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 CF_4 and CO_2 has also been found to be catalyzed by metal and inhibited by oxygen.[17] 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 COF_2 instead of a molecule of $F_3COC(O)F$.

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.[4a] 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 O_2 and formation of HF;[18] the analogous decomposition of acetyl hypofluorite to HF, CO_2, and C_2H_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.[19]

Acknowledgment. Mass spectrometric analysis of gas ratios was carried out by A. G. Engelkemeir of the Argonne Analytical Laboratory. NMR measurements were made by A. G. Kostka and A. Svirmickas. E.H.A. wishes to thank Dr. A. J. Downs of Oxford University both for extremely profitable discussions and for providing a practical environment in which to develop techniques for the matrix isolation of highly reactive fluorine compounds. We thank Drs. Mirko Diksic and Shlomo Rozen for helpful discussions and for making the manuscripts of ref 8a,b available to us prior to their publication. And we are grateful to Dr. Felix Schreiner for illuminating discussion of our vapor-pressure measurements.

Registry No. F_2, 7782-41-4; 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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Effect of Thiolate vs. Nitrogen-Base Ligands on O_2 Stretching Frequencies of (Oxytetraphenylporphyrinato)cobalt

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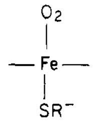
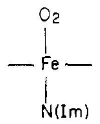
Abstract: The resonance Raman spectra of model compounds of oxycytochrome P-450, $K^{Cr}[Co(TPP)(SC_6H_5)^{16}O_2]$ (K^{Cr}: potassium 18-crown-6 ether) and its $^{18}O_2$ analogue were located at 1122 and 1058 cm^{-1}, respectively, in CH_2Cl_2 solution at ~185 K with 457.9-nm excitation. The $\nu(^{16}O_2)$ of this compound is lower by 22 cm^{-1} than that of a model compound of oxyhemoglobin, $Co(TPP)(1\text{-}MeIm)^{16}O_2$ (1144 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 π overlap. The $\nu(O_2)$ of $K^{Cr}[Co(TPP)(SCH_2C_6H_5)^{16}O_2]$ and its $^{18}O_2$ analogue are observed at 1120 and 1055 cm^{-1}, respectively, by 476.5-nm excitation. The small shift of $\nu(O_2)$ observed by replacing the $SC_6H_5^-$ with $SCH_2C_6H_5^-$ ion indicates that the degree of total electron donation to dioxygen via σ and π overlap is similar for these two compounds. When a CH_2Cl_2 solution of crystalline $K^{Cr}[Co(TPP)(SC_6H_5)](HSC_6H_5)$ is saturated with dioxygen at ~185 K and warmed to ~225 K, a new $\nu(O_2)$ band appears at 1137 cm^{-1} which is assigned to $[Co(TPP)(HSC_6H_5)O_2]$. The electronic spectrum of $K^{Cr}[Co(TPP)(SC_6H_5)O_2]$ in CH_2Cl_2 solution exhibits the α and β bands at 620 and 522 nm, respectively, and a split Soret band at 468 and 423 nm. The excitation profile of the $\nu(O_2)$ (1122 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[1] 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 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.[2] 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.



$$\begin{array}{c} O_2 \\ | \\ —Fe— \\ | \\ SR^- \end{array}$$

I



$$\begin{array}{c} O_2 \\ | \\ —Fe— \\ | \\ N(Im) \end{array}$$

II

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

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In 1979, Caughey et al.[3] observed two O_2 stretching bands ($\nu(O_2)$) at 1155 and 1107 cm^{-1} for oxyhemoglobin by using IR difference techniques and attributed this splitting to Fermi resonance between the $\nu(O_2)$ ($\sim$1130 cm^{-1}) and the first overtone of the $\nu(Fe-O_2)$ at 567 cm^{-1}. However, their interpretation was questioned by Tsubaki and Yu[4] based on resonance Raman (RR) studies of cobalt-substituted oxyhemoglobin and oxymyoglobin. The $\nu(O_2)$ of oxycytochrome P-450 has not been observed either by IR or RR spectroscopy. As to their model compounds, Collman et al.[5] observed the $\nu(O_2)$ of $Fe(T_{piv}PP)(1\text{-}MeIm)O_2$($T_{piv}PP$: picket-fence porphyrin) at 1159 cm^{-1} (Nujol mull), and Weiss et al.[6] located the $\nu(O_2)$ of $[Fe(T_{piv}PP)(SC_6HF_4)O_2]^-$ and its cobalt analogue at 1139 and 1126 cm^{-1}, respectively, by using IR difference spectroscopy. Recently, Chottard et al.[7] made the first observation of $\nu(O_2)$ of oxyiron porphyrins by RR spectroscopy. Using 440-nm excitation, these workers were able to observe the $\nu(O_2)$ of $[Fe(T_{piv}PP)(SC_6HF_4)O_2]^-$ at 1140 cm^{-1}, in good agreement with the IR frequency mentioned above. However, similar attempts to resonance-enhance $\nu(O_2)$ of other oxyiron porphyrins have been unsuccessful. In contrast, the $\nu(O_2)$ of oxycobalt porphyrins are observed without exception by using exciting lines between 406.7 and 514.5 nm.[8]

In this work, we have measured for the first time the $\nu(O_2)$ of an "unprotected" porphyrin, $K^{Cr}[Co(TPP)(SC_6H_5)O_2]$ (K^{Cr} = potassium 18-crown-6 ether; TPP = tetraphenylporphyrin) and its $SCH_2C_6H_5$ analogue by using our minibulb techniques[9] and discussed the effect of thiolate vs. N-base ligand on bound dioxygen.

Experimental Section

Compounds. (Tetraphenylporphyrinato)cobalt(II), Co(TPP), was prepared according to the literature method.[10] TPP was purchased from Midcentury, Posen, IL, and purified by the procedure reported previously.[11] 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 CaH_2. The $^{16}O_2$ and $^{18}O_2$ (97.8% pure) gases were purchased from AIRCO Inc. and Monsanto Research, respectively. The potassium 18-crown-6 ether (abbreviated as K^{Cr}) salt, $K^{Cr}[Co(TPP)(SC_6H_5)](HSC_6H_5)$ 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 Co(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 $K^{Cr}[Co(TPP)(SC_6H_5)](HSC_6H_5)$: 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.[12]

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[9] were employed to measure the spectra at low temperatures. The excitation profiles (Figure 5) were obtained by measuring the intensities of the $\nu(O_2)$ at 1137 and 1122 cm^{-1} and ν(TPP) at 1237 cm^{-1} relative to that of the solvent band at 1155 cm^{-1}. No intensity corrections were made since these frequencies are close to each other.

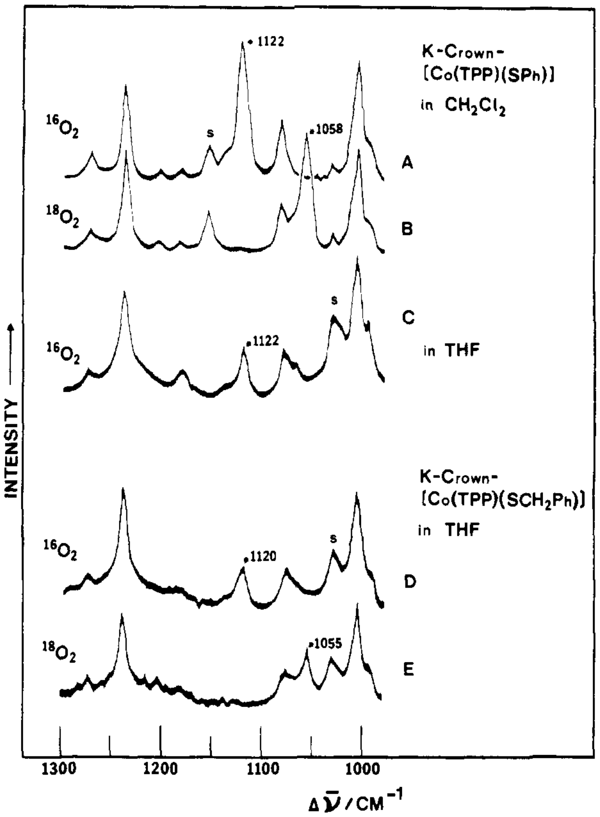

Figure 1. RR spectra of dioxygen adducts of $K^{Cr}[Co(TPP)(SR)]$ at $\sim$185 K. (A) $^{16}O_2$, R = C_6H_5, CH_2Cl_2 solution; (B) $^{18}O_2$, R = C_6H_5, CH_2Cl_2 solution; (C) $^{16}O_2$, R = C_6H_5, THF solution; (D) $^{16}O_2$, R = $SCH_2C_6H_5$, THF solution; and (E) $^{18}O_2$, R = $SCH_2C_6H_5$, 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.

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 $K^{Cr}[Co(TPP)(SC_6H_5)](HSC_6H_5)$ was placed. After oxygen was added, the minibulb was sealed and kept at $\sim$80 K with liquid nitrogen until the spectral measurement began. The $Co(TPP)/SC_6H_5$ 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 C_6H_5 or $CH_2C_6H_5$. A benzene solution of $K^{Cr}[SR]$ was introduced into a minibulb, and benzene was removed by pumping. To this bulb was added Co(TPP) in approximately 1/20 M ratio of Co(TPP)/SR. THF was transferred to this minibulb, and oxygen was added. The bulb was sealed and kept at $\sim$80 K until the spectral measurement began.

The electronic spectrum of $K^{Cr}[Co(TPP)(SC_6H_5)O_2]$ at $\sim$205 K (Figure 5) was measured on a Perkin-Elmer Model 320 spectrophotometer. The solution ($\sim 10^{-5}$ 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 $K^{Cr}[Co(TPP)(SC_6H_5)](HSC_6H_5)$ dissolved in methylene chloride which was saturated with $^{16}O_2$ and $^{18}O_2$, respectively, at $\sim$185 K. The former exhibits a strong band at 1122 cm^{-1} which is shifted to 1058 cm^{-1} by $^{16}O_2$–$^{18}O_2$ substitution. The magnitude of this shift (64 cm^{-1}) is in perfect agreement with that expected for a perturbed O_2 molecule. Figure 1C shows the RR spectrum of a THF solution of Co(TPP) containing a large excess of $K^{Cr}[SC_6H_5]$ ($Co(TPP)/K^{Cr}[SC_6H_5]$ = 1/20) which was saturated with $^{16}O_2$ at $\sim$185 K. This solution also exhibits a band at 1122 cm^{-1}. Hence, we assign the bands at 1122 and 1058 cm^{-1} to the $\nu(O_2)$ of $K^{Cr}[Co(TPP)(SC_6H_5)^{16}O_2]$ and its $^{18}O_2$ analogue, respectively. The $\nu(^{16}O_2)$ of $Co(TPP)(1\text{-}MeIm)O_2$ is at 1144 cm^{-1}

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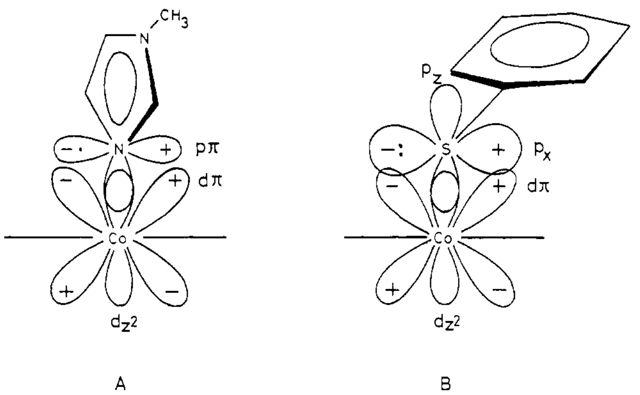

Figure 2. Bonding schemes of 1-methylimidazole (A) and benzene-thiolate (B) to cobalt(II) porphyrin. The horizontal line points to the direction of pyrrole nitrogen atoms of the porphyrin ring.

under similar experimental conditions.[13] Thus, the $\nu(O_2)$ has been lowered by 22 cm^{-1} by changing the axial ligand from 1-MeIm to the $SC_6H_5^-$ ion. This value is very close to that observed when 1-MeIm of Fe(T$_{piv}$PP)(1-MeImO$_2$)(1159 cm^{-1})[5] is replaced by the $SC_6HF_4^-$ ion (1139 cm^{-1}).[6]

As we have shown previously,[9,14,15] the $\nu(O_2)$ 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 σ or π overlap or both. Base-free Co(TPP)O$_2$ exhibits the $\nu(O_2)$ at 1278 cm^{-1} in an Ar matrix.[16] On the other hand, Co(TPP)(*n*-BuNH$_2$)O$_2$ in methylene chloride exhibits the $\nu(O_2)$ at 1139 cm^{-1}.[13] Since *n*-butylamine is a pure σ donor, the observed shift (139 cm^{-1}) in going from Co(TPP)O$_2$ to Co(TPP)(*n*-BuNH$_2$)O$_2$ must be attributed to the increased electron density on the dioxygen resulting from σ donation alone.

Different from *n*-butylamine, base ligands such as 1-MeIm and pyridine are able to transmit electrons to the metal via the σ as well as π overlap as shown in Figure 2A. The σ-donating ability as measured in terms of pK_a values of their conjugate acids is larger for *n*-BuNH$_2$ (10.6) than for 1-MeIm (7.2).[9] On this basis alone, we predict that the $\nu(O_2)$ of Co(TPP)(*n*-BuNH$_2$)O$_2$ (1139 cm^{-1}) is lower than that of the 1-MeIm derivative (1144 cm^{-1}). We thus conclude that the π donation by 1-MeIm is negligible probably because the $p_\pi(N)$–$d_\pi(Co)$ overlap shown in Figure 2A is diminished considerably by the deviation of the 1-MeIm plane from the d_π orbital plane. X-ray analysis[17] shows that this deviation amounts to 20° in Fe(T$_{piv}$PP)(1-MeIm)O$_2$.

The thiolate ion such as $SC_6H_5^-$ coordinates to iron porphyrin with its benzene ring approximately parallel to the porphyrin plane.[18,19] Then, it may transmit electrons to the metal via σ as well as π overlap as shown in Figure 2B. However, the degree of σ donation should not differ appreciably between $SC_6H_5^-$ and 1-MeIm since their basicities are similar (the pK_a values of their conjugate acids are 6.5[20] and 7.2, respectively). Thus, the observed shift of $\nu(O_2)$ (22 cm^{-1}) in going from Co(TPP)(1-MeIm)O$_2$ to [Co(TPP)(SC$_6$H$_5$)O$_2$]$^-$ must be attributed largely to the difference in π donation which is negligible in the former but substantial in the latter. π Donation by the $SC_6H_5^-$ ion is promoted by two factors: (1) Extra lone-pair electrons reside in the p_x orbital of the sulfur atom. (2) The thiolate ion in TPP complexes tends to take an orientation which maximizes the p_x–d_π overlap (Figure 2B) and minimizes the steric repulsion from the *meso*-phenyl groups. The concept of the p_x–d_π overlap is not new; Ozaki et al.[21] observed the oxidation-state marker band of reduced cytochrome P-450$_{cam}$ at an unusually low frequency (1346 cm^{-1}) and attributed its origin to the electron donation from the cysteinyl residue to the porphyrin via the $p_x(S)$–$d_\pi(Fe)$–$\pi^*(e_g,por)$ overlap.

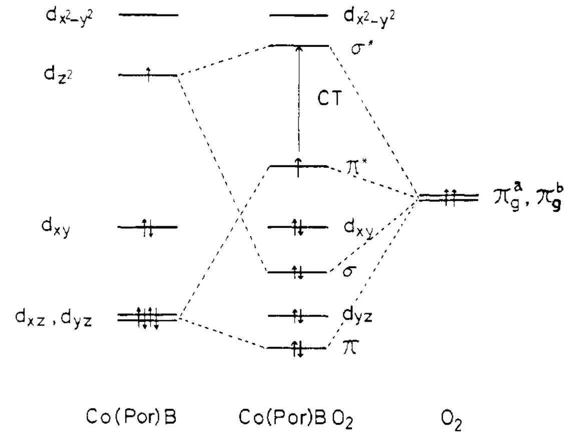

Figure 3. Approximate MO energy level diagram of the Co(porphyrin)(base)O$_2$ system.

Figure 3 shows an approximate MO energy diagram for the dioxygen adduct of a cobalt porphyrin containing a base (B) ligand.[4,22] It is seen that the Co(II) atom forms a σ bond via the $d_{z^2}(Co)$–$\pi_g^a(O)$ overlap and a π bond via the $d_\pi(Co)$–$\pi_g^b(O)$ overlap where the $\pi_g^a(O)$ and $\pi_g^b(O)$ orbitals denote the p orbitals which are parallel and perpendicular to the Co–O–O plane, respectively.[22] As in the case of iron porphyrin (low spin), part of this electron density will be diverted to the porphyrin ring system via the $d_\pi(Co)$–$\pi^*(e_g,por)$ mixing.[23] Again, the $d_\pi(Co)$–$\pi_g^b(O)$ overlap is maximized when the $\pi_g^b(O)$ orbital is parallel to the d_π plane. In Fe(T$_{piv}$PP)(1-MeIm)O$_2$,[17] the Fe–O–O plane approximately bisects the two d_π planes where the $d_\pi(Fe)$–$\pi_g^b(O)$ 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 [Fe(T$_{piv}$PP)(SC$_6$HF$_4$)O$_2$]$^-$ [19] is much closer to the d_π plane than that of the 1-MeIm derivative. If the dioxygen in [Co(TPP)(SC$_6$H$_5$)O$_2$]$^-$ takes such an orientation, there would be no difficulty in transmitting π electrons from the thiolate to dioxygen. Presumably, this extra π-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 π effect is much smaller than the σ effect discussed earlier as evidenced by the $\nu(O_2)$ shift (22 vs. 130–140 cm^{-1}).

Figure 1D shows the RR spectrum (476.5-nm excitation) of a THF solution containing Co(TPP) and K^{Cr}[SCH$_2$C$_6$H$_5$] in a 1:2 ratio which is saturated with $^{16}O_2$ at ~185 K. In this cases, a new band appears at 1120 cm^{-1}, and this band is shifted to 1055 cm^{-1} by $^{16}O_2$–$^{18}O_2$ substitution (Figure 1E). Thus, we assign these bands to the $\nu(O_2)$ of K^{Cr}[Co(TPP)(SCH$_2$C$_6$H$_5$)^{16}O$_2$] and its $^{18}O_2$ analogue, respectively. The pK_a values of HSCH$_2$C$_6$H$_5$ and HSC$_6$H$_5$ are 9.4 and 6.5, respectively.[20] Then, we expect more σ donation for the former than for the latter. Yet the $\nu(O_2)$ of these thiolato complexes are surprisingly similar. This may suggest that the degree of π donation is less for the former than for the latter. It is probable that a better spatial separation between the

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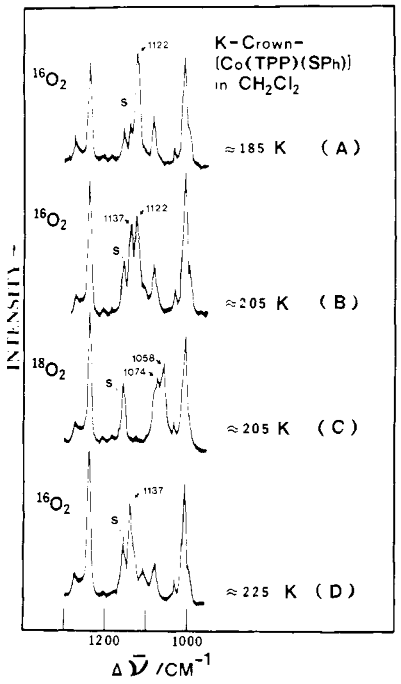

Figure 4. RR spectra of CH_2Cl_2 solutions of $K^{Cr}[Co(TPP)(SC_6H_5)](HSC_6H_5)$ saturated with dioxygen. (A) $^{16}O_2$, ~185 K, (B) $^{16}O_2$, ~205 K, (C) $^{18}O_2$, ~205 K, and (D) $^{16}O_2$, ~225 K. All the spectra were obtained with the 457.9-nm excitation. S denotes the solvent band.

$SCH_2C_6H_5$ group and the *meso*-phenyl groups of TPP reduces the p_x–d_π overlap discussed earlier.

Figure 4 shows the temperature dependence of the RR spectrum of $K^{Cr}[Co(TPP)(SC_6H_5)O_2]$ which was prepared by oxygenation of crystalline $K^{Cr}[Co(TPP)(SC_6H_5)](HSC_6H_5)$ dissolved in methylene chloride. As discussed previously, the band at 1122 cm^{-1} in trace A (~185 K) is due to the $\nu(O_2)$ of $K^{Cr}[Co(TPP)(SC_6H_5)O_2]$. When the temperature of this solution was raised to ~205 K, a new band appeared at 1137 cm^{-1} as shown in trace B. Similar experiments with $^{18}O_2$ shifted these bands to 1074 and 1058 cm^{-1}, respectively (trace C). At ~225 K, however, only the band at 1137 cm^{-1} remains as shown in trace D. The 1137-cm^{-1} band does not appear when a solution of Co(TPP) with excess $K^{Cr}[SC_6H_5]$ is saturated with dioxygen and warmed to higher temperatures. Previously, Collman and Sorrell[24] noted that the $\nu(CO)$ of $Fe(T_{piv}PP)(HS\text{-}n\text{-}Bu)(CO)$ (1970 cm^{-1}) is higher than that of its SCH_3^- derivative (1954 cm^{-1}). In accordance with this trend, we assign the 1137-cm^{-1} band to $Co(TPP)(HSC_6H_5)O_2$. Namely, the π donation from the thiolate ion is responsible for the observed low-frequency shifts of $\nu(CO)$ and $\nu(O_2)$ relative to those of mercaptan complexes. In fact, the $\nu(O_2)$ of $Co(TPP)(HSC_6H_5)O_2$ (1137 cm^{-1}) is close to that of $Co(TPP)(n\text{-}BuNH_2)O_2$ (1139 cm^{-1}) for which no π donation from the base ligand is expected.

The electronic spectrum of $K^{Cr}[Co(TPP)(SC_6H_5)]$ in methylene chloride at ~185 K shows the α and β bands at 662 and 620 nm, respectively, and a split Soret band at 480 and 398 nm. Upon oxygenation at this temperature, the α and β bands are shifted to 620 and 522 nm, respectively, and three bands appear in the Soret region (468, 423, and 414 nm) as shown in Figure 5. When the temperature is raised to ~225 K, the bands at 468 and 423 nm disappear while the band at 414 nm remains. The α and β bands remain at 620 and 522 nm, respectively. As demonstrated in Figure 4, the $\nu(O_2)$ band of $K^{Cr}[Co(TPP)(SC_6H_5)O_2]$ at 1122 cm^{-1} disappears when the temperature is raised from ~205 to ~225 K. We, therefore, attribute the 468- and 423-nm bands to this dioxygen adduct. Then, the remaining band at 414 nm must be assigned to $[Co(TPP)(HSC_6H_5)O_2]$ which exhibits the $\nu(O_2)$ at 1137 cm^{-1}. Previously, Hanson et al.[25] predicted from 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 Co(II) complexes.

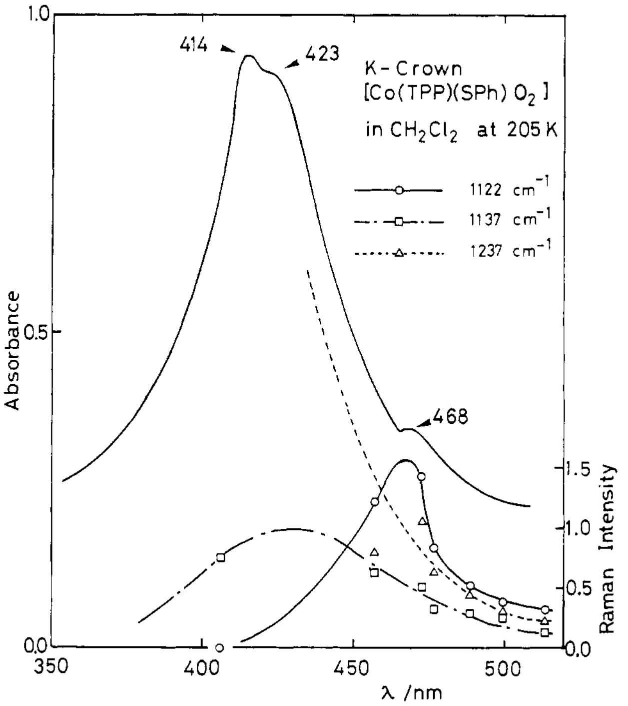

Figure 5. Electronic spectra and excitation profiles of $K^{Cr}[Co(TPP)(SC_6H_5)O_2]$ and $Co(TPP)(HSC_6H_5)O_2$ in CH_2Cl_2. The intensity of the 1237-cm^{-1} band at 406 nm is not shown since it is ca. 13 on the scale shown.

Figure 5 also shows the excitation profiles of the $\nu(O_2)$ of $K^{Cr}[Co(TPP)(SC_6H_5)O_2]$ (1122 cm^{-1}) and $[Co(TPP)(HSC_6H_5)O_2]$ (1137 cm^{-1}) together with that of a TPP vibration ($\nu(C\text{–}C_6H_5)$, 1237 cm^{-1}).[26] It is seen that the intensity of the former $\nu(O_2)$ maximizes near 468 nm, whereas that of the latter appears to be shifted near 414 nm. These results suggest that the 468-nm component of the split Soret bands of the former O_2 adduct contains substantial Co–O_2 CT character and that the 414-nm band of the latter O_2 adduct is responsible for resonance enhancement of the $\nu(O_2)$ as seen in oxycobalt porphyrins containing N-base ligands.[13] According to Figure 3, the Co–O_2 charge transfer occurs via the π^* to σ^* transition. As discussed earlier, the π^* level would be higher in the thiolate than in the mercaptan complex although the σ^* level is expected to be of similar energy for the two. The net result is a bathochromic shift of the Co–O_2 CT band in going from the mercaptan to the thiolate complex, as observed. Finally, the intensity of the TPP vibration at 1237 cm^{-1} increases markedly near the Soret band as expected for all totally symmetric TPP vibrations.[23]

Acknowledgment. This work was supported by the National Science Foundation (PCM-8114676). We express our sincere thanks to Prof. T. Kitagawa (Institute for Molecular Science, Japan), Prof. D. P. Strommen (Carthage College), and Dr. T. Isobe (Marquette University) for their valuable comments. Professor R. Weiss kindly sent us reprints and preprints of his papers related to this work.

Registry No. $K[Co(TPP)(SC_6H_5)](HSC_6H_5)$, 98652-73-4; $K[Co(TPP)(SC_6H_5)O_2]$, 98677-64-6; $K[Co(TPP)(SC_6H_5)^{18}O_2]$, 98677-66-8; $K[Co(TPP)(SCH_2C_6H_5)O_2]$, 98677-68-0; $K[Co(TPP)(SCH_2C_6H_5)^{18}O_2]$, 98677-70-4; $Co(TPP)(HSC_6H_5)O_2$, 98677-71-5.

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