


Figure 2. Linear voltammograms at a DME: (a) 3.5 × 10^{-4} M $Mn^{II}TPP$ in DMSO, under inert atmosphere; (b) initial solution + $O_2^{\bullet -}$; (c) solution from (b) after the addition of dioxygen.

Physical Measurements. Linear voltamperometry was performed by using a dropping mercury electrode (DME) or a rotating platinum electrode as the working electrode, a platinum wire as the auxiliary electrode, and a commercial saturated calomel electrode (SCE) as the reference. Potential was delivered by a Tacussel PRG5 potentiostat connected to a Tacussel EPL1 recorder. Cyclic voltamperometry was performed at a scan rate of 0.1 V s^{-1}, using a platinum working electrode and a saturated calomel reference electrode. Measurements were made by using a Tacussel type PRT20 potentiostat coupled with a Tektronix type 564 storage oscilloscope. The electrochemical experiments were performed under nitrogen in a thermostated cell at 25 ± 0.1 °C, using porphyrin concentrations of 3.5 × 10^{-4} M, saturated solutions of KO_2, and supporting electrolyte concentrations (tetrabutylammonium perchlorate) of 10^{-1} M. Visible spectra were recorded on a Perkin-Elmer Lambda 5 spectrophotometer, and infrared spectra were recorded on a Beckman Acculab 10 spectrophotometer. The EPR spectra were recorded on a Bruker ER-200 E spectrometer, operating in the X-band frequencies and modulated at 100 kHz. Low temperature was achieved by using the Bruker liquid-nitrogen accessory, and the temperature control was accurate to ±1 °C. Magnetic field strength was calibrated by an NMR proton probe, and a sample of the lithium salt of tetracyanoquinodimethane radical anion (Li^+TCNQ^-) was employed as a *g* marker. Quartz tubes of 1-mm thickness and 2-mm internal diameter were used.

Results

Voltamperometric Data. Dioxygen is reduced at a DME, in DMSO, in two successive monoelectronic steps:[24]

$$O_2/O_2^{\bullet -}: \quad E_{1/2} = -0.75 \text{ V vs SCE}$$

$$O_2^{\bullet -}/O_2^{2-}: \quad E_{1/2} = -2.05 \text{ V vs SCE}$$

---

(7) De Poorter, B.; Meunier, B. *J. Chem. Soc., Perkin Trans. 2* **1985**, 1735.

(8) (a) Tabushi, I.; Koga, N. *J. Am. Chem. Soc.* **1979**, *101*, 6456. (b) Perrée-Fauvet, M.; Gaudemer, A. *J. Chem. Soc., Chem. Commun.* **1981**, 874.

(9) (a) Tabushi, I.; Yazaki, A. *J. Am. Chem. Soc.* **1981**, *103*, 7371. (b) Tabushi, I.; Morimitsu, K. *J. Am. Chem. Soc.* **1984**, *106*, 6871.

(10) Mansuy, D.; Fontecave, M.; Bartoli, J. F. *J. Chem. Soc., Chem. Commun.* **1983**, 253.

(11) Tabushi, I.; Kodera, M. *J. Am. Chem. Soc.* **1986**, *108*, 1101.

(12) Battioni, P.; Bartoli, J. F.; Leduc, P.; Fontecave, M.; Mansuy, M. *J. Chem. Soc., Chem. Commun.* **1987**, 791.

(13) Creager, S. E.; Raybuck, S. A.; Murray, R. W. *J. Am. Chem. Soc.* **1986**, *108*, 4225.

(14) Perrée-Fauvet, M.; Chung, M. Unpublished results.

(15) Lever, A. B. P.; Wilshire, J. P.; Quan, S. K. *J. Am. Chem. Soc.* **1979**, *101*, 3668 and references therein.

(16) (a) Hoffman, B. M.; Weschler, C. J.; Basolo, F. *J. Am. Chem. Soc.* **1976**, *98*, 5473. (b) Hoffman, B. M.; Szymanski, T.; Brown, T. G.; Basolo, F. *J. Am. Chem. Soc.* **1978**, *100*, 7253.

(17) Creager, S. E.; Murray, R. W. *Inorg. Chem.* **1987**, *26*, 2612.

(18) Valentine, J. S.; Quin, A. E. *Inorg. Chem.* **1976**, *15*, 1997.

(19) Shirazi, A.; Goff, H. M. *J. Am. Chem. Soc.* **1982**, *104*, 6318.

(20) Van Atta, R. B.; Strouse, C. E.; Hanson, L. S.; Valentine, J. S. *J. Am. Chem. Soc.* **1987**, *109*, 1425.

(21) (a) Schardt, B. C.; Hollander, F. J.; Hill, C. L. *J. Am. Chem. Soc.* **1982**, *104*, 3964. (b) Smegal, J. A.; Schardt, B. C.; Hill, C. L. *J. Am. Chem. Soc.* **1983**, *105*, 3510.

(22) Dismukes, G. C.; Sheats, J. E.; Smegal, J. A. *J. Am. Chem. Soc.* **1987**, *109*, 7202.

(23) Adler, A. D.; Longo, F. R.; Kampas, F.; Kim, J. *J. Inorg. Nucl. Chem.* **1970**, *32*, 2443.

(24) Goolsby, A. D.; Sawyer, D. T. *Anal. Chem.* **1968**, *40*, 83.

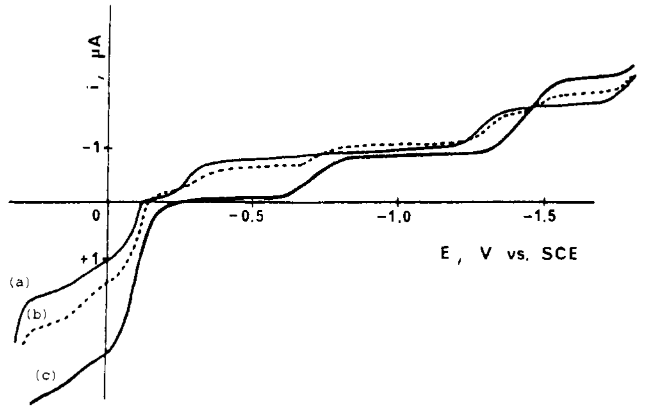


Figure 3. Linear voltammograms at a DME: (a) 3.5×10^{-4} M $ClMn^{III}TPP$ in DMSO, under inert atmosphere; (b, c) initial solution + increasing amounts of $O_2^{\bullet-}$.

Under inert atmosphere, $ClMn^{III}TPP$ is also reduced at a DME in two successive monoelectronic steps: in DMSO, the first reduction occurs at -0.31 V,[25] and the second one, which corresponds to the formation of the anion radical, is observed at -1.31 V:

$$\mathrm{Mn(III)/Mn(II)}: E_{1/2} = -0.31 \text{ V vs SCE}$$

$$\mathrm{Mn(II)/Mn(II)^-}: E_{1/2} = -1.31 \text{ V vs SCE}$$

In the presence of dioxygen, the -1.31-V wave is replaced by a double wave at -1.28 and -1.45 V, the total intensity of which corresponds to a bielectronic exchange (Figure 1). The species obtained at the electrode are $[Mn^{II}TPP]_{el}$ and $[O_2^{\bullet-}]_{el}$ resulting respectively from the electrochemical reduction of $Mn^{III}TPP^+$ at -0.31 V and O_2 at -0.75 V. The simplest hypothesis would be to consider that the two electrogenerated species react together to form $[MnTPPO_2]^-$. However, the existence of such a species does not account for the bielectronic reaction observed.

$Mn^{II}TPP$ and $O_2^{\bullet-}$. In order to study the electrochemical behavior of the postulated $[MnTPPO_2]^-$ species, we have prepared it by reaction of KO_2 with $Mn^{II}TPP$, which itself was electrochemically or chemically generated (as $Mn^{II}TPP(py)$; see Experimental Section). The I/E curve of $Mn^{II}TPP$ displays an oxidation wave at -0.27 V corresponding to the electrochemical oxidation

$$Mn^{II}TPP \rightarrow Mn^{III}TPP^+ + e^-$$

and a reduction wave at -1.31 V corresponding to the electrochemical reduction (Figure 2a)

$$Mn^{II}TPP + e^- \rightarrow Mn^{II}TPP^-$$

Addition of KO_2 results in fast changes in the voltamperogram: an ill-defined wave appears in oxidation, together with the double wave previously observed in reduction at -1.28 and -1.45 V (Figure 2b). The total intensity of this double wave does not exceed one electron, which might indicate that the complex $[MnTPPO_2]^-$ is effectively formed. After bubbling of dioxygen into the solution, the intensity of the double wave increases, indicating the formation of a new species, which can be reduced by two electrons (Figure 2c). The wave in oxidation at -0.6 V could indicate that $O_2^{\bullet-}$ is formed. This wave does not appear in Figure 2b, showing that there is no excess of KO_2. However, we want to emphasize that only the currents observed in reduction give well-defined and reproducible waves. In oxidation, the waves usually appear ill-defined and hardly reproducible, due probably to the existence of complex chemical reactions with the solvent.

$Mn^{III}TPP^+$ and $O_2^{\bullet-}$. Addition of increasing amounts of superoxide ion to a DMSO solution of $ClMn^{III}TPP$ results first in the appearance, in oxidation, of a wave at -0.27 V,[26] which shows that $Mn^{II}TPP$ is initially formed, and then the double wave at -1.28 and -1.45 V appears, with an intensity corresponding to a bielectronic exchange (Figure 3). In the presence of a large excess of KO_2, this double wave is replaced by a single one of the same intensity, at -1.43 V, which might indicate the formation of another complex.

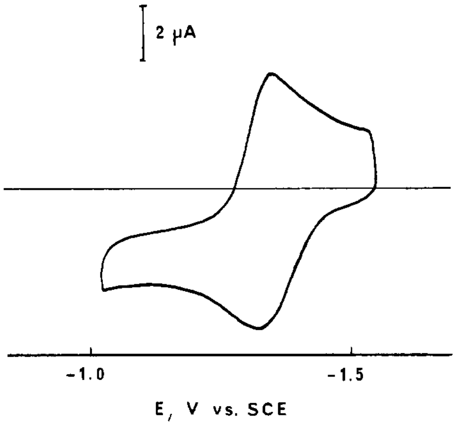


Figure 4. Cyclic voltammogram at a Pt electrode of 3.5×10^{-4} M $Mn^{II}TPP$ in DMSO in the presence of $O_2^{\bullet-}$.

The presence of a two-electron wave gives evidence for the formation of a new species. This species and the $[MnTPPO_2]^-$ complex are dependent on the concentration of KO_2, and their thermodynamic stabilities are very comparable, as seen from the similar values of their half-wave potentials. We have shown, in further experiments, that these reactions are quantitative and that the intensities of the waves correspond exactly to a bielectronic and to a monoelectronic exchange. The presence of a double wave at the electrode instead of a single wave might result from a rate-dependent electrochemical phenomenon that was not elucidated. As a matter of fact, a single wave is observed if a rotating platinum electrode is used instead of the dropping mercury electrode, the number of exchanged electrons being constant. However, the DME is preferred to avoid the absorption effects.

Very similar variations of the voltamperograms, including comparable values of the potentials of the double wave, are observed if the experiments are performed in DMF instead of DMSO. Linear voltammetry was preferred to cyclic voltammetry, because it can detect the existence in solution of new species and give information on their stabilities. However, a cyclic voltammetric study has been carried out. It shows that, in all cases, the reduction of the complexes formed is reversible (Figure 4).

The presence of these reduced complexes has not been observed previously by electrochemistry. The formation of the $MnTPPO_2$ species has been pointed out,[17] but a voltamperometric study performed at more reducing potentials, should have been necessary to detect its reduced form.

$O_2^{\bullet-}$ in DMSO. The electrochemical behavior of a DMSO solution of superoxide ion alone was studied. The voltamperogram displays an oxidation wave at -0.73 V and two reduction waves at -0.77 and -2.10 V. If small amounts of ClMnTPP are added to this solution, the wave at -0.73 V disappears and the double wave at -1.28 and -1.45 V appears. It would be consistent to attribute the wave in reduction at -0.77 V to the presence of dioxygen. However, this is not supported by the fact that its intensity does not decrease after bubbling argon. This wave, which was also present in Figure 3, corresponds probably to a reaction product between $O_2^{\bullet-}$ and DMSO. Actually, in spite of the use of drying reagents and cautions, there is always some residual water in DMSO, and it is well known that, in the presence of water, superoxide ion decomposes into OH^- and OOH^-:[27,24]

$$2O_2^{\bullet-} + H_2O \rightarrow OH^- + OOH^- + O_2$$

$$OOH^- + DMSO \rightarrow OH^- + DMSO_2$$

However, the hydroxide ion produced in the decomposition of superoxide ion cannot be considered as responsible for the for-

---

(25) Kadish, K. M.; Kelly, S. *Inorg. Chem.* **1979**, *18*, 2968.

(26) This wave is observed unambiguously at a rotating platinum electrode. At a DME, it is masked by the oxidation wave of the mercury, in the presence of the chloride ion of the porphyrin.

(27) Maricle, D. L.; Hodgson, W. G. *Anal. Chem.* **1965**, *37*, 1562.

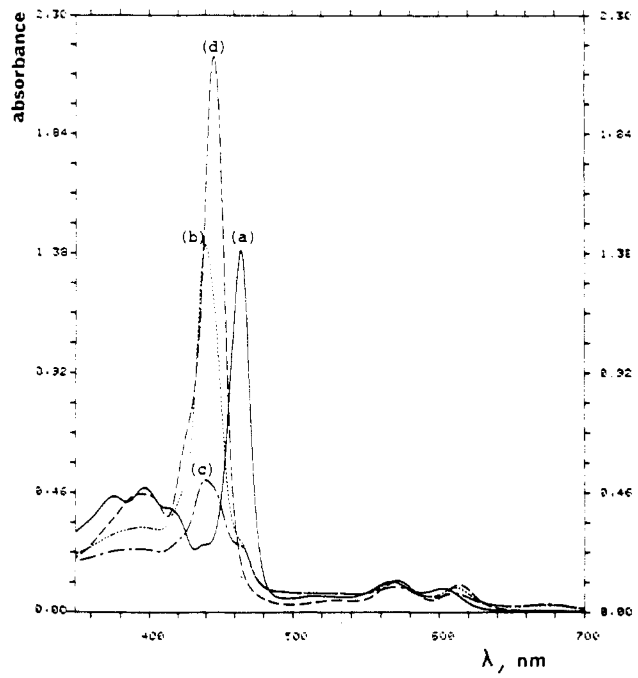


Figure 5. Visible absorption spectra: (a) 10^{-5} M ClMn^{III}TPP in DMSO; (b–d) initial solution + increasing amounts of $O_2^{\bullet-}$.

mation of the complex, which is reducible by two electrons at −1.28 and −1.45 V, since this complex can also be produced in situ at the electrode from electrochemically generated $O_2^{\bullet-}$ and Mn^{II}TPP. It results most likely from a fast and quantitative chemical reaction between these two species.

Visible Spectra. The effects of adding increasing amounts of KO_2 to solutions of Mn^{II}TPP(py) and Mn^{III}TPP$^+$ can be monitored by visible spectroscopy. In DMSO, Mn^{II}TPP(py) and Mn^{III}TPP$^+$ display a strong absorption (Soret band) at 438 and 464 nm, respectively. In the presence of excess KO_2, the intensity of the Soret band of a deaerated DMSO solution of Mn^{II}TPP(py) decreases considerably. If dioxygen is introduced, a rapid shift of the band at 445 nm is observed. On the other hand, if KO_2 is added to a solution of Mn^{III}TPP$^+$, the band at 438 nm corresponding to Mn^{II}TPP appears first, then decreases, and is replaced by the Soret band at 445 nm (Figure 5). Very similar results are obtained in DMF.

These results confirm those obtained by electrochemistry: addition of KO_2 to Mn^{II}TPP generates the complex [MnTPPO$_2$]$^-$, which might present an absorption band at 438 nm, like Mn^{II}TPP, though less intense. In the presence of dioxygen or Mn^{III}TPP$^+$, a new species with a Soret band at 445 nm is formed.

Infrared Spectra. The peroxide adduct MnTPPO$_2$ exhibits its ν_{O-O} at 983 cm^{-1},[28] while metalloporphyrin superoxide complexes show their ν_{O-O} in the 1100–1200-cm^{-1} region,[29] and dimeric (μ-oxo)manganese porphyrins display an intense absorption band near 800 cm^{-1}.[21]

Infrared spectra of Mn^{III}TPP$^+$, either in KBr pellets or in solution in DMF, display three principal absorption bands at 695, 740, and 800 cm^{-1}. If excess KO_2 is added to the DMF solution of Mn^{III}TPP$^+$, two other bands appear at 920 and 970 cm^{-1}, which are not present in the spectrum of KO_2 alone. As they appear in the peroxo region, they can presumably be assigned as the ν_{O-O} of a peroxomanganese porphyrin.

EPR Study. Mn^{III}TPP$^+$ and $O_2^{\bullet-}$. The reaction of 1 equiv of superoxide ion (as the crown ether complex) with 1 equiv of Mn^{III}TPP$^+$ in CH_2Cl_2 produces dioxygen and generates Mn^{II}TPP, which is characterized by its six-line EPR spectrum at $g_\perp = 6$.[16] In the presence of an excess of KO_2, the signal of Mn^{II}TPP decreases and a new signal is observed, with an apparent 16-line hyperfine coupling pattern centered at $g = 2$ and a total spectral width of 1220 G (Figure 6a). This signal, which was observed at 110 K, with CH_2Cl_2, toluene, DMF, or THF as the solvent, strongly suggests the presence of a mixed-valence dimeric porphyrin complex, denoted in the following by dimer 1. Similar spectra have been previously reported in the literature for dimeric manganese complexes.[30]

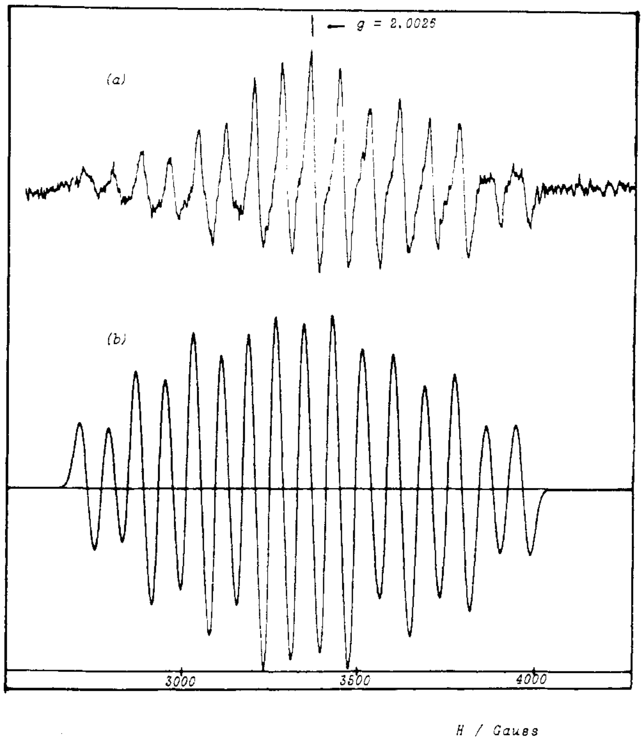


Figure 6. X-Band EPR spectra: (a) a CH_2Cl_2 solution of ClMn^{III}TPP and excess $O_2^{\bullet-}$ at 110 K (field modulation 4.0 G); (b) simulation of (a) using $A_1 = 163$ G and $A_2 = 81$ G.

Mn^{II}TPP and O_2. We have reproduced a recently published experiment that was proved to yield a mixed-valence dimeric manganese porphyrin[22] by bubbling air in a C_6H_5Cl solution of Mn^{II}TPP prepared according to ref 31. The EPR spectrum of the solution exhibits, at 110 K, a 16-line signal centered at $g = 2$ with a total spectral width of 1410 G, which is the value measured by the authors at 10 K. This means that temperature does not affect the coupling constants, and it proves that the dimeric complex detected in this experiment (dimer 2) and formulated as [TPPmn^{II}–O$_x$–Mn^{III}TPP]$^-$ differs from the dimeric species we have obtained with superoxide ion (dimer 1). Performing this experiment in toluene instead of chlorobenzene results in formation of small amounts of dimer 1 exclusively. Besides, we have evidence that the signal of dimer 2 decreases considerably after addition of a reducing agent (borohydride) to give place to an intense signal of dimer 1.

Mn^{II}TPP and $O_2^{\bullet-}$. Addition of superoxide ion to a deaerated C_6H_5Cl or toluene solution of Mn^{II}TPP leads to the formation of dimer 1 exclusively, while its addition to a C_6H_5Cl solution of Mn^{III}TPP$^+$ provides both dimers. This is consistent with the fact that, in the latter case, Mn^{II}TPP and dioxygen are initially formed, and this again shows the role of the solvent in the formation of these dimers. As Mn^{II}TPP is very unstable, the use of Mn^{II}TPP(py), stable in its crystalline form, was preferred for

---

(28) Urban, M. W.; Nakamoto, K.; Basolo, F. *Inorg. Chem.* **1982**, *21*, 3406.

(29) (a) Collman, J. P.; Brauman, J. I.; Halbert, T. R.; Suslick, K. S. *Proc. Natl. Acad. Sci. U.S.A.* **1976**, *73*, 3333. (b) Cheung, S. K.; Grimes, C. J.; Wong, J.; Reed, C. A. *J. Am. Chem. Soc.* **1976**, *98*, 5028. (c) Kozuka, M.; Nakamoto, K. J. *J. Am. Chem. Soc.* **1981**, *103*, 2162.

(30) (a) Cooper, S. R.; Dismukes, G. C.; Klein, M. P.; Calvin, M. *J. Am. Chem. Soc.* **1978**, *100*, 7248. (b) Sheats, J. E.; Czernuszewicz, R. S.; Dismukes, G. C.; Rheingold, A. L.; Petrouleas, V.; Stubbe, J.; Armstrong, W. H.; Beer, R. H.; Lippard, S. J. *J. Am. Chem. Soc.* **1987**, *109*, 1435. (c) Mabad, B.; Tuchagues, J. P.; Hwang, Y. T.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1985**, *107*, 2801. (d) Hagen, K. S.; Armstrong, W. H.; Hope, H. *Inorg. Chem.* **1988**, *27*, 969.

(31) Camenzind, M. J.; Hollander, F. J.; Hill, C. L. *Inorg. Chem.* **1982**, *21*, 4301.

quantitative experiments. Addition of superoxide ion to a dried and deaerated CH_2Cl_2 solution of $Mn^{II}TPP(py)$ in a ratio 1/1 yields the $[MnTPPO_2]^-$ species, which is EPR silent. Only traces of the postulated dimer are observed. Addition of dioxygen or $Mn^{III}TPP^+$ does not modify the EPR spectrum. The formation of significant amounts of dimer 1 is observed only in the ratio $[Mn^{II}TPP(py)]/[O_2^{\bullet-}] = 2/1$ and is always accompanied by residual traces of $Mn^{II}TPP$.

These experiments strongly support the hypothesis of the formation of two distinct dimeric species: one resulting from the reaction of air with $Mn^{II}TPP$ in chlorobenzene and giving a 1410 G wide EPR signal and the other, 200-G narrower, obtained in more reducing conditions ($Mn^{II}TPP$ and $O_2^{\bullet-}$ and $Mn^{II}TPP$, O_2, and borohydride). We could not obtain a well-defined spectrum of dimer 1 at 10 K, because its signal was overlapped by the signal of KO_2, which was revealed as very intense at low temperature, even if it was present as traces. Its simulation was obtained with an isotropic spin Hamiltonian for a spin $S = {}^1/_2$ state with $g = 2.00$, $A_1^{1/2} = 163$ G, $A_2^{1/2} = -81$ G, and a line width of 40 G with Gaussian lines (Figure 6b). $A_1^{1/2}$ and $A_2^{1/2}$ refer to the isotropic hyperfine coupling constants between electronic spin $S = {}^1/_2$ and the nuclear spin of sites 1 and 2.

Magnetic Susceptibility. The magnetic susceptibility at room temperature of dimer 1 was found by the Evans method such that, for a dimer formulation, the product $\chi_M T = 0.54$ cm^3 mol^{-1} K. This value is to be compared to the expected one for noninteracting manganese ions (n_1 and n_2 unpaired electrons):

$$\mu_{\text{eff}}^2 = 8\chi_M T = \tfrac{1}{4}g_1^2 n_1(n_1 + 2) + \tfrac{1}{4}g_2^2 n_2(n_2 + 2)$$

If one supposes $g_1 = g_2 = 2$, we obtain $\chi_M T = 7.375$ for a Mn(II)/Mn(III) formulation and $\chi_M T = 4.875$ for a Mn(III)/Mn(IV) formulation. In both hypotheses, we see that the complex is strongly antiferromagnetically coupled.

Discussion

The electrochemical mechanisms indicate that two different complexes are formed by reaction of $Mn^{III}TPP^+$ or $Mn^{II}TPP$ with superoxide ion. The first one is reduced by one electron and can be assigned as $[MnTPPO_2]^-$. According to the EPR spectra, the second one could be a dimer. These complexes are thermodynamically stable and have very similar apparent formation constants, as seen from the value of their reduction potentials.

The spin $S = {}^1/_2$ state observed in EPR spectra arises from exchange coupling in a Mn(III)/Mn(II) pair or in a Mn(III)/Mn(IV) pair. Such a situation can be described by the following spin Hamiltonian:

$$\mathcal{H} = -J\vec{S}_A\cdot\vec{S}_B + a_A\vec{S}_A\cdot\vec{I}_A + a_B\vec{S}_B\cdot\vec{I}_B + g_A\beta H S_{AZ} + g_B\beta H S_{BZ}$$

where J denotes the exchange coupling constant and g_A, g_B denote the Lande factors, $\vec{S}_A$, $\vec{S}_B$ the electronic spin moments, $\vec{I}_A$, $\vec{I}_B$ the nuclear spin moments, and a_A, a_B the hyperfine coupling constants of ions A and B. In the Mn(III)/Mn(II) formulation, we will have $S_A = 2$ and $S_B = {}^5/_2$, and in the Mn(III)/Mn(IV) case, we get $S_A = 2$ and $S_B = {}^3/_2$. The difference between those two formulations has effect on the way the hyperfine parameters of the pair are related to those of the individual ions. For a trapped Mn(III)/Mn(II) pair and for the case where the exchange coupling is large versus other effects, one obtains[32]

$$A_{Mn(II)}^{1/2} = \tfrac{7}{3}a_{Mn(II)} \qquad A_{Mn(III)}^{1/2} = -\tfrac{4}{3}a_{Mn(III)} \tag{1a}$$

and for the same hypotheses, a Mn(III)/Mn(IV) pair will yield

$$A_{Mn(III)}^{1/2} = 2a_{Mn(III)} \qquad A_{Mn(IV)}^{1/2} = -a_{Mn(IV)} \tag{1b}$$

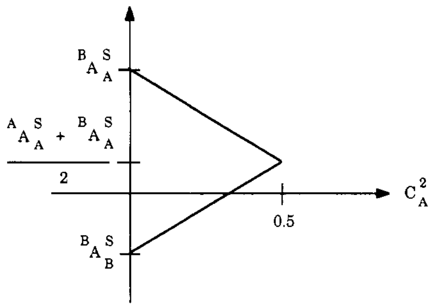


Figure 7. Hyperfine coupling constants of site A and site B in a dimer AB versus the amount of delocalization.

Table I. Hyperfine Parameters for Manganese(II) and Manganese(IV) Porphyrins

		ref
$Mn^{II}TPP$	$a_\perp = 73$ G	this work
$Mn^{II}TPP\cdot py$	$a_\parallel = a_\perp = 74$ G	16
$[TPPMn^{II}-O_x-Mn^{III}TPP]^-$	$a_{Mn(II)\parallel} = a_{Mn(II)\perp} = 77$ G	22
$Mn^{IV}TPP(OCH_3)_2$	$a = 72$ G	34
$Mn^{IV}TPP(NCO)_2$	$a = 69$ G	34
$[Mn^{IV}TPPCl]^+$	$a_{av} = 81$ G	36
$Mn^{IV}TPPCl_2$	$a_{av} = 73$ G	36
$Mn^{IV}TPPO_2$	$a_{av} = 78$ G	16
$[TPPMn^{III}-O-Mn^{IV}TPP]-X$	$a_{Mn(IV)\parallel} = a_{Mn(IV)\perp} = 74$ G	35

We would like to stress that those relations are valid only for trapped mixed-valence dimers. One of us[33] has recently studied the effect of delocalization on electronic spin coupling: delocalization modifies eq 1. If the wave function of the pair is $|S\rangle = C_A|S\rangle^A + C_B|S\rangle^B$, where $|S\rangle^A$ means the wave function of the pair when the extra electron is on site A, we have

$$\begin{aligned} A_A^S &= C_A^2\,{}^{A}A_A^S + (1 - C_A^2)\,{}^{B}A_A^S \\ A_B^S &= C_A^2\,{}^{A}A_B^S + (1 - C_A^2)\,{}^{B}A_B^S \end{aligned} \tag{2}$$

where ${}^{i}A_k^S$ stands for the hyperfine parameter of site k when the extra electron is on site i for a pair of spin S. When the valences are trapped, we again find eq 1. When the valences are fully delocalized ($C_A^2 = {}^1/_2$), we find two equivalent sites, with

$$A_A^S = A_B^S = \tfrac{1}{2}({}^{A}A_A^S + {}^{B}A_A^S) \tag{3}$$

If we suppose that the mixed-valence dimer is symmetric, so that ${}^{A}A_A^S = {}^{B}A_B^S$ and ${}^{B}A_A^S = {}^{A}A_B^S$, we have the condition

$$A_A^S + A_B^S = {}^{A}A_A^S + {}^{B}A_A^S \tag{4}$$

This behavior is summarized in Figure 7.

We want now to consider the two hypotheses for the oxidation-state assignment.

Mn(II)/Mn(III). If we assume that dimer 1 is a Mn(II)/Mn(III) trapped species, we have $a_{Mn(II)} = 70$ G. In Table I, we have collected data on $Mn^{II}TPP$ from the literature. The value we obtained appears too small. A value of 77 G was found for the Mn(II)–Mn(III) postulated dimer 2,[22] which is coherent with the fact its EPR spectrum is larger. One possible explanation is that, due to a different bridging species or a more symmetrical environment, dimer 1 would be somewhat delocalized. Dimer 2 would be valence trapped. Using their observed values and ours, we remark that our sum rule is obeyed: $A_A^{1/2} + A_B^{1/2} = 181 - 99 = 163 - 81 = 82$ G. Using our theory, we can evaluate $C_A^2 = 0.06$, which reflects 6% delocalization. One fact that goes against this Mn(II)/Mn(III) assignment is the observation of a strong antiferromagnetic coupling: so far, no strongly coupled Mn(II)/Mn(III) species has been observed.

Mn(III)/Mn(IV). If we make this assignment for the oxidation state of dimer 1, we find $a_{Mn(IV)} = 81$ G. This agrees with some of thc data of Table I, more precisely with the data corresponding

---

[32] Dismukes, G. C.; Siderer, Y. *Proc. Natl. Acad. Sci. U.S.A.* **1981**, *78*, 274.

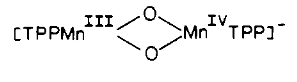
[33] Papaefthymiou, V.; Girerd, J. J.; Moura, I.; Moura, J. J. G.; Munck, E. *J. Am. Chem. Soc.* **1987**, *109*, 4703. Munck, E.; Papaefthymiou, V.; Surerus, K. K.; Girerd, J. J. In *Metals in Proteins*; Que, L., Ed.; ACS Symposium Series; American Chemical Society: Washington, DC, 1988.

[34] Camenzind, M. J.; Hollander, F. J.; Hill, C. L. *Inorg. Chem.* **1983**, *22*, 3776.

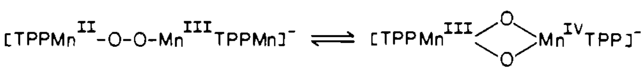
[35] Camenzind, M. J.; Schardt, B. C.; Hill, C. L. *Inorg. Chem.* **1984**, *23*, 1984.

[36] Konishi, S.; Hoshino, M.; Imamura, M. *J. Phys. Chem.* **1982**, *86*, 4537.

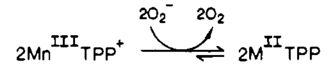
to Mn(IV) bound on one side of the porphyrin ring. Such a formulation would also agree with the large exchange coupling observed from magnetic susceptibility measurement: known Mn(III)/Mn(IV) pairs bridged by oxygen atoms are strongly coupled. A large gap between the ground state $S = {}^1/_2$ and the first excited state $S = {}^3/_2$ is also consistent with a slow relaxation rate allowing the observation of the EPR signal of dimer 1 at 110 K (we would like to stress that the signal of dimer 2 can also be observed at the same temperature).[37] Dimer 1 must be different from the [TPPMn^{III}–O–Mn^{IV}–TPP]–X observed in ref 35 since the EPR spectra are different (signal width 1070 G). This difference is also expected from redox behavior, dimer 1 being reduced at a very negative potential. A possible structure would be



This complex could be related to the peroxo-bridged species [TPPMn^{II}–O$_2$–Mn^{III}TPP]$^-$, postulated in ref 22, by a change in the geometry and oxidation level of the bridge. The value $a_{\mathrm{Mn(IV)}}$ = 81 G close to the one of asymmetrical Mn(IV) monomer could be in agreement with our hypothesis. The equilibrium



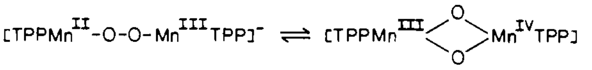
could exist. Consequently, the following mechanism is proposed:



$$2\mathrm{Mn^{III}TPP^+} \overset{2O_2^- \quad 2O_2}{\rightleftharpoons} 2\mathrm{M^{II}TPP} \qquad (5)$$

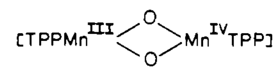
$$\mathrm{Mn^{II}TPP} + O_2^{\bullet -} \rightleftharpoons [\mathrm{Mn^{III}TPPO_2}]^- \qquad (6)$$

$$[\mathrm{Mn^{III}TPPO_2}]^- + \mathrm{Mn^{II}TPP} \rightleftharpoons [\mathrm{TPPMn^{II}{-}O{-}O{-}Mn^{III}TPP}]^- \qquad (7)$$



(8)

[Mn^{III}TPPO$_2$]$^-$ and [TPPMn^{II}–O–O–Mn^{III}TPP]$^-$ or



would be the species reduced at the dropping mercury electrode with one electron and two electrons, respectively, at the same half-wave potentials: −1.28 and −1.45 V. The fact that [Mn^{III}TPPO$_2$]$^-$ is reduced at the same potential as Mn^{II}TPP is strong evidence that $O_2^{\bullet -}$ does not strongly bind to Mn^{II}TPP in coordinating solvents (DMSO or DMF). Equation 5 is supported by polarography, visible spectroscopy, and EPR spectroscopy, though we failed electrochemically to give absolute evidence for O$_2$ formation. With Mn^{II}TPP as the starting material, two situations can occur: with less than 1 equiv of superoxide ion, the above mechanism is valid starting from eq 6; with 1 equiv or a slight excess of superoxide, all the Mn^{II}TPP is converted into [Mn^{III}TPPO$_2$]$^-$ and the reaction cannot go further. The effect of adding dioxygen in DMSO solutions can be so interpreted: dioxygen may partly cause the decomposition of [Mn^{III}TPPO$_2$]$^-$, which proves to be not very stable in DMSO (vide supra), into the Mn^{II}TPP necessary for the reaction to proceed (eq 7). A reviewer suggested to us that the initiation of dimer formation could be provoked by further reduction of Mn(II) to Mn(II)$^-$, which then would react rapidly with the $O_2^{\bullet -}$ in the diffusion layer. This is consistent with the first reduction wave at −1.28 V, the dimer being reduced once further at −1.45 V. This is a possible notion, consistent with the reversible cyclic voltammetry, but we could not get evidence for it: Coulometric experiments performed at those potentials to identify the reduction products produced at the electrode induced decomposition of the porphyrin.

The mixed-valence dimeric manganese porphyrin we identified did not prove stable enough to be isolated. In solution, it slowly decomposes to Mn^{II}TPP. So it may be possible that, like [Mn-TPPO$_2$]$^-$, it plays a role in the manganese porphyrin catalyzed oxidation by dioxygen. Moreover, we have detected its formation by EPR spectroscopy in the oxidation reaction of 2,4,6-tri-*tert*-butylphenol by Mn^{II}TPP and dioxygen, in toluene or CH$_2$Cl$_2$.

Acknowledgment. We gratefully acknowledge Dr. J. Huet (Laboratoire de Chimie Bioorganique et Bioinorganique), who recorded the first EPR spectra.

---

[37] Chang, H. S.; Larsen, S. K.; Boyd, P. D. W.; Pierpont, C. G.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1988**, *110*, 4565.

Contribution from the Department of Chemistry,
University of California, Berkeley, California 94720

Isomerization and Solution Structures of Desferrioxamine B Complexes of Al^{3+} and Ga^{3+} [1]

Brandan Borgias, Alain D. Hugi, and Kenneth N. Raymond*

Received August 26, 1988

The Ga(III) and Al(III) complexes of desferrioxamine B (H$_4$DFO$^+$) have been prepared and purified by cation-exchange liquid chromatography. Both complexes elute as single bands, with elution rates comparable to those measured for the trans isomer(s) of the kinetically inert Cr(HDFO)$^+$ complex. The solution thermodynamics of Ga(HDFO)$^+$ show that the cationic complex is the only significant species from pH 2 to pH 9. Above pH 9 the complex undergoes hydrolysis. Its stability constant, log K_{ML}, is 27.56 (compared to 30.60 for Fe(III)). The NMR spectra of both the Ga and Al complexes indicate the presence of two isomers in solution, whose rapid interconversion prevents chromatographic separation. The kinetics of isomerization of Ga(HDFO)$^+$ were studied by variable-temperature ^{13}C measurements in D$_2$O, methanol-d_4, and dimethyl-d_6 sulfoxide. The following kinetic parameters were obtained at 25 °C: k (s^{-1}), ΔH^* (kcal·mol^{-1}) and ΔS^* (cal·mol^{-1}·K^{-1}): 13 (1), 13 (1), and −10 (3) in water; 73 (7), 17 (2), and +8 (8) in methanol; 4.1 (6) × 10^2, 17 (5), and +10 (15) in DMSO. These results, and the observation that in water isomerization is pH independent, are discussed in terms of a possible I$_d$ mechanism. Attempts to further characterize the isomers of Ga(HDFO)$^+$ by 2D NMR were only partially successful, due to the complexity of the spectra. The results of these combined studies show that Ga is a good substitute metal for Fe in the M–DFO system. Further, it shows that there are only two significant isomers in solution for the labile Ga(III) complex, and these are most likely the N-cis,cis and C-trans,trans isomers.

Introduction

One of the tangential results of research on the siderophores[2] has been the development of clinical iron sequestering agents modeled after, or actually composed of, the natural products.[3] Desferrioxamine B (DFO) is a siderophore produced by *Strep-*

---

* Author to whom correspondence should be addressed.

[1] Coordination Chemistry of Microbial Iron Transport. 41. For the previous paper, see: Cass, M. E.; Garrett, T. M.; Raymond, K. N. *J. Am. Chem. Soc.* **1989**, *111*, 1677.

0020-1669/89/1328-3538$01.50/0