J. Am. Chem. Soc. **1981,** *103,* 4275-4277 4275

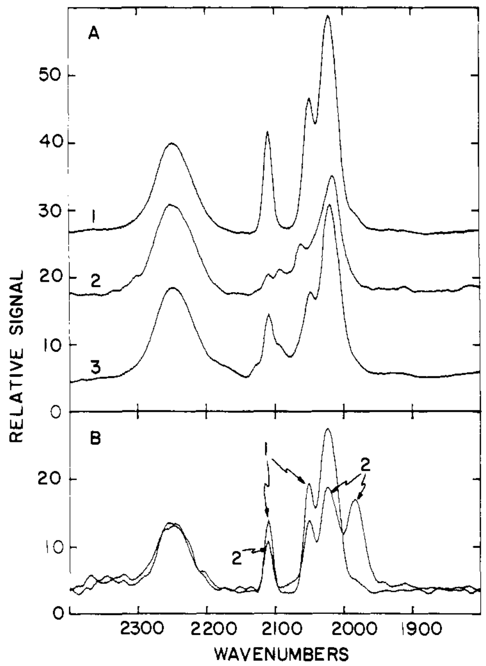

Figure 3. (A) Curve 1 is the initial FTIR/PAS spectrum of a sample of $[S]{>}SiCo(CO)_4$ and curve 2 is the spectrum obtained after near-UV irradiation, of the sample characterized in 1, for 10 min under 1-atm PF_3. The product is $[S]{>}SiCo(CO)_n(PF_3)_{4-n}$. Curve 3 is the spectrum that results when the sample characterized in 2 is irradiated under 1 atm of CO to regenerate $[S]{>}SiCo(CO)_4$. These spectra are recorded using 1-atm Ar as the coupling gas. (B) Spectral changes accompanying the near-UV irradiation of $[S]{>}SiCo(CO)_4$ (curve 1) at low temperature, ~−50 °C, under ~100-torr isobutylene for 10 min to form $[S]{>}SiCo(CO)_3$(isobutylene) (curve 2).

FTIR/PAS can also be used to monitor photosubstitution of the $[S]{>}SiCo(CO)_4$ by using gas-phase entering groups such as PF_3 and olefins (Figure 3). At 25 °C, the chemistry represented by (5) is detectable. The main infrared feature is at ~2000 cm^{-1}

$$[S]{>}SiCo(CO)_4 + PF_3 \xrightarrow{h\nu} [S]\text{-}SiCo(CO)_n(PF_3)_{4-n} \qquad (5)$$

and is associated with $[S]{>}SiCo(CO)_3PF_3$, with the PF_3 occupying an axial position trans to the >Si–, as found for $R_3SiCo(CO)_3P(OPh)_3$ prepared by photosubstitution.[1,10] Irradiation of $[S]\text{-}SiCo(CO)_n(PF_3)_{4-n}$ under 1-atm CO leads to the regeneration of a large fraction of the $[S]{>}SiCo(CO)_4$. Irradiation of $[S]{>}SiCo(CO)_4$ under ethylene or propylene at 25 °C yields loss of all metal carbonyls; $Et_3SiCo(CO)_3$(alkene) was shown previously to decompose at 25 °C.[1] But irradiation of the $[S]{>}SiCo(CO)_4$ at −50 °C under ethylene, propylene, isobutylene, or propyne and monitored by FTIR/PAS at that temperature leads to the generation of new surface metal carbonyl species (Figure 3). The signal at ~1990 cm^{-1} would logically be attributed to $[S]{>}SiCo(CO)_3$(alkene), where the alkene is trans to the >Si–, paralleling solution studies. A signal that grows in at ~2050 cm^{-1} for ethylene, propylene, or propyne, but not isobutylene, is unidentified at this time. Such a signal could be due to another isomer of the $[S]{>}SiCo(CO)_3$(alkene) where the alkene is cis to the >Si–, or the peak could be due to multiple substitution. This point is currently under investigation, but it does appear that the species association with the ~2050 cm^{-1} peak is a primary product, since it appears even at short irradiation times. Interestingly, the ~2050-cm^{-1} peak does not appear in low-temperature irradiations of $Ph_3SiCo(CO)_4$ in solutions containing 1-pentene or ethylene, but the Ph_3Si– group may offer more steric restriction than the $[S]{>}Si$–.

To summarize, we have established the primary photoreaction of $[S]{>}SiCo(CO)_4$ to be loss of CO. This can be exploited to study the oxidation of CO by O_2, prepare inert or labile substitution products, and elaborate the mechanism of the reactions of immobilized, photogenerated, coordinatively unsaturated intermediates. The technique of FTIR/PAS is shown to be a molecular specific tool having unique capabilities for the study of photoreactions of the surface species on high-surface-area supports.

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(9) The cobalt oxide product is detected as an absorber in the visible at ~620 nm.[1b] Monitoring a sample by FTIR/PAS and PAS in the visible shows the decline of metal carbonyl to be accompanied by the growth of the ~620-nm feature attributed to cobalt oxide.

(10) Many metal carbonyls undergo photosubstitution under PF_3 (Geoffroy, G. L; Wrighton, M. S. "Organometallic Photochemistry"; Academic Press: New York, 1979) including Co carbonyls related to those under study here: Udovich, C. A.; Clark, R. J. *Inorg. Chem.* **1969**, *8*, 938.

Structure of Molecular Complexes of Copper Uroporphyrin with Aromatic Heterocycles[†]

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The molecular complexes formed between metalloporphyrins and aromatic ring structures are of interest in a number of areas. These molecular complexes are involved in redox catalysis,[1-3] photosynthesis,[4-10] herbicidal activity,[11] and malaria drug binding to hemoglobin-based pigments.[12] They are also models for the residue–porphyrin interactions in heme proteins that may be involved in control of O_2 affinity in hemoglobin.[13-15]

Recently, I have undertaken a study of these molecular complexes by using Raman difference spectroscopy (RDS). The RDS technique[13,16-18] is sensitive to small frequency differences in the resonance Raman lines of metalloporphyrins, resulting from differences in their protein environment.[13-16] These differences, while small (~1.0 cm^{-1}), indicate large redistributions of the π electrons of the ring, since they represent about 10% of the changes

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(1) Manassen, J. *Catal. Rev—Sci. Eng.* **1974**, *9*, 223.
(2) Manassen, J.; Bar-Ilan, A. *J. Catal.* **1970**, *17*, 86.
(3) Fuhrhop, J. H.; Baccouche, M.; Grabow, H.; Aryounanian, H. *J. Mol. Catal.* **1980**, *7*, 245.
(4) Calvin, M. *J. Theor. Biol.* **1961**, *1*, 258.
(5) Hill, H. A. O.; McFarlane, A. J.; Mann, B. E.; Williams, R. J. P. *Chem. Commun.* **1968**, 123.
(6) Hill, H. A. O.; McFarlane, A. J.; Williams, R. J. P. *Chem. Commun.* **1967**, 905.
(7) Ho, T. F.; McIntosh, A. R.; Bolton, J. R. *Nature* (*London*) **1980**, 286.
(8) Willner, I.; Mettee, H.; Ford, W. E.; Otvos, J. W.; Calvin, M. *Sol. Power Fuels*, [*Proc. Int. Conf.*] **1980**, *3*, 221.
(9) Pileni, M. P.; Grätel, M. *J. Phys. Chem.* **1980**, *84*, 1822.
(10) Tanno, T.; Wöhrle, D.; Kaneko, M.; Yamada, A. *Sol. Power Fuels*, [*Proc. Int. Conf.*] **1980**, *3*, 161.
(11) Boon, W. R., *Chem. Ind.* (*London*) **1965**, 782.
(12) Chou, A. C.; Chevli, R.; Fitch, C. D. *Biochemistry* **1980**, *19*, 1543.
(13) Shelnutt, J. A.; Rousseau, D. L.; Friedman, J. M.; Simon, S. R. *Proc. Natl. Acad. Sci. U.S.A.* **1979**, *76*, 4409.
(14) Shelnutt, J. A.; *Proc. Int. Conf. Raman Spectrosc., 7th* **1980**, 516.
(15) Abbott, E. H.; Piafson, P. A. *J. Am. Chem. Soc.* **1974**, *96*, 7378.
(16) Shelnutt, J. A.; Rousseau, D. L.; Dethmers, J. K.; Margoliash, E. *Proc. Natl. Acad. Sci. U.S.A.* **1979**, *76*, 3865.
(17) Rousseau, D. L.; Shelnutt, J. A.; Simon, S. R. *FEBS Lett.* **1980**, *111*, 235.
(18) Rousseau, D. L.; Shelnutt, J. A.; Henry, E. R.; Simon, S. R. *Nature* (*London*) **1980**, *285*, 49.

0002-7863/81/1503-4275$01.25/0

Table I. Frequency Shifts[a] in Some Copper Uroporphyrin Raman lines upon Molecular Association with Various Addends

addend	buffer	shifts					
		1309 cm^{-1}	1379 cm^{-1}	1403 cm^{-1} [c]	1500 cm^{-1}	1582 cm^{-1} [c]	1637 cm^{-1}
1,10-phen	NaOH (Tris)		+0.4 (+0.2)		+1.8 (+1.6)	+ (+)	+1.9 (+1.6)
1,7-phen	NaOH	<0.8	+0.8[b]	−0.4	+2.1	+1.3	+2.2
4,7-phen	NaOH	<1.0	+0.4	−0.6	+1.9	+1.4	+2.3
4-Me-1,10-phen	NaOH		b	−0.4	+1.8	+1.4	+1.9
5-Me-1,10-phen	NaOH	<0.4	+0.3	b	+1.6	+1.3	+1.8
5-chloro-1,10-phen	NaOH	+0.7	+0.4	<0.2	+2.1	+1.7	+2.7
5-nitro-1,10-phen	NaOH	<0.3	<0.2	−0.3	+1.5	+0.8	+1.8
5-phenyl-1,10-phen	NaOH	<0.4	+0.1	<0.1	+0.2	+0.1	+0.1
2,9-Me_2-1,10-phen	Tris		+0.2		+1.1	+0.6	+1.3
4,7-Me_2-1,10-phen	NaOH	−0.2	+0.2	−0.4	+1.1	+1.1	+1.5
5,6-Me_2-1,10-phen	Tris		<0.3	<0.2	+1.0	+1.0	+1.4
4,7-Ph_2-1,10-phen	Tris	<0.3	<0.2		<0.4	<0.1	<0.1
2,9-Me_2-4,7-Ph_2-1,10-phen	Tris	<0.3	<0.2		<0.4	<0.1	<0.1
1,10-phen-5,6-dione	NaOH	<0.6	<0.2	<0.2	+1.3	+0.8	+1.5
1,10-phen-4,7-diol	NaOH (Tris)	<0.4	b (b)	<0.2 (<0.2)	<0.2 (+)	+0.3[b] (+0.2[b])	+0.3 (+0.3)
pyridine	Tris	−0.8	+0.4	−0.3	+0.5	+	+0.6
methyl viologen	NaOH (Tris)		−2.4 (−2.2)		−2.2 (−2.4)	−4.3 (−4.0)	−1.3 (−1.8)

[a] Frequency differences, $\nu(\text{CuURO} + \text{addend}) - \nu(\text{CuURO})$, are calculated from $\Delta\nu = 0.38\ \Gamma(I_D/I_0)$, where Γ is the full width at half-maximum and I_0 is the intensity of the line. I_D is the peak-to-valley intensity in the balanced difference spectrum.[16] Line widths for the 1309, 1379, 1403, 1500, 1582, and 1637 cm^{-1} lines are 10, 15, 10, 10, 17, and 12 cm^{-1}, respectively. [b] Line shape variation. [c] Overlapping lines increase possible error in $\Delta\nu$ for this line.

in frequency that occur on metal oxidation or ring reduction.

The shifts in frequency of the Raman lines of copper(II) uroporphyrin I (CuURO) that result from complex formation have been detected by using RDS to compare the Raman spectrum of the metalloporphyrin *plus* addend to that of the metalloporphyrin alone. At the concentrations employed, the Raman spectrum of the addend is not observed. The structure of the complex is inferred from the addend-induced frequency shifts of the vibrations of the porphyrin macrocycle that are selectively enhanced. These complexes have not been studied previously by vibrational spectroscopy; however, studies of similar molecular complexes using visible absorption spectroscopy[19,20] and ESR[21] spectroscopy have appeared.

The complexes formed in aqueous alkaline solution between CuURO and 15 derivatives of phenanthroline have been investigated in detail. The porphyrin concentration was about 2×10^{-5} M. Except for the diol derivative, the phenanthroline addends were at saturation, and all except the phenyl derivatives were at least 80% complexed as judged from spectrophotometric titration experiments. Table I shows the frequency shifts of the Raman lines in the 1300–1700-cm^{-1} region that are induced by formation of a complex of CuURO with each of the 15 phenanthroline (phen) derivatives, methyl viologen, and pyridine.

Of particular interest are the shifts in the lines at 1379, 1500, 1582, and 1637 cm^{-1}. In the iron porphyrins these lines are sensitive to variations in the π-electron density in the antibonding orbitals of the porphyrin ring caused by changes in the state of axial ligation,[22] oxidation,[23] and changes in the protein environment.[13,16] These lines all shift to lower (higher) frequency when the π-electron density of the ring increases (decreases). This behavior has been explained in terms of increased density in antibonding π orbitals of the porphyrin ring which would generally lower the force constants. Similarly, for the CuURO complexes these lines shift either to higher frequency or to lower frequency as a group. Also, if the same interpretation holds for CuURO, we would infer lower π density in the porphyrin ring for the molecular complexes with the phenanthrolines and pyridine and higher π-electron density for the methyl viologen complex.

Copper was chosen to minimize the interaction at the metal site through the lone pairs of the addends. 1,10-Phenanthroline could interact with the Cu ion through the nitrogen lone pairs if the Cu ion were moved out of plane slightly. 2,9-Dimethyl-1,10-phenanthroline is sterically hindered, however, and it cannot interact with the Cu ions in a perpendicular orientation. Nevertheless, the shifts for the 2,9-dimethyl-1,10-phenanthroline complex is only slightly less than for the 1,10-phenanthroline complex. The three dimethyl derivatives have about the same shifts so that they exhibit either a similar steric effect or an inductive effect. Therefore, interaction directly between the lone pairs and the metal is unlikely.

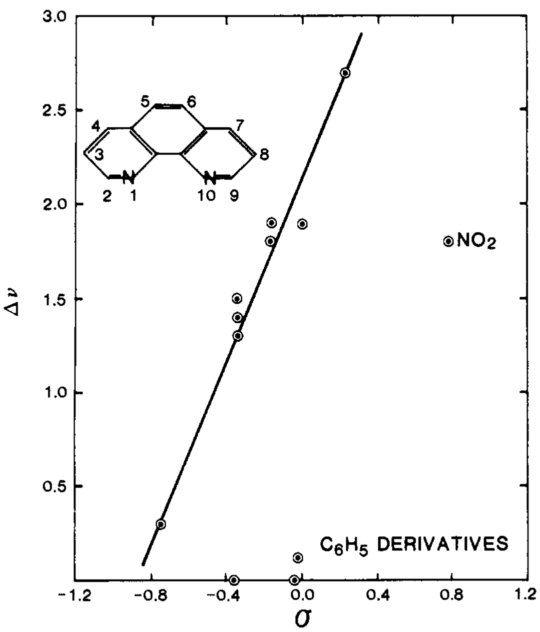

Figure 1. Raman frequency shift in the 1637-cm^{-1} line for CuURO–phen complexes vs. Hammett constants for the substituted phenanthrolines. The acceptor properties increase with increasing σ. Error in $\Delta\nu$ for this line is ±0.1 cm^{-1}.

The phenyl derivatives are sterically hindered from lying flat on the porphyrin ring. The 5-nitro-1,10-phenanthroline derivative may also be hindered, since the NO_2 group is bulky. Since shifts for these complexes are the smallest detected, a π–π charge-transfer complex with the planes of the rings parallel is indicated. This is consistent with the fact that the position of the heteroatom in the phenanthroline ring has little effect on the structure of the complex as judged by the Raman shifts.

Figure 1 shows a plot of the Hammett constants σ, which give a measure of the electron-withdrawing properties of parasubsti-

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(19) Mauzerall, D. *Biochemistry* **1965**, *4*, 1801.

(20) Heathcote, J. G.; Hill, G. J.; Rothwell, P.; Slifkin, M. A. *Biochem. Biophys. Acta.* **1968**, 153, 13.

(21) Blumberg, W. E.; Peisach, J. *J. Biol. Chem.* **1965**, *240*, 870.

(22) Spiro, T. G.; Burke, J. M. *J. Am. Chem. Soc.* **1976**, *98*, 5482.

(23) Spiro, T. G.; Strekas, T. C. *J. Am. Chem. Soc.* **1974**, *96*, 338.

tuents,[24] vs. the frequency shifts of the 1637-cm^{-1} Raman line. Only the sterically hindered 5-nitro and phenyl derivatives lie off the line. The correlation with phen acceptor properties (Figure 1), together with a pattern of shifts in the Raman lines consistent with changes in π density, provides strong evidence for charge-transfer stabilization of the molecular complex.

Visible absorption spectral studies give a rough correlation between log K and the shift in frequency of the 1637-cm^{-1} Raman line. Charge transfer accounts for more than 1 order of magnitude in K or about 20% of the binding energy (ΔG). The tightness (log $K > 6$) of the methyl viologen dication complex is explained by the strong electrostatic interaction, which presumably induces an "unfavorable" charge transfer in the ground state, making viologen (normally a stronger acceptor then phen) a donor.

Recently, Shelnutt el al., observed that the O_2 affinity properties of hemoglobin[13] and myoglobin[25] correlate with the shifts in the π-electron density marker lines. A charge-transfer model for cooperative O_2 binding was suggested.[13,14] We also pointed out that nearby aromatic amino acid residues could form donor-acceptor complexes with the porphyrin. The present data shows for the first time that molecular complexes give shifts in the π-density marker lines like those observed in hemoglobin.[26]

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(24) Hine, J. "Physical Organic Chemistry"; McGraw Hill: New York, 1962; p 87.

(25) Shelnutt, J. A.; Rousseau, D. L., unpublished result.

(26) Shelnutt, J. A., submitted to *Biochemistry*.

New Bonding Mode for a Bridging Dioxygen Ligand: Crystal and Molecular Structure of [K·dibenzo-18-crown-6][$Al_2(CH_3)_6O_2$]·1.5C_6H_6

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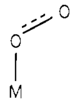
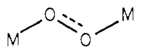
Dioxygen adduct complexes of metal ions have been the subject of many recent investigations.[1,2] Four types of structures have been observed (I–IV),[3] and correlations between the O–O bond

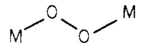


I



II

III



IV

length and the O–O symmetrical stretch have been made. I and II are formulated as the superoxide ion, O_2^-. With a bond order of 1.5, the bond distances for II fall in the range 1.10–1.30 Å, and ν_{O-O} 1075–1195 cm^{-1}.[4] For the bridged peroxo situation (IV), the lengths reside between 1.40 and 1.50 Å, and ν_{O-O} 790 and 930 cm^{-1}.[4] The ionic compounds KO_2 and Na_2O_2 exhibit values of 1.28 Å and 1145 cm^{-1}, and 1.49 Å and 842 cm^{-1}, respectively,[3] for bond distances and ν_{O-O}.

In the course of our studies on high-oxygen content organoaluminum compounds, we have carried out the reaction of KO_2 and $Al(CH_3)_3$ according to

$$KO_2 + 2Al(CH_3)_3 + \text{dibenzo-18-crown-6 (V)} \xrightarrow{\text{aromatic}} [\text{K}\cdot\text{dibenzo-18-crown-6}][Al_2(CH_3)_6O_2]$$

To our surprise the new complex is thermally stable for at least 24 h in refluxing toluene. More interesting, the single-crystal X-ray structure[5] has revealed a new type of coordination mode for the superoxide ion (See VI and Figure 1). The dioxygen

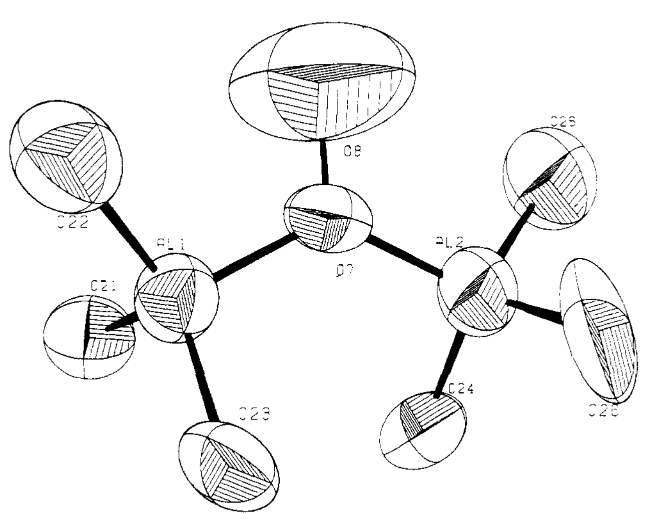
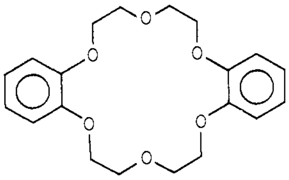
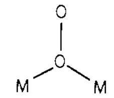


Figure 1. Structure of the anion [$Al_2(CH_3)_6O_2$]$^-$, with the atoms represented by their 50% probability ellipsoids for thermal motion.



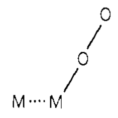
V



VI

moiety must be regarded as O_2^- for charge balance, but the O–O bond length is much longer than any previously found for a superoxide ion. Unfortunately, the distance is not known with great accuracy because of the high thermal motion of the nonbridging oxygen atom. The O–O value is 1.47 (2) Å. The weakness of the O–O linkage is also substantiated by the IR spectrum (Nujol mull) in which the ν_{O-O} is assigned to the band at 851 cm^{-1}.

The importance of the new bonding mode is underscored by a consideration of the hemerythrins, a group of oxygen-carrying proteins. The resonance Raman spectrum of oxyhemerythrin shows an assigned O–O stretch at 844 cm^{-1}.[6] The two oxygen atoms have also been shown to exist in two different environments. Structures VI and VIII were proposed.[6] Our investigation



VII

demonstrates that a low ν_{O-O} and long O–O length may be associated with not only a peroxo group but also with the superoxo

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(1) Sugiura, Y. *J. Am. Chem. Soc.* **1980**, *102*, 5216.

(2) Bertini, I.; Luchinat, C.; Scozzafava, A. *J. Am. Chem. Soc.* **1980**, *102*, 7349.

(3) Jones, R. D.; Summerville, D. A.; Basolo, F. *Chem. Rev.* **1979**, *79*, 139.

(4) Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry"; Interscience: New York, 1980; pp 156–157.

(5) The space group is the triclinic $P\bar{1}$ with unit cell parameters a = 13.210 (8), b = 13.671 (8), c = 14.090 (8) Å; α = 68.11 (4), β = 65.46 (4), γ = 87.42 (4)°; D_c = 1.08 g cm^{-3} for Z = 2; λ = 0.71069 Å, and T = 22 °C. Least-squares refinement based on 1509 observed reflections led to a final R value of 0.084. The hydrogen atoms of the crown ether were included with fixed contributions and those of the anion were located on a difference Fourier map, but their parameters were not refined. The nonhydrogen atoms of the crown, the anion, and the potassium ion were refined with anisotropic thermal parameters. The overall accuracy of the structure is impaired by the disorder (or high thermal motion) associated with the benzene molecules.

(6) Dunn, J. B.; Shriver, D. F.; Klotz, I. M. *Biochemistry* **1975**, *14*, 2689. Kurtz, D. M.; Shriver, D. F.; Klotz, I. M. *J. Am. Chem. Soc.* **1976**, *98*, 5033.

0002-7863/81/1503-4277$01.25/0