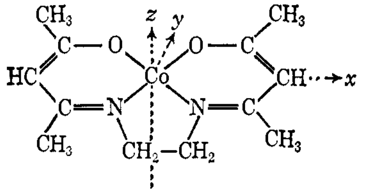
Electron Paramagnetic Resonance Studies of Some Cobalt(II) Schiff Base Compounds and Their Monomeric Oxygen Adducts

Brian M. Hoffman, Damon L. Diemente, and Fred Basolo

Contribution from the Department of Chemistry, Northwestern University, Evanston, Illinois 60201. *Received June 19, 1969*

Abstract: The epr spectra have been observed for a series of molecular oxygen adducts prepared from Co(acacen) [acacen = $(CH_3—C(O^-)=CHC(CH_3)=NCH_2—)_2$]. These reversibly formed adducts, which in general contain an additional base, are unambiguously shown to be monomeric in both fluid and frozen solution. They are further shown to be best characterized as superoxo (O_2^-) adducts of Co(III). Suggestion is also made as to the probable geometry of these complexes.

Cobalt complexes carrying molecular O_2 have been the object of extensive investigations.[1–7] Until recently the oxygen adducts studied have generally been dimeric, containing two atoms of cobalt for one molecule of oxygen. However, several examples of monomeric 1:1 complexes of molecular oxygen with cobalt(II) have now been chemically characterized.[7–9a] We have examined the epr absorption of a series of adducts of Co(acacen),[10] A, in order to confirm their postulated monomeric nature and to elucidate their electronic structures. These adducts are designated as B–A–Y (or ABY) where B = py, CN-py, Me-py, DMF, H_2O, or open, and Y = O_2 or open. Abbreviations are explained in Table I.



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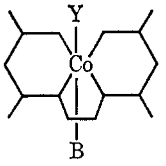

B–A–Y

The parent compound A contains a low-spin cobalt(II) ion, as indicated by a magnetic moment of 2.16 BM. Although resolvable epr spectra of A were not usually observed at 77°K, or above,[11] 1:1 adducts of A with a pyridine base, *e.g.*, py–A, exhibit epr spectra in frozen solution which are quite comparable to those shown by adducts of cobalt(II) phthalocyanine[12] or by vitamin B_{12r}.[13]

Crystalline oxygen adducts of A with pyridines, *e.g.*, py–A–O_2, in the sixth coordination position exhibit magnetic moments[8] ranging from 1.49 to 1.89 BM, indicating the presence of a single unpaired electron. Our epr measurements in both liquid and frozen solution clearly demonstrate the monomeric nature of these adducts by the presence of eight resolved hyperfine splittings from a single cobalt ^{59}Co nucleus. Furthermore, a careful consideration of the spin Hamiltonian parameters for the compounds studied indicates that the unpaired electron resides primarily on the oxygen molecule, and that in partitioning charges the adducts are best thought of as superoxide adducts of cobalt(III). We have also observed that it is possible to form a solution-stable oxygen adduct of A with water as the base in the sixth coordination position, H_2O–A–O_2, and there is evidence to suggest a pentacoordinate oxygen adduct in the absence of a base, A–O_2, although these two adducts have not been isolated as crystalline solids.

Experimental Section

The preparation of A and the characterization of its adducts, as well as the purification of solvents, were described previously.[8] Unoxygenated samples for epr measurements were prepared on a vacuum line. Solid A (sufficient to yield *ca.* 0.01 *M* solution) was placed in a sample tube provided with a vacuum O-ring joint and stopcock. Dry, degassed toluene was then trap-distilled into the tube. If a liquid base was required, a dry, degassed sample was distilled into the tube immediately after the toluene. If a solid base was needed, it was mixed dry with the sample of A prior to the introduction of toluene. The frozen heterogeneous samples were then thawed, warmed to −20°, and allowed to achieve homogeneity. The homogeneous samples were stored frozen in liquid nitrogen prior to use.

These samples could be oxygenated at will by exposure to 100 mm of oxygen pressure at *ca.* −20°. Samples of oxygenated species could also be prepared directly by dissolving A in toluene in the open air at −10° or below, and then adding any required base. In all cases, samples were made up with a large molar excess of base.

Spectra were taken on a Varian Associates epr spectrometer or Bruker Scientific spectrometer. *g* values were determined by calibration with DPPH powder (g = 2.0036) in a Varian Associates V-4532 dual cavity, using a Hewlett-Packard x532-B frequency meter. Magnetic field calibrations for the Bruker spectrometer were performed with a built-in nmr gaussmeter. Cooling was provided either by boiling nitrogen or by a conventional variable temperature apparatus using cold nitrogen gas, with a thermocouple placed directly below the sample in the nitrogen stream. This thermocouple gives temperatures accurate to within ±2°K.

Results

The epr spectrum of py–A, in frozen toluene solution (T = 77°K), displayed in Figure 1, indicates a nearly axial symmetry about the cobalt(II) ion, but with

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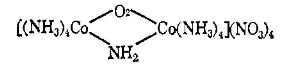
(1) S. Fallab, *Angew. Chem. Intern. Ed. Engl.*, **6**, 496 (1967).
(2) M. Mori and J. A. Weil, *J. Am. Chem. Soc.*, **89**, 3732 (1967).
(3) M. Mori, J. A. Weil, and M. Ishiguro, *ibid.*, **90**, 615 (1968).
(4) J. Simplicio and R. Wilkins, *ibid.*, **89**, 6092 (1967).
(5) J. Simplicio and R. Wilkins, *ibid.*, **91**, 1325 (1969).
(6) F. Miller, J. Simplicio, and R. Wilkins, *ibid.*, **91**, 1962 (1969).
(7) C. Floriani and F. Calderazzo, *J. Chem. Soc.*, *A*, 946 (1969).
(8) A. Crumbliss and F. Basolo, *J. Am. Chem. Soc.*, **92**, 55 (1970).
(9) After completion of this manuscript, an epr study of monomeric oxygen adducts of vitamin B_{12r} appeared, with results similar to ours: J. H. Bayston, N. K. King, F. D. Looney, and M. E. Winfield, *ibid.*, **91**, 2775 (1969).
(9a) NOTE ADDED IN PROOF. Also brought to our attention is the epr study of a monomeric species reported by H. Kon and N. E. Sharpless, *Spectrosc. Lett.*, 49 (1968).
(10) acacen = $(CH_3C(O^-)=CHC(CH_3)NCH_2-)_2$.
(11) This could be due to the formation of a dimeric species in solution. Other square-planar cobalt(II) Schiff base complexes are known to form dimers in the solid state; see S. Brückner, M. Calligaris, G. Nardin, and L. Randaccio, *Acta Cryst.*, in press.
(12) J. M. Assour, *J. Am. Chem. Soc.*, **87**, 4701 (1965).
(13) G. N. Schrauzer and L. P. Lee, *ibid.*, **90**, 6541 (1968).

Table I. Epr Parameters of Some Cobalt(III)–Superoxo Complexes[a]

Compound[b]	$g_\perp$[c]	$g_\parallel$[c]	g_{iso}	$A_\perp^{Co}$, G	$A_\parallel^{Co}$,[c] G	a^{Co}, G	$A_\parallel^{N}$,[c] G
Co(acacen)CN-py	2.39[e]	2.0128			101.17		16.24
Co(acacen)Me-py	2.44[e]	2.0123			98.74		15.75
Co(acacen)py	2.44[e]	2.0110			97.53		15.72
Co(acacen)(O_2)			2.0247[h]			13.26[h]	
Co(acacen)H_2O(O_2)	(1.9966)[f]	2.0878	2.0270[g]	(13.72)[f]	28.85	18.76[g]	
Co(acacen)DMF(O_2)	(1.9962)[f]	2.0859	2.0261[h]	(9.92)[f]	20.15	13.33[h]	
Co(acacen)CN-py(O_2)	(1.9965)[f]	2.0796	2.0242[h]	(10.30)[f]	20.11	13.57[h]	
Co(acacen)Me-py(O_2)	(1.9972)[f]	2.0824	2.0256[h]	(10.00)[f]	19.63	13.21[h]	
Co(acacen)py(O_2)	(1.9987)[f]	2.0816	2.0263[g]	(10.73)[f]	19.64	13.70[g]	
$[(NH_3)_5CoO_2Co(NH_3)_5](NO_3)_5$			2.0249[d]			11.4[d]	
 $[(NH_3)_4Co\overset{O_2}{\underset{NH_2}{\diamond}}Co(NH_3)_4](NO_3)_4$			2.0342[d]			12.4[d]	

[a] Estimated errors for g values are ±0.0005; for hyperfine splitting, ±0.05, unless otherwise noted. [b] py = pyridine; CN-py = 4-cyanopyridine; Me-py = 4-methylpyridine. [c] Measured in frozen toluene solution at 77°K. [d] From ref 20. [e] Approximate value. [f] Calculated from $g_\perp = {}^1/_2(3g_{iso} - g_\parallel)$ or $A_\perp = {}^1/_2(3a - A_\parallel)$. [g] Measured in toluene solution at −74°. [h] Measured in toluene solution at −61°.

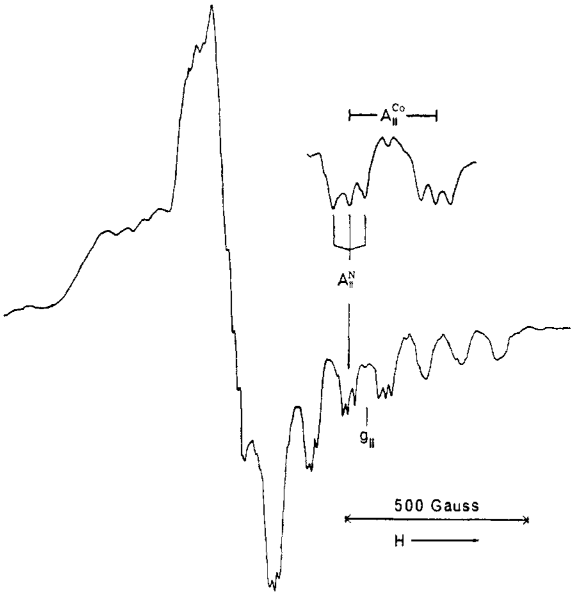


Figure 1. Epr spectrum of Co(acacen)py in frozen toluene solution at 77°K.

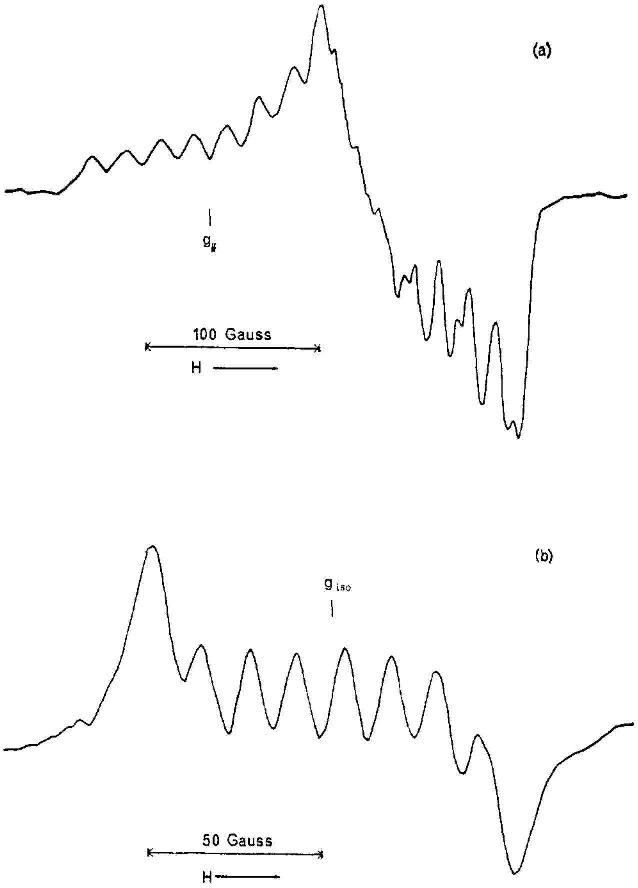


Figure 2. Epr spectra of Co(acacen)py(O_2). (a) Frozen toluene solution at 77°K. (b) Fluid toluene solution at −58°.

the "perpendicular" region split by a rhombic distortion. Seven of the eight ^{59}Co hyperfine lines ($I = {}^7/_2$) for the high field, "parallel," direction are observable, and several are seen to be split into equal intensity triplets by the single nitrogen nucleus of one coordinated pyridine molecule. The substituted pyridine analogs give qualitatively identical spectra. These spectra may be interpreted in terms of the following spin Hamiltonian

$$\mathcal{H} = \beta H \cdot \mathbf{g} \cdot S + \sum_{i = Co,N} S \cdot \mathbf{A}^i \cdot I^i \qquad (1)$$

The appropriate parameters for py–A and the substituted analogs are listed in Table I. Values for the parallel direction ($g_\parallel = g_1$ and $A_\parallel = A_1$) are obtained unambiguously, but those for the perpendicular region ($g_\perp = {}^1/_2(g_2 + g_3)$) are approximations due to incomplete spectral resolution. For unoxygenated adducts such as py–A, the principal axes of the $\mathbf{A}^{Co}$ and $\mathbf{g}$ tensors are expected to coincide. Further, as discussed below, the parallel direction of these tensors is expected to coincide with the z symmetry axis normal to the plane of the Schiff base.

No toluene fluid solution spectra of the pyridine adducts are observed from room temperature to approximately the melting point of toluene (−95°), presumably because of rapid spin-lattice relaxation.

If oxygen is admitted to a sample tube containing a solution of py–A, the spectrum shown in Figure 2a is obtained upon cooling to 77°K. Upon warming to −58°, the eight-line fluid solution spectrum of Figure 2b is observed. At temperatures above −39° the resolved hyperfine splittings wash out. Identical spectra are observed from solutions made by directly dissolving crystalline py–A–O_2 in toluene, proving that the spectra in Figure 2 are indeed those of the same material characterized by Crumbliss and Basolo.[8] The eigth line solution spectrum of Figure 2b, arising from interaction of an unpaired electron with a single ^{59}Co nucleus, clearly proves the monomeric nature of py–A–O_2.

The frozen solution spectrum of Figure 2a may be analyzed using the spin Hamiltonian of eq 1, with exclusion of the term describing resolved nitrogen superhyperfine splitting (shf). The observation of a fluid solution spectrum allows direct measurement of the isotropic g value and cobalt hyperfine splitting constant, a^{Co}.

Spectra similar to those of Figure 2 are obtained from monomeric cobalt–oxygen adducts using a variety of bases, and the apparent spin Hamiltonian parameters for these compounds are included in Table I. However, for oxygenated complexes the principal axes of the A^{Co} and g tensors need not coincide, nor, as is discussed later, need the g tensor axes coincide with the symmetry axis system defined by the plane of the Schiff base.

Since Crumbliss and Basolo[8] found that adducts of A with oxygen were unstable without a base in the sixth coordination site, we were surprised to observe that addition of oxygen to a solution of A in the absence of added base gave rise to both frozen and fluid solutions quite similar to those of Figure 2. When A is oxygenated in rigorously dried toluene solution, a poorly resolved frozen solution spectrum is observed, with an envelope characteristic of well-defined oxygen adducts such as py–A–O_2. In fluid solution, a well-resolved eight-line spectrum is observed with an isotropic ^{59}Co hyperfine splitting constant a_E = 13.26 G. If trace amounts of water are added, or if slightly damp toluene is used initially, well-resolved spectra are obtained in both frozen and fluid solution, and the isotropic splitting constant changes to a_D = 18.76 G. Thus, it appears that E is A–O_2, an oxygen adduct of A without a base in the sixth coordination site; it is formed in dilute, dry, toluene solution and is sufficiently stable to be studied by epr, although such a species is not stable to isolation and chemical analysis. The difference caused by traces of water indicates that D is H_2O–A–O_2, another new monomeric adduct of A. The existence of H_2O–A–O_2 and A–O_2 means that considerable care is called for in degassing crystals of A in order sufficiently to remove adsorbed oxygen and thus avoid observation of oxygen adduct spectra when attempting to observe spectra of unoxygenated species.

We have shown that it is possible to prepare H_2O–A–O_2 from solutions of A–O_2, by adding deoxygenated water, and that it is possible to prepare py–A–O_2 by adding deoxygenated pyridine to solutions of H_2O–A–O_2. Thus, starting from an oxygenated solution of the parent Schiff base complex, A, it is possible to form an oxygen adduct with a stronger base from a similar adduct with a weaker base by direct displacement. All adducts studied may be reversibily deoxygenated.

Discussion

The results presented above unambiguously verify the evidence presented by Crumbliss and Basolo[8] for the existence of monomeric oxygen adducts of A in fluid solution, in the presence of added base. All the oxygen adducts we have studied show fluid solution spectra of eight lines with equal intensity, characteristic of interaction of the unpaired spin with a single ^{59}Co nucleus. Frozen solution spectra of the oxygen adducts also show clear evidence of interaction with but one Co nucleus, in particular the low-field region about $g_\parallel$ where generally seven of the expected eight lines are clearly resolved. Figure 2 gives representative spectra for an adduct in which pyridine is in the axial position. In addition to the earlier observations,[8] we have added evidence for the existence of oxygen adducts both with water as a base and in the absence of added base. These adducts are stable enough in solution to be characterized by epr, although it has been demonstrated that they are not stable to isolation and chemical analysis.[8]

A. Electronic Structure. Consideration of the spin Hamiltonian parameters for the various species studied also allows us to draw definite conclusions about their electronic structures. The g values and hyperfine splitting constants of py–A and substituted analogs are very similar to those found for a variety of low-spin Co(II) complexes.[12–15] As with these other complexes, the result $g_\perp > g_\parallel \cong 2.0$, the absence of in-plane nitrogen atom superhyperfine (shf) splitting, and the sensitivity to changes in the environments, as evidenced by the observation of shf splitting from the nitrogen atom of the coordinating base, establish that the unpaired electron is associated with the $3d_{z^2}$ orbital. (The (x, y, z) axis system is fixed in the framework of A, as in the drawing above.) The observation of a three-line shf pattern produced by interaction with the nitrogen of *one* pyridine indicates that in the presence of base, A adds only one such axial ligand.

Oxygenation of A, with or without added base, produces a drastic change in the observed epr spectra in frozen solution and makes it possible to observe resolvable epr spectra in fluid solution. Magnetic moment data indicate a spin (S) of $^1/_2$ and the presence of only one unpaired spin in the crystalline adducts, and the epr measurements indicate a similar conclusion for the adducts in solution. In frozen solution spectra (77°K) there is no evidence of the zero-field splitting terms (zfs) which are quadratic in the electron spin and which might be expected if $S > {}^1/_2$. An even more sensitive indication of the absence of any appreciable zfs comes from the ready observation of resolved nuclear hyperfine structure of solution. Molecular tumbling in solution causes a zfs to act as a strong source of line broadening. Since the Co(II) ion of A has a single unpaired electron, and the gaseous molecular oxygen possesses two unpaired electrons (S = 1), then in solution as well as in a solid there has been a "pairing up" of spins to leave a resultant adduct with $S = {}^1/_2$. In attempting to qualitatively understand the electronic structure of these adducts it is convenient to begin the analysis by assuming that upon coordination the symmetry of the oxygen molecule is sufficiently reduced to split the otherwise degenerate $2p\pi^*$ orbitals and to constrain the two antibonding electrons to be paired in the orbital thus stabilized.

If the Co(II) of A is not formally oxidized upon complexation with oxygen, the oxygen adducts such as py–

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(14) A. H. Maki, N. Edelstein, A. Davison, and R. H. Holm, *J. Am. Chem. Soc.*, **86**, 4580 (1964).

(15) See A. Carrington and A. D. McLachlan, "Introduction to Magnetic Resonance," Harper and Row, New York, N. Y., 1967.

A–O_2 would also contain low-spin Co(II). However, the spin hamiltonian parameters for these adducts are completely inconsistent with a formulation in which the unpaired electron is in the $3d_{z^2}$ orbital.[14,16,17] It is seen that $g_\perp = {}^1/_2(g_2 + g_3)$ is less than $g_\parallel = g_1$ although the reverse must be true for the electron in the $3d_{z^2}$ orbital. Although postulating an inversion of the order of the energy levels, leading to an electron in a $3d_{xy}$ orbital upon complexation with oxygen, correctly predicts that $g_\parallel > g_\perp$, this suggestion may be ruled out by the absence of shf splittings from the in-plane nitrogen atoms. Consideration of the various alternative formulations for the energy level ordering of a low-spin Co(II) complex, many of which have recently been discussed,[14,16,17] leads to the conclusion that there is no convincing way to formulate the g values of these monomeric oxygen adducts in terms of a low-spin Co(II) species.

Furthermore, by use of well-known methods[14,16,18] expressions for the principal values of the ^{59}Co hyperfine interaction may be derived which depend on

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

and also on α^2, where the molecular orbital of the unpaired electron includes a cobalt 3d atomic orbital with coefficient α. Taking $\alpha = 1$ for py–A, we use the parameters from Table I in equations for the hyperfine interaction constants of an electron in a $3d_{z^2}$ orbital[16] to estimate that $P_{\text{py–A}} \cong 0.012$ cm^{-1}. We may estimate α^2 for the oxygen adducts without specifying the 3d orbital involved, although the equations for the hyperfine constants differ for different orbitals. Recognizing that P is intrinsically positive for cobalt, the magnitudes of observed hyperfine splitting parameters for the oxygen adducts require that signs be attributed to these parameters such that in first order (zeroth order in the cobalt spin-orbit interaction)

$$|A_\parallel^{\text{Co}}| \cong |A_\perp^{\text{Co}}| = |a^{\text{Co}}| + 4\alpha^2P/7$$

independent of the identity of the 3d orbital involved. For py–A–O_2 the result is $\alpha^2 \approx 0.1$, indicating $\sim$90% transfer of spin density from cobalt upon oxygen adduct formation. Estimates discussed below suggest that the value of α^2 is not increased by second-order corrections.

These considerations suggest that in the monomeric molecular oxygen adducts the Co(II) of parent molecule A is oxidized to Co(III) and that the oxygen is reduced to the superoxide ion, O_2^-. The observation that $g_\parallel > g_\perp$ for oxygen adducts is consistent with results for O^{2-} in halide crystals[19] if $g_\parallel$ for the adduct corresponds to the oxygen–oxygen (z') axis. Nearly complete electron transfer from cobalt to oxygen will also account for the low value of α^2 in the adducts.

Further evidence for formulating the monomeric oxygen adducts as Co(III)–O_2^- comes from comparison of the spin Hamiltonian parameters for these adducts with the parameters for the μ-superoxo- and μ-amido-μ-superoxodicobalt(III) complexes. Epr studies[20,21] have confirmed that in both solution and solid state, these complexes contain equivalent cobalt nuclei. Several X-ray structures[20–25] have been reported which clarify that the bridging O–O unit must be formulated as O_2^-. Taken together, these studies require that the dimeric cobalt–oxygen complexes contain two *cobalt(III)* ions. As can be seen in Table I, the isotropic g values and cobalt hyperfine splitting constants for our monomeric cobalt oxygen–adducts are in quantitative agreement with the values found for the series of bridged cobalt complexes studied by Weil.[20] These comparisons, along with the more general considerations above, are compelling evidence that the electronic structure of the oxygen adducts reported in this paper should be *formally* described as Co(III)–O_2^-.

The unpaired electron will of course be located in a molecular orbital, one involving an antibonding $2p\pi_g$ oxygen molecular orbital and a cobalt $3d_t$ orbital

$$|\psi\rangle \approx \beta|2p\pi_g\rangle + \alpha|3d_t\rangle$$

Neglecting oxygen–cobalt overlap, $\beta^2 \approx 1 - \alpha^2 \approx 0.9$ py–A–O_2. To first order, deviations from the free-electron g value come *solely* from spin density on superoxide. For an approximate analysis, first-order g-value expressions may be modified from those of Känzig and Cohen[19] to include delocalization of spin density from superoxide onto cobalt

$$g_\parallel = g_e + \beta^2\left(\frac{\lambda^2}{\lambda^2 + \Delta^2}\right)^{1/2} l$$

$$g_\perp = g_e\left[\alpha^2 + \beta^2\left(\frac{\Delta^2}{\lambda^2 + \Delta^2}\right)\right]^{1/2}$$

We find $\Delta/\lambda \lesssim 15$ and $l \lesssim 0.7$ for py–A–O_2, where λ is the spin-orbit splitting of the molecule ion, Δ corresponds to a splitting of the $2p\pi_g$ oxygen orbitals upon adduct formation, and l represents a correction to the angular momentum about the superoxide z' axis and is unity for the free molecule ion.[19,26]

This picture of the oxygen adducts is not qualitatively altered by considering second-order corrections to the formulas for hyperfine constants and g values resulting from spin density on cobalt. Taking $3d_t = 3d_{xz}$ (see section B) and using $\alpha^2 \approx 0.1$, a very crude estimate gives $0 > \Delta g_\parallel^{\text{Co}} \gtrsim -0.03$ and $0 < \Delta g_\perp^{\text{Co}} \lesssim 0.02$. These values may in turn be used in second-order equations for the hyperfine constants in order to iterate the calculation of α^2. They do not tend to increase α^2, but do change Δ and l.

The ^{59}Co nuclear hyperfine splitting may also be used to further the understanding of the functions of the ligand in the second axial position. Among the oxygen adducts for which a value of α^2 may be estimated, this parameter generally decreases with increasing base strength, and is largest for those adducts with weakest coordinating base. This is readily understood by considering that electron *pair* donation to the cobalt ion by

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[16] W. C. Lin, C. A. McDowell, and D. J. Ward, *J. Chem. Phys.*, **49**, 2883 (1968).

[17] J. M. Assour, *ibid.*, **43**, 2477 (1965).

[18] J. S. Griffiths, "Theory of Transition Metal Ions," Cambridge University Press, Cambridge, 1961.

[19] W. Känzig and M. H. Cohen, *Phys. Rev. Lett.*, **3**, 509 (1959).

[20] M. Mori, J. A. Weil, and J. K. Kinnaird, *J. Phys. Chem.*, **71**, 103 (1967).

[21] J. A. Weil and J. K. Kinnaird, *ibid.*, **71**, 3341 (1967).

[22] W. P. Schaefer and R. E. Marsh, *J. Am. Chem. Soc.*, **88**, 178 (1966).

[23] W. P. Schaefer and R. E. Marsh, *Acta Cryst.*, **21**, 735 (1966).

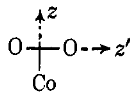
[24] R. E. Marsh and W. P. Schaefer, *ibid.*, **B24**, 246 (1968).

[25] G. G. Christoph, R. E. Marsh, and W. P. Schaefer, *Inorg. Chem.*, **8**, 291 (1969).

[26] N. Gerloch and J. R. Miller, *Progr. Inorg. Chem.*, **10**, 1 (1968).

the lone pair of the base reduces the *actual* charge which develops on the cobalt, and that the greater the pair donation to cobalt from the base, the more unpaired spin density is transferred from cobalt to oxygen.

B. Geometry. We next consider the disposition of the superoxide ion with respect to the cobalt(III) ion, in the light of the magnetic resonance and magnetic moments data. Of the three plausible geometries, where III is a limiting case of II, we may safely rule out III in both solid and fluid systems. The essentially spin-only magnetic moment and the observation of epr at $T > 77\,°\mathrm{K}$ indicate that the geometry about the oxygen–oxygen bond departs appreciably from axial symmetry, splitting the $2p\pi_g$ orbitals of the oxygen molecule, and considerably reducing l from its free ion value. It does not seem plausible to assign such a departure to geometry III, with the necessary asymmetry arising from interactions with the nonaxially symmetric square plane of the Schiff base ligand.



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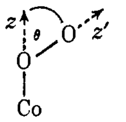

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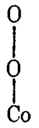

III

The epr results may also be used to attempt to distinguish between geometries I and II. The observation of a distinct, although not readily resolvable, g_x and g_y, A_2 and A_3, for the oxygen adducts demonstrates that at 77 °K the adducts do not possess axial symmetry, and thus that the superoxide ion is not rotating (geometry I) or precessing (geometry II) about the axial direction with frequencies approaching 1–10 MHz. As discussed above, the **g** tensor anisotropy is determined principally by the (large) spin density on the superoxide ion, and the direction of $g_{z'} = g_{\parallel}$ is that of the interoxygen axis. The cobalt hyperfine splitting tensor is principally determined by the 3d orbital on the cobalt ion which contributes to the molecular orbital of the unpaired electron. If geometry I is adopted with, say, the z' axis along x, then $g_{\parallel} = g_{z'}$ will also lie along x. However, in this geometry, $3d_{zz}$ is the only cobalt 3d orbital which is allowed by symmetry to bond to $2p\pi_g$. The maximum hyperfine splitting for spin density in $3d_{zz}$ lies along y, and would thus correspond to $A_{\perp}$, associated with $g_{\perp}$. This is contrary to observation that $A_{\parallel}^{\mathrm{Co}} > A_{\perp}^{\mathrm{Co}}$. Thus the epr observations tend to support the conclusions of Crumbliss and Basolo[8] from ir data that structure I does not obtain, leaving II as the preferred structure.

Considering geometry II, when the Co–O–O and x–z planes coincide the $2p\pi_g$ molecular orbital containing the unpaired electron will mix only with the $3d_{yz}$ orbital of cobalt. Following Griffiths[27] the simplest model involves an angle $\theta = \pi/3$. This angle (or greater) puts z' largely along x, which is also the direction of largest hyperfine splitting for $3d_{yz}$. Therefore, geometry II is consistent with experiment.

Acknowledgments. We thank Dr. A. L. Crumbliss for helpful discussions. D. L. D. expresses his appreciation to the National Science Foundation for a predoctoral fellowship. B. M. H. acknowledges support by the Advanced Research Projects Agency of the Department of Defense through the Northwestern University Materials Research Center. This research was also supported in part by National Institutes of Health Grant GM-07488.

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(27) J. S. Griffiths, *Proc. Roy. Soc., Ser. A*, 235, 23 (1956).