line in the $g_{\parallel}$ region is apparent at S-band in comparison with X-band frequency. Thus, a decrease in the g strain at low frequencies may allow for increased resolution of the hyperfine structure and the detection of closely related cupric complexes.

With a secure understanding of the room-temperature ESR spectrum of $CuKTSM_2$ in hand, it was hoped that details of its interaction with cells could be extracted from an EPR analysis of this process. This seemed a particularly attractive experiment because previous work had indicated that $CuKTSM_2$ localizes in membrane.[15,19] Thus the complex might have the behavior of a membrane-bound spin label. However, in this case, the nature of the interaction was clear without extensive use of simulations from multiple-frequency data. At low concentration $CuKTSM_2$ is essentially immobilized in its association with the Ehrlich cell. The nature of the membrane reaction will require further study. Nevertheless, without the use of ambient-temperature ESR spectroscopy, this phenomenon would not have been discovered.

As the concentration of $CuKTSM_2$ is increased, an apparent end point for the immobilization reaction occurs and mobile $CuKTSM_2$ is noted. It is in this part of the titration that the complex also displays a concentration-dependent cytotoxicity toward the Ehrlich cell. Whether the completion of the immobilization reaction or the availability of mobile $CuKTSM_2$ is related to cytotoxicity has yet to be determined.

Registry No. CuKTS, 19976-05-7; $CuKSM_2$, 19976-18-2; CuKSM, 19976-16-0.

Contribution from the Department of Chemistry and Biochemistry
and Molecular Biology Institute, University of California, Los Angeles, Los Angeles, California 90024

Reactivity of the Peroxo Ligand in Metalloporphyrin Complexes. Reaction of Sulfur Dioxide with Iron and Titanium Porphyrin Peroxo Complexes To Give Sulfato Complexes or Sulfate

ANDREW R. MIKSZTAL and JOAN SELVERSTONE VALENTINE*

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The reaction of sulfur dioxide with metal-coordinated peroxide to give metal–sulfato complexes has been found in the past to be characteristic of a wide variety of group 8 metal complexes. Similar reactions with metalloporphyrin peroxo complexes have not been reported, however. The present paper describes an investigation of such reactions for three different types of metalloporphyrin peroxo complexes: $(TPP)Fe{-}O_2{-}Fe(TPP)$ (TPP = tetraphenylporphinato) (**1**), a μ-peroxo ferric porphyrin complex formed by reaction of FeTPP with dioxygen at low temperature; $TiP(O_2)$ (P = TPP or OEP; OEP = octaethylporphinato) (**2a,b**), mononuclear Ti(IV) porphyrin peroxo complexes formed by reaction of TiP(O) with hydrogen peroxide; and $FeP(O_2)^-$ (**3a,b**), mononuclear ferric porphyrin peroxo complexes formed by reaction of FeP with superoxide, O_2^-. In all three cases, sulfate was obtained as a product, in the form of sulfato complexes for **1** and **2** and in the form of free ionic sulfate for **3**.

Introduction

A number of metalloporphyrin complexes with peroxo ligands have been synthesized and characterized in recent years.[1-5] One of these, a mononuclear ferric porphyrin peroxo complex, was originally reported by us in 1978.[3a] We have been interested in characterizing this complex because it may be analogous to intermediates in reactions of heme-containing oxygenase enzymes such as cytochrome P_{450}.[6] Attempted oxidations of organic substrates typical of those oxygenated by the enzyme systems (i.e. olefins, hydrocarbons) have so far failed to show any pronounced reactivity of this peroxo complex. This observation is not surprising because the so-called "nucleophilic" group 8 metal–peroxo complexes of this type are not generally reactive toward such substrates.[6b] One reaction that is very characteristic of group 8 metal–peroxo complexes is that with sulfur dioxide, SO_2, to give metal–sulfato complexes.[7] In fact, we are not aware of any metal–peroxo complex of this type that fails to give sulfate when exposed to SO_2. It therefore appeared logical to us to study the reaction of some metalloporphyrin peroxo complexes with SO_2 in order to ascertain if these new types of peroxo complexes showed reactivity patterns similar to those of previously characterized group 8 peroxo complexes. Our results, described below, demonstrate that the metalloporphyrin peroxo

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(1) (a) Chin, D. H.; Del Gaudio, J.; La Mar, G. N.; Balch, A. L. *J. Am. Chem. Soc.* **1977**, *99*, 5486. (b) Chin, D. H.; La Mar, G. N.; Balch, A. L. *J. Am. Chem. Soc.* **1980**, *102*, 4344. (c) Chin, D. H.; La Mar, G. N.; Balch, A. L. *J. Am. Chem. Soc.* **1980**, *102*, 5945.

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(4) (a) Chevrier, B.; Diebold, Th.; Weiss, R. *Inorg. Chim. Acta* **1976**, *19*, L57. (b) Ledon, H.; Bonnet, M.; Lallemand, J. Y. *J. Chem. Soc., Chem. Commun.* **1979**, 702. (c) Kadish, K. M.; Chang, D.; Malinski, T.; Ledon, H. *Inorg. Chem.* **1983**, *22*, 3490.

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Table I. Vibrational Frequencies Assigned to Sulfate in Ionic Sulfate and Various Sulfato Complexes

compd	mode of coordination	ν_1	ν_2	ν_3	ν_4	ref
SO_4^{2-} ion				1104	613	24
$[Co(NH_3)_5(SO_4)]Br$	unidentate	970	438	1130 1038	645 605	27
$[(NH_3)_3Co(SO_4)_2(OH)Co(NH_3)_3]Cl$	bridging bidentate	966		1180 1101 1048	645 598	28
$[(NH_3)_4Co(SO_4)(NH_2)Co(NH_3)_4](NO_3)_3$	bridging bidentate	995	462	1170 1105 1055	641 610 571	27
$Pd(PPh_3)_2SO_4$	chelating bidentate	920		1265 1155 1110		29
$Ir(PPh_3)_2(CO)I(SO_4)$	chelating bidentate	856	549	1296 1172 880	662 610	30
5a		860	555	1325 1182 985	685 665	
5b		855	560	1318 1180 914	690 672	

complexes do have this characteristic reactivity, i.e. that they react with SO_2 to give sulfate.

Experimental Section

All manipulations and reactions were performed under He in a Vacuum Atmospheres glovebox ($O_2 < 1$ ppm) or in Schlenk glassware. FeTPP(Cl)[8,9] and FeOEP(Cl)[10] were prepared by literature methods. The ferrous porphyrins were prepared by reducing the corresponding ferric porphyrin with Zn(Hg).[11] TiTPP(O_2) and TiOEP(O_2) were generous gifts from Dr. Jean-Marc Latour.[2] TiOEP(O) and TiTPP(O) were prepared by literature methods.[12] Tetramethylammonium superoxide was prepared by literature methods; analyzed superoxide content was >95%.[13] Tetrahydrofuran (Mallinckrodt, reagent grade) and toluene (Mallinckrodt, reagent grade) were refluxed and distilled from Na/benzophenone and stored over 4-Å molecular sieves. Dichloromethane (Mallinckrodt, reagent grade) was distilled from calcium hydride and stored over 4-Å molecular sieves. Sulfur dioxide (Matheson, 99.9% purity) and dioxygen (Liquid Carbonic, technical grade) were passed through Aquasorb columns (Mallinckrodt) to remove residual moisture.

Visible spectra were recorded in 0.1-mm or 0.1-cm path length quartz cells on a Beckman UV 5270 spectrophotometer. Infrared spectra were recorded on a Beckman IR 4260 spectrophotometer. IR samples were prepared in the glovebox as Nujol mulls between KBr windows and calibrated with polystyrene. The IR data were collected and stored in a Digital Minc-11 computer. Electron spin resonance spectra were recorded on a Varian E-9 instrument at 77 K using a low-temperature Dewar. The magnetic field was calibrated with an NMR gaussmeter, and g values were determined from the DPPH reference signal. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

Preparation of (TPP)Fe–O_2–Fe(TPP) and Reaction with SO_2. Dioxygen was bubbled for 10 min through a 3 mM solution of FeTPP in toluene at −77 °C to form (TPP)Fe–O_2–Fe(TPP) (**1**).[1] The formation of **1** was confirmed by examination of the visible spectrum at the same temperature. SO_2 was bubbled into the solution for 10 min, resulting in a color change from scarlet red to brown. The solution was allowed to warm to room temperature, and a 0.3-mL aliquot was transferred into an ESR tube. The remaining solution was evaporated to dryness in vacuo to remove the excess SO_2 and further heated to 80 °C for 1 h. The visible, IR, and ESR spectra were identical with those of a sample of (TPP)Fe–SO_4–Fe(TPP) (**4**), prepared by the method of Phillippi et al. from (TPP)Fe–O–Fe(TPP) and H_2SO_4.[14a] The visible spectrum of **4** in CH_2Cl_2 showed absorbances with λ_{max} = 347, 372, 407, 508, 574, 652, and 682 nm. The IR spectrum of **4** showed non-porphyrin bands at 1277, 1138, 912, and 880 cm^{-1}, which are assigned to sulfate. The ESR spectrum of **4** in toluene at 77 K gave no observable signals.

Reactions of TiP(O_2) with SO_2. SO_2 was bubbled for 30 min through 10 mL of a 1 mM solution of TiOEP(O_2) (**2b**) in toluene, causing the cherry red solution to turn brown. The vessel was evacuated for 2 min to remove excess SO_2 from the solution. Heptane (15 mL) was layered on top of the toluene solution. After 2 days at room temperature, microcrystals had formed, which were collected by filtration and were washed five times with 1-mL portions of heptane. The moisture-sensitive solid was dried in vacuo for 2 days. The visible spectrum of the solid dissolved in toluene had bands at 388 (sh), 407, 538, and 574 nm. The IR spectrum of the reaction product had numerous non-porphyrin bands that are assignable to sulfate (see Table I). Elemental analysis was consistent with the formulation TiOEP(SO_4)·tol (**5b**). Anal. Calcd for $TiC_{43}H_{52}N_4O_4S$: C, 67.18; H, 6.82; N, 7.29; S, 4.16. Found: C, 66.25; H, 7.11; N, 6.98; S, 4.15.

TiTPP(SO_4) (**5a**) was prepared in a similar manner by reacting TiTPP(O_2) with SO_2. Infrared bands assigned to sulfate are listed in Table I.

Preparation of FeP(O_2)$^-$ and Reaction with SO_2. FeTPP (25 mg, 0.014 mmol) was stirred with tetramethylammonium superoxide, (TMA)O_2 (75 mg, 0.28 mmol), for 4–5 h in 7 mL of THF. Unreacted (TMA)O_2 was removed by filtration. Complete formation of FeTPP(O_2)$^-$ (**3a**) was confirmed by visible and ESR spectroscopy. The visible spectrum of **3a** in THF was essentially identical with that of **3a** in Me_2SO, with bands at 434, 546 (sh), 564, 592 (sh), and 608 nm.[3b] The ESR spectrum of a 1.5 mM solution of **3a** in THF at 77 K showed a large narrow signal at g = 4.3 and weak signals at g = 2 and 8, indicative of a rhombic, high-spin, ferric porphyrin complex.[3a,b] The ESR spectrum of the filtered product also established that no free superoxide was present.[15]

Sulfur dioxide was bubbled through a 2 mM solution of FeTPP(O_2)$^-$ in THF for 1 h at room temperature. The exothermic heat of solvation of SO_2 in THF required that the solution be occasionally cooled in ice water to maintain the temperature near 25 °C. The immediate

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(8) Abbreviations: P = Dianion of porphyrin (OEP or TPP); THF, tetrahydrofuran; Me_2SO, dimethyl sulfoxide; DPPH, α,α-diphenyl-β-picrylhydrazyl; TMA, tetramethylammonium cation; (TMA)O_2, tetramethylammonium superoxide.

(9) FeTPP(Cl) was prepared by metalating chlorin-free *meso*-tetraphenylporphyrin (Midcentury Chemicals) by the method of: Adler, A. D.; Longo, F. R.; Kampas, F.; Kim, J. *J. Inorg. Nucl. Chem.* **1970**, *32*, 2443.

(10) FeOEP(Cl) was prepared by metalating octaethylporphyrin (Midcentury Chemicals) by the method of: Dolphin, D.; Sams, J. R.; Tsin, T. B.; Wong, K. L. *J. Am. Chem. Soc.* **1976**, *98*, 6970.

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(12) Fournari, P.; Guilard, R.; Fontesse, M.; Latour, J. M.; Marchon, J. C. *J. Organomet. Chem.* **1976**, *110*, 205.

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(14) (a) Phillippi, M. A.; Baenziger, N.; Goff, H. M. *Inorg. Chem.* **1981**, *20*, 3904. (b) Scheidt, W. R.; Lee, Y. J.; Bartzcak, T.; Hatano, K. *Inorg. Chem.* **1984**, *23*, 2552.

(15) Free superoxide ion in aprotic solvents has a characteristic ESR spectrum with signals at g = 2.11, 2.00: Sawyer, D. T.; Valentine, J. S. *Acc. Chem. Res.* **1981**, *14*, 393.

formation of precipitate was accompanied by a color change of the solution from green-brown to deep green. Excess SO_2 was removed by evaporating the mixture to dryness in vacuo and then heating the residue to 120 °C for 1 h. The dried products were redissolved in toluene, leaving an insoluble yellow residue, which was removed by filtration. The yellow solid was washed five times with 3-ml portions of toluene and dried in vacuo. A standard qualitative test for sulfate was performed on the yellow solid by reacting it with $BaCl_2$ under acidic aqueous conditions.[16] A white precipitate of $BaSO_4$ confirmed the presence of sulfate in the solid. An IR spectrum of this white precipitate was identical with that of an authentic sample of $BaSO_4$. The presence of the tetramethylammonium cation was observed in the IR spectrum of the yellow solid (3020 (s), 1490 (s), 950 cm^{-1} (m)). Elemental analysis of the yellow solid also confirmed the presence of tetramethylammonium cation and sulfate ion.[17]

A control experiment was carried out by reacting SO_2 with FeTPP(Cl) in THF. No precipitate was observed during the SO_2 addition. The workup was identical with that of analyzing the SO_2 plus peroxo complex reaction products. The only bands in the IR spectrum of the control reaction products were those due to FeTPP(Cl). The visible spectrum also indicated that FeTPP(Cl) did not react with SO_2.

$FeOEP(O_2)^-$ (**3b**) was prepared in a fashion similar to that used to prepare **3a** but starting with FeOEP. The visible absorption spectrum of **3b** in THF showed bands at 422, 528 (sh), 546, 572, and 585 (sh) nm. The ESR spectrum of a 1 mM solution of **3b** in THF at 77 K was identical with that of **3a**, with weak signals at $g = 2$ and 8 and a large narrow signal at $g = 4.3$. Reaction with SO_2 led to the formation of a similar yellow precipitate.

Results and Discussion

Reaction of the μ-Peroxo Ferric Porphyrin Complex with SO_2. Characterization of a binuclear μ-peroxo ferric porphyrin complex was first reported by Balch, La Mar, and co-workers as one aspect of their study of the mechanism of oxidation of ferrous porphyrins by dioxygen.[1a] They found that the reaction of O_2 with ferrous tetra-*m*-tolylporphyrin (T-*m*-TP) in toluene at low temperatures proceeded through several intermediates before the final product, (T-*m*-TP)Fe–O–Fe(T-*m*-TP), was formed. The proposed mechanism is summarized in Scheme I.

Scheme I

$$(\text{T-}m\text{-TP})\text{Fe}^{\text{II}} + \text{O}_2 \rightarrow (\text{T-}m\text{-TP})\text{FeO}_2$$

$$(\text{T-}m\text{-TP})\text{FeO}_2 + (\text{T-}m\text{-TP})\text{Fe}^{\text{II}} \rightarrow (\text{T-}m\text{-TP})\text{Fe}^{\text{III}}\text{–O–O–Fe}^{\text{III}}(\text{T-}m\text{-TP})$$

$$(\text{T-}m\text{-TP})\text{Fe}^{\text{III}}\text{–O–O–Fe}^{\text{III}}(\text{T-}m\text{-TP}) \rightarrow 2(\text{T-}m\text{-TP})\text{Fe}^{\text{IV}}\text{O}$$

$$(\text{T-}m\text{-TP})\text{Fe}^{\text{IV}}\text{O} + (\text{T-}m\text{-TP})\text{Fe}^{\text{III}}\text{–O–O–Fe}^{\text{III}}(\text{T-}m\text{-TP}) \rightarrow (\text{T-}m\text{-TP})\text{Fe}^{\text{III}}\text{–O–Fe}^{\text{III}}(\text{T-}m\text{-TP}) + (\text{T-}m\text{-TP})\text{FeO}_2$$

$$(\text{T-}m\text{-TP})\text{Fe}^{\text{IV}}\text{O} + (\text{T-}m\text{-TP})\text{Fe}^{\text{II}}\text{O}_2 \rightarrow (\text{T-}m\text{-TP})\text{Fe}^{\text{III}}\text{–O–Fe}^{\text{III}}(\text{T-}m\text{-TP}) + \text{O}_2$$

The μ-peroxo ferric porphyrin complex, was found to be stable at −80 °C for over 2 weeks. It was characterized by proton NMR and visible spectroscopy. As it was warmed to room temperature, it was observed to disappear, giving the μ-oxo dimer as the final product. Our intention was to determine if the μ-peroxo ferric porphyrin complex would react with SO_2.

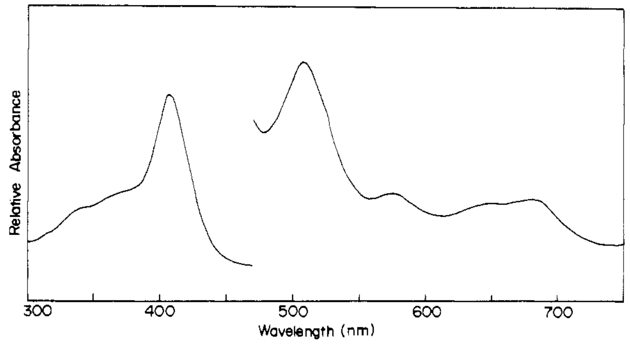


Figure 1. Visible absorption spectrum of **4** in CH_2Cl_2.

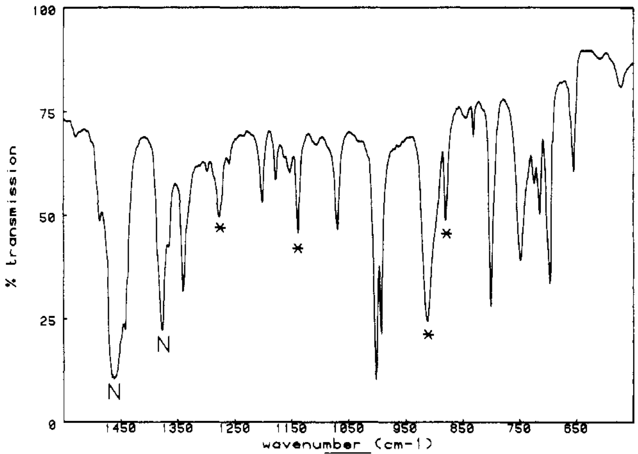
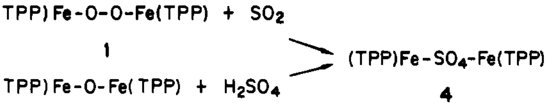
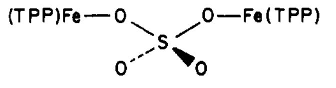


Figure 2. Infrared spectrum of a Nujol mull of **4**. The four bands labeled with an asterisk are assigned to sulfate. The two bands labeled N are due to Nujol.

The μ-peroxo ferric porphyrin complex was prepared by bubbling dioxygen through a 3 mM solution of FeTPP in toluene at −77 °C for 10 min. Addition of a gentle stream of SO_2 at −77 °C for 10 min caused the scarlet red solution to turn brown. The resulting product was found to have visible, IR, and ESR spectral properties identical with those of (TPP)Fe–(SO_4)–Fe(TPP), which we prepared by the method of Phillippi et al. by reaction of (TPP)Fe–O–Fe(TPP) with sulfuric acid in CH_2Cl_2.[14a]



Goff characterized **4** by elemental analysis and IR, visible, NMR, and ESR spectroscopy.[14a] An X-ray crystal structural study of this complex carried out by Scheidt and co-workers[14b] revealed that the bridging sulfate is bound in a monodentate fashion to each of the two iron porphyrins, i.e.



The visible spectrum of the reaction product obtained by reaction of **1** and SO_2 in CH_2Cl_2 is shown in Figure 1. The band positions and extinction coefficients are identical with those for **4** as reported by Goff.[14a] The region from 450 to 750 nm is similar to the spectra of other high-spin ferric porphyrin complexes.[18] The position of the Soret band at 407 nm is reminiscent of the Soret band of (TPP)Fe–O–Fe(TPP),

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[16] Sorum, C. H. "Introduction to Semimicro Qualitative Analysis"; Prentice-Hall: Englewood Cliffs, NJ, 1967; p 236.

[17] Anal. Found for the unpurified yellow solid: C, 36.30; H, 7.15; N, 8.56; S, 13.43; Fe, 1.75. The TMA cation is $C_4H_{12}N^+$. The C:H:N ratio found for the yellow solid is 4.9:11.8:1. We believe that the yellow solid is predominantly $(TMA)_2SO_4$ but that it contains in addition some $(TMA)_2S_2O_7$ (or other higher polysulfates). This conclusions is based on our observation that the IR spectrum of the yellow solid has some bands characteristic of $S_2O_7^{2-}$, in addition to those assigned to sulfate. These non-sulfate bands disappear and the sulfate bands increase when the solid is treated with water, as would be expected for a polysulfate. See: (a) Walrafen, G. E.; Irish, D. E.; Young, T. F.; *J. Chem. Phys.* **1962**, *37*, 662. (b) Brown, R. G.; Ross, S. D. *Spectrochim. Acta, Part A* **1972**, *28A*, 1263.

[18] (a) Buchler, J. W. "Porphyrins and Metalloporphyrins"; Smith, K. M., Ed.; Elsevier: Amsterdam, 1975; Chapter 5. (b) Gouterman, M. "The Porphyrins"; Dolphin, D., Ed., Academic Press: New York, 1978; Vol. 3, Chapter 1.

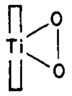
which is blue shifted relative to monomeric ferric porphyrin complexes. This blue shift is thought to be characteristic of metalloporphyrin dimers in which the porphyrin rings are parallel and close to each other.[19]

The IR spectrum of **4** obtained from the SO_2 reaction, shown in Figure 2, has non-porphyrin bands at 1277, 1138, 912, and 880 cm^{-1}. The remaining IR bands are all assignable to the porphyrin ligand and are very similar to those of FeTPP(Cl). The absence of bands at 890 and 870 cm^{-1} indicates that (TPP)Fe–O–Fe(TPP) was not present.[20]

The ESR spectrum at 77 K of a 1.5 mM solution of the reaction product in toluene showed no observable signals. Phillippi et al.[14a] also reported that 2 mM solutions of **4** prepared by the sulfuric acid route in CH_2Cl_2/toluene are ESR silent at 77 K. Apparently, the proximity of the two high-spin ferric centers leads to short electronic relaxation times.[14a]

We also found that we could prepare **4** simply by adding dioxygen to a solution of FeTPP saturated with SO_2 at room temperature, indicating that, even at room temperature, the μ-peroxo complex can be trapped by SO_2 prior to its dissociation to give (TPP)Fe^{IV}O. We conclude from our studies described above that SO_2 will react with the μ-peroxo ferric porphyrin complex, **1**, to form a μ-sulfato product. This is the first known chemical reaction of the μ-peroxo ferric porphyrin complex that oxidizes a substrate without prior dissociation of the O–O bond. The reaction is reminiscent of a similar reaction of a μ-peroxo Co(III) complex, $(en)_2Co(O_2)(NH_2)Co(en)_2^{3+}$, with SO_2 to give the corresponding μ-sulfato complex, $(en)_2Co(SO_4)(NH_2)Co(en)_2^{3+}$.[21]

Reactions of Mononuclear Titanium Porphyrin Peroxo Complexes with SO_2. The best characterized mononuclear metalloporphyrin peroxo complexes are $TiTPP(O_2)$ (**2a**) and $TiOEP(O_2)$ (**2b**).[2] The crystal structure of **2b** shows that the peroxo ligand is bound in a triangular fashion:



The two Ti–O bond lengths are 1.827 (4) and 1.822 (4) Å, and Ti lies 0.620 (6) Å out of the mean plane of the four pyrrole nitrogens toward the oxygens. The O–O bond distance is 1.445 (5) Å, close to the O–O bond length in sodium peroxide (1.49 Å) and other peroxide complexes. The IR spectrum of **2a** shows an O–O stretch at 895 cm^{-1}, characteristic of peroxide complexes,[7] that shifts to 857 cm^{-1} with $^{18}O_2$ substitution. All of this evidence establishes that the dioxygen ligand is in the reduced form of peroxide.

The reaction of SO_2 with $TiOEP(O_2)$ leads to a new product as seen in its visible spectrum. The α band for $TiOEP(O_2)$ is split into to bands at 567 and 576 nm while the β band at 535 has a shoulder at 522 nm. This splitting of the α and β bands is similar to that observed for $FeP(O_2)^-$ [3a,b] and may be due to a lowering of the symmetry of the complex by bidentate bonding of the peroxide ligand. The visible spectrum after reaction with SO_2 is quite different. The α and β absorption bands of the product, **5b**, have maxima at 574 and 538 nm, respectively. They are very symmetrical bands without any shoulders and have lower extinction coefficients than the α and β bands in the peroxo species. The corresponding oxo complex, TiOEP(O), has absorption bands at 573 and 536 nm, but the bands have a different shape. The visible spectrum of a toluene solution of the sulfato complex, **5b**, rapidly changed to that of TiOEP(O) upon exposure to the atmosphere. We conclude from that observation that the sulfate complex is readily hydrolyzed by the moisture in the air, forming H_2SO_4 and TiOEP(O).[22]

A study of the IR spectra of the reaction product **5b** revealed that the band at 890 cm^{-1} due to the peroxo stretch in $TiOEP(O_2)$ as well as the bands at 590 and 635 cm^{-1} that are assigned to the Ti–O symmetric and asymmetric stretches, respectively, had disappeared. In addition, no band at 970 cm^{-1} was present, indicating that the TiOEP(O) complex had not been formed. As can be seen from examination of Table I, the new bands in the IR spectra of the reaction product **5b** are very similar to those of other metal sulfato complexes.

Free sulfate ion has tetrahedral symmetry. It has four fundamental vibrations, of which only ν_3 and ν_4 are IR active. When the sulfate ion is coordinated to a metal, its IR spectrum changes drastically.[23] When the sulfate ligand is bound in a monodentate fashion, its symmetry is lowered to C_{3v}. In such complexes, ν_3 and ν_4 are split into two bands each and both ν_1 and ν_2 appear with medium intensity. When sulfate acts as a bidentate ligand, its symmetry is lowered further to C_{2v}. In such cases, ν_3 and ν_4 are split into three bands each while ν_1 and ν_2 still appear with medium intensity.

Sulfate can act bidentately as either a chelating ligand bound to one metal ion or a bridging ligand bound to two metal ions. Bridging and chelating bidentate sulfato complexes can generally be distinguished on the basis of their IR spectra because chelating bidentate sulfato complexes have ν_3 vibrations at higher energies than that of bridging sulfato complexes.[23] Table I lists the vibrational frequencies of various sulfato complexes along with their modes of coordination.

In the IR spectrum of $TiOEP(SO_4)$ (**5b**) the ν_3 vibrations lie at 1318, 1180, and 914 cm^{-1}. A comparison with the other sulfato complexes in Table I indicates that these vibrations lie at rather high energies for ν_3 vibrations and therefore suggests that sulfate binds to titanium in a chelating bidentate manner.

The reaction between SO_2 and $TiTPP(O_2)$ (**2a**) proceeded in a fashion similar to that described for **2b**. New bands in the IR spectrum of $TiTPP(SO_4)$ (**5a**) are listed in Table I. These new bands are very similar to those of **5b**, suggesting that sulfate is coordinated similarly in both complexes.

The bands at 570 and 615 cm^{-1} in the IR spectrum of **5b** and at 572 and 610 cm^{-1} in the spectrum of **5a** are tentatively assigned to Ti–O symmetric and asymmetric stretches. They provide further evidence for the bidentate mode of binding of sulfate to titanium. These vibrations are at lower frequencies than the Ti–O stretches in the corresponding titanium peroxo complexes.

Reactions of Mononuclear Ferric Porphyrin Peroxo Complexes with SO_2. Initial studies of the reaction of SO_2 with $FeTPP(O_2)^-$ (**3a**) were carried out in Me_2SO but were found to be complicated by apparent side reactions of Me_2SO itself with the reaction products. Subsequent experiments were therefore carried out in THF. $FeTPP(O_2)^-$ (**3a**) and $FeOEP(O_2)^-$ (**3b**) were cleanly prepared in THF by stirring excess $(TMA)O_2$ with FeP for several hours and then filtering off unreacted $(TMA)O_2$.

During the reaction of SO_2 with **3a**, the solution changed from green-brown to deep green and a solid precipitated out of solution. This yellow solid was separated by filtration,

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[20] Phillippi et al.[14] reported the sulfate stretches for (TPP)Fe–SO_4–Fe(TPP) at 1282, 1145, 922, and 890 cm^{-1}. When we prepared **4** by their method, we found the sulfate bands positioned at 1276, 1138, 913, and 881 cm^{-1}.

[21] Garbett, K.; Gillard, R. D. *J. Chem. Soc. A* **1968**, 1725.

[22] It was previously observed that solutions of $TiTPP(F)_2$, $TiTPP(Cl)_2$, and $TiTPP(Br)_2$ in dichloromethane are readily hydrolyzed by traces of residual water ($TiTPP(X)_2 + H_2O \rightarrow TiTPP(O) + 2HX$): Nakajima, M.; Latour, J. M.; Marchon, J. C. *J. Chem. Soc, Chem. Commun.* **1977**, 763.

[23] Nakamoto, K. "Infrared and Raman Spectra of Inorganic and Coordination Compounds", 3rd ed.; Wiley: New York, 1978; p 239.

washed with toluene, and dried. The solid was dissolved in water, the solution filtered and then evaporated to dryness, and the residue dried in vacuo. The IR spectrum of the grayish solid had strong bands at 1115 and 612 cm^{-1}. Free sulfate has bands at 1110 and 615 cm^{-1}.[24] The IR spectrum also showed the presence of the TMA cation with bands at 3020, 1490, and 950 cm^{-1}. These three bands are common to all the TMA salts of Cl^-, Br^-, I^-, OH^-, O_2^-, and OAc^-. The remaining solid was further analyzed by reaction with $BaCl_2$ and gave a positive test for sulfate ion (see Experimental Section).

The visible spectrum of the soluble reaction products after removal of the precipitate indicated that the initial ferric porphyrin peroxo complex had disappeared and a new porphyrin species with visible bands at 415, 575, and 615 (sh) was formed. This new species was identified as FeTPP(OH) by comparison of its visible spectrum with that of a solution prepared by reaction of FeTPP(Cl) with OH^- in THF.[25] While the yield of sulfate recovered from the yellow solid produced in this reaction was 60–70% of the theoretical yield, the yield of FeTPP(OH) calculated from the visible absorption spectrum was only 40–50%. Thin-layer chromatography in CH_2Cl_2 established that only one iron porphyrin species was present. These results indicate that the reaction of the peroxo complex with SO_2 results not only in a high yield of sulfate ion but also in substantial degradation of the porphyrin ligand. This degradation occurs very rapidly upon exposure of the peroxo complex to SO_2, as judged by the immediate partial bleaching of the solution. The mechanism of this observed porphyrin degradation is not understood. Possibly the initial reaction of SO_2 with the peroxo ligand forms a reactive peroxide-containing intermediate, that attacks the porphyrin ligand.[26]

The reaction of $FeOEP(O_2)^-$ with SO_2 produced similar results. The evidence described above demonstrates that SO_2 reacted with the mononuclear ferric porphyrin peroxo complexes to produce sulfate, which precipitated out of solution as a TMA salt, and FeP(OH), but that in addition a substantial fraction of the starting porphyrin complex was degraded to a nonchromophoric material. Difficulties in scaling up the preparation of the highly unstable starting peroxo complexes, **3a,b**, prevented us from identifying the degradation products.

Conclusions. Reactions of three different types of peroxo complexes with SO_2 have resulted in the production of sulfate complexes or free ionic sulfate. These results support our hypothesis that this type of reactivity is a general property of peroxo complexes and, furthermore, suggest that these peroxide complexes may have properties similar to those of other known non-porphyrin peroxide complexes. The unusual porphyrin degradation that was observed when the mononuclear ferric porphyrin peroxo complex was reacted with SO_2 may provide a clue to the mode of activation of dioxygen when bound to iron porphyrins in oxygenase enzyme intermediates. Continuing experiments are planned to elucidate the reactivity of the peroxide ligand in such complexes.

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Registry No. 1, 73146-62-0; **2b**, 60217-35-8; **3a**, 83160-26-3; **3b**, 91711-52-3; **4**, 72895-19-3; **5a**, 91687-02-4; $TiTPP(O_2)$, 65651-28-7; FeTPP, 16591-56-3; FeOEP, 61085-06-1; $TiOEP(SO_4)$, 91687-03-5; FeTPP(OH), 25482-26-2; O_2^{2-}, 14915-07-2; SO_2, 7446-09-5; SO_4^{2-}, 14808-79-8.

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