

temperature factors, and structure factor table appear in Tables III-V.<sup>9</sup>

**Supplementary Material Available.** Tables III-V will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number JACS-74-6763.

(9) See paragraph at end of paper regarding supplementary material.

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### Evidence against the O<sub>2</sub><sup>-</sup> Formulation of Cobalt(II) Adducts of Dioxygen

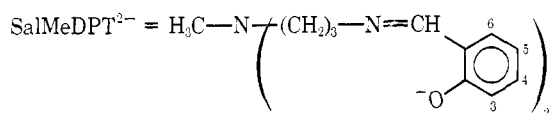
Sir:

The reversible binding of dioxygen, O<sub>2</sub>, to form six-coordinate cobalt(II) Schiff base and porphyrin complexes has led to much recent work concerning the electronic structure of the cobalt-oxygen adduct<sup>1-6</sup> and the enthalpy of adduct formation.<sup>7-10</sup> Binding of O<sub>2</sub> usually takes place in the presence of a coordinating base, B, and can be represented as



where CoL represents the Schiff base or porphyrin complex. These adducts have been formulated as superoxo (O<sub>2</sub><sup>-</sup>) adducts of Co(III) through esr<sup>2-6</sup> and X-ray diffraction studies.<sup>11</sup> In this communication we present results on a complex which is best viewed as one involving bound singlet O<sub>2</sub> and show its esr spectral behavior is not very different than other reported cobalt-oxygen complexes formulated as O<sub>2</sub><sup>-</sup>.

We report nmr and esr investigations of the O<sub>2</sub> and CO adducts of the pentadentate Schiff base complex Co<sup>II</sup>(salMeDPT), salMeDPT = bis(salicylidene-γ-



iminopropyl)methylamine, as shown below. Nmr studies on this system are more feasible than those previously reported due to enhanced solubility. Co(salMeDPT) is high spin ( $\mu = 4.29$  BM in solid, 4.28 BM

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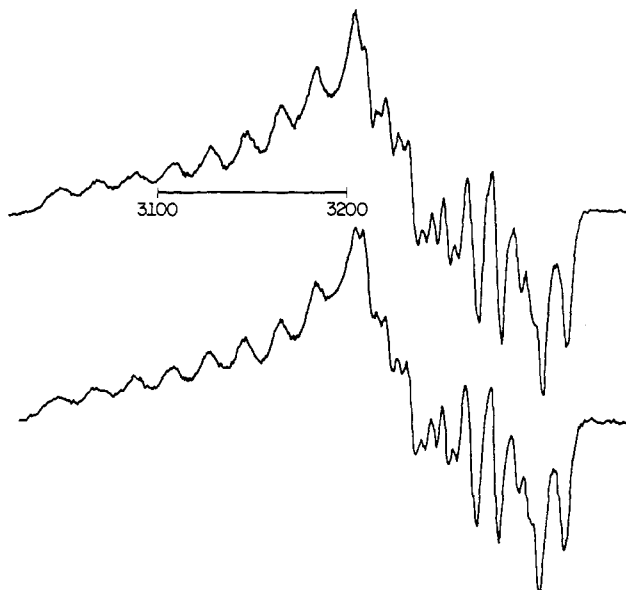


Figure 1. X-Band esr spectra of Co(salMeDPT) adducts in CH<sub>2</sub>Cl<sub>2</sub>-toluene glass: O<sub>2</sub> (top), CO (bottom).

in CH<sub>2</sub>Cl<sub>2</sub> solution) and is likely five-coordinate, as is the case with the Ni(II) complex of this ligand.<sup>12</sup> Since the combined effects of spin-orbit coupling and zero-field splitting cause a short  $T_1$ , the contact-shifted <sup>1</sup>H nmr is easily observable. The isotropic shifts exhibit Curie behavior.

Addition of 1 atm of O<sub>2</sub> to the complex in degassed CDCl<sub>3</sub> solution produces a marked change in the nmr. As the temperature is lowered below -10°, new peaks appear in the 0-6 ppm range and they gain intensity as the temperature is lowered. The 4, 5, and 6 ring proton peaks lose intensity, but their chemical shifts remain identical with those of a low temperature degassed sample. At -50°, the 4-H peak has lost ~40% of its room temperature intensity. These observations are reversible with temperature. We attribute these new peaks to the O<sub>2</sub> adduct. Since separate resonances are observed for the adduct and free complex, there is slow exchange of O<sub>2</sub> over the temperature range observed. Further evidence for slow exchange comes from the fact that resonances due to free Co(salMeDPT) in the O<sub>2</sub> solution fall on the same Curie plot as the degassed sample.

The esr of free Co(salMeDPT) in a degassed solution of CH<sub>2</sub>Cl<sub>2</sub>-toluene or a dilute powder in Zn<sup>II</sup>(salMeDPT) shows a very broad signal observable at 77°K with a  $g$  value of approximately 4.3, consistent with its high spin configuration. Upon addition of O<sub>2</sub> to a CH<sub>2</sub>Cl<sub>2</sub>-toluene solution, the spectrum sharpens and  $g$  value anisotropy is evident and is better resolved than in any previously reported spectra of O<sub>2</sub> adducts. A precise computer simulation has not as yet been obtained because of field dependent line widths as seen in Figure 1 and the possible misalignment of the  $g$  and  $A$  tensors. The spectrum observed when CO is complexed to the cobalt is practically identical with that of the O<sub>2</sub> adduct. Coordination of CO is established from the very broad infrared absorption of complexed CO at ~2090 cm<sup>-1</sup> and from a +23.8 ppm shift

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from free CO for the stopped exchange peak in the  $^{13}\text{C}$  nmr of a 90.5%  $^{13}\text{C}$  enriched CO adduct.

Further evidence for the similarity in the  $\text{O}_2$  and CO adducts comes from their  $^{13}\text{C}$  nmr. The adducts were run at *ca.*  $-50^\circ$  in tubes sealed under 1 atm of gas at that temperature. High-spin Co(salMeDPT) shows irresolvable broad peaks. Relatively sharp resonances with small isotropic shifts are observed for the adducts consistent with the  $^1\text{H}$  nmr conclusion of slow exchange on the nmr time scale. A definite similarity again exists between the chemical shifts of the ligand resonances in both the  $\text{O}_2$  and CO adducts.

The observed cobalt(II) hyperfine coupling constants are  $\sim 5$  to  $20 \times 10^{-4} \text{ cm}^{-1}$  and comparable to those reported for other adducts of  $\text{O}_2$  with cobalt(II) complexes. The unusual esr behavior in the present CO adduct, relative to previously studied five coordinate CO adducts, likely is due to the fact that Co(salMeDPT)·CO is six-coordinate, and, as is the case with the  $\text{O}_2$  adduct, the geometry is likely very distorted. There are several possible reasons for the reduced cobalt hyperfine coupling constants in these adducts. They are based on variations in 3d and 4s and 4p atomic orbital contributions in the MO containing the unpaired electron in addition to variations in other crystal field parameters included in the esr analysis.<sup>13</sup> In the past, the reduced value has been interpreted as an indication of  $\text{O}_2^-$  by comparison to low spin four- and five-coordinate cobalt(II) species.<sup>13-18</sup> The presence of additional ligands in the six-coordinate complexes has a considerable effect on the relative 3d-orbital energies. It is significant to point out that the coordination of methyl isocyanide or CO to this  $\text{Co}^{\text{II}}$ -(salMeDPT) complex results in an esr spectrum similar to that of  $\text{O}_2$ . The observed isotropic proton nmr shift of the  $\text{CH}_3\text{NC}$  ligand ( $\sim 4$  ppm downfield from free  $\text{CH}_3\text{NC}$ ) and the small  $^{13}\text{C}$  shift of the CO ligand preclude the possibility of these fragments being formulated as  $\text{CH}_3\text{NC}^-$  or  $\text{CO}^-$  and provide a precedent for a six-coordinate, low spin cobalt(II) complex with a lower coupling constant than the four- or five-coordinate systems. Subsequent to submission of this manuscript, Wayland, *et al.*,<sup>19</sup> reported a five-coordinate CO adduct of cobalt(II) tetraphenylporphyrin which behaves quite differently from our CO adduct. This does not alter our conclusions in view of the difference in coordination and geometry.

Since  $\text{CH}_3\text{NC}$  is not reduced and it is unlikely that CO is formally reduced in its adduct, we feel it best to describe both the CO and  $\text{O}_2$  adduct as Co(II) in nature with the unpaired spin being largely in a cobalt(II) orbital instead of an  $\text{O}_2 \pi^*$  orbital (as in  $\text{O}_2^-$ ). The coordinated  $\text{O}_2$  is then formulated as a bound singlet state with possible stabilization from metal to  $\text{O}_2 \pi$  back-bonding. The spin pairing is caused by the lift-

ing of the degeneracy of the  $\pi^*$  orbitals of  $D_{\infty h} \text{O}_2$  upon coordination. Since the reduced cobalt hyperfine was the main evidence for  $\text{O}_2^-$  in previous studies, there is nothing to suggest that the other reported  $\text{O}_2$  complexes of cobalt(II) should not be similarly formulated even though the  $\text{O}_2$  adduct reported here may have a very different geometry than those in which part of the ligand set is rigorously planar.

These conclusions are contrary to those recently reported from an  $^{17}\text{O}$  labeled study of dioxygen coordinated to a cobalt(II) ammonia complex in a  $\gamma$  Zeolite.<sup>20</sup> The resolution of the  $^{17}\text{O}$  hyperfine on these systems is badly obscured by the cobalt, and the spectra do not provide independent support for the  $\text{O}_2^-$  model advocated by these authors. A recent  $^{17}\text{O}$  enrichment study<sup>21</sup> of  $\text{Co}(\text{bzacen})\text{pyO}_2$  in  $\text{CH}_2\text{Cl}_2$  solution showed both oxygens equivalent, though the crystal structure shows the geometry of the Co- $\text{O}_2$  moiety to be bent with an angle of  $126^\circ$ . Spin densities were calculated from the observed isotropic  $\langle a \rangle_{^{17}\text{O}} = 21.6 \text{ G}$ , by assuming that the unpaired electron was in an  $\text{O}_2 \pi^*$  MO. Since it was found that both oxygens are equivalent, it is possible that a rapid equilibrium between two  $\sigma$ -bonded structures exists with unpaired spin delocalization arising from the interaction of cobalt  $d_{z^2}$  and  $\text{O}_2 \text{ sp}^2$  orbitals (similar to  $\text{Co}(\text{bzacen})\text{py}$ ). This situation would put spin directly into the oxygen 2s orbitals and require a very small spin density on the  $\text{O}_2$  molecule to produce a 21.6 G hyperfine splitting.

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### Singlet Oxygen Reaction. III. "Solvent and Temperature Effects" on the Photosensitized Oxygenation of Vinyl Sulfides and Vinyl Ethers

Sir:

Reactions of singlet oxygen with vinyl ethers have been extensively developed,<sup>1-6</sup> but relatively few studies have been reported in which sulfur substituted ethylenes are oxidized.<sup>7,8</sup> We previously reported that vinyl sulfides, which have an activated double bond as well as allylic hydrogen atoms, give dithiooxalate, thiocarbonate, and disulfide, presumably *via* 1,2-dioxetane intermediates.<sup>9,10</sup> Recently, however, several reports have

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