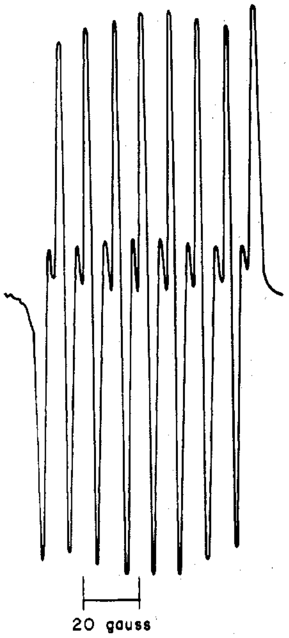

Figure 2. Solution ESR spectrum of [Co(trien)(DBcat)]Cl obtained at 25 °C in methanol solution.

intense band at 1440 cm^{-1} which can be assigned to a C–O stretching vibration of the *o*-semiquinone complex.[1] On the other hand, 3,5-di-*tert*-butyl-*o*-benzoquinone shows a C–O vibration of 1660 cm^{-1}. The uv–visible spectrum of the isolated complex is identical in all respects with the spectrum of the material produced by in situ oxidation of [Co(trien)(DBcat)]Cl, Figure 1. The peak maxima in the visible region occur at 512 nm (ϵ 1270) and 360 nm (ϵ 1145) while the peak maximum in the uv region occurs at 300 nm (ϵ 6680). The ESR spectrum of the isolated complex is also identical in all respects with that given in Figure 2. The molar conductance was found to be 237 Ω^{-1} in water confirming that the complex is indeed a 2:1 electrolyte. The solution magnetic moment was found to be 1.86 μ_B.

Discussion

The ESR spectrum shown in Figure 2. is the most convincing evidence that the complex is correctly formulated as an *o*-benzosemiquinone complex. The eight-line pattern due to ^{59}Co coupling shows a hyperfine coupling constant of 9.76 G. This is a small value compared to the coupling constants found for low-spin cobalt(II) complexes.[3] Additionally, the further splitting due to the proton at C-4 of the *o*-semiquinone ligand shows a coupling constant of approximately 3.5 G which is very close to the hyperfine coupling constant for that proton in free 3,5-di-*tert*-butyl-*o*-benzosemiquinone.[4] Thus the unpaired electron appears to be located largely on the ligand. The position of the C–O stretching vibration (1440 cm^{-1}) is also consistent with this formulation. Therefore, the complex is correctly characterized as containing the 3,5-di-*tert*-butyl-*o*-benzosemiquinone coordinated to cobalt(III) rather than, for example, a quinone coordinated to cobalt(II).

There have been other reports of *o*-semiquinone–metal complexes in the literature. Eaton has reported the ESR spectra of *o*-benzosemiquinone coordinated to a number of metals, primarily non transition metal ions.[5] In that work no complexes were isolated from solution or characterized. Röhrscheid et al. have reported the occurrence of what probably corresponds to coordinated *o*-semiquinone by oxidation of certain bis(catecholato)metal complexes.[6] However, no well-characterized *o*-benzosemiquinone complexes were isolated.

Floriani et al. have reported a series of binary 9,10-phenanthrenequinone complexes of iron, cobalt, and nickel.[7] It appears as if these workers viewed the complexes as quinone complexes of zero-valent metals. However, the C–O stretching vibration in these systems occurs around 1460 cm^{-1}, and based on the work reported here, it seems that Floriani's systems would be more correctly formulated as complexes of the 9,10-phenanthrenequinone and 1,2-naphthoquinone with Fe(salen) which may well be correctly formulated as containing a semiquinone ligand.[8] Balch has reported *o*-semiquinone complexes of tetrahalo-*o*-semiquinones with a number of heavy transition metals.[9] These were prepared and characterized in solution but not isolated.

Of the other cobalt(III) catecholato complexes which we have reported, none gives as stable an *o*-semiquinone complex as the one reported here. This is undoubtedly due to the fact that the bulky *tert*-butyl groups render the *o*-semiquinone ligand kinetically more stable than other *o*-semiquinone ligands. Nevertheless, several of the catecholato complexes show spectra indicating the definite existence of an oxidation product similar to [Co(trien)(DBsq)]Cl$_2$.

Experimental Section

Preparation of Semiquinone Complex. The starting material, [Co(trien)DBcat]Cl, was prepared as described previously.[1] To prepare the semiquinone complex, [Co(trien)(DBcat)]Cl, 1.00 g (2.2 mmol), was dissolved in 100 ml of vigorously deoxygenated 95% ethanol. To this solution was added 0.13 ml (1.1 mmol) of 30% H_2O_2 and 0.18 ml (2.2 mmol) of concentrated HCl. This mixture was allowed to stir under nitrogen for 2 h during which time the solution turned a deep red. After this time the semiquinone complex was obtained quantitatively by evaporation of solvent. The complex was dried under vacuum over P_2O_5.

Physical Measurements. The infrared spectra were obtained as KBr disks on a PE 621 spectrometer. Electronic spectra were measured with a Beckman DB-G. The magnetic moment was determined in aqueous solution by the method of Evans.[10] The ESR spectrum was obtained on a Varian V4502 spectrometer at room temperature in methanol solution.

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Registry No. [Co(trien)(DBsq)]Cl$_2$, 59204-56-7; [Co(trien)(DBcat)]Cl, 57396-04-0.

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Reaction of Superoxide with the Manganese(III) Tetraphenylporphine Cation

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The oxidation of transition metal complexes by dioxygen has been of interest to chemists and biochemists for a long time.[1,2] Nevertheless, the mechanisms of such oxidations are only understood in a small number of systems. We have recently become interested in the possibility of using superoxide anion, O_2^-, as a probe of oxidation mechanism in such systems. We have begun, therefore, a study of the reactions of superoxide with the *oxidized* form of transition metal complexes whose *reduced* form is reactive with dioxygen. We have previously communicated our results relating to the reaction of superoxide with a complex of copper(II).[3] We report here the reaction of $MnTPP^+$ (TPP = tetraphenylporphine) and superoxide.

There are several porphyrin,[4] Schiff base,[5] and macrocyclic[6] complexes of manganese(II) that are reported to be very reactive toward dioxygen. $Mn^{II}TPP$[7] and its monopyridine complex[8] have been shown to combine reversibly with dioxygen in toluene at low temperatures. In toluene at room temperature, however, they are rapidly and irreversibly oxidized to an unidentified $Mn^{III}TPP$ product. We have found that $Mn^{III}TPP^+$ reacts rapidly and quantitatively with O_2^- in dimethyl sulfoxide (DMSO) to give $Mn^{II}TPP$. The implications of this result for the mechanism of oxidation of the manganese(II) porphyrins by dioxygen are discussed below.

Experimental Section

Materials. $MnTPP(Cl){\cdot}CHCl_3$ was prepared by literature methods.[9] It was converted to MnTPP(Cl)·3tol by recrystallization from toluene (tol). MnTPP·2tol was a generous gift from Professor C. A. Reed. Potassium superoxide was purchased from K & K Laboratories. Dicyclohexyl-18-crown-6 was either prepared by literature methods,[10] purchased from Fluka and used without purification, or purchased from Aldrich and purified by chromatography on alumina. Dimethyl sulfoxide (MCB) was vacuum distilled from CaH_2 and stored over freshly activated 4A molecular sieves.

Preparation of Solutions of Superoxide. Potassium superoxide was ground to a fine powder with a mortar and pestle in a dry atmosphere. Powdered KO_2 and dicyclohexyl-18-crown-6 were placed in a dry Schlenk tube containing a Teflon-coated magnetic stirring bar and the flask was evacuated and flushed with dry argon. Dimethyl sulfoxide was introduced into the Schlenk tube by syringe. Stirring the mixture for 1–3 h gave a clear yellow solution.

Titration of $MnTPP^+$ with O_2^- in DMSO. Two milliliters of a 10^{-5} M solution of MnTPP(Cl)·3tol in DMSO was placed in a capped 1-cm quartz cuvette. Aliquots (0.001–0.005 ml) of a 10^{-3} M solution of KO_2/dicyclohexyl-18-crown-6 were added by syringe, the cuvette was shaken, and visible spectra were recorded immediately.

Reaction of MnTPP with O_2. Solutions of MnTPP·2tol (10^{-3}–10^{-5} M) in DMSO were prepared. Dioxygen was bubbled through the solutions until the visible spectra showed oxidation to be complete or nearly complete. These solutions were then sealed in EPR tubes and frozen, and their spectra at 77 K were recorded immediately.

Spectra. Visible and EPR spectra were recorded on Cary 118C and Varian E-12 spectrophotometers.

Results

MnTPP(Cl) is known to dissociate in DMSO to give $MnTPP^+$ and Cl^-.[4] When superoxide, O_2^-, was added to solutions of $MnTPP^+$ by addition of a DMSO solution of KO_2 solubilized by use of dicyclohexyl-18-crown-6, rapid reduction of $MnTPP^+$ to MnTPP was observed. MnTPP (which presumably coordinates one DMSO[7]) was identified by its characteristic visible spectral properties in DMSO (λ_{max} (nm): $MnTPP^+$, 374, 395, 414 sh, 463 (ϵ 1.4×10^5), 515, 566, 600; MnTPP, 437 (ϵ 2.5×10^5), 530, 569, 607). A titration of $MnTPP^+$ with O_2^- (see Experimental Section) indicated that the reduction was complete upon addition of approximately 1 equiv of superoxide. Moreover, the presence of two isosbestic points demonstrated the absence of any long-lived intermediate (Figure 1). The reduction of $MnTPP^+$ to MnTPP was also observed upon addition of solid KO_2 to a DMSO solution of $MnTPP^+$. Thus the presence of crown ether was not required for this reaction to take place.

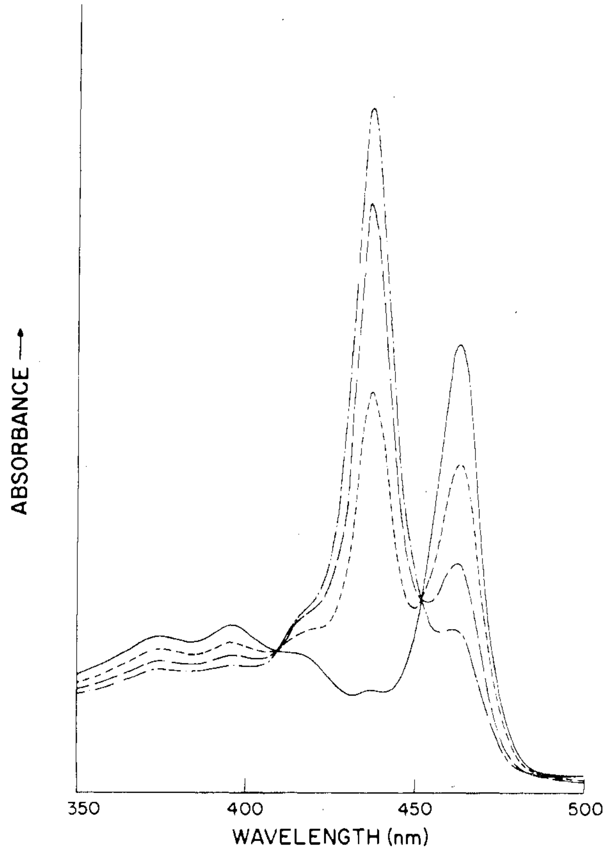

Figure 1. Titration of $MnTPP^+$ with O_2^- (see Experimental Section): (a) $MnTPP^+$ (–); (b) plus 0.005 ml of KO_2 solution (- - -); (c) plus another 0.005 ml of KO_2 solution (– –); (d) plus another 0.003 ml of KO_2 solution (– · –). The exact end point is is not shown because the 437-nm band starts to shift when 1 equiv is exceeded.

Addition of a second equivalent of superoxide resulted in some small but distinct spectral shifts. The Soret band moved from 437 to 446 nm with a new broad, weak band appearing at 398 nm. The α, β region was somewhat changed also with bands observed at 530, 572, and 614 nm. The spectral shifts observed upon addition of more than 1 equiv of O_2^- to $MnTPP^+$ could be duplicated by addition of O_2^- to solutions of MnTPP prepared by dissolution of MnTPP·2tol in DMSO.

We also investigated the reaction of MnTPP with O_2 in DMSO. Although toluene solutions of MnTPP and MnTPPpy reacted very rapidly with O_2 to give an unidentified manganese(III) porphyrin product,[7,8] in DMSO the reaction was considerably slower requiring 15–20 min for oxidation of a 10^{-4} M solution. Moreover the product had a visible absorption spectrum identical with that of $MnTPP^+$. The possibility that superoxide was a product of this oxidation ($MnTPP + O_2 \rightarrow MnTPP^+ + O_2^-$) was investigated by observation of the EPR spectra of oxidized solutions. The characteristic EPR spectrum of O_2^- is easily detected in DMSO[3] at concentrations $>10^{-5}$ M. Oxygenated solutions of MnTPP in DMSO at several concentrations (10^{-3}–10^{-5} M) gave no evidence of superoxide. A very small signal at $g = 2$ was observed, but its intensity was not related to the concentration of MnTPP. If it was due to superoxide, the concentration was $<10^{-5}$ M. In several samples, a faint signal developed identical with that obtained from solutions of free Mn^{2+} in DMSO implying that a small amount of demetalation of the porphyrin had occurred.

The stoichiometry of the oxygenation reaction was also investigated. Oxygenation of a 10^{-5} M solution of MnTPP in DMSO resulted in a visible spectrum identical with that of $MnTPP^+$ in DMSO. The resulting concentration of $MnTPP^+$ calculated from the absorption spectrum was 7.7 ×

10^{-6} M. The presence of two isosbestic points (identical with those observed in the superoxide reaction) throughout the oxygenation demonstrated that no stable porphyrin intermediates or by-products were present.

Discussion

Dioxygen is a very powerful four-electron oxidizing agent.[1] The one-electron reduction of O_2, however, is not a particularly favored reaction. The reduction potential for O_2 in DMSO[11] demonstrates this fact:

$$O_2 + e^- \rightarrow O_2^- \quad -0.73 \text{ V vs. SCE} \qquad (1)$$

Because dioxygen is a poor one-electron oxidizing reagent, superoxide is rarely found to be the product of oxidation of transition metal complexes by O_2. Instead it is more commonly found either that oxidations by O_2 require the presence of protons as in the case of several Cu(I) complexes[3,12] or that oxidation occurs through a two-electron step where dioxygen obtains two electrons at once either from one metal[13] or by forming a binuclear μ-peroxo species.[14]

Although the reduction of $MnTPP^+$ by superoxide in DMSO is quantitative, the oxygenation reaction of MnTPP in DMSO is clearly neither quantitative nor clean. Oxygenation of solutions of MnTPP in DMSO gives a 77% yield of $MnTPP^+$ and evidence for free Mn^{2+} (from EPR). There is no evidence for superoxide as a product nor for stable peroxo or μ-oxo intermediates. The results from the superoxide reaction allow us to rule out a one-electron oxidation resulting in the formation of superoxide. Thus the most likely mechanism is a two-electron oxidation occurring either through a μ-peroxo intermediate or a mononuclear peroxo intermediate such as $Mn^{IV}TPP(O_2^{2-})$.[8] Such peroxo species or peroxide, O_2^{2-}, itself are unlikely to be stable in DMSO since hydrogen peroxide, H_2O_2, reacts with DMSO.[15,16] It is also possible that some oxygenation of the porphyrin ligand is occurring perhaps catalyzed by MnTPP and resulting in the presence of free Mn^{2+}. This might occur in DMSO where the reaction with O_2 is slow and might not be observed in other solvents such as toluene where the oxidation is instantaneous at room temperature. In toluene, MnTPPpy is oxidized very rapidly by O_2 with the stoichiometry O_2:Mn = 1:4.[17] Unfortunately, we cannot study the superoxide reaction in toluene or benzene because superoxide is not stable enough in these solvents to allow quantitative studies.[18]

In conclusion, observation of the quantitative reduction of $MnTPP^+$ by O_2^- in DMSO provides information pertaining to the mechanism of oxidation of MnTPP by O_2 in the same solvent, a reaction that is itself difficult to study because of secondary reactions.

The product of the reaction of superoxide with MnTPP has not yet been identified. The possibility that this complex is $[Mn^{II}TPP(O_2^-)]^-$ or $[Mn^{III}TPP(O_2^{2-})]^-$ is under investigation.

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Registry No. $MnTPP^+$, 59388-92-0; MnTPP, 31004-82-7; O_2^-, 11062-77-4.

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Crystal Structure of Monoclinic Sulfur[1]

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Monoclinic sulfur is the form which is stable at normal pressure from 95 °C to the melting point (115 °C). Below 95 °C the orthorhombic form ("rhombic sulfur") is stable, but pure crystals of the metastable monoclinic form can be preserved for weeks at room temperature. Sands[2] determined the structure of the monoclinic crystals from photographic x-ray diffraction patterns and reported preliminary atomic coordinates, but the data were not accurate enough for good refinement.[3] In this paper we report more precise parameters, derived from diffractometer data, which confirm Sands' conclusion about the structure.

Experimental Section

Crystals of monoclinic sulfur were produced accidentally by Dr. R. Gradl in an attempt to make a substituted diethietene complex of uranium, and their identity was not recognized until one of them (a nine-faced crystal with dimensions about 0.3 × 0.3 × 0.2 mm mounted in a quartz capillary) was examined by x-ray diffraction. Unit cell dimensions were derived from the setting angles of 12 reflections (with $40° < 2\theta < 45°$) measured with a Picker FACS-I diffractometer with a graphite monochromator and Mo radiation (λ 0.709 26 Å for $K\alpha_1$). The same instrument was used to measure intensities using a θ–2θ scan technique with a scanning rate of 2°/min from 1° below 2θ for $K\alpha_1$ to 1° above 2θ for $K\alpha_2$. Background was counted for 4 s with an offset of 0.5° from each end of the scan. Three strong reflections (333, 060, $22\bar{4}$) checked at intervals of 200 measurements indicated no decay within the accuracy of the experiment.

Absorption corrections calculated by an analytical integration[4] ranged from 1.338 to 1.808. Their validity was verified by multiple measurements of several reflections at various azimuthal angles.

Measurements were made of 4577 reflections not excluded by the space group in the hemisphere $\pm h$, k, $\pm l$ and up to $2\theta = 50°$. These reflections represent 2254 unique reflections; for 1627, $F^2 > \sigma(F^2)$; and for 1140, $F^2 > 3\sigma(F^2)$.

Crystal Data. The space group is $P2_1/c$; at 24 °C, $a = 10.926$ (2), $b = 10.855$ (2), $c = 10.790$ (3) Å, $\beta = 95.92$ (2)°, $Z = 48$ atoms, $d_x = 2.008$ g cm^{-3}.

Determination of the Structure. The structure was solved with the MULTAN program,[5] to give an independent check of the previous work. With anisotropic thermal parameters (for the 16 atoms in the asymmetric unit) the full-matrix least-squares refinement reduced $R_2 = [\sum w(\Delta F)^2/\sum wF_o^2]^{1/2}$, the quantity minimized, to 0.030 and also $R_1 = \sum|\Delta F|/\sum|F_o|$ to 0.030 for 1140 reflections with $F^2 > 3\sigma(F^2)$. We used $\sigma^2(F^2) = s^2(F^2) + (0.035F^2)^2$; $s^2(F^2)$ is the variance of F^2 based on counting statistics or alternatively that based on the scatter of measurements of equivalent reflections when the latter exceeds 16 times the former. The factor 0.035 which reduced the effect of strong