

Rearrangement 3 would appear to be catalyzed by metal surfaces.

The stabilizing action of molecular oxygen presumably results from its reaction with atoms and free radicals to produce less reactive peroxy species. The role of oxygen in enhancing the yield of methyl fluoroformate is not clear. It may have the effect of stabilizing the acetate radical, allowing more time for rearrangement 3 to take place.

The analogous decomposition of trifluoroacetyl hypofluorite to  $\text{CF}_4$  and  $\text{CO}_2$  has also been found to be catalyzed by metal and inhibited by oxygen.<sup>17</sup> Hexafluoroethane is a minor product of this decomposition, though trifluoromethyl fluoroformate is not. However, carbonyl fluoride is formed. It may be that in the trifluoroacetyl system, the reaction analogous to reaction 5 produces two molecules of  $\text{COF}_2$  instead of a molecule of  $\text{F}_3\text{COC}(\text{O})\text{F}$ .

The authors of the first report on acetyl hypofluorite took special note of the fact that it was the only hypofluorite to contain an unfluorinated alkyl radical.<sup>4a</sup> Indeed, aside from HOF itself, it is the only hypofluorite that contains hydrogen. This fact, however, appears to be of considerably less significance for acetyl hypofluorite than for HOF. Decomposition of HOF proceeds with elimination of  $\text{O}_2$  and formation of HF;<sup>18</sup> the analogous decomposition of acetyl hypofluorite to HF,  $\text{CO}_2$ , and  $\text{C}_2\text{H}_4$  does not take place. The decomposition of acetyl hypofluorite appears to be closely analogous to that of trifluoroacetyl hypofluorite, and at least to a first approximation, there is no reason to expect their stabilities to be grossly different. In fact, the two compounds do appear to be of very roughly comparable stability.

In view of its instability, the isolation of acetyl hypofluorite may be of only limited significance for its use as a synthetic reagent.

For such applications, it would appear safest to continue to use the compound without isolation, either by addition of substrate to a dilute solution of the reagent or by carrying the reagent with a gas stream into a solution of a substrate. In the latter case, our observations indicate that it will be advantageous to use oxygen rather than nitrogen as a carrier.

Finally, it seems worthwhile to note that hazards may exist even if the acetyl hypofluorite is not explicitly isolated. Fluorination of acetates in Freon at low temperatures can, at least in principle, produce dangerously high concentrations of acetyl hypofluorite, and delivery of acetyl hypofluorite in a gas stream into a cold reaction medium can lead to condensation of the reagent. An explosion resulting from the latter conditions has already been reported.<sup>19</sup>

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**Registry No.**  $\text{F}_2$ , 7782-41-4;  $\text{O}_2$ , 7782-44-7; KOAc, 127-08-2; HOAc, 64-19-7; AcF, 557-99-3; FC(O)OMe, 1538-06-3; acetyl hypofluorite, 78948-09-1.

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(19) Adam, M. J. *Chem. Eng. News* **1985**, *63* (No. 7), 2.

## Effect of Thiolate vs. Nitrogen-Base Ligands on $\text{O}_2$ Stretching Frequencies of (Oxytetraphenylporphyrinato)cobalt

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**Abstract:** The resonance Raman spectra of model compounds of oxycytochrome P-450,  $\text{K}^{\text{Cr}}[\text{Co}(\text{TPP})(\text{SC}_6\text{H}_5)^{16}\text{O}_2]$  ( $\text{K}^{\text{Cr}}$ : potassium 18-crown-6 ether) and its  $^{18}\text{O}_2$  analogue were located at 1122 and 1058  $\text{cm}^{-1}$ , respectively, in  $\text{CH}_2\text{Cl}_2$  solution at  $\sim 185$  K with 457.9-nm excitation. The  $\nu(^{16}\text{O}_2)$  of this compound is lower by 22  $\text{cm}^{-1}$  than that of a model compound of oxyhemoglobin,  $\text{Co}(\text{TPP})(1\text{-MeIm})^{16}\text{O}_2$  (1144  $\text{cm}^{-1}$ ), measured under similar conditions. The observed shift has been attributed to the presence of lone-pair electrons on the thiolate sulfur atom which donate extra electron density to dioxygen via  $\pi$  overlap. The  $\nu(\text{O}_2)$  of  $\text{K}^{\text{Cr}}[\text{Co}(\text{TPP})(\text{SCH}_2\text{C}_6\text{H}_5)^{16}\text{O}_2]$  and its  $^{18}\text{O}_2$  analogue are observed at 1120 and 1055  $\text{cm}^{-1}$ , respectively, by 476.5-nm excitation. The small shift of  $\nu(\text{O}_2)$  observed by replacing the  $\text{SC}_6\text{H}_5^-$  with  $\text{SCH}_2\text{C}_6\text{H}_5^-$  ion indicates that the degree of total electron donation to dioxygen via  $\sigma$  and  $\pi$  overlap is similar for these two compounds. When a  $\text{CH}_2\text{Cl}_2$  solution of crystalline  $\text{K}^{\text{Cr}}[\text{Co}(\text{TPP})(\text{SC}_6\text{H}_5)](\text{HSC}_6\text{H}_5)$  is saturated with dioxygen at  $\sim 185$  K and warmed to  $\sim 225$  K, a new  $\nu(\text{O}_2)$  band appears at 1137  $\text{cm}^{-1}$  which is assigned to  $[\text{Co}(\text{TPP})(\text{HSC}_6\text{H}_5)\text{O}_2]$ . The electronic spectrum of  $\text{K}^{\text{Cr}}[\text{Co}(\text{TPP})(\text{SC}_6\text{H}_5)\text{O}_2]$  in  $\text{CH}_2\text{Cl}_2$  solution exhibits the  $\alpha$  and  $\beta$  bands at 620 and 522 nm, respectively, and a split Soret band at 468 and 423 nm. The excitation profile of the  $\nu(\text{O}_2)$  (1122  $\text{cm}^{-1}$ ) suggests that the 468-nm component contains substantial Co-O $_2$  character.

It is generally recognized that the active site of oxycytochrome P-450 during the reaction cycle<sup>1</sup> is a six-coordinate iron protoporphyrin (low spin) in which dioxygen is coordinated trans to the thiolate sulfur of a cysteinyl residue (structure I). This



(1) For example, see: Alexander, L. S.; Goff, H. M. *J. Chem. Educ.* **1982**, *59*, 179.

structure is similar to that of oxyhemoglobin (low spin) except that the group trans to its dioxygen in oxyhemoglobin is the imidazole nitrogen of the proximal histidine (structure II). In cytochrome P-450, the O-O bond is cleaved after one-electron reduction by NADH, and the activated oxygen thus produced or released from the ferryl (FeO) bond is utilized for hydroxylation of a substrate.<sup>2</sup> On the other hand, hemoglobin binds dioxygen reversibly without the O-O bond cleavage. It is, therefore, of great interest to compare the effect of these two axial ligands on the bound dioxygen.

(2) Groves, J. T.; McClusky, G. A. "Biochemical and Clinical Aspects of Oxygen"; Caughey, W. S., Ed.; Academic Press: New York, 1979; p 277.

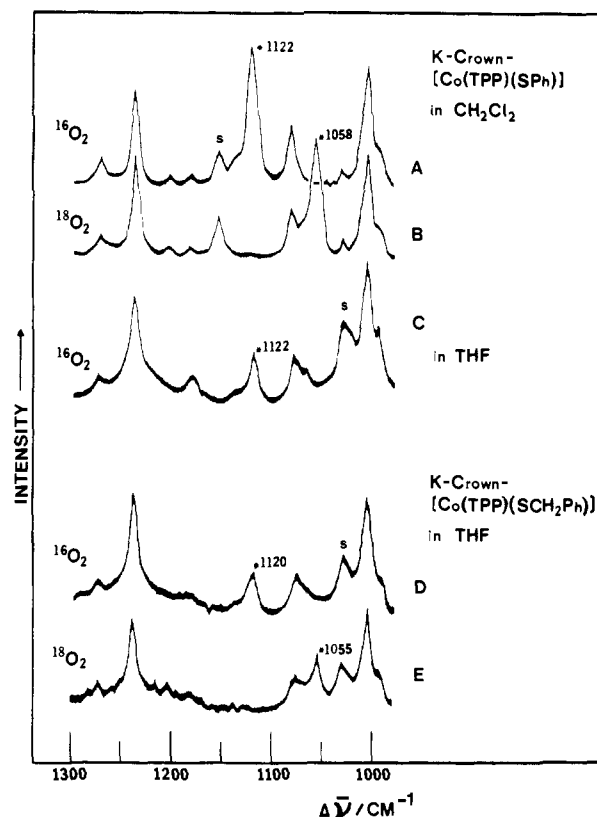
In 1979, Caughey et al.<sup>3</sup> observed two  $\text{O}_2$  stretching bands ( $\nu(\text{O}_2)$ ) at 1155 and 1107  $\text{cm}^{-1}$  for oxyhemoglobin by using IR difference techniques and attributed this splitting to Fermi resonance between the  $\nu(\text{O}_2)$  ( $\sim 1130 \text{ cm}^{-1}$ ) and the first overtone of the  $\nu(\text{Fe}-\text{O}_2)$  at 567  $\text{cm}^{-1}$ . However, their interpretation was questioned by Tsubaki and Yu<sup>4</sup> based on resonance Raman (RR) studies of cobalt-substituted oxyhemoglobin and oxymyoglobin. The  $\nu(\text{O}_2)$  of oxycytochrome P-450 has not been observed either by IR or RR spectroscopy. As to their model compounds, Collman et al.<sup>5</sup> observed the  $\nu(\text{O}_2)$  of  $\text{Fe}(\text{T}_{\text{piv}}\text{PP})(1\text{-MeIm})\text{O}_2$  ( $\text{T}_{\text{piv}}\text{PP}$ : picket-fence porphyrin) at 1159  $\text{cm}^{-1}$  (Nujol mull), and Weiss et al.<sup>6</sup> located the  $\nu(\text{O}_2)$  of  $[\text{Fe}(\text{T}_{\text{piv}}\text{PP})(\text{SC}_6\text{HF}_4)\text{O}_2]^-$  and its cobalt analogue at 1139 and 1126  $\text{cm}^{-1}$ , respectively, by using IR difference spectroscopy. Recently, Chottard et al.<sup>7</sup> made the first observation of  $\nu(\text{O}_2)$  of oxyiron porphyrins by RR spectroscopy. Using 440-nm excitation, these workers were able to observe the  $\nu(\text{O}_2)$  of  $[\text{Fe}(\text{T}_{\text{piv}}\text{PP})(\text{SC}_6\text{HF}_4)\text{O}_2]^-$  at 1140  $\text{cm}^{-1}$ , in good agreement with the IR frequency mentioned above. However, similar attempts to resonance-enhance  $\nu(\text{O}_2)$  of other oxyiron porphyrins have been unsuccessful. In contrast, the  $\nu(\text{O}_2)$  of oxycobalt porphyrins are observed without exception by using exciting lines between 406.7 and 514.5 nm.<sup>8</sup>

In this work, we have measured for the first time the  $\nu(\text{O}_2)$  of an "unprotected" porphyrin,  $\text{K}^{\text{Cr}}[\text{Co}(\text{TPP})(\text{SC}_6\text{H}_5)\text{O}_2]$  ( $\text{K}^{\text{Cr}}$  = potassium 18-crown-6 ether; TPP = tetraphenylporphyrin) and its  $\text{SCH}_2\text{C}_6\text{H}_5$  analogue by using our minibulb techniques<sup>9</sup> and discussed the effect of thiolate vs. N-base ligand on bound dioxygen.

## Experimental Section

**Compounds.** (Tetraphenylporphyrinato)cobalt(II),  $\text{Co}(\text{TPP})$ , was prepared according to the literature method.<sup>10</sup> TPP was purchased from Midcentury, Posen, IL, and purified by the procedure reported previously.<sup>11</sup> All other chemicals were purchased from Aldrich Chemical Co., Milwaukee, WI. Both benzene and THF were dried by metallic sodium while methylene chloride was dried by  $\text{CaH}_2$ . The  $^{16}\text{O}_2$  and  $^{18}\text{O}_2$  (97.8% pure) gases were purchased from AIRCO Inc. and Monsanto Research, respectively. The potassium 18-crown-6 ether (abbreviated as  $\text{K}^{\text{Cr}}$ ) salt,  $\text{K}^{\text{Cr}}[\text{Co}(\text{TPP})(\text{SC}_6\text{H}_5)](\text{HSC}_6\text{H}_5)$  was prepared by using the following procedure. The crown ether (40 mg), potassium hydride (6 mg), and benzenethiol (0.1 mL) were dissolved in degassed benzene (70 mL), and the solution was stirred overnight. A sample of  $\text{Co}(\text{TPP})$  (100 mg) in 20 mL of degassed benzene was added to the solution. The solution was concentrated under reduced pressure, and the black crystals thus obtained were filtered and washed with benzene. Anal. Calcd for  $\text{K}^{\text{Cr}}[\text{Co}(\text{TPP})(\text{SC}_6\text{H}_5)](\text{HSC}_6\text{H}_5)$ : C, 68.37; H, 5.31; N, 4.69; S, 5.36. Found: C, 68.02; H, 5.17; N, 4.74; S, 5.64. This complex was formulated as a five-coordinate rather than a six-coordinate species since the former is more stable than the latter in cobalt(II) porphyrins.<sup>12</sup>

**Spectral Measurements.** The RR spectra were recorded on a Spex Model 1401 double monochromator equipped with a Spex DPC-2 digital photometer system. Excitations at 457.9, 472.7, 476.5, 488.0, 501.7, and 514.5 nm were made with a Spectra-Physics Model 164-05 Ar-ion laser and that at 406.7 nm with a Spectra-Physics Model 164-01 Kr-ion laser. The frequency reading was calibrated by using the solvent bands. The minibulb techniques described previously<sup>9</sup> were employed to measure the spectra at low temperatures. The excitation profiles (Figure 5) were obtained by measuring the intensities of the  $\nu(\text{O}_2)$  at 1137 and 1122  $\text{cm}^{-1}$  and  $\nu(\text{TPP})$  at 1237  $\text{cm}^{-1}$  relative to that of the solvent band at 1155



**Figure 1.** RR spectra of dioxygen adducts of  $\text{K}^{\text{Cr}}[\text{Co}(\text{TPP})(\text{SR})]$  at  $\sim 185 \text{ K}$ . (A)  $^{16}\text{O}_2$ ,  $\text{R} = \text{C}_6\text{H}_5$ ,  $\text{CH}_2\text{Cl}_2$  solution; (B)  $^{18}\text{O}_2$ ,  $\text{R} = \text{C}_6\text{H}_5$ ,  $\text{CH}_2\text{Cl}_2$  solution; (C)  $^{16}\text{O}_2$ ,  $\text{R} = \text{C}_6\text{H}_5$ , THF solution; (D)  $^{16}\text{O}_2$ ,  $\text{R} = \text{SCH}_2\text{C}_6\text{H}_5$ , THF solution; and (E)  $^{18}\text{O}_2$ ,  $\text{R} = \text{SCH}_2\text{C}_6\text{H}_5$ , THF solution. The 457.9-nm excitation was used for (A), (B), and (C), while the 476.5-nm excitation was employed for (D) and (E). S denotes the solvent band.

$\text{cm}^{-1}$ . No intensity corrections were made since these frequencies are close to each other.

Two different procedures were employed to prepare the sample solution. (a) The spectra shown in Figures 1A and B and 4 were obtained as follows: Degassed methylene chloride was transferred to a minibulb in which crystalline powder of  $\text{K}^{\text{Cr}}[\text{Co}(\text{TPP})(\text{SC}_6\text{H}_5)](\text{HSC}_6\text{H}_5)$  was placed. After oxygen was added, the minibulb was sealed and kept at  $\sim 80 \text{ K}$  with liquid nitrogen until the spectral measurement began. The  $\text{Co}(\text{TPP})/\text{SC}_6\text{H}_5$  ratio was 1/1 in these experiments. (b) The spectra shown in Figure 1C–E were obtained in large excess of the thiolate ligand SR where R is  $\text{C}_6\text{H}_5$  or  $\text{CH}_2\text{C}_6\text{H}_5$ . A benzene solution of  $\text{K}^{\text{Cr}}[\text{SR}]$  was introduced into a minibulb, and benzene was removed by pumping. To this bulb was added  $\text{Co}(\text{TPP})$  in approximately 1/20 M ratio of  $\text{Co}(\text{TPP})/\text{SR}$ . THF was transferred to this minibulb, and oxygen was added. The bulb was sealed and kept at  $\sim 80 \text{ K}$  until the spectral measurement began.

The electronic spectrum of  $\text{K}^{\text{Cr}}[\text{Co}(\text{TPP})(\text{SC}_6\text{H}_5)\text{O}_2]$  at  $\sim 205 \text{ K}$  (Figure 5) was measured on a Perkin-Elmer Model 320 spectrophotometer. The solution ( $\sim 10^{-5} \text{ M}$ ) was prepared by using dry methylene chloride as the solvent, and the measurements were made by using a Dewar cell at the desired temperature.

## Results and Discussion

Figure 1A and B shows the RR spectra (457.9-nm excitation) of  $\text{K}^{\text{Cr}}[\text{Co}(\text{TPP})(\text{SC}_6\text{H}_5)](\text{HSC}_6\text{H}_5)$  dissolved in methylene chloride which was saturated with  $^{16}\text{O}_2$  and  $^{18}\text{O}_2$ , respectively, at  $\sim 185 \text{ K}$ . The former exhibits a strong band at 1122  $\text{cm}^{-1}$  which is shifted to 1058  $\text{cm}^{-1}$  by  $^{16}\text{O}_2$ - $^{18}\text{O}_2$  substitution. The magnitude of this shift (64  $\text{cm}^{-1}$ ) is in perfect agreement with that expected for a perturbed  $\text{O}_2$  molecule. Figure 1C shows the RR spectrum of a THF solution of  $\text{Co}(\text{TPP})$  containing a large excess of  $\text{K}^{\text{Cr}}[\text{SC}_6\text{H}_5]$  ( $\text{Co}(\text{TPP})/\text{K}^{\text{Cr}}[\text{SC}_6\text{H}_5] = 1/20$ ) which was saturated with  $^{16}\text{O}_2$  at  $\sim 185 \text{ K}$ . This solution also exhibits a band at 1122  $\text{cm}^{-1}$ . Hence, we assign the bands at 1122 and 1058  $\text{cm}^{-1}$  to the  $\nu(\text{O}_2)$  of  $\text{K}^{\text{Cr}}[\text{Co}(\text{TPP})(\text{SC}_6\text{H}_5)^{16}\text{O}_2]$  and its  $^{18}\text{O}_2$  analogue, respectively. The  $\nu(^{16}\text{O}_2)$  of  $\text{Co}(\text{TPP})(1\text{-MeIm})\text{O}_2$  is at 1144  $\text{cm}^{-1}$

(3) Caughey, W. S.; Choc, M. G.; Houtchens, R. A. "Biochemical and Clinical Aspects of Oxygen"; Caughey, W. S., Ed.; Academic Press: New York, 1979; p 4.

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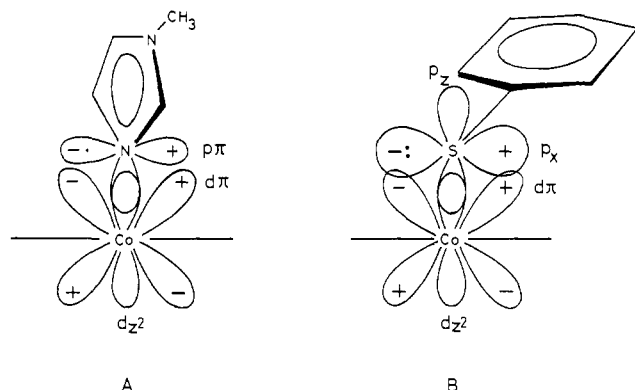
(7) Chottard, G.; Schappacher, M.; Ricard, L.; Weiss, R. *Inorg. Chem.* **1984**, *23*, 4557.

(8) For example, see: Bajdor, K.; Nakamoto, K.; Kincaid, J. J. *Am. Chem. Soc.* **1983**, *105*, 678.

(9) Nakamoto, K.; Nonaka, Y.; Ishiguro, T.; Urban, M. W.; Suzuki, M.; Kozuka, M.; Nishida, Y.; Kida, S. *J. Am. Chem. Soc.* **1982**, *104*, 3386.

(10) Rothmund, P.; Menotti, A. R. *J. Am. Chem. Soc.* **1948**, *70*, 1808.

(11) Rosseau, K.; Dolphin, D. *Tetrahedron Lett.* **1974**, *48*, 4251.



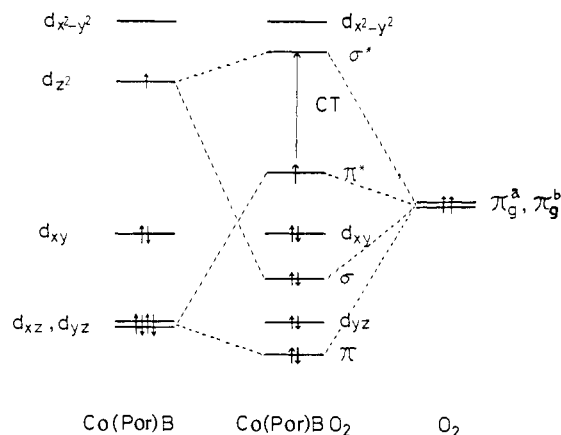
**Figure 2.** Bonding schemes of 1-methylimidazole (A) and benzene-thiolate (B) to cobalt(II) porphyrin. The horizontal line points to the direction of pyrrole nitrogen atoms of the porphyrin ring.

under similar experimental conditions.<sup>13</sup> Thus, the  $\nu(\text{O}_2)$  has been lowered by  $22\text{ cm}^{-1}$  by changing the axial ligand from 1-MeIm to the  $\text{SC}_6\text{H}_5^-$  ion. This value is very close to that observed when 1-MeIm of  $\text{Fe}(\text{T}_{\text{piv}}\text{PP})(1\text{-MeImO}_2)$  ( $1159\text{ cm}^{-1}$ )<sup>5</sup> is replaced by the  $\text{SC}_6\text{HF}_4^-$  ion ( $1139\text{ cm}^{-1}$ ).<sup>6</sup>

As we have shown previously,<sup>9,14,15</sup> the  $\nu(\text{O}_2)$  of a dioxygen adduct of a Co(II) chelate becomes lower as more electrons are transmitted from the in-plane and axial base ligands to the dioxygen. Electron donation from the axial ligand may occur either via  $\sigma$  or  $\pi$  overlap or both. Base-free  $\text{Co}(\text{TPP})\text{O}_2$  exhibits the  $\nu(\text{O}_2)$  at  $1278\text{ cm}^{-1}$  in an Ar matrix.<sup>16</sup> On the other hand,  $\text{Co}(\text{TPP})(n\text{-BuNH}_2)\text{O}_2$  in methylene chloride exhibits the  $\nu(\text{O}_2)$  at  $1139\text{ cm}^{-1}$ .<sup>13</sup> Since *n*-butylamine is a pure  $\sigma$  donor, the observed shift ( $139\text{ cm}^{-1}$ ) in going from  $\text{Co}(\text{TPP})\text{O}_2$  to  $\text{Co}(\text{TPP})(n\text{-BuNH}_2)\text{O}_2$  must be attributed to the increased electron density on the dioxygen resulting from  $\sigma$  donation alone.

Different from *n*-butylamine, base ligands such as 1-MeIm and pyridine are able to transmit electrons to the metal via the  $\sigma$  as well as  $\pi$  overlap as shown in Figure 2A. The  $\sigma$ -donating ability as measured in terms of  $\text{p}K_{\text{a}}$  values of their conjugate acids is larger for *n*-BuNH<sub>2</sub> (10.6) than for 1-MeIm (7.2).<sup>9</sup> On this basis alone, we predict that the  $\nu(\text{O}_2)$  of  $\text{Co}(\text{TPP})(n\text{-BuNH}_2)\text{O}_2$  ( $1139\text{ cm}^{-1}$ ) is lower than that of the 1-MeIm derivative ( $1144\text{ cm}^{-1}$ ). We thus conclude that the  $\pi$  donation by 1-MeIm is negligible probably because the  $\text{p}_{\pi}(\text{N})-\text{d}_{\pi}(\text{Co})$  overlap shown in Figure 2A is diminished considerably by the deviation of the 1-MeIm plane from the  $\text{d}_{\pi}$  orbital plane. X-ray analysis<sup>17</sup> shows that this deviation amounts to  $20^\circ$  in  $\text{Fe}(\text{T}_{\text{piv}}\text{PP})(1\text{-MeIm})\text{O}_2$ .

The thiolate ion such as  $\text{SC}_6\text{H}_5^-$  coordinates to iron porphyrin with its benzene ring approximately parallel to the porphyrin plane.<sup>18,19</sup> Then, it may transmit electrons to the metal via  $\sigma$  as well as  $\pi$  overlap as shown in Figure 2B. However, the degree of  $\sigma$  donation should not differ appreciably between  $\text{SC}_6\text{H}_5^-$  and 1-MeIm since their basicities are similar (the  $\text{p}K_{\text{a}}$  values of their conjugate acids are 6.5<sup>20</sup> and 7.2, respectively). Thus, the observed shift of  $\nu(\text{O}_2)$  ( $22\text{ cm}^{-1}$ ) in going from  $\text{Co}(\text{TPP})(1\text{-MeIm})\text{O}_2$  to  $[\text{Co}(\text{TPP})(\text{SC}_6\text{H}_5)\text{O}_2]^-$  must be attributed largely to the difference in  $\pi$  donation which is negligible in the former but substantial



**Figure 3.** Approximate MO energy level diagram of the Co(porphyrin)(base) $\text{O}_2$  system.

in the latter.  $\pi$  Donation by the  $\text{SC}_6\text{H}_5^-$  ion is promoted by two factors: (1) Extra lone-pair electrons reside in the  $\text{p}_x$  orbital of the sulfur atom. (2) The thiolate ion in TPP complexes tends to take an orientation which maximizes the  $\text{p}_x-\text{d}_{\pi}$  overlap (Figure 2B) and minimizes the steric repulsion from the *meso*-phenyl groups. The concept of the  $\text{p}_x-\text{d}_{\pi}$  overlap is not new; Ozaki et al.<sup>21</sup> observed the oxidation-state marker band of reduced cytochrome P-450<sub>cam</sub> at an unusually low frequency ( $1346\text{ cm}^{-1}$ ) and attributed its origin to the electron donation from the cysteinyl residue to the porphyrin via the  $\text{p}_x(\text{S})-\text{d}_{\pi}(\text{Fe})-\pi^*(e_g, \text{por})$  overlap.

Figure 3 shows an approximate MO energy diagram for the dioxygen adduct of a cobalt porphyrin containing a base (B) ligand.<sup>4,22</sup> It is seen that the Co(II) atom forms a  $\sigma$  bond via the  $\text{d}_{z^2}(\text{Co})-\pi_g^a(\text{O})$  overlap and a  $\pi$  bond via the  $\text{d}_{xy}(\text{Co})-\pi_g^b(\text{O})$  overlap where the  $\pi_g^a(\text{O})$  and  $\pi_g^b(\text{O})$  orbitals denote the p orbitals which are parallel and perpendicular to the Co-O-O plane, respectively.<sup>22</sup> As in the case of iron porphyrin (low spin), part of this electron density will be diverted to the porphyrin ring system via the  $\text{d}_{\pi}(\text{Co})-\pi^*(e_g, \text{por})$  mixing.<sup>23</sup> Again, the  $\text{d}_{\pi}(\text{Co})-\pi_g^b(\text{O})$  overlap is maximized when the  $\pi_g^b(\text{O})$  orbital is parallel to the  $\text{d}_{\pi}$  plane. In  $\text{Fe}(\text{T}_{\text{piv}}\text{PP})(1\text{-MeIm})\text{O}_2$ ,<sup>17</sup> the Fe-O-O plane approximately bisects the two  $\text{d}_{\pi}$  planes where the  $\text{d}_{\pi}(\text{Fe})-\pi_g^b(\text{O})$  overlap is minimal. This geometry further limits the possibility of electron drift from 1-MeIm to the dioxygen. On the other hand, the Fe-O-O plane in  $[\text{Fe}(\text{T}_{\text{piv}}\text{PP})(\text{SC}_6\text{HF}_4)\text{O}_2]^-$ <sup>19</sup> is much closer to the  $\text{d}_{\pi}$  plane than that of the 1-MeIm derivative. If the dioxygen in  $[\text{Co}(\text{TPP})(\text{SC}_6\text{H}_5)\text{O}_2]^-$  takes such an orientation, there would be no difficulty in transmitting  $\pi$  electrons from the thiolate to dioxygen. Presumably, this extra  $\pi$ -electron density donated to dioxygen by the thiolate facilitates the O-O bond cleavage when oxycytochrome P-450 accepts the second electron from NADH in its reaction cycle. It should be noted, however, that this  $\pi$  effect is much smaller than the  $\sigma$  effect discussed earlier as evidenced by the  $\nu(\text{O}_2)$  shift ( $22$  vs.  $130\text{--}140\text{ cm}^{-1}$ ).

Figure 1D shows the RR spectrum (476.5-nm excitation) of a THF solution containing  $\text{Co}(\text{TPP})$  and  $\text{K}^{\text{Cr}}[\text{SCH}_2\text{C}_6\text{H}_5]$  in a 1:2 ratio which is saturated with  $^{16}\text{O}_2$  at  $\sim 185\text{ K}$ . In this case, a new band appears at  $1120\text{ cm}^{-1}$ , and this band is shifted to  $1055\text{ cm}^{-1}$  by  $^{16}\text{O}_2-^{18}\text{O}_2$  substitution (Figure 1E). Thus, we assign these bands to the  $\nu(\text{O}_2)$  of  $\text{K}^{\text{Cr}}[\text{Co}(\text{TPP})(\text{SCH}_2\text{C}_6\text{H}_5)_2]^{16}\text{O}_2$  and its  $^{18}\text{O}_2$  analogue, respectively. The  $\text{p}K_{\text{a}}$  values of  $\text{HSCH}_2\text{C}_6\text{H}_5$  and  $\text{HSC}_6\text{H}_5$  are 9.4 and 6.5, respectively.<sup>20</sup> Then, we expect more  $\sigma$  donation for the former than for the latter. Yet the  $\nu(\text{O}_2)$  of these thiolate complexes are surprisingly similar. This may suggest that the degree of  $\pi$  donation is less for the former than for the latter. It is probable that a better spatial separation between the

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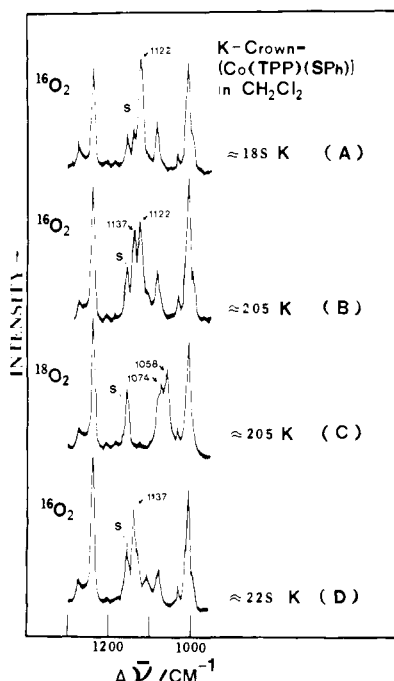
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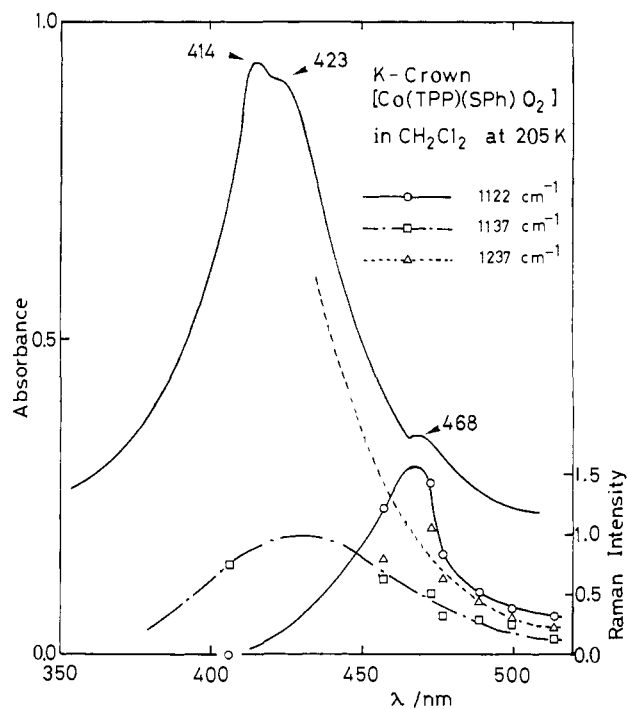


**Figure 4.** RR spectra of  $\text{CH}_2\text{Cl}_2$  solutions of  $\text{K}^{\text{Cr}}[\text{Co}(\text{TPP})(\text{SC}_6\text{H}_5)](\text{HSC}_6\text{H}_5)$  saturated with dioxygen. (A)  $^{16}\text{O}_2$ ,  $\sim 185$  K, (B)  $^{16}\text{O}_2$ ,  $\sim 205$  K, (C)  $^{18}\text{O}_2$ ,  $\sim 205$  K, and (D)  $^{16}\text{O}_2$ ,  $\sim 225$  K. All the spectra were obtained with the 457.9-nm excitation. S denotes the solvent band.

$\text{SCH}_2\text{C}_6\text{H}_5$  group and the *meso*-phenyl groups of TPP reduces the  $p_x$ - $d_{\pi}$  overlap discussed earlier.

Figure 4 shows the temperature dependence of the RR spectrum of  $\text{K}^{\text{Cr}}[\text{Co}(\text{TPP})(\text{SC}_6\text{H}_5)\text{O}_2]$  which was prepared by oxygenation of crystalline  $\text{K}^{\text{Cr}}[\text{Co}(\text{TPP})(\text{SC}_6\text{H}_5)](\text{HSC}_6\text{H}_5)$  dissolved in methylene chloride. As discussed previously, the band at  $1122\text{ cm}^{-1}$  in trace A ( $\sim 185$  K) is due to the  $\nu(\text{O}_2)$  of  $\text{K}^{\text{Cr}}[\text{Co}(\text{TPP})(\text{SC}_6\text{H}_5)\text{O}_2]$ . When the temperature of this solution was raised to  $\sim 205$  K, a new band appeared at  $1137\text{ cm}^{-1}$  as shown in trace B. Similar experiments with  $^{18}\text{O}_2$  shifted these bands to  $1074$  and  $1058\text{ cm}^{-1}$ , respectively (trace C). At  $\sim 225$  K, however, only the band at  $1137\text{ cm}^{-1}$  remains as shown in trace D. The  $1137\text{ cm}^{-1}$  band does not appear when a solution of  $\text{Co}(\text{TPP})$  with excess  $\text{K}^{\text{Cr}}[\text{SC}_6\text{H}_5]$  is saturated with dioxygen and warmed to higher temperatures. Previously, Collman and Sorrell<sup>24</sup> noted that the  $\nu(\text{CO})$  of  $\text{Fe}(\text{T}_{\text{pv}}\text{PP})(\text{HS}-n\text{-Bu})(\text{CO})$  ( $1970\text{ cm}^{-1}$ ) is higher than that of its  $\text{SCH}_3$  derivative ( $1954\text{ cm}^{-1}$ ). In accordance with this trend, we assign the  $1137\text{ cm}^{-1}$  band to  $\text{Co}(\text{TPP})(\text{HSC}_6\text{H}_5)\text{O}_2$ . Namely, the  $\pi$  donation from the thiolate ion is responsible for the observed low-frequency shifts of  $\nu(\text{CO})$  and  $\nu(\text{O}_2)$  relative to those of mercaptan complexes. In fact, the  $\nu(\text{O}_2)$  of  $\text{Co}(\text{TPP})(\text{HSC}_6\text{H}_5)\text{O}_2$  ( $1137\text{ cm}^{-1}$ ) is close to that of  $\text{Co}(\text{TPP})(n\text{-BuNH}_2)\text{O}_2$  ( $1139\text{ cm}^{-1}$ ) for which no  $\pi$  donation from the base ligand is expected.

The electronic spectrum of  $\text{K}^{\text{Cr}}[\text{Co}(\text{TPP})(\text{SC}_6\text{H}_5)]$  in methylene chloride at  $\sim 185$  K shows the  $\alpha$  and  $\beta$  bands at  $662$  and  $620\text{ nm}$ , respectively, and a split Soret band at  $480$  and  $398\text{ nm}$ . Upon oxygenation at this temperature, the  $\alpha$  and  $\beta$  bands are shifted to  $620$  and  $522\text{ nm}$ , respectively, and three bands appear in the Soret region ( $468$ ,  $423$ , and  $414\text{ nm}$ ) as shown in Figure 5. When the temperature is raised to  $\sim 225$  K, the bands at  $468$  and  $423\text{ nm}$  disappear while the band at  $414\text{ nm}$  remains. The  $\alpha$  and  $\beta$  bands remain at  $620$  and  $522\text{ nm}$ , respectively. As demonstrated in Figure 4, the  $\nu(\text{O}_2)$  band of  $\text{K}^{\text{Cr}}[\text{Co}(\text{TPP})(\text{SC}_6\text{H}_5)\text{O}_2]$  at  $1122\text{ cm}^{-1}$  disappears when the temperature is raised from  $\sim 205$  to  $\sim 225$  K. We, therefore, attribute the  $468$ - and  $423$ -nm bands to this dioxygen adduct. Then, the remaining band at  $414\text{ nm}$  must be assigned to  $[\text{Co}(\text{TPP})(\text{HSC}_6\text{H}_5)\text{O}_2]$  which exhibits the  $\nu(\text{O}_2)$  at  $1137\text{ cm}^{-1}$ . Previously, Hanson et al.<sup>25</sup> predicted from



**Figure 5.** Electronic spectra and excitation profiles of  $\text{K}^{\text{Cr}}[\text{Co}(\text{TPP})(\text{SC}_6\text{H}_5)\text{O}_2]$  and  $\text{Co}(\text{TPP})(\text{HSC}_6\text{H}_5)\text{O}_2$  in  $\text{CH}_2\text{Cl}_2$ . The intensity of the  $1237\text{ cm}^{-1}$  band at  $406\text{ nm}$  is not shown since it is ca. 13 on the scale shown.

MO calculations that split Soret bands are expected for dioxygen adducts of low-spin ferrous porphyrin mercaptides whereas single Soret bands are anticipated for the corresponding mercaptan complexes. The present results show that these predictions are applicable to analogous  $\text{Co}(\text{II})$  complexes.

Figure 5 also shows the excitation profiles of the  $\nu(\text{O}_2)$  of  $\text{K}^{\text{Cr}}[\text{Co}(\text{TPP})(\text{SC}_6\text{H}_5)\text{O}_2]$  ( $1122\text{ cm}^{-1}$ ) and  $[\text{Co}(\text{TPP})(\text{HSC}_6\text{H}_5)\text{O}_2]$  ( $1137\text{ cm}^{-1}$ ) together with that of a TPP vibration ( $\nu(\text{C}-\text{C}_6\text{H}_5)$ ,  $1237\text{ cm}^{-1}$ ).<sup>26</sup> It is seen that the intensity of the former  $\nu(\text{O}_2)$  maximizes near  $468\text{ nm}$ , whereas that of the latter appears to be shifted near  $414\text{ nm}$ . These results suggest that the  $468\text{-nm}$  component of the split Soret bands of the former  $\text{O}_2$  adduct contains substantial  $\text{Co}-\text{O}_2$  CT character and that the  $414\text{-nm}$  band of the latter  $\text{O}_2$  adduct is responsible for resonance enhancement of the  $\nu(\text{O}_2)$  as seen in oxycobalt porphyrins containing N-base ligands.<sup>13</sup> According to Figure 3, the  $\text{Co}-\text{O}_2$  charge transfer occurs via the  $\pi^*$  to  $\sigma^*$  transition. As discussed earlier, the  $\pi^*$  level would be higher in the thiolate than in the mercaptan complex although the  $\sigma^*$  level is expected to be of similar energy for the two. The net result is a bathochromic shift of the  $\text{Co}-\text{O}_2$  CT band in going from the mercaptan to the thiolate complex, as observed. Finally, the intensity of the TPP vibration at  $1237\text{ cm}^{-1}$  increases markedly near the Soret band as expected for all totally symmetric TPP vibrations.<sup>23</sup>

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**Registry No.**  $\text{K}[\text{Co}(\text{TPP})(\text{SC}_6\text{H}_5)](\text{HSC}_6\text{H}_5)$ , 98652-73-4;  $\text{K}[\text{Co}(\text{TPP})(\text{SC}_6\text{H}_5)\text{O}_2]$ , 98677-64-6;  $\text{K}[\text{Co}(\text{TPP})(\text{SC}_6\text{H}_5)^{18}\text{O}_2]$ , 98677-66-8;  $\text{K}[\text{Co}(\text{TPP})(\text{SCH}_2\text{C}_6\text{H}_5)\text{O}_2]$ , 98677-68-0;  $\text{K}[\text{Co}(\text{TPP})(\text{SCH}_2\text{C}_6\text{H}_5)^{18}\text{O}_2]$ , 98677-70-4;  $\text{Co}(\text{TPP})(\text{HSC}_6\text{H}_5)\text{O}_2$ , 98677-71-5.

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