P. Schaefer, and R. E. Marsh, *Acta Crystallogr., Sect. B*, **27**, 1461 (1971); (c) J. R. Fritch, G. G. Christoph, and W. P. Schaefer, *Inorg. Chem.*, **12**, 2170 (1973).
(23) W. P. Schaefer and R. E. Marsh, *Acta Crystallogr., Sect. B*, **25**, 1675 (1969); C. L. Freinkel, J. S. Sherfinski, W. P. Schaefer, and G. G. Christoph, in preparation.
(24) M. Calligaris, G. Nardin, and L. Randaccio, *Coord. Chem. Rev.*, 7, 385 (1972).
(25) The structure of the monomeric dioxygen adduct of *N,N'*-{1,1,2,2-tetramethyl}ethylenebis(3-fluorosalicylideniminato)cobalt(II) with 1-methylimidazole as the axial base has been determined (A. Avdeef and W. P. Schaefer, *J. Am. Chem. Soc.*, in press. At −171 °C the crystal structure is completely ordered including two molecules of acetone solvent. The O-O bond length is 1.302 (3) Å and the Co-O-O angle is 117.3 (2)°.
(26) B. S. Tovrog and R. S. Drago, *J. Am. Chem. Soc.*, **96**, 6765 (1974).
(27) B. M. Hoffman, T. Syzmanski, and F. Basolo, *J. Am. Chem. Soc.*, **97**, 673 (1975).
(28) D. Getz, F. Melamud, B. L. Silver, and Z. Dori, *J. Am. Chem. Soc.*, **97**, 3846 (1975).
(29) B. M. Hoffman and D. H. Petering, *Proc. Natl. Acad. Sci. U.S.A.*, **67**, 637 (1970); G. S. Hsu, C. A. Spilburg, C. Bull, and B. M. Hoffman, *ibid.*, **69**, 2122 (1972).
(30) M. J. Carter, D. P. Rillema, and F. Basolo, *J. Am. Chem. Soc.*, **96**, 392 (1974).
(31) L. G. Marzilli and P. A. Marzilli, *Inorg. Chem.*, **11**, 457 (1972), and references therein.
(32) R. G. Little and J. A. Ibers, *J. Am. Chem. Soc.*, **96**, 4440 (1974); J. W. Lauher and J. A. Ibers, *J. Am. Chem. Soc.*, **96**, 4447 (1974).
(33) F. R. Fronczek and W. P. Schaefer, *Inorg. Chim. Acta*, **9**, 143 (1974), and references therein.
(34) C. Busetto, F. Cariati, A. Fasi, M. Gullotti, F. Morazzoni, A. Pasini, R. Ugo, and V. Valenti, *J. Chem. Soc., Dalton Trans.*, 754 (1973).
(35) M. Calligaris, G. Nardin, and L. Randaccio, *J. Chem. Soc., Dalton Trans.*, 419 (1973).
(36) O. L. Harle and M. Calvin, *J. Am. Chem. Soc.*, **68**, 2612 (1946).
(37) Strikingly similar intermolecular interactions of the dioxygen ligand with acetone solvent molecules and the *N*-methylimidazole base are found in the crystal structure of Co(3-Fsaltmen)(MeImid)(O_2).[25]
(38) L. Pauling, "The Nature of the Chemical Bond", 3d ed, Cornell University Press, Ithaca, N.Y., 1960, p 260.

Nature of the Bound O_2 in a Series of Cobalt Dioxygen Adducts

Benjamin S. Tovrog, David J. Kitko, and Russell S. Drago*

Contribution from the School of Chemical Sciences, William A. Noyes Laboratory, University of Illinois, Urbana, Illinois 61801. *Received October 10, 1974*

Abstract: A new series of dioxygen adducts of cobalt(II) complexes is reported whose EPR parameters span a considerably larger range than those reported earlier. The EPR spectra of these and other reported complexes are analyzed in detail, leading to a qualitative molecular orbital description of the adducts. The model shows that the unpaired electron resides on dioxygen regardless of the amount of electron transfer from cobalt(II) to oxygen. It is shown that the only source of electron transfer information lies in the spin polarization of a filled cobalt-oxygen σ bond by the unpaired electron residing in an essentially dioxygen π^* molecular orbital. The interpretation of these results indicates that there is a wide variation in the amount of electron transfer to O_2 in a series of adducts which depends on the ligands coordinated to the cobalt. Electron transfer into O_2 ranging from 0.1 to 0.8 of an electron is found in different adducts. The bonding interaction involves essentially a spin pairing of an unpaired electron in an antibonding orbital of O_2 with an unpaired electron in a d_{z^2} orbital of cobalt(II). This model is consistent with the observed magnetic properties of reported iron-dioxygen and manganese-dioxygen adducts. A previously unrecognized source of spin polarization is proposed and found to make a significant contribution to the observed coupling constants.

The ability of transition metal ions to reversibly coordinate O_2 has been known for a long time. Some of the first synthetic systems reported to bind O_2 were cobalt(II) complexes.[1] However, only recently has it been demonstrated that a wide variety of ligand environments about cobalt(II) result in reversible systems.[2-8] Neutral complexes in which the ligands contain N_2O_2 and N_4 donor atoms that are bound in a planar array and which also contain a fifth axial donor that is a σ donor,[3] π-acceptor,[7] sterically hindered base, or aromatic solvent molecule[8] have been reported. The complexes $Co(CN)_5{}^{3-}$,[9] $Co(pfp)_2$[10] (pfp = perfluoropinacol), and several derived from pentadentate ligands[11,12] have also been recently described. The reversible coordination of O_2 to iron(II) has also been an area in which significant recent advances have been made.[13]

Much of the recent activity in this area has been motivated by a desire to elucidate the factors which lead to reversible O_2 binding, to enhance the kinetic reactivity of O_2 by coordination, and to understand the transport of O_2 and oxidations by it in biological systems. Systematic approaches to these problems will require an understanding of the electronic nature of the coordinated O_2 fragment. The cobalt(II) complexes are particularly well suited for an investigation of the electronic structure because they contain at least one unpaired electron, making them ideal for electron spin resonance studies. Accordingly, we have directed our initial efforts toward a study of these complexes.

An EPR study[2] of Co(acacen)pyO_2 and other similar O_2 adducts has shown greatly reduced anisotropy ($A_{\parallel} - A_{\text{iso}}$) in the cobalt hyperfine coupling constants when compared to the parent five-coordinate cobalt(II) complex. These results along with some structural[14] and infrared data to be discussed shortly led to the formulation of the cobalt-O_2 adducts as Co(III)-$O_2{}^-$ with "nearly complete electron transfer from cobalt(II) to oxygen". In a subsequent EPR study of an enriched $^{17}O_2$ adduct,[14] the *isotropic* ^{17}O hyperfine coupling constant was reported and also interpreted in terms of an $O_2{}^-$ formulation.

The EPR spectra of the O_2 adduct of the pentadentate Schiff base complex CoSMDPT (SMDPT = bis(salicylidene-γ-iminopropyl)methylamine) and that of an isocyanide adduct have been reported.[11] The existence of this adduct was subsequently confirmed by Hoffman et al., who also agreed that, in both the O_2 and CH_3NC adducts, the cobalt hyperfine coupling constant in the parallel direction was reduced considerably below that of typical five-coordinate adducts.[15] The small observed proton contact shifts in the NMR of the six-coordinate isocyanide adduct enabled us to conclude that the observed reduction in the hyperfine coupling constant of the adduct occurred without "oxidation of cobalt" and formation of Co(III) $CNCH_3{}^-$. An interpretation of the isotropic ^{17}O hyperfine coupling constant in terms of a coordinated singlet O_2 formulation was presented.

The experimental result needed to resolve the question of the singlet nature of the adducts was the ^{17}O EPR anisotropic hyperfine coupling constants. Correspondence with Dori et al.[16] revealed that they had obtained but unfortunately had not reported these results for their Co–O_2 adduct. One could conclude from the anisotropy in the ^{17}O hyperfine coupling that the unpaired electron resides in a molecular orbital which was mainly composed of oxygen p orbitals. This result conclusively rules out the bound singlet O_2 formulation as these authors subsequently reported.[16]

Elimination of the singlet O_2 structure does not establish the electronic nature of the bound O_2 fragment in the complex as O_2^- with "nearly complete electron transfer", i.e., Co(III) O_2^- in the formal sense. Remaining are structures with ranges of electron transfer from zero to one, i.e., from Co(II) O_2 to Co(III) O_2^-. A more complete description of what is meant by bound O_2 or O_2^- is provided in the text. In this section, our main concern is to evaluate the short-comings of data interpretation which led to an O_2^- description for all Co–O_2 adducts.

EPR, x-ray, and infrared results were employed to formulate the adduct as Co(III) O_2^-. The inconsistencies in the EPR analysis have been reported[11] and will be discussed in more detail in this article. The single-crystal x-ray diffraction interpretation leading to an O_2^- formulation is based upon a comparison[17a,b] of the O–O distance in an O_2 adduct (1.26 Å) with that in free O_2 and that in the ionic potassium superoxide salt (1.28 Å). However, the ionic salt sodium superoxide has a reported[17c,d] distance of 1.31 Å while O_2^- in the gas phase has a distance[17e] of 1.34 Å. Recently,[17b] an O–O distance of 1.24 Å was reported for $CoCN_5O_2^{3-}$. Even in the absence of the above mentioned ambiguities inferences of the electronic nature of materials from bond distances are known historically to be extremely risky when good model compounds are not available. For example, the O–O distance to be expected for a coordinated singlet or neutral triplet O_2 molecule with possible metal to ligand π back-bonding cannot be predicted from the structure of free O_2. The O–O σ bond in a complex in which a Co–O bond has formed will have different s and p orbital contributions than that in free O_2. With two antibonding electrons, a slight weakening of the σ bond could result in an appreciable increase in the O–O distance upon coordination even if electron transfer did not occur. Similar complications exist in the interpretation of the reported infrared frequency lowerings upon complexation.

In this article, we report new five-coordinate cobalt(II) complexes which bind O_2. We offer an alternative interpretation of the cobalt hyperfine coupling which provides a consistent rationalization of all aspects of the results from this experiment. The ligand field strengths of the bound ligands provide a reasonable basis for predicting the variation in the spectra for a series of complexes. The spectral results are interpreted in terms of a qualitative molecular orbital model of the adducts and provide a crude estimate of the extent of electron transfer into the bound O_2 fragment. Finally, a model for the end on binding of O_2 is presented in which the interaction is viewed mainly as a spin pairing of one of the unpaired antibonding electrons of O_2 with an unpaired electron in the d_{z^2} orbital of cobalt(II). This model is used to rationalize the magnetic and EPR behavior of dioxygen complexes of iron(II) and manganese(II).

Experimental Section

General. Salicylaldehyde, 5-bromosalicylaldehyde, 5-methoxysalicylaldehyde, 3,3′-bis(diaminopropyl)methylamine, bis(2-cyanoethyl) ether, and boron trifluoride etherate were purchased from Aldrich. 5-Nitrosalicylaldehyde and diphenylglyoxime were purchased from Eastman. 3,3′-Diaminopropyl ether was prepared via the catalytic hydrogenation of bis(2-cyanoethyl) ether.[18] The Co complexes used as starting materials for the Co(X-salDAPE) series were prepared by the reaction of an aqueous solution of cobalt(II) acetate tetrahydrate and the appropriate salicylaldehyde in ethanol, washed with ethanol and ether and dried over P_2O_5.

Co(SMDPT) was prepared as reported.[19]

Preparation of Co(salDAPE)[20] and Substituted Derivatives. 3,3′-Diaminopropyl ether (1.32 g) in 10 ml of anhydrous deaerated EtOH was added to a slurry of 3.37 g of $Co(sal)_2 \cdot 2H_2O$ in 20 ml of anhydrous deaerated EtOH at reflux under N_2. The resulting slurry turned a deep reddish brown and the solid dissolved. The reaction was continued at reflux for 1 h and allowed to cool to ambient temperature. The tan solid that formed was collected on a fritted funnel under a stream of N_2, washed twice with EtOH and twice with Et_2O and dried in vacuo over P_2O_5.

The substituted derivatives were prepared in an analogous manner from $Co(X\text{-}sal)_2 \cdot 2H_2O$ (X = 5-Br, 5-OMe, 5-NO_2) an 3,3′-diaminopropyl ether. The complexes are tan in color, not sensitive to O_2 in the solid state, but are slowly oxidized in solution. They are only sparingly soluble in CH_2Cl_2, $CHCl_3$, and EtOH, and are insoluble in H_2O and hydrocarbons.

Analyses: **Co(salDAPE).** $CoC_{20}H_{22}N_2O_3$. Calcd: Co, 14.83; C, 60.45; H, 5.58; N, 7.05. Found: Co, 14.92; C, 60.33; H, 5.57; N, 7.06. **Co(5-NO_2-salDAPE).** $CoC_{20}H_{20}N_4O_7$. Calcd: Co, 12.09; C, 49.29; H, 4.14; N, 11.50. Found: Co, 12.01; C, 49.42; H, 4.18; N, 11.63. **Co(5-Br-salDAPE).** $CoC_{20}H_{20}N_2O_3Br_2$. Calcd: Co, 10.62; C, 43.27; H, 3.63; N, 5.04. Found: Co, 10.44; C, 43.30; H, 3.49; N, 4.94. **Co(5-OMe-salDAPE).** $CoC_{22}H_{26}N_2O_5$. Calcd: Co, 12.88; C, 57.77; H, 5.73; N, 6.12. Found: Co, 12.65; C, 57.64; H, 5.83; N, 6.30.

Preparation of $Co(DPGB)_2 \cdot 2CH_3OH$. Bis(diphenylglyoximato)cobalt(II) $[Co(DPGH)_2]$ was prepared by a reported procedure.[21] The BF_2 capped species $[Co(DPGB)_2]$ was prepared in a manner similar to that developed by Schrauzer.[22] A suspension of 5.0 g of $Co(DPGH)_2$ in 75 ml of Et_2O was deoxygenated with dry N_2. To this was added 10 ml of freshly distilled $BF_3 \cdot OEt_2$, the resulting mixture stirred for 24 h under N_2. The ether was evaporated and the residue recrystallized from methanol and isolated as a bismethanol adduct. All manipulations were carried out in Schlenk apparatus under N_2.

Anal. Calcd for $CoC_{30}H_{28}N_4O_6B_2F_4$: C, 51.68; H, 4.05; N, 8.04; Co, 8.45. Found: C, 51.54; H, 3.99; N, 7.95; Co, 8.40.

Electron spin resonance spectra were collected on a Varian Model E-9 spectrometer equipped with a Hewlett-Packard frequency counter. Cooling was provided by cold nitrogen gas, the probe temperature was approximately −180 °C for all samples. The field was calibrated using a Varian weak pitch sample with $g = 2.0070$.

Results and Discussion

Complexes Formed. The series of complexes illustrated in Figure 1 has been prepared for this investigation. The EPR spectra at ca. −180 °C in a CH_2Cl_2/toluene glass of the O_2 adducts of Co(X-salDAPE), Co(SMDPT), and $Co(DPGB)_2 \cdot (CH_3)_2CO$ are shown in Figure 2. The $Co(DPGB)_2$ complex serves as the basis for preparing a large number of new reversible dioxygen adducts. The complex is isolated as the trans dimethanol adduct. Stoichiometric amounts of many different bases, e.g., quinuclidine, piperidine, pyridine, *N*-methylimidazole, triethylamine, trimethylamine, 3,5-dichloropyridine, 4-cyanopyridine, acetonitrile, acetone, tetrahydrofuran, and *N*,*N*-dimethylacetamide all displace one molecule of methanol forming a mixed base–methanol adduct. The methanol is readily displaced from these complexes by O_2 forming reversible dioxygen adducts at low temperature. The first eight bases listed form 2:1 adducts when excess base is used, but the others do not. Excessses of these eight bases displace O_2 from the cobalt, so a greatly reduced tendency for O_2 coordination occurs in excess base.

The EPR spectra in Figure 2 indicate significant changes in the magnitude and anisotropy of A_{Co} in the series of complexes studied. Spin Hamiltonian values from computer simulation of the spectra of the O_2 adducts are listed in Table I, along with previously reported results for O_2 adducts formed from five-coordinate, square pyramidal cobalt(II) complexes. The variation in these values suggests differences in the electronic structures of the complexes, and these differences must

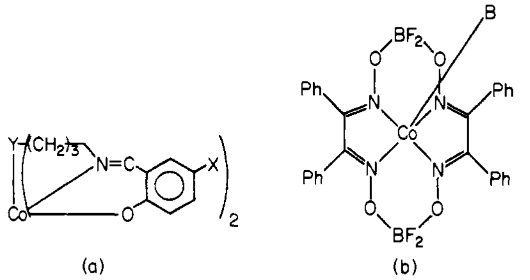


Figure 1. A series of pentadentate cobalt(II) complexes: (a) when Y = NCH_3, the ligand is abbreviated as salMeDPT; when Y is O, as salDAPE; (b) the bisdiphenylglyoximatocobalt(II) complex is abbreviated as

be understood if we are to understand the electronic structure of bound O_2.

Inconsistencies in a Simplified EPR Interpretation. Previous workers have analyzed the ESR of O_2 adducts in terms of the unpaired electron residing primarily on the O_2 moiety.[2-8,23] The cobalt hyperfine has been interpreted to indicate an almost complete transfer of an electron to O_2,[2,3,8] leading to a formal Co(III) O_2^- description of the complex. We now will proceed to demonstrate that this analysis of the EPR spectra is not internally consistent by considering more completely the data in Table I. First, the following equations pertinent to d^7 complexes with a $(d_{z^2})^1$ ground state in axial symmetry including interactions with excited doublet states[24] are summarized:

$$g_\parallel = 2.00 \qquad (1)$$

$$g_\perp = 2.00 - \frac{6\xi}{\Delta E(xz, yz - z^2)} \qquad (2)$$

$$A_\parallel = P\left[-K + \frac{4}{7} - \frac{1}{7}(g_\perp - 2.00)\right] \qquad (3)$$

$$A_\perp = P\left[-K - \frac{2}{7} + \frac{15}{14}(g_\perp - 2.00)\right] \qquad (4)$$

$$\langle A \rangle = P\left[-K + \frac{2}{3}(g_\perp - 2.00)\right] \qquad (5)$$

$$P = g_e\beta_e g_N\beta_N \left\langle \frac{1}{r^3} \right\rangle_{3d} \qquad (6)$$

where K is the Fermi contact parameter and P is proportional to the average value of the inverse of the metal-unpaired electron distance cubed $\langle 1/r^3 \rangle$. In complexes, P is reduced from the free ion value of 0.0254 cm^{-1}.[25] The Fermi contact parameter, K, in many cobalt(II) complexes has two main contributions: (1) polarization of filled 1s, 2s, and 3s orbitals inducing net negative spin at the cobalt nucleus, and (2) admixture of the 4s orbital into the $(d_{z^2})^1$ ground state[7b,23] (4s and d_{z^2} transform with the same irreducible representation in many symmetries) contributing positive spin. An equation describing these two contributions is:

$$-P \cdot K = \rho_{4s}[A(\mathrm{Co4s})] + \rho_{3d}[A(\mathrm{Co3d})]$$

where ρ_{3d}, ρ_{4s} are the cobalt 3d and 4s spin densities, respectively, $A(\mathrm{Co4s}) = 1232 \times 10^{-4}$ cm^{-1}, $A(\mathrm{Co3d}) = -4 \times 10^{-4}$ cm^{-1}.

EPR parameters for low spin five-coordinate cobalt(II) complexes, typified by Co(p-OCH_3)TPP·B (see Table I), fall in the range $g_\perp \sim 2.3$, $g_\parallel \sim 2.0$, $A_\parallel \sim 80 \times 10^{-4}$ cm^{-1}, and $A_\perp \sim -12 \times 10^{-4}$ cm^{-1}. This translates into P values of (180–200) × 10^{-4} cm^{-1} and $-P{\cdot}K$ of ca. -20×10^{-4} cm^{-1}. Anisotropy, given by $A_\parallel - \langle A \rangle$ is typically 60×10^{-4} cm^{-1}. Six-coordinate low spin cobalt(II) complexes (e.g., Co(p-OCH_3)TPP·B_2) possess typically $g_\perp \sim 2.2$, $g_\parallel \sim 2.0$, $A_\parallel \sim 65 \times 10^{-4}$ cm^{-1}, and $A_\perp \sim 50 \times 10^{-4}$ cm^{-1}, which translates into P values of (180–200) × 10^{-4} cm^{-1}, $-P{\cdot}K$ ca. -40×10^{-4} cm^{-1}, and $A_\parallel - \langle A \rangle \sim (69\text{–}79) \times 10^{-4}$ cm^{-1}. The solution of eq 3–5 and the requirement that P be positive make $A_\parallel > 0$, $A_\perp < 0$.

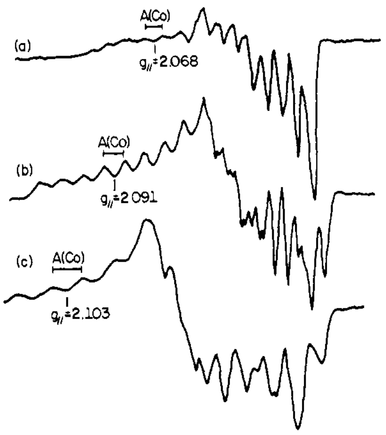


Figure 2. ESR of various new dioxygen adducts derived from $Co(DPGB)_2$ and five-coordinate cobalt(II) complexes at −180 °C in a CH_2Cl_2/toluene mixture: spectrum (a) is $Co(DPGB)_2$·acetone·O_2, (b) is Co(SMDPT)·O_2, and (c) is Co(salDAPE)·O_2.

The above equations have been written for a full electron in the d_{z^2} orbitals. For the O_2 adducts, a prior analysis[2] corrected for fractional occupation, α^2, of the d orbital and derived the following equation from eq 3 and 5:

$$|A_\parallel| = |\langle A \rangle| + \frac{4}{7}P\alpha^2$$

When the EPR parameters for O_2 adducts are substituted, the resulting α^2 values are approximately 0.1. The authors[2] concluded that nearly complete electron transfer from cobalt to oxygen occurred. However, an inconsistency exists in this interpretation of the EPR. The isotropic A_{Co} values observed for typical O_2 adducts (which is largely due to a Fermi contact interaction, see below) are roughly one-half of the isotropic A_{Co} values obtained for other six-coordinate cobalt(II) complexes. The values can be calculated from the reported values of $A_\parallel$ and $A_\perp$ in Table II. By no less rigorous a set of approximations than used on the anisotropic hyperfine coupling,[2] this leads to the conclusion that the electron residues in a molecular orbital with about 50% cobalt 3d character. We do not advocate this analysis, but only wish to conclude that the early EPR interpretations are inconsistent on this point and must be incomplete. We shall next develop an alternate interpretation of the EPR which overcomes the above inconsistency and leads to a new model for the electronic structure of these adducts.

Origin of the Cobalt Hyperfine. The interpretation of the cobalt hyperfine is complicated by the fact that it could arise from either a direct or indirect mechanism. The anisotropic $^{17}O_2$ hyperfine results are very important for this reason. A solution study of Co(bzacen)·py·O_2 showed equivalent oxygens[14] with $\langle A(^{17}O) \rangle = 21.6$ G. As we pointed out,[11] this is not unequivocal evidence for substantial unpaired spin on O_2, for a very small amount of unpaired electron density delocalized directly into the oxygen 2s orbital could give rise to a value of this magnitude. The critical experiment, determination of the anisotropic components of the ^{17}O hyperfine tensor, had been carried out but regrettably was not reported until recently.[16] The oxygens are shown to be nonequivalent, possessing 60 and 40% spin densities on the terminal and middle oxygens, respectively. This experiment indicates unequivocally that the unpaired electron in the adduct residues predominantly on the O_2 fragment. However, as we shall show, contrary to these authors' conclusion, this result gives no indication of the extent of electron transfer to O_2.

Table I. EPR Parameters for Some O_2 Adducts of Cobalt(II) Complexes

Complex	g_1 ±0.003	g_2 ±0.01	g_3 ±0.01	$-A_1{}^a$ +0.5	$-A_2{}^a$ ±1	$-A_3{}^a$ ±1	$-\langle A\rangle^a$	$\rho_{3d}(\times 10^2)$	$\rho_{4s}(\times 10^2)$	%4s	%$4s_{corr}$	Ref
Co(acacen)py·O_2	2.082	2.00	2.00	19.1	10	10	13.0	4.3	1.05	20	24	2
Co(acacen)H_2O·O_2	2.088	2.00	2.00	28.1	13	13	17.9	7.1	1.5	17	21	2
Co(*p*-OCH_3TPP)pyO_2	2.077	2.00	2.00	16.6	11	11	12.3	2.5	1.0	29	32	3, 6
Co(*p*-OCH_3TPP)MeImidO_2	2.080	2.00	2.00	16.2	10	10	11.6	2.9	0.9	25	28	3, 6
Co(salen)pyO_2	2.079	2.03	2.00	17.0	13	13	14.4	1.8	1.2	39	42	6
Co(SMDPT)·O_2	2.092	2.00	2.00	19.3	11	14	14.5	3.4	1.2	26	29	*b*
Co$(DMGH)_2$pyO_2	2.065	2.00	2.00	15.4	11	13	12.6	2.0	1.0	34	37	*b*
$Co(DPGB)_2$·$(CH_3)_2CO$·O_2	2.08	2.02	2.02	18.0	16	16	16.9	0.8	1.4	64	65	*b*
$Co(DPGB)_2$·$(CH_3CN$·O_2	2.068	2.00	2.00	19.3	17	17	17.7	1.1	1.4	56	57	*b*
$Co(DPGB)_2$·HMPA·O_2	—	2.01	2.01	15.4	12	12	13.3	1.3	1.1	45	49	*b*
Co(X-salDAPE)·O_2												
X = 5-H	2.103	1.996	1.994	33.0	14.5	22.5	22.3	6.6	1.9	22	26	*b*
= 5-OMe	2.099	2.000	1.997	28.5	13.0	19.0	20.2	5.7	1.6	22	26	*b*
= 5-Br	2.097	2.000	1.998	27.5	13.5	19.0	20.0	5.1	1.6	24	28	*b*
= 5-NO_2	—	1.993	1.993	—	21.0	21.0	—	—	—	—	—	*b*

[a] *A* values in 10^{-4} cm^{-1}. [b] This work.

Table II. Spin Hamiltonian Parameters for Some Typical Five- and Six-Coordinate Co(II) Complexes[3]

	$g_\perp$	$g_\parallel$	$-A_\perp{}^a$	$A_\parallel{}^a$	P^a	PK^a	%4s
Five-Coordinate, Co(*p*-OCH_3)TPP·B							
B = pyridine	2.327	2.025	12	79.8	198.3	24.3	3.3
4-picoline	2.323	2.028	11	78.9	192.2	22.1	3.4
3,5-lutidine	2.316	2.029	11	76.4	183.5	20.2	3.3
piperidine	2.318	2.026	13	77.4	190.8	23.0	3.3
quinuclidine	2.322	2.032	11	81.2	196.6	22.2	3.5
Six-Coordinate Co(*p*-OCH_3)TPP·B_2							
B = pyridine	2.216	2.047	57	60	195.8	45.9	1.5
4-picoline	2.226	2.060	50	61	188.4	40.6	1.8
3,5-lutidine	2.228	2.062	52.1	66	200.8	42.3	2.0
piperidine	2.214	2.054	53.8	61	191.3	42.5	1.7
quinuclidine	2.299	2.027	23	80.5	208.3	29.7	3.2

[a] Values in 10^{-4} cm^{-1}.

In our analysis, the cobalt hyperfine arises mainly from an indirect mechanism as opposed to a direct mixing of the d orbital into the MO containing the unpaired electron. A molecular orbital model can be proposed which accommodates this polarization mechanism. It is similar to that proposed by Wayland et al.[7] to explain observations pertinent to coordination of O_2 and other diatomic molecules, e.g., CO, NO. We will focus on the portion of the model most pertinent to the EPR interpretation (Figure 3). A π^* orbital of O_2 overlaps with metal $a_1(d_{z^2})$ to form a σ molecular orbital (ψ_1) containing two electrons. The second π^* orbital of O_2 is orthogonal to the above σ MO and contains the unpaired electron. Neglecting for convenience overlap with other orbitals, ψ_1 to ψ_3 have the form:

$$\psi_3 = \beta(d_{z^2}) - \alpha(\pi^*)$$

$$\psi_2 = \pi^*$$

$$\psi_1 = \alpha(d_{z^2}) + \beta(\pi^*)$$

where $\beta = (1 - \alpha^2)^{1/2}$. In this model, when $\alpha = 0$, the complex is Co(III) $O_2{}^-$; when $\beta = 0$, Co(I) $O_2{}^+$; and when $\alpha = \beta$, Co(II) O_2. *The fact that the unpaired electron residues mainly on O_2 does not necessitate that an electron has been transferred into O_2 to form $O_2{}^-$.* Furthermore, whether the complex consists of $O_2{}^+$, O_2, or $O_2{}^-$ depends on the coefficients of a molecular orbital which does not contain unpaired electrons. Accordingly, if a direct delocalization interpretation were[2] invoked, to explain the cobalt hyperfine, the molecular orbital description suggests the *A* values would be insensitive to the nature of the bound O_2 for the different possibilities are not related to the cobalt character in the MO containing the unpaired electron. Our only source of information in the EPR experiment about the nature of the bound O_2 arises from the spin polarization of ψ_1 as manifested in the cobalt hyperfine.

The Polarization Mechanism. The predominant metal contribution to ψ_1 is from the $3d_{z^2}$ orbital of cobalt. We know from studies on five- and six-coordinate complexes that 4s is also mixed in to the extent of 2–5%[7] of the d_{z^2} contribution. Thus, a more complete description of the ψ_1 molecular orbitals in Figure 3 is given by

$$\psi_1 = \alpha' d_{z^2} + \gamma 4s + \beta\pi^*$$

Since ψ_1 is close in energy to ψ_2, polarization of ψ_1 by ψ_2 can introduce negative spin density in d_{z^2} by virtue of the $\alpha' d_{z^2}$ component. Thus, one contribution to the nonzero cobalt hyperfine anisotropy could arise from $\alpha' \neq 0$. The existence of anisotropic cobalt hyperfine from this effect implies that a limiting $O_2{}^-$ description is not accurate in any of the reported complexes for there is cobalt character in ψ_1.

Signs of Hyperfine Constants. The signs of A_1, A_2, and A_3 in Table I are all the same, as can be seen by the $\langle A\rangle$ value observed in fluid solution for Co(acacen)pyO_2 and Co(SMDPT)·O_2. The similarity in the hyperfine components of the other complexes where $\langle A\rangle$ has not been observed suggests a similar situation. Further, the expected signs of the

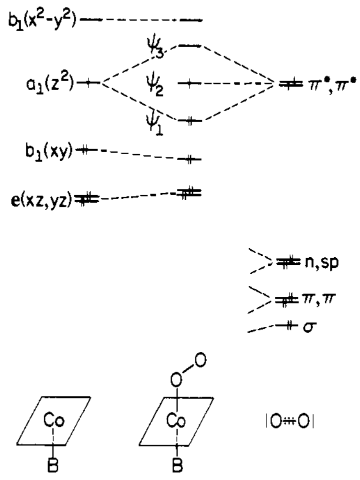


Figure 3. Molecular orbital model for the coordination of dioxygen to cobalt(II) complexes.

A values are negative due to the fact that the source of hyperfine is indirect in nature.

Our polarization mechanism would predict β unpaired spin density in ψ_1. For d_{z^2} character in ψ_1, polarization will produce anisotropic hyperfine contributions proportional to

$$A_{\text{Aniso}} \propto P\alpha^2 \begin{array}{ccc} z & x & y \\ \left| -\frac{4}{7} \right. & +\frac{2}{7} & \left. +\frac{2}{7} \right| \end{array} \tag{7}$$

(Note the opposite signs from eq 3 and 4 for α spin in d_{z^2}.) As can be seen in Table I, the O_2 adducts give rise for negative $\langle A \rangle$ to anisotropic components consistent with this form for:

$$\text{Co(acacen)py}\cdot\text{O}_2 \begin{array}{ccc} z & x & y \\ |-6.1 & 3.0 & 3.0| \end{array}$$

$$\text{and Co}(p\text{-OCH}_3\text{TPP})\text{pyO}_2 \begin{array}{ccc} z & x & y \\ |-3.5 & +1.6 & +1.6 \end{array}$$

In these higher symmetry complexes, d_{z^2} apparently is making the principal d-orbital contribution to ψ_1.

Polarization Analysis. The only information regarding the electron transfer that is available from this experiment comes from the interpretation of the spin polarization of ψ_1. A rigorous quantitative analysis cannot be made, but a crude semiquantitative analysis is possible, which provides us with insight about the nature of the bound O_2. First, we must critically examine literature procedures for carrying out this analysis, for we have discovered some inconsistencies when reported procedures are employed.

An equation which relates the *isotropic* polarization hyperfine to molecular orbital parameters is that basically of Symons:[27]

$$\frac{\langle A \rangle_{\text{Co}}}{A_{4s}} = U_{\text{O-Co}}\rho_{\text{O}} \tag{8}$$

$\langle A \rangle_{\text{Co}}$ = observed isotropic cobalt hyperfine, A_{4s} = isotropic hyperfine for one full electron in a cobalt 4s orbital, 1232 × 10^{-4} cm^{-1}, ρ_{O} = spin density on neighboring oxygen, and $U_{\text{O-Co}}$ = spin polarization constant representing polarization of cobalt by unpaired spin on neighboring oxygen atom.

This equation has been applied to systems characterized as ligand radicals bound to diamagnetic metals.[28-30] In such systems, the unpaired electron resides in a π-symmetry ligand orbital. Metal hyperfine is proposed to result by spin polarization of the metal-ligand σ bond. In the use of eq 8, polarization of the σ bond by the ligand unpaired electron is assumed the only source for isotropic hyperfine. It is also assumed that the isotropic hyperfine arises solely from 4s contribution to the σ bond. This crucial assumption will be considered later in more detail.

After obtaining the s character by analyzing the isotropic hyperfine, the d character in the σ bond is determined by analyzing the anisotropic hyperfine which arises from unpaired spin in a d orbital. The "apparent 3d spin density" is arrived at by an equation similar to eq 8:

$$\frac{A_{\text{aniso obsd}}}{A_{\text{aniso(3d)}}} = \rho_{3d} \tag{9}$$

$A_{\text{aniso obsd}}$ = observed anisotropy, $A_{\parallel} - \langle A \rangle$ and $A_{\text{aniso(3d)}}$ = anisotropy for one full electron in a 3d orbital,[35] $\sim 146 \times 10^{-4}$ cm^{-1}. Values of $\langle A \rangle$ were obtained from isotropic solution spectra or calculated from $\frac{1}{3}A_{\parallel} + \frac{2}{3}(A_x + A_y)$. Knowledge of ρ_{3d} and $U_{\text{O-Co}}\cdot\rho_{\text{O}}$ which gives the 4s character enables one to calculate the percent 4s character (i.e., [4s/(4s + 3d)] × 100) which is shown in Table I for Co-O_2 adducts. Other radical bound species[31-33] are listed in Table III. It is interesting to compare the results for 4s character in the metal-ligand bond deduced in Tables I and III with those found in systems where the unpaired electron is localized on the metal. In cobalt(II) complexes, analyses can be made, utilizing the data by Walker[3] for 1:1 and 2:1 adducts of Co(p-OCH$_3$TPP), employing the ligand field analysis outlined in eq 1-6. The results are shown in Table II. Similar results are obtained from consideration of base adducts of Co(salen)·B, Co(acacen)·B, Co(dmg)·B, etc.

An obvious disparity exists in comparing the percent 4s results from Table II with I and III. Though one would not expect the 4s character of the species in the tables to be the same, the large differences obtained by these procedures are unexpected. Within the Co-O_2 series, the uncorrected s character is calculated to vary from 20 to 64%. It is possible in the porphyrin, Schiff base, and DPGB series that the cobalt is pulled out of the ligand plane toward the O_2, inducing more s character in the Co-O_2 bond. However, the crystal structure of Co(bzacen)pyO_2 did not indicate a dramatic distortion. Though the electronic structures of all O_2 adducts in Table I are not expected to be identical, the range in 4s character of 20-64% is also unexpected. Such drastic differences suggest the polarization analysis reported in the literature is incomplete.

The shortcomings of the above approach can be understood by first considering the source of Fermi-contact interaction in paramagnetic complexes where the unpaired electron resides in a d orbital. This unpaired electron in the 3d orbital polarizes filled 1s, 2s, and 3s core orbitals, and usually leads to a negative sign for $A_{\text{F.C.}}$. When this mechanism dominates, a negative value for $A_{\text{F.C.}}$ will result. In certain complexes, direct contributions of 4s into the molecular orbital containing the unpaired electron complicates this analysis, as this contribution adds positive spin to 4s, which tends to cancel in part the polarization contribution.

The observed values of $A_{\text{F.C.}}$ (i.e., $\langle A \rangle$ in Table I) in O_2 adducts or in radical bound species cannot be accounted for by the core type of polarization mechanism. Spin polarization of ψ_1 puts spin in the opposite direction in the 3d orbital, so the contribution to $A_{\text{F.C.}}$ from this mechanism is of opposite sign. Considering Co(acacen)py·O_2 (Table I), for example, the apparent 3d spin density of 4.3% from eq 9 suggests the core polarization contribution to $A_{\text{F.C.}}$ will be $+3.6 \times 10^{-4}$ cm^{-1}. As mentioned above, polarization of the 4s contribution to ψ_1 would require unreasonably large s character in this MO.

Previous workers in this area have utilized the 4s explanation. To be accurate, this analysis should be modified to incorporate the secondary core polarization of s orbitals by the unpaired spin density in the 3d orbital. When this is done, the results reported in the column labeled %4s$_{\text{corr}}$ in Table I are

Table III. EPR Parameters for Radical Species Bound to Diamagnetic Metal Complexes

	g_3	g_2	g_1	$\lvert A_{2,3}\ (\mathrm{M})\rvert^a$	$\lvert A_1\ (\mathrm{M})\rvert^a$	$\lvert\langle A\rangle\rvert^a$	$\rho_{3d}(\times 10^2)$	$\rho_{4s}(\times 10^3)$	%4s	$\%4s_{corr}$	Ref
$Co(CN)_5 \cdot RNO$											
R = C_6H_5	2.002	2.008	2.008	7.7	14.1	9.8	2.96	8.0	21.	25	30
C_6D_5	2.008	2.008	2.012	7.9	14.1	10.0	2.83	8.1	22.	26	30
$C_6H_2Cl_3$	1.999	2.007	2.012	9.3	16.9	11.8	3.49	9.6	21.	26	30
C_6HCl_4	1.998	2.007	2.010	8.2	18.8	11.7	4.90	9.5	16.	21	30
L_nVOO	2.002	2.002	2.033	—	6.2	4.5	1.73^b	5.2	23	—	28
L_nAlOO	2.009	2.002	2.038	—	6.3	5.2	2.73^c	5.7	17	—	33
NbO_4^{2-}	2.0061	2.0146	2.0480	—	29.2	28.4	1.01	20	66	—	29
$DTBN \cdot AlCl_3{}^d$	—	—	—	14.6^e	16.2^e	15.1^e	2.73	15	35	—	32
DTBN·silica[d] alumina	—	—	—	16.6^e	17.1^e	16.8^e	0.74	17	70	—	32
$DTBN \cdot SnCl_4$	—	—	—	$\sim 165^f$	$\sim 165^f$	$\sim 165^f$	~0.0	22^g	~100	—	31
	$\langle g\rangle = 2.00521$										

[a] A values in 10^{-4} cm^{-1}, M refers to particular metal involved. [b] Utilizing $\lvert A_{aniso}\rvert = 98.3 \times 10^{-4}$ cm^{-1}, from ref 35. [c] Utilizing $\lvert A_{aniso}\rvert = 40.3 \times 10^{-4}$ cm^{-1}, from ref 35. [d] DTBN is di-*tert*-butyl nitroxide. [e] A(Al) in G. [f] A(Sn) in G. [g] Utilizing $\lvert A_{iso}\rvert = 7603$ G from ref 35.

obtained and also show large variations. The disparity between the s orbital contribution to the MO containing the unpaired electron in the five-coordinate cobalt complexes (Table II) and the O_2 adducts and radical bound species (Tables I and III) is now even greater. An additional contribution is needed to account for the large negative $A_{F.C.}$ in the O_2 adducts.

Considering the specific case of $Co-O_2$ systems, the π^* orbital containing the unpaired electron has a nonzero differential overlap with the filled cobalt 3s orbital. By virtue of this nonzero differential overlap, spin polarization of the cobalt 3s orbital by the ligand orbital containing the unpaired electron is possible. The polarization occurs without direct delocalization of unpaired electron density into d orbitals. The important point is that this polarization by unpaired spin on the ligand induces negative spin density at the cobalt nucleus *without producing d spin density*. This enables cobalt $A_{F.C.}$ to increase in magnitude without an increase in the anisotropic hyperfine coupling constant. Because this mechanism does not involve d orbitals, the s character can appear to increase at the expense of the d character. Though the differential overlap of the ligand π^* orbital is expected to be small, a significant contribution to A_{iso} could result because one unpaired electron in 3s produces a huge hyperfine coupling of 3666 G.[35] Furthermore, the radial character of 3s is actually slightly greater than that of 3d suggesting that this mechanism can be efficient at introducing unpaired spin in cobalt s orbitals. We suggest this polarization mechanism to be the source of the anomalously large s characters in other systems listed in Table III.

Since isotropic hyperfine coupling constants have contributions from polarization of 3s by spin density in metal d orbitals and orthogonal ligand orbitals, as well as 4s admixture to the molecular orbital containing the unpaired electron, we feel more reliable information about the cobalt character in metal–ligand bonds can be gained by examining the anisotropic hyperfine data. This anisotropy arises from the d orbital contributions to the ψ_1 molecular orbital formed from essentially d_{z^2} and oxygen π^*.

In the analysis of $Co-O_2$ systems, we strive to obtain α'^2 in ψ_1, employing an equation of the form:

$$\frac{A_{aniso\ obsd}}{A_{aniso(3d)}} = U_{O-Co}\rho_O\alpha'^2 \qquad (10)$$

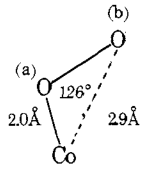
where U_{O-Co} and ρ_O are as defined in eq 8. In this equation, α'^2 and U_{O-Co} are unknown. An independent determination of an appropriate U_{O-Co} is needed. This requires a system where α'^2 is known. The aryl nitroso compounds bound to $Co(CN)_5{}^{3-}$ which are listed in Table III are as good a system as we can find for this purpose. The one unpaired electron resides in a π^* orbital localized on the nitroso moiety, essentially forming a nitroso anion radical. The radicals are bound through the nitrogen, so, for the sake of a qualitative discussion, the complex can be viewed as a Lewis acid–base adduct in which the Co–N σ bond involves the nitrogen lone pair and an essentially Co(III) acceptor. In the nitroso anion radical series, the nitrogen spin density is 0.7 for the R = $C_6H_2Cl_3$ derivative. Assuming[42] that the cobalt character in the metal–nitrogen bond[36,37] of the Co NRO adducts is 10–20%, and that the spin polarization constants of Co–N and Co–O are similar, one is in a position to estimate α^2 in ψ_1.

Dipolar Coupling of Oxygen Unpaired Spin and Cobalt Nuclear Spin. Before the cobalt character in the cobalt-O_2 bond can be estimated, it is necessary to correct for an additional source of cobalt hyperfine. This is dipolar coupling contributions from unpaired spin on O_2 with the cobalt nuclear spin. The equations pertinent for metal–ligand distances of 2 Å or greater are given below:[35]

$$A_{x,y} = \frac{-g\beta_e g_N\beta_N}{r^3}$$

$$A = \frac{2g\beta_e g_N\beta_N}{r^3}$$

Assuming the $Co-O_2$ geometry shown below,[14] the dipolar contributions are readily calculated.



The dipolar cobalt hyperfine resulting from 0.4 unpaired spin density on the middle oxygen (O_a) is (in 10^{-4} cm^{-1})

$$\begin{array}{cccc} & z & x & y \\ A_{Co-O_a} = & \lvert +0.66 & -0.33 & -0.33\rvert \end{array}$$

Though the z axis for the dipolar contribution from O_b is 20° off from that of O_a, this effect is very minimal on the magnitudes of the dipolar components, since these interactions fall off as $1/r^3$. As has been pointed out previously, the A and cobalt g tensors are likely not coincident. Since it is not known what directions diagonalize these tensors, the dipolar components will not be corrected for their noncoincidences. The dipolar cobalt hyperfine resulting from 0.6 unpaired spin density on the terminal oxygen is (in 10^{-4} cm^{-1})

$$\begin{array}{cccc} & z & x & y \\ A_{Co-O_b} = & \lvert +0.33 & -0.16 & -0.16\rvert \end{array}$$

The total dipolar components are then

$$\begin{array}{lccc} & z & x & y \\ A_{\text{Co-O}_a} + A_{\text{Co-O}_b} = & |+1.0 & -0.5 & -0.5| \end{array}$$

One should also note that the $[Co(CN)_5 \cdot RNO]^{3-}$ complexes listed in Table III have this dipolar contribution to their cobalt hyperfines. In the $C_6H_2Cl_3NO$ derivative, a spin density of 0.7 is reported to reside on the coordinated nitroso nitrogen and 0.3 on the oxygen. Assuming a similar geometrical situation as that utilized above for the dioxygen adducts, one can calculate the following dipolar components (in 10^{-4} cm^{-1}).

$$\begin{array}{lccc} & z & x & y \\ A_{\text{Co-N}} = & |+1.16 & -0.58 & -0.58| \end{array}$$

$$\begin{array}{lccc} & z & x & y \\ A_{\text{Co-O}} = & |+0.16 & -0.08 & -0.08| \end{array}$$

$$\begin{array}{lccc} & z & x & y \\ A_{\text{Co-N}} + A_{\text{Co-O}} = & |+1.3 & -0.66 & -0.66| \end{array}$$

In the following section where the cobalt d_{z^2} contribution to ψ_1 is calculated, these dipolar couplings will be taken into consideration.

Cobalt Contribution to the Cobalt–Dioxygen σ Bond. Utilizing equations of the form of eq 10, both for Co-O_2 and CoRNO, one can derive an equation to calculate α'^2 of the form:

$$\alpha'^2_{\text{Co-O}} = \frac{[A_{\text{aniso}}(\text{Co-O}_2) - A_{\text{dip}}(\text{Co-O}_2)]}{[A_{\text{anisb}}(\text{Co-RNO}) - A_{\text{dip}}(\text{Co-RNO})]} \times \left(\frac{\rho_N}{\rho_O}\right)(\alpha^2_{\text{Co-N}}) \quad (11)$$

$\alpha'^2_{\text{Co-O}}$ is cobalt 3d character in the Co-O bond, $\alpha'^2_{\text{Co-N}}$ is cobalt 3d character in the Co-N bond in $Co(CN)_5RNO$, $A_{\text{aniso}}(\text{Co-O}_2) = A_{\parallel} - \langle A \rangle$ observed in the Co-O_2 complex, $A_{\text{aniso}}(\text{Co-RNO}) = A_{\parallel} - \langle A \rangle$ observed in the Co-RNO complex, $A_{\text{dip}}(\text{Co-O}_2)$ is dipolar coupling in the z direction in the Co-O_2 complex, $+1.0 \times 10^{-4}$ cm^{-1}, A_{dip}(Co-RNO) is dipolar coupling in the z direction in the Co-RNO complex $+1.3 \times 10^{-4}$ cm^{-1}, ρ_N is spin density on N in CoRNO, 0.7 for the $C_6H_2Cl_3NO$ derivative, and ρ_O is spin density on the middle oxygen in Co-O_2, 0.4.

Using the α'^2 values from this analysis, we can calculate the amount of electron density in this molecular orbital which would be assigned to oxygen by a Mulliken population type analysis with zero overlap, i.e., the cobalt density is $2\alpha'^2$ and the oxygen $2(1 - \alpha'^2)$ (the two arises from the two electrons in ψ_1). The results are indicated in Table IV. It should be realized that if $2(1 - \alpha'^2)$ equals 1.0, the cobalt would be formally in the two oxidation state and the oxygen neutral. When $2(1 - \alpha'^2)$ equals 2.0, the oxygen moiety is O_2^- and the cobalt formally Co(III). Thus, the amount of electron density transferred, E-T, into the O_2 fragment upon complexation is given by: $2(1 - \alpha'^2) - 1$. Though the α'^2 values are semiquantitative, we should note that, regardless of how much lower or higher the correct α'^2 values are, there is a large range in anisotropy (10.2×10^{-4} cm^{-1} to 1.1×10^{-4} cm^{-1} for $Co(acacen)H_2O \cdot O_2$ and $Co(DPGB)_2 \cdot CH_3CN \cdot O_2$, respectively) implying a wide difference in the α'^2 value in the various complexes. Values of α'^2 range from 0.5 to 0.1, respectively. The trend observed in the α'^2 values spans a range of electron transfer from cobalt(II) to oxygen of 0.1–0.8 electron. This span is reasonable and provides support for the logic of the assumptions employed in our analysis. Some compounds can clearly be assigned as predominantly bound neutral O_2, e.g., the Co(X-salDAPE) O_2 series and others would be better described as approaching bound O_2^-, e.g., $Co(DPGB)_2 \cdot B \cdot O_2$ series. The $Co(acacen) \cdot py \cdot O_2$ adduct previously inferred[2] to involve nearly complete electron transfer, i.e., Co(III) O_2^- is seen to be borderline with only 0.4 of an electron transferred. Although the formal oxidation state of cobalt is III in all these complexes, one certainly would not be justified in writing this formula as Co(III) O_2^- for $Co(acacen)py \cdot O_2$ any more than one would write H(I) F$^-$ for HF.

Table IV. α^2 Values and Electron Transfer in Some O_2 Adducts of Cobalt(II) Complexes

	$\alpha'^{2\,b}$	$\alpha'^{2\,c}$	α'^2_{av}	E.T.[a] $2(1 - \alpha'^2) - 1$
Co(acacen)·py·O_2	0.19	0.39	0.29	0.4
Co(acacen)·H_2O·O_2	0.31	0.61	0.46	0.1
Co(p-OCH_3TPP)·py·O_2	0.13	0.27	0.20	0.6
Co(p-OCH_3TPP)·Me-Imid·O_2	0.15	0.31	0.23	0.5
Co(salen)·py·O_2	0.16	0.32	0.24	0.5
Co(SMDPT)·O_2	0.16	0.32	0.24	0.5
Co(DMGH)·py·O_2	0.11	0.21	0.16	0.7
$Co(DPGB)_2 \cdot CH_3CN \cdot O_2$	0.06	0.12	0.09	0.8
$Co(DPGB)_2$·acetone·O_2	0.07	0.15	0.11	0.8
$Co(DPGB)_2$·HMPA·O_2	0.09	0.17	0.13	0.7
Co(X-salDAPE)O_2				
X = 5-H	0.28	0.56	0.42	0.2
= 5-OMe	0.24	0.48	0.36	0.3
= 5-Br	0.23	0.46	0.35	0.3

[a] $2(1 - \alpha'^2) - 1$ is the electron transfer from Co(II) to O_2. The results are semiquantitative but the trends are accurate. [b] Calculated assuming cobalt character in Co–N bond of nitroso anion radicals is a lower limit 10%. [c] Calculated assuming cobalt character in Co–N bond of nitroso anion radicals is as an upper limit 20%.

Dioxygen adduct formation is best viewed as a spin pairing of an electron in a d_{z^2} orbital of cobalt with an unpaired electron in a π^* orbital of oxygen. As the ligand field strength around th cobalt increases, d_{z^2} is raised in energy relative to the π^* of O_2 and the complex becomes more O_2^- in character. A decreasing ligand field lowers the cobalt d_{z^2} orbital energy and causes it to approach the energy of the oxygen π^* orbital. This lowering results in increased cobalt character in the molecular orbital. Roughly, the N_2O_3 ligand environments generate lower ligand fields than N_3O_2 which in turn are lower than N_4O and N_5. We find that the amount of electron transfer from these four sets is 0.1–0.3, 0.4–0.6, 0.7–0.8, and 0.5–0.8, respectively. It should be noted at this point that α'^2 in Table IV is the d_{z^2} component of ψ_1. In Figure 2, cobalt 4s is also mixed into ψ_1, though a value for it cannot be calculated due to the many contributions to the isotropic coupling constant. However, in discussing the cobalt contribution to ψ_1, the 4s contribution should be added to α^2 in Table IV. The result of this effect is to make the ET values reported here *upper* limits. We have assumed that Q is the same for an electron on oxygen and nitrogen in writing eq 11. We have also assumed that Q does not change appreciably with the change in the energy difference of ψ_1 and ψ_2. These assumptions are drastic enough to make the actual reported values crude estimates of the electron transfer. The net effect of all approximations is expected to cause the reported ET numbers to be high.

With this model we have elucidated those factors which are essential to the binding of O_2 (matching of the d_{z^2} and O_2 π^* energies) as well as those factors which perturb the bound oxygen molecule by transferring electron density into it. Next, we examine the role that π back-bonding plays in this chemistry.

The arguments presented so far are based on the assumption that all the observed anisotropy in the cobalt hyperfine is due to spin polarization of the mainly d_{z^2} + O_2 π^* molecular or-

Table V. EPR Parameters for O_2 Adducts of Co(TPP)·X[8]

	g_1	g_2	g_3	$\lvert A_1\rvert^a$	$\lvert A_2\rvert^a$	$\lvert A_3\rvert^a$	$\lvert\langle A\rangle\rvert^a$
X = sterically hindered base							
2,4,6-Collidine	2.080	2.002	2.002	20.9	12.7	12.7	15.4
Acridine	2.080	1.997	2.001	22.1	15.4	13.6	17.0
2,4-Lutidine	2.085	2.001	2.001	21.7	13.4	13.4	16.2
X = solvent							
Toluene	2.083	1.988	1.985	29.2	24.5	28.8	27.50
Pyrene	2.062	1.996	1.997	21.2	18.7	23.2	21.03
1,3-Dinitrobenzene	2.083	1.998	2.006	21.6	17.3	18.7	19.20
Picric acid	—	1.993	1.974	—	24.2	26.1	—
1,3,5-Trinitobenzene	—	1.986	1.973	—	34.2	34.2	—

[a] A values in 10^{-4} cm^{-1}.

bitals and dipolar couplings. This effect gives rise to the following dipolar contributions to the anisotropic cobalt hyperfine coupling:

$$\begin{array}{cccc} & z & x & y \\ \rho_O U_{\text{O-Co}}\alpha'^2 & \left|-\frac{4}{7}\right. & +\frac{2}{7} & \left.+\frac{2}{7}\right| \end{array} \qquad (12)$$

Deviations from this −2,1,1 ratio can arise via several mechanisms. For example, spin polarization of an essentially filled d_{xz} or d_{yz} orbital could occur. In a low symmetry complex other d orbitals besides d_{z^2} could be involved in the ψ_1 MO. The dipolar contribution will reflect contributions from all contributing d orbitals. This effect probably accounts for the anisotropy observed in Co(H-salDAPE), i.e.,

$$\begin{array}{ccc} z & x & y \\ \left|-9.7\right. & +8.8 & \left.+0.8\right| \end{array}$$

A direct mechanism exists for transmitting unpaired spin to cobalt, that is π back-bonding of the metal d_{xz} (or d_{yz}) orbital with an oxygen π^* orbital mixing d_{xz} (or d_{yz}) into ψ_2. This direct delocalization will put positive spin in a d orbital of cobalt. The addition of this contribution changes the expected anisotropic hyperfine as outlined below.

π-Back-bonding of ψ_2 with d_{xz} ($\psi_2 = \epsilon\pi^* + \alpha''(d_{xz})$)

$$\begin{array}{cccc} & z & x & y \\ P\alpha''^2 & \left|+\frac{2}{7}\right. & +\frac{2}{7} & \left.-\frac{4}{7}\right| \end{array} \qquad (13)$$

Defining $f = \rho_O U_{\text{O-Co}}\alpha'^2$ and $g = P\alpha''^2$, the resultant is:

$$A_x - \langle A\rangle = \frac{2}{7}(f+g) \qquad (14)$$

$$A_y - \langle A\rangle = \frac{2}{7}(f-2g) \qquad (15)$$

$$A_z - \langle A\rangle = \frac{2}{7}(-2f+g) \qquad (16)$$

In eq 13-16, $P = g\beta g_N\beta_N \langle 1/r^3\rangle_{d_{xz}}$, α^2 is the d_{z^2} contribution to ψ_1 (see Figure 3). We can see that although the two mechanisms put spin of opposite sign in d orbitals, since the d orbitals involved are different in this particular case, the anisotropy does not cancel in all directions and is additive in the x direction (if d_{yz} is involved, anisotropy will be additive in the y direction). Rapid rotation of the O_2 molecule would average the xy anisotropy.

There are a number of reasons we feel the π-back-bonding mechanism is a small contributor for the complexes listed in Table I. First, if we assume no rotation of the O_2 molecule about the cobalt-oxygen bond, the ^{17}O hyperfine suggests that the d_{xz} contribution to the orbital containing the unpaired electron can be no greater than 2% or anisotropic component of at most about (in 10^{-4} cm^{-1})

$$\begin{array}{ccc} z & x & y \\ \left|+0.75\right. & +0.75 & \left.-1.5\right| \end{array}$$

Since it is not known whether or not the O_2 molecule is fixed in our glass at low temperatures, a second argument can be made from a series of Co(TPP)·B·O_2 adducts where B is a phosphorus donor. Phosphorus hyperfine is observed both in the parent compound, where d_{z^2} is mixed with a phosphorus sp^n hybrid, and in the O_2 adducts, where it is geatly reduced from the deoxy adduct. Wayland[7b] has pointed out that the trends in isotropic ^{31}P hyperfine in the O_2 adducts parallel the donor orbital s character in the $Co^{II}TPP{\cdot}PX_3$ complexes. Such a trend suggests the primary source of ^{31}P hyperfine arises from the polarization of the ($Co d_{z^2} + P_\sigma$) orbital.

A series of compounds which exhibits quite different EPR spectra are shown in Table V. These complexes arise when there is a solvent molecule or sterically hindered Lewis base bonded to a cobalt(II) porphyrin trans to the coordinated O_2. The fact that one obtains a small g and A anisotropy as well as a large $A_{\text{iso}}/A_{\text{aniso}}$ ratio suggests that the unpaired electron is localized on the O_2. Considering first the anisotropic A values, one observes considerable x, y anisotropy (i.e., $A_x \neq A_y$). The anisotropic tensor components for the following species have the form:

$$\begin{array}{cccc} & 1 & 2 & 3 \\ \text{acridine} & \left|-5.1\right. & +1.6 & \left.+3.4\right|, \end{array}$$

$$\begin{array}{cccccccc} & 1 & 2 & 3 & & 1 & 2 & 3 \\ \text{toluene} & \left|-1.7\right. & +3.0 & \left.-1.3\right|, & \text{pyrene} & \left|-0.2\right. & +2.3 & \left.-2.2\right| \end{array}$$

These components are obviously far different from those of Table I, the A_1 anisotropy is much smaller, and the difference in A_2 and A_3 very large. It is interesting to speculate and note that these differences are those expected if increased π-back-bonding occurs (eq 14-16) and the metal d_{xz} or d_{yz} orbital is mixed into ψ_2 resulting in a direct delocalization of the electron onto cobalt. It would be interesting to know the structures of these adducts.

Conclusion

Though the interpretation of the EPR spectrum is involved and indirect, it does lead to a relatively simple model for the binding of O_2 in cobalt(II) complexes. This model views the bonding of O_2 as arising from a coupling of the spins of an electron in an antibonding O_2 molecular orbital with an unpaired electron on cobalt. For adducts in which the metal-oxygen-oxygen bond angle is ~120°, the interaction involves an electron in the metal d_{z^2} orbital. The magnitude of the interaction and the amount of electron transfer into the coordinated O_2 fragment are related to the ligand field strength of

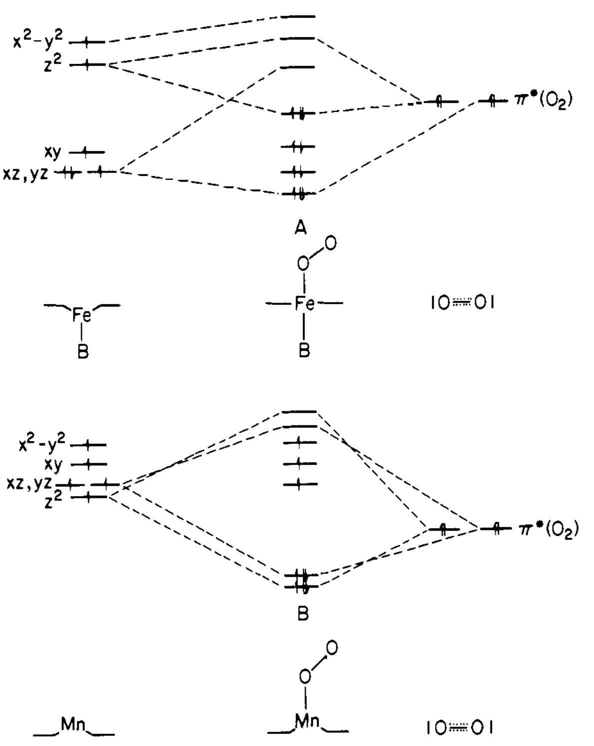


Figure 4. A qualitative molecular orbital scheme for the O_2 adducts (A) iron(II) and (B) manganese(II). (Relative energies are indicated.)

the donor atoms around cobalt(II). This is simply a consequence of the influence of the ligands on the initial energies of the orbitals which overlap to form the metal-oxygen bond. Rough estimates ranging from 0.1 to 0.8 of an electron transferred result from an analysis of the anisotropic cobalt hyperfine coupling.

The model presented here is also consistent with the observed diamagnetism of synthetic and natural iron(II) reversible oxygen carriers as well as with the observed paramagnetism of the adduct[38] of *meso*-tetraphenylporphyrinmanganese(II) with O_2. In using our model, the key feature is that the metal have an unpaired electron in d_{z^2} with high enough energy to spin pair with an odd electron in the oxygen antibonding orbital. In cobalt(II), this is the essential interaction binding the oxygen to the complex. In iron(II) complexes and Mn(II) complexes where there are unpaired electrons in metal orbitals with "π-symmetry" which permit interaction with the second unpaired electron in O_2, spin-pairing of these electrons can also occur. Square planar, four-coordinate iron(II) complexes are generally low or intermediate spin. Coordination of an axial base in the systems which reportedly pick up O_2 reversibly leads to a high spin complex. A low spin O_2 adduct results as shown in Figure 4. The $d_{x^2-y^2}$ orbital in the O_2 adduct would be driven higher in energy via a stronger interaction of in-plane ligands with this orbital. This accounts for the observed diamagnetic O_2 adducts observed in the reversible iron(II) systems reported to date. The model could accommodate a paramagnetic O_2 adduct of iron(II) which would result by fine tuning the ligand field so as to decrease the $d_{x^2-y^2}$ and d_{xy} separations in the adduct. A weak interaction of the axial base on d_{z^2} could also lower the d_{z^2}-O_2 π^* antibonding orbital to a place where it becomes populated. An intermediate initial spin state for a five-coordinate adduct could also lead to a reversible-O_2 system if the energy of d_{z^2} were high enough.

Similar considerations apply to the reported Mn(II) complexes. The d-orbital separations are smaller in this complex, and the d_{z^2} orbital energy is higher than that in iron(II). Reportedly, axial bases are not required to bind O_2. This would be predicted by our model for a higher initial d_{z^2} energy. With a small $d_{x^2-y^2}$ separation, a complex with three unpaired electrons would result.[38] (See Figure 4b.) If the ligand field were to raise the energy of $d_{x^2-y^2}$ one unpaired electron residing on Mn(II) could result with the electrons paired in a lower energy orbital. Thus, the basic model we are proposing here can account for the electronic structure of a wide variety of O_2 adducts.

Subsequent to the submission of this article for publication, three independent studies have been reported which provide strong support for our conclusions. Ab initio, generalized valence bond, and configuration interaction calculations[39] corroborate the model offered above and are reported to be consistent with Mossbauer studies and *z*-polarized charge transfer transitions in the hemoglobin system.

The second report is an ESCA study[40] of O_2 adducts. Although it is not possible to ascertain the extent of electron transfer from ESCA experiments, electron density is reported to be transferred into the O_2 fragment of the adduct upon complex formation in varying amounts in the series of complexes studied.

The third report is a recent[41] INDO-UHF calculation on Co(acacen)NH_3O_2. Within the calculation, O_2 adduct formation is shown to be consistent with a spin-pairing interaction of one unpaired O_2 electron and one on cobalt, which agrees with our model. The delocalization of unpaired spin over O_2 also agrees well with the ^{17}O hyperfine results: 0.38 and 0.61 electron on the middle and terminal oxygen π^* orbital. A very interesting feature of this study is the spin densities calculated in cobalt d orbitals: d_{z^2} (−0.0816), d_{xz} (0.0005), d_{yz} (0.005), d_{xy} (−0.0060), $d_{x^2-y^2}$ (−0.0001), s (−0.0028). These spin densities, especially the negative values in d_{z^2} and cobalt s, which we predicted on the basis of polarization arguments, are in excellent agreement with our model. The very small densities in d_{xz} and d_{yz} confirm our claim that little unpaired spin is delocalized from ψ_2 to metal π orbitals. Finally, the amount of electron transfer from cobalt to O_2 is calculated to be 0.3, compared to our upper limit of 0.4 in Co(acacen)py·O_2.

Acknowledgment. The authors acknowledge the generous support of this research by the National Science Foundation.

References and Notes

(1) R. H. Bailes and M. Calvin, *J. Am. Chem. Soc.*, **69**, 1886 (1947).
(2) (a) B. M. Hoffman, D. L. Diemente, and F. Basolo, *J. Am. Chem. Soc.*, **92**, 61 (1970); (b) A. L. Crumbliss and F. Basolo, *ibid.*, **92**, 55 (1970).
(3) F. A. Walker, *J. Am. Chem. Soc.*, **92**, 4235 (1970).
(4) G. N. Schrauzer and L. P. Lee, *J. Am. Chem. Soc.*, **90**, 6541 (1968).
(5) J. H. Bayston, N. K. King, F. D. Looney, and M. E. Winfield, *J. Am. Chem. Soc.*, **91**, 2775 (1969).
(6) E.-I. Ochiai, *J. Inorg. Nucl. Chem.*, **35**, 1727 (1973).
(7) (a) B. B. Wayland, J. V. Minkiewiez, and M. E. Abd-Elmageed, *J. Am. Chem. Soc.*, **96**, 2795 (1974); (b) B. B. Wayland and M. E. Abd-Elmageed, *ibid.*, **96**, 9809 (1974).
(8) F. A. Walker, *J. Magn. Reson.*, **15**, 201 (1974).
(9) L. D. Brown and K. N. Raymond, *J. Chem. Soc., Chem. Commun.*, 470 (1974).
(10) C. J. Willis, *J. Chem. Soc., Chem. Commun.*, 117 (1974).
(11) B. S. Tovrog and R. S. Drago, *J. Am. Chem. Soc.*, **96**, 6765 (1974).
(12) H. Kon and N. E. Sharpless, *Spectrosc. Lett.*, 49 (1968).
(13) (a) J. E. Baldwin and J. Huff, *J. Am. Chem. Soc.*, **95**, 5757 (1973); (b) J. P. Collman, R. R. Gagne, and C. A. Reed, *ibid.*, **96**, 2629 (1974), and references therein; (c) W. S. Brinigar, C. K. Chang, J. Geibel, and T. G. Traylor, *ibid.*, **96**, 5598 (1974), and references therein; (d) D. L. Anderson, C. J. Weschler, and F. Basolo, *ibid.*, **96**, 5599 (1974), and references therein.
(14) E. Melamud, B. L. Silver, and Z. Dori, *J. Am. Chem. Soc.*, **96**, 4689 (1974).
(15) B. M. Hoffman, T. Symanski, and F. Basolo, *J. Am. Chem. Soc.*, **97**, 673 (1975). We have previously incorrectly communicated[11] the existence of a low spin CO adduct. Attempts to repeat this result on a vacuum line were not successful and cause us to conclude in agreement with Hoffman et al. that O_2 impurities in our sample led to our observing an O_2 adduct which we attributed to CO. However, the essential conclusions of our previous communication are not effected because these authors confirmed the existence of our low spin isocyanide adduct. The reduced cobalt hyperfine coupling constant $A_{\parallel}$ in the six-coordinate CH_3NC demonstrates that $A_{\parallel}$

in a five-coordinate complex is not a good model to compare with the six-coordinate O_2 adduct to infer Co(III)–O_2^-.

(16) D. Getz, E. Melamud, B. L. Silver, and Z. Dori, *J. Am. Chem. Soc.*, **97**, 3846 (1975), and references therein.

(17) (a) G. A. Rodley and W. T. Robinson, *Nature (London)*, **235**, 438 (1972); (b) L. D. Brown and K. N. Raymond, *Inorg. Chem.*, **14**, 2590 (1975), and references therein; (c) D. H. Templeton, C. H. Dauben, *J. Am. Chem. Soc.*, **72**, 2251 (1950); (d) G. S. Zhdanov and Z. V. Zvonkova, *Dokl. Akad. Nauk. SSSR*, **82**, 743 (1952); (e) R. J. Celotta et al., *Phys. Rev. A*, **6**, 631 (1972).

(18) M. Israel, J. S. Rosenfield, and E. J. Modest, *J. Med. Chem.*, 7, 710 (1964).

(19) L. Sacconi and I. Bertini, *J. Am. Chem. Soc.*, **88**, 5180 (1966).

(20) R. H. Niswander, A. K. St. Clair, S. R. Edmondson, and L. T. Taylor, *Inorg. Chem.*, **14**, 478 (1975).

(21) G. N. Schrauzer, *Inorg. Synth.*, **11**, 61 (1968).

(22) G. N. Schrauzer and R. J. Windgassen, *J. Am. Chem. Soc.*, **88**, 3738 (1966).

(23) J. B. Raynor, *Inorg. Nucl. Chem. Lett.*, **10**, 867 (1974).

(24) A. H. Maki, N. Edelstein, A. Davison, and R. H. Holm, *J. Am. Chem. Soc.*, **86**, 4580 (1964). The unpaired electron in this system resides on O_2. In terms of the cobalt hyperfine, which arises from spin polarization, we are essentially treating this as a d^7 cobalt system except that a full unpaired electron is not involved, but only fractional spin density from the spin polarization. Since the unpaired electron in these complexes resides on O_2 (vide infra), the *g* tensor is probably determined by the orientation of the coordinated O_2. Co(bzacen)pyO_2 possesses a bent Co–O–O linkage and the EPR spectrum is similar to the other Co–O_2 systems listed in Table I. It is then likely that most (if not all) complexes in Table I possess bent Co–O–O units. As the cobalt hyperfine tensor is likely determined by the surrounding nitrogen and oxygen donor atoms, there is little chance the *g* and cobalt *A* tensors are coincident because of the symmetry of the adduct. The noncoincidence of these two tensors has been shown in a single crystal study of oxycobaltmyoglobin.[26] Though the principal values of the *A* tensor will be larger than those listed in Table I, the reported single-crystal study indicates that frozen solution spectra are a good gauge of the actual anisotropy. The errors introduced in our parameters by these assumptions render them semiquantitative. Under the circumstances, it was not deemed significant to further refine them by incorporating contributions from mixing in quartet states (B. R. McGarvey, *Can. J. Chem.*, **53**, 2498 (1975)). The correction for quartet states is not straightforward in this system for the *g* value observed is associated with the electron on O_2 which even in O_2^- has a value different from that of the free electron. We have made the quartet correction in a series of five- and six-coordinate low spin d^7 complexes and have found it to have only a minor influence on the *A* values and to cause no reversals in trends. The reader is cautioned about these complications in the event he is tempted to use our results for other purposes than the conclusions we draw.

(25) B. R. McGarvey, *J. Phys. Chem.*, **71**, 51 (1967).

(26) J. C. W. Chien and L. C. Dickinson, *Proc. Natl. Acad. Sci. U.S.A.*, **69**, 2783 (1972).

(27) T. F. Hunter and M. C. R. Symons, *J. Chem. Soc. A*, 1770 (1967).

(28) M. C. R. Symons, *J. Chem. Soc. A*, 1889 (1970).

(29) P. R. Edwards, S. Subramanian, and M. C. R. Symons, *J. Chem. Soc. A*, 2985 (1968).

(30) M. C. R. Symons and J. G. Wilkinson, *J. Chem. Soc., Faraday Trans. 2*, **68**, 1265 (1972).

(31) A. H. Cohen and B. M. Hoffman, *Inorg. Chem.*, **13**, 1484 (1974).

(32) G. P. Lozos and B. M. Hoffman, *J. Phys. Chem.*, **78**, 200 (1974).

(33) K. M. Wang and J. H. Lunsford, *J. Phys. Chem.*, **73**, 2069 (1969).

(34) W. R. Scheidt, *J. Am. Chem. Soc.*, **96**, 90 (1974).

(35) B. A. Goodman and J. B. Raynor, *Adv. Inorg. Chem. Radiochem.*, **13**, 135 (1970).

(36) B. S. Tovrog and R. S. Drago, to be submitted.

(37) L. F. Mehne and B. B. Wayland, *Inorg. Chem.*, **14**, 881 (1975).

(38) C. J. Weschler, B. M. Hoffman, and F. Basolo, *J. Am. Chem. Soc.*, **97**, 5278 (1975).

(39) W. A. Goddard, III, and B. D. Olafson, *Proc. Natl. Acad. Sci. U.S.A.*, **72**, 2335 (1975).

(40) J. H. Burness, J. G. Dillard, and L. T. Taylor, *J. Am. Chem. Soc.*, **97**, 6080 (1975).

(41) P. Fantucci and V. Valenti, private communication.

(42) Our main conclusion will be shown to be relatively independent of this estimate.

Reversible Oxygen Carriers. The Synthesis and Low Temperature (−171°) Structure of an Unstable Monomeric Dioxygen Adduct of *N,N′*-(1,1,2,2-Tetramethyl)ethylenebis(3-fluorosalicylideniminato)(1-methylimidazole)cobalt(II), Co(3-F-Saltmen)(1-Me-Imid)(O_2)·2(CH_3)$_2$CO

Alex Avdeef and William P. Schaefer*

Contribution No. 5230 from the Arthur Amos Noyes Laboratory of Chemical Physics,
California Institute of Technology, Pasadena, California 91125.

Received December 1, 1975

Abstract: The structure at −171° of *N,N′*-(1,1,2,2-tetramethyl)ethylenebis(3-fluorosalicylideniminato)(1-methylimidazole)superoxocobalt(III) diacetone solvate, Co(3-F-Saltmen)(1-Me-Imid)(O_2)·2(CH_3)$_2$CO, has been determined from three-dimensional x-ray data collected by counter methods and has been refined on F^2 using 6078 reflections, including those with negative intensities. The conventional R_F factor based on the portion of the data with F^2 greater than $3\sigma(F^2)$ is 6.0%. The monomeric adduct (Co:O_2 = 1:1) of cobalt(II) crystallizes in the monoclinic space group C^5_{2h}-$P2_1/c$ (No. 14), with four formula units in a cell with the low-temperature dimensions a = 11.934 (6) Å, b = 13.864 (5) Å, c = 18.018 (8) Å, and β = 92.35 (2)°. The superoxide ligand, O_2^-, is bonded "end-on" to the cobalt atom of the chelate, with a Co–O–O angle of 117.4 (2)° and an O–O bond length of 1.302 (3) Å. The dioxygen group lies nearly in the plane defined by the methylimidazole trans to it. The Co–O (dioxygen) and Co–N (imidazole) bond distances are 1.881 (2) and 2.004 (3) Å, respectively. The other coordination bonds average 1.893 (Co–N) and 1.901 Å (Co–O). The molecular packing in the vicinity of the coordinated dioxygen ligand is similar to that found in the hydrophobic "distal imidazole" pocket of myoglobin. Crystals of the cobalt oxygen adduct are not stable at ambient conditions and evolution of O_2 may be readily observed, as the crystals change from dark burgundy red to golden yellow upon decomposition.

Understanding molecular oxygen transport and storage in living systems has been enhanced by studies of reversibly bound dioxygen adducts of simple transition metal complexes.[1] Much effort has been directed towards the mimicry of myoglobin and hemoglobin, as demonstrated so well by the characterization of the dioxygen adduct of the iron "picket fence porphyrin" complex by Collman and co-workers.[2]

Schiff base complexes of cobalt(II) have been studied as oxygen carriers since 1938.[3] The relevance and importance of such dioxygen-carrying cobalt complexes as models has been