Cobaloximes(II) and Vitamin B_{12r} as Oxygen Carriers. Evidence for Monomeric and Dimeric Peroxides and Superoxides

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Abstract: Bisdimethylglyoximatocobalt(II) complexes ("cobaloximes(II)") and related cobalt chelates react with molecular oxygen to yield intensely colored, diamagnetic μ-peroxo-cobaloximes, $B{-}Co(D_2H_2){-}O_2{-}Co(D_2H_2){-}B$ (D = dianion of dimethylglyoxime; B = base, *e.g.*, pyridine). Although the oxygen adducts are very labile and can be readily deoxygenated the cobaloximes are only incompletely reversible oxygen carriers due to their subsequent oxidation of μ-superoxo-cobaloximes, $B{-}Co(D_2H_2){-}O_2{-}Co(D_2H_2){-}B^+$. Esr analysis of the latter species reveals the unpaired electron to be symmetrically delocalized over the Co–O–O–Co system. The μ-superoxo-cobaloximes decompose with bases into derivatives of the cobaloxime(III) anhydrobase, $Co(D_2H)$, and the monomeric peroxoradicals, $B{-}Co(D_2H_2){-}O_2\cdot$. The esr spectrum of $Py{-}Co(D_2H_2){-}O_2\cdot$ closely resembles that of peroxocobalamin, indicating a close similarity of the electronic environment of the $Co{-}O_2\cdot$ system in both compounds.

Although the oxygen-carrying propensities of cobalt(II) chelates have received considerable attention in the past three decades[2,3] many questions concerning the nature and electronic structure of the oxygen adducts still remain to be answered. To obtain some new insight into factors influencing the Co(II) ion to bind oxygen we have continued earlier investigations[4] on the oxygen carrying properties of bisdimethylglyoximatocobalt(II) complexes ("cobaloximes(II)"), whose similarity to vitamin B_{12r} made them particularly attractive for further study as possible models of the oxygen carrying properties of the vitamin.

Cobaloximes(II): Properties and Structure in Solution

Bisdimethylglyoximatocobalt(II), $Co(D_2H_2)$ (D = dianion of dimethylglyoxime),[4] is paramagnetic (μ_{eff} = 1.70 BM), insoluble in all noncoordinating solvents, and hence probably associated in the solid state.[5] It reacts with various bases to form 1:1 and 1:2 adducts which are soluble in a variety solvents including CH_2Cl_2, benzene, or acetone. The 1:2 adducts of composition $Co(D_2H_2)\cdot 2B$ (B = *e.g.*, pyridine, triphenylphosphine, or -arsine) dissociate in solution according to eq 1.

$$Co(D_2H_2)\cdot 2B \rightleftharpoons Co(D_2H_2)\cdot B + B \qquad (1)$$

Equilibrium 1 is shifted to the left upon the addition of excess base. Solutions of cobaloximes(II) containing excess pyridine accordingly exhibit the esr signals of the 1:2 base adducts (Figure 1).[6] The solutions of the 1:1 base adducts of cobaloximes(II) in noncoordinating solvents such as CH_2Cl_2, CH_3CHCl_2, or $ClCH_2CH_2Cl$ are either paramagnetic or diamagnetic and may contain varying amounts of monomeric or dimeric species depending on the nature of the axial base. The triphenylphosphine, -arsine, or -antimony adducts are essentially monomeric and paramagnetic (Table I). The adducts with pyridine or cyclohexyl isocyanide are dimeric or essentially dimeric in the concentration range applied for the molecular weight determination (Table I) and show no esr signals. The solubility of the pyridine adducts in CD_2Cl_2 is sufficient for ^1H nmr measurements. The signal of the phenyl protons of bisdiphenylglyoximato(pyridine)cobalt(II) dimer was observed as a single peak at 7.30 ppm and was only slightly broadened due to traces of paramagnetic species present. The solid complex was found to be diamagnetic (observed gram susceptibility at 293°K: -0.92×10^{-6} cgs). Solid (cyclohexyl isocyanide)cobaloxime(II) possesses only a slight paramagnetism of approximately 0.22 BM. The signal of the methyl protons of bisdimethylglyoximato(pyridine)cobalt(II) in CD_2Cl_2 occurs as a single peak at 1.43 ppm. The electronic structure of cobaloximes(II) has been discussed elsewhere.[6] Since the unpaired electron is essentially localized in the $3d_{z^2}$ orbital the dimerization of the five-coordinate cobaloxime(II) units could occur through metal–metal bond formation.[6a] The degree of dissociation into paramagnetic monomers depends on the basicity of the axial component and the polarity of the solvent. In DMF, for example, dissociation is essentially complete as evidenced by the molecular weight measurements. An alternative way in which cobaloxime(II) 1:1 base adducts could dimerize is through the pairwise interaction of the Co(II) ions with oxime oxygen anions as, *e.g.*, in bisdimethylglyoximatocopper. Dimers of this kind should be paramagnetic, however. The remark-

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[1] UCSD Predoctoral Fellow, 1967–1970.

[2] L. H. Vogt, H. M. Faigenbaum, and S. E. Wiberley, *Chem. Rev.*, **63**, 269 (1963).

[3] A. E. Martell and M. Calvin, "Chemistry of Metal Chelate Compounds," Prentice-Hall Inc., New York, N. Y., 1952, and references cited therein.

[4] G. N. Schrauzer and R. J. Windgassen, *Chem. Ber.*, **99**, 602 (1966).

[5] Bis(dimethylglyoximatocobalt) is not isostructural with the corresponding nickel complex. The solid state association of $Co(D_2H_2)$ presumably involves the coordination of the cobalt ion by oxime oxygen anions of neighboring molecules.

[6] G. N. Schrauzer and L. P. Lee, *J. Amer. Chem. Soc.*, **90**, 6541 (1968).

[6a] NOTE ADDED IN PROOF. The structure anticipated for dimeric cobaloximes(II) has since been observed for a related bisdimethylglyoximatorhodium(II) complex. See K. G. Caulton and F. A. Cotton, *J. Amer. Chem. Soc.*, **91**, 6517 (1969).

Table I. Molecular Weights of Cobaloximes(II) in Solution

No.	Compound	Molecular weights (concn, *M*)[a] Calcd	In CH_3CHCl_2	In DMF
I	$Co(D_2H_2)\cdot 2Py$	447.4	238 (0.012)	240 (0.012)
II	$Co(D_2H_2)\cdot 2P(C_6H_5)_3$	813.7	402 (0.009)	400 (0.009)
III	$Co(D_2H_2)\cdot 2P(n\text{-}C_4H_9)_3$	693.3	360 (0.011)	350 (0.011)
IV	$Co(D_2H_2)\cdot Py$	368.7	720 (0.026)	477 (0.026)
V	$Co(Dpg_2H_2)\cdot Py$[b]	618.8	1240 (0.015)	*c*
VI	$Co(D_2H_2)\cdot P(C_6H_5)_3$	554.4	497 (0.013)	*c*
VII	$Co(D_2)H_2)\cdot As(C_6H_5)_3$	598.3	*d*	*c*
VIII	$Co(D_2H_2)\cdot Sb(C_6H_5)_3$	645.2	530 (0.022)	*c*
IX	$Co(D_2H_2)\cdot CN\text{-}C_6H_{11}$	398.2	692 (0.025)	390 (0.01)
X	$(Co(D_2H_2)\cdot Py)_2O_2$	772.5	760 (0.013)	*c*
XI	$(Co(Dpg_2H_2)\cdot Py)_2O_2$[b]	1268	1250 (0.01)	*c*

[a] Determined osmometrically with a TEM Mechrolab Instrument at 37° under nitrogen. All runs are duplicate; the reproducibility was about 1%. The estimated accuracy of the measurements is better than 5% for the range between 400 and 700, and about 10% for the range of 1500. [b] Dpg is dianion of diphenylglyoxime. [c] Not determined. [d] Insoluble.

able insensitivity of the solid cobaloxime(II) 1:1 base adducts to oxygen would seem to indicate that the complexes are also dimeric in the solid state. Vitamin B_{12r}, which cannot form a dimer for steric reasons, is extremely oxygen sensitive. The structure of the solid cobaloxime(II) 1:1 base adducts is as yet unknown. It is of interest that the complexes can apparently exist both in a diamagnetic[4] and in a paramagnetic[7] modification, whose formation seems to depend on details of the method of preparation.

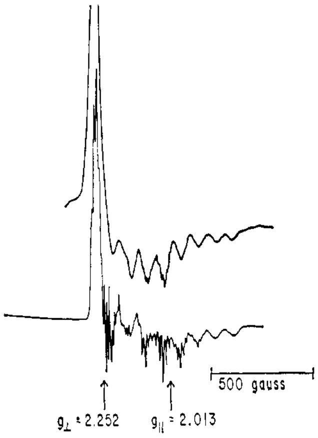
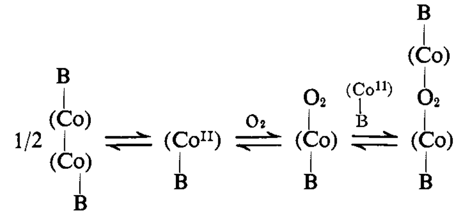


Figure 1. Esr spectra of solutions of pyridine(dimethylglyoximato)-cobalt(II) (upper curve) and of pyridine(diphenylglyoximato)-cobalt(II) (lower curve) in CH_2Cl_2–pyridine glass at 110°K. The fivefold shf splitting due to the interaction of cobalt with two molecules of pyridine is resolved in both cases, particularly clearly in the derivative of diphenylglyoximatocobalt. Solutions of the 1:1 base adducts in CH_2Cl_2 glass in the absence of added excess of pyridine show no esr signal due to formation of dimeric species.

Cobaloximes(II) as Oxygen Carriers

Solutions of both the 1:1 and 1:2 adducts of cobaloximes(II) with bases in aprotic solvents such as benzene or methylene chloride absorb 0.5 mol of oxygen per mol of cobalt. The oxygen in the intensely colored adducts is held only loosely and can be removed by a stream of nitrogen and argon, or by heating of the solutions to about 40°. In strictly anhydrous media the oxygen absorption–desorption can be repeated many times. The cobaloximes(II) nevertheless are only incompletely reversible oxygen carriers due to the occurrence of irreversible side reactions (oxidation to Co(III) derivatives), which taken place particularly in the presence of traces of water. These reactions have been shown previously to lead to the formation of the cobaloxime(III) "anhydrobase," $Co(D_2H)$.[4] The initial oxygen adducts are diamagnetic binuclear μ-peroxides as evidenced by the absence of esr signals in solutions of freshly oxygenated cobaloxime(II) solutions and molecular weight measurements (Table I). The initial reactions of the cobaloximes(II) with oxygen thus may be represented by eq 2. The oxygen adducts were isolated in solid form by adding *n*-hexane to solutions in CH_2Cl_2 at −20°. The purple μ-peroxo-bis(pyridinecobaloxime) or the blue μ-peroxo-bis(triphenylphosphinecobaloxime) are unstable on storage, slowly decomposing with oxygen evolution even at 0°. The μ-peroxide of pyridinecobaloxime appears to be more stable than the corresponding triphenylphosphine, triphenylarsine, or cyclohexyl isocyanide derivatives. The intense color of the adducts is due to strong charge transfer absorptions in the visible region. Usually two CT bands are resolved between 800 and 500 mμ, whose λ_{max} depend on the nature of the axial bases. The observed bathochromic shifts in the order $N(C_2H_5)_3 \simeq Py < (CH_3)_2S < P(C_6H_5)_3 < As(C_6H_5)_3$ (Table II) suggest that strong σ-donor ligands increase the energy of



$$\tfrac{1}{2}\,\text{B–(Co)–(Co)–B} \rightleftharpoons \text{(Co}^{II}\text{)–B} \xrightleftharpoons{O_2} \text{O}_2\text{–(Co)–B} \xrightleftharpoons{\text{(Co}^{II}\text{)–B}} \text{B–(Co)–O}_2\text{–(Co)–B} \qquad (2)$$

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(7) P. W. Schneider, P. F. Phelan, and J. Halpern, *J. Amer. Chem Soc.*, **91**, 77 (1969).

Table II. Observed Maxima of Charge Transfer Bands of Oxygenated Cobaloximes(II) in CH_2Cl_2 (Approximate Extinction Coefficients in Parentheses) as a Function of the Axial Base

Axial base	Color	Observed transitions, λ_{max}, mμ (ϵ)[a]		
$N(C_2H_5)_3$	Purple	530 (3.5×10^3)	700 (1.15×10^3)	1175 (1×10^2)
Pyridine	Purple	550 (3.6×10^3)	700 (1.2×10^3)	1200 (1.1×10^2)
Dimethyl sulfide	Violet	580 (4×10^3)	730 (1×10^3)	1140 (*ca.* 10^2)
$P(C_6H_5)_3$	Blue	620 (5.2×10^3)	768 (1.9×10^3)	1200 (5.8×10^2)
$As(C_6H_5)_3$	Blue	625 (5.3×10^3)	780 (1.2×10^3)	*b*

[a] Extinction coefficients are approximate due to instability of the oxygen adducts. The transition around 1200 mμ is possibly a forbidden transition. [b] Not observed.

the CT transitions by increasing the charge density on cobalt. Triphenylphosphine, even though it is a more polarizable ligand than pyridine or triethylamine, acts as a weaker donor presumably because of its significant acceptor properties. The spectral properties observed are consistent with an excitation mechanism in which an electron from a MO largely localized on oxygen is transferred to an orbital with greater metal character. Absorption spectra of oxygenated cobaloximes are shown in Figure 2.

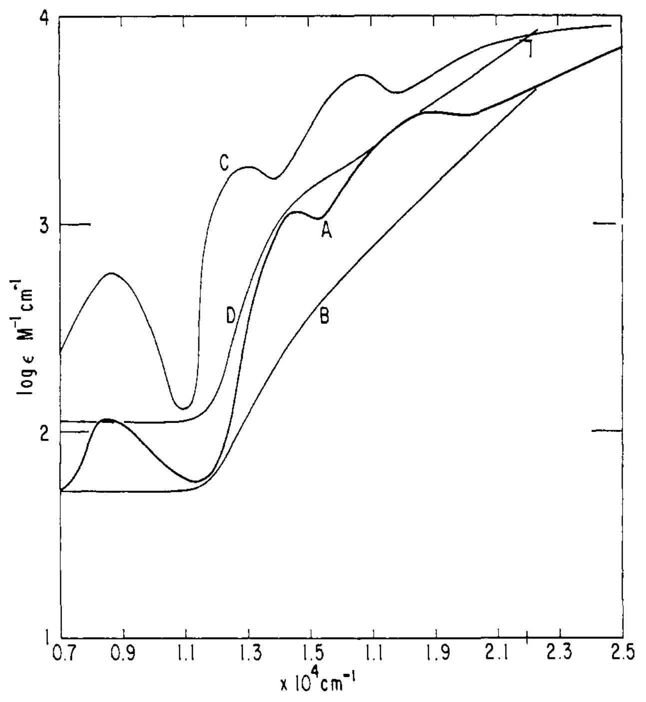

Figure 2. Spectra of oxygenated pyridine–cobaloxime (A) and of triphenylphosphinecobaloxime (C) in CH_2Cl_2, immediately after preparation. Spectra of the same after standing for 60 min (pyridinecobaloxime, B; triphenylphosphinecobaloxime, D).

The formation of μ-peroxides does not occur in the presence of electron acceptors competing with oxygen. Tetracyanoethylene (TCNE) forms short-lived CT complexes with cobaloximes(II) recognized by their green color. These adducts are quite unstable, decomposing rapidly into cobaloxime(III) and the $TCNE^-$ radical anion which was detected by esr measurements. Fumaronitrile still prevents the appearance of the characteristic color of the μ-peroxides if present during the oxygenation of cobaloximes(II). Acrylonitrile, a sufficiently weak acceptor, does not interfere under the same conditions.

Binuclear Cobaloxime Superoxo Radicals

On standing the μ-peroxo-cobaloximes undergo further reaction accompanied by oxygen evolution. The purple solutions of $Py–Co(D_2H_2)–O_2–Co(D_2H_2)–Py$ turn brown with the simultaneous appearance of a 15-line esr spectrum shown in Figure 3. The radical species responsible for this signal must be the μ-superoxo radical cation $Py–Co(D_2H_2)–O_2–Co(D_2H_2)–Py^+$ in which the unpaired electron is delocalized over the $Co–O_2–Co$ unit. The magnitude of the hf splitting due to ^{59}Co of 12 G indicates that the highest occupied MO has approximately 20% metal character (the value of $\langle a \rangle$ due to ^{59}Co in cobaloximes(II) is 80–113 G[6]). The 15-line signals are not entirely symmetric and vary with changes of the solvent, temperature, and viscosity of the solutions similarly as has been observed in other cases, *e.g.*, in the spectra of the ion $(NH_3)_5Co–O_2–Co(NH_3)_5^{+5}$[5,8,9] which is attributed to anisotropy and relaxa-

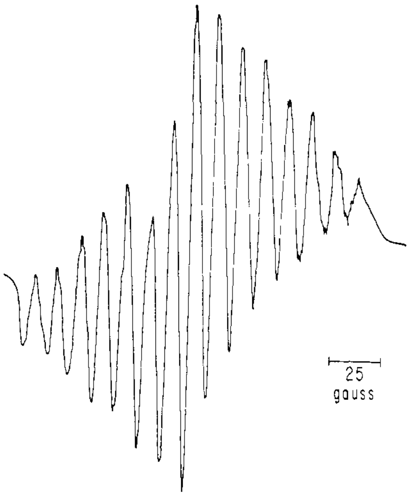

Figure 3. Esr spectrum (15-line) of $Py–Co(D_2H_2)–O_2–Co(D_2H_2)–Py^+$ in CH_2Cl_2 at 298 °K (for *g* value see Table III).

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(8) E. A. V. Ebsworth and J. A. Weil, *J. Phys. Chem.*, **63**, 1890 (1959).

Table III. Esr Data of Peroxocobaloxime Radicals and of Related Species

Radical[a]	$\langle g \rangle$ isotropic, mostly at 298° (solvent)	$\langle a \rangle$ isotropic, G	Hfs multiplicity ^{59}Co, (I = 7/2)	Anisotropy at 100°K				Re-marks
				$\langle g_{\parallel} \rangle$	$\langle g_{\perp} \rangle$	$\langle a_{\parallel} \rangle$	$\langle a_{\perp} \rangle$	
$Py{-}Co(L_1){-}O_2{-}Co(L_1){-}Py^+$	2.030 (C_6H_6)	12	15	[b]				[d]
$Py{-}Co(L_2){-}O_2{-}Co(L_2){-}Py^+$	2.022 (CH_3CHCl_2)	13	15	[b]				[d]
$(C_6H_5)_3P{-}Co(L_1){-}O_2{-}Co(L_1){-}P(C_6H_5)_3^+$	2.013 (C_6H_6)	12.5	15	[b]				[e]
$C_6H_{11}NC{-}Co(L_1){-}O_2{-}Co(L_1){-}CNC_6H_{11}^+$	2.012 (C_6H_6)	~10	15	[b]				[e]
$(NC)_5Co{-}O_2{-}Co(CN)_5^{-5}$ [9]	2.0203 (H_2O, acidic)	8	15	[b]				[d]
$(H_3N)_5Co{-}O_2{-}Co(NH_3)_5^{+5}$ [9]	2.025 (50% H_2SO_4)	11.4	15	[b]				[d]
$Py{-}Co(L_1){-}O_2\cdot$	2.014 (C_6H_6)	8.5	8	2.065	2.000	16	12	[d]
$Py{-}Co(L_2){-}O_2\cdot$	2.014 (C_6H_6)	8.5	8	2.066	2.022	13	12	[d]
$(C_6H_5)_3P{-}Co(L_1){-}O_2\cdot$	2.013 (C_6H_6)	8.5	8	[c]				[d]
$C_6H_{11}NCCo(L_1){-}O_2\cdot$	2.013 (C_6H_6)	10	8	[c]				[e]
Vitamin $B_{12r}{}^{-}O_2$ [10,11]	2.02 (DMF), 174°K	~12	8	2.069	2.002	16	13	[d]
Vitamin $B_{12r}{-}O_2$ [10,11]	2.02 (CH_3OH), 174°K	~14	8	2.079	2.003	18	13	[d]

[a] L_1 and L_2 denote the bisdimethylglyoximato- and bisdiphenylglyoximato-ligand systems, respectively. [b] Anisotropy not resolved. [c] Anisotropy not resolved. [c] Anisotropy not determined. [d] Signal due to a single species. [e] Solution contains mono- and binuclear peroxo radicals.

tion effects. At 100°K the signal of $Py{-}Co(D_2H_2){-}O_2{-}Co(D_2H_2){-}Py^+$ is observed as a broad line without recognizable anisotropy or hf structure at $\langle g \rangle = 2.030$. The formation of the superoxo radical from the diamagnetic μ-peroxide is probably initiated by a disproportionation into the radical cation and an anionic species. The latter could subsequently undergo decomposition into OH^- and oxygen. The overall stoichiometry of the reaction hence could be as shown in eq 3 (the axial base is not included). Equation 3 is supported by the isolation of the cobaloxime anhydro base $Co(D_2H)$ out of solutions of irreversibly oxygenated cobaloximes and the amount of oxygen evolved in the reaction, which very nearly corresponds to the quantity expected according to eq 3.[4]

$$2Co(D_2H_2){-}O_2{-}Co(D_2H_2) \longrightarrow Co(D_2H_2){-}O_2{-}Co(D_2H_2)^+ + 2Co(D_2H) + 1/2\,O_2 + H_2O \quad (3)$$

The stability of the μ-superoxo radicals depends markedly on the nature of the axial base. Although we have been able to identify the 15-line signal of $(C_6H_5)_3P{-}Co(D_2H_2){-}O_2{-}Co(D_2H_2){-}P(C_6H_5)_3^+$, the esr spectrum indicated the presence of a monomeric radical species to be discussed in the next section. The situation is similar in the superoxo-radical spectrum of the cobaloxime with cyclohexyl isocyanide as the axial base, where again only a composite signal due to a mono- and binuclear radical was observed. We have been unable to observe a 15-line signal in oxygenated solutions of the cobaloximes with $As(C_6H_5)_3$ and $Sb(C_6H_5)_3$ as the axial components. Esr data on cobaloxime μ-superoxo radicals are summarized in Table III.

Mononuclear Peroxocobaloxime Radicals

On standing, benzene solutions of $Py{-}Co(D_2H_2){-}O_2{-}Co(D_2H_2){-}Py^+$ exhibiting the 15-line esr signal undergo further chemical change, indicated by the slow conversion of the esr spectrum to an 8-line signal shown in Figure 4. Judging from the observed hf splitting multiplicity the radical must be due to a peroxo species containing only one cobalt ion, presumably $Py{-}Co(D_2H_2){-}O_2\cdot$. Subsequent experiments revealed a remarkable sensitivity of the binuclear μ-peroxo radicals to nucleophilic attack. The addition of a small amount of pyridine or DMF to solutions of $Py{-}Co(D_2H_2){-}O_2{-}Co(D_2H_2){-}Py^+$ in benzene caused the diasppearance of the 15-line esr spectrum. A new signal exhibiting axial symmetry was observed at 100°K, with $\langle g_{\parallel} \rangle = 2.065$, $\langle a \rangle = 16$ G, and $\langle g_{\perp} \rangle = 2.000$, $\langle a \rangle = 13$ G, respectively, with the hf splitting multiplicity of 8. The signal proved to be similar to that shown in Figure 4, if measured at liquid nitrogen temperature. The reaction of the binuclear peroxocobaloxime radicals with pyridine thus may be formulated according to eq 4. The formation of the bispyridine adduct of the anhydro base according to eq 5 has been demonstrated previously.[4] Due to the greater lability of the μ-peroxo radicals of cobaloximes with triphenylphosphine or cyclohexylisocyanide as the axial base, cleavage of the binuclear species to the mononuclear peroxo radicals in these compounds occurs even in the absence of added base. Two spectra of a benzene solution of oxygenated triphenylphosphine–cobaloxime(II) in benzene are shown in Figure 5. Shortly after preparation of the solutions the esr spectra still consist of superimposed signals due to the binuclear and the mononuclear peroxo radicals. After 80 min the intensity of the 8-line signal of the monomeric species is increased relative to the 15-line signal, the latter disappearing altogether on further standing. We have been unable to observe binuclear or mononuclear peroxo radicals of cobaloximes in water as the solvent. Instability of the peroxo radicals in

$$Py{-}Co(D_2H_2){-}O_2{-}Co(D_2H_2){-}Py^+ + 2Py = Py{-}Co(D_2H_2){-}O_2\cdot + Co(D_2H)\cdot 2Py + PyH^+ \quad (4)$$

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

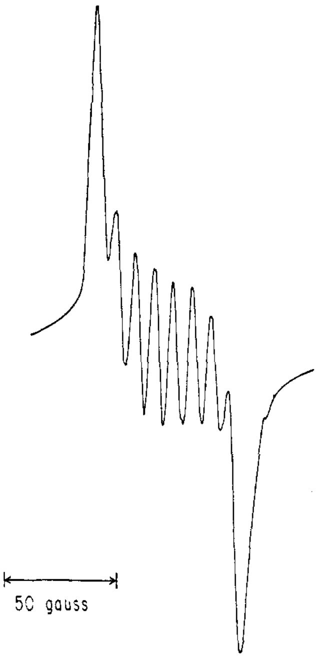

Figure 4. Esr spectrum (8-line) due to Py-Co(D_2H_2)-O_2· observed in "aged" solutions of Py-Co(D_2H_2)-O_2-Co(D_2H_2)-Py$^+$ in CH_2Cl_2 at 298°K (*g* value is listed in Table III).

water is indicated by the fact that the 15-line signal due to Py-Co(D_2H_2)-O_2-Co(D_2H_2)-Py$^+$ rapidly changes to the 8-line signal of Pr-Co(D_2H_2)-O_2· upon the addition of a few drops of water to benzene solutions of the oxygenated cobaloxime. The mononuclear peroxocobaloxime radicals are more stable under these conditions, but also disappear over a period of 24 hr.

Comparison with Oxygenated Vitamin B_{12r}

Vitamin B_{12r} reacts with oxygen to produce a peroxo radical recently characterized by Bayston, *et al.*,[10] and independently studied by us.[11] A binuclear μ-peroxo radical in this case is not formed for steric reasons, preventing the close approach of two cobalamin molecules. The esr spectrum of peroxocobalamin is shown in Figure 6 together with that of Py-Co(D_2H_2)-O_2·. The near identity of the two signals demonstrates that the electronic environment of the Co-O_2· radical unit must be very similar in both cases. Thus, although cobaloximes(II) are not sterically hindered they may still serve as models for the oxygen-carrying properties of vitamin B_{12r}.

The possible formation of peroxo radicals of vitamin B_{12} must be considered in all reactions involving vitamin B_{12r} in the presence of oxygen. The photolysis of complexes between methylcobalamin and the enzyme ethanolamine deaminase, for example, produced solutions exhibiting esr signals around $g = 2.000$, which were claimed to be similar to those formed on photolysis of 5′-deoxyadenosylcobalamin under anaerobic conditions.[12] The signal is not identical with vitamin B_{12r}, however, but is due to peroxocobalamin, which is also formed on aerobic photolysis of methylcobalamin[13] and hence does not necessarily indicate a special behavior of enzyme-bound methylcobalamin. The formation of peroxocobalamin derivatives also occurs on exposing solutions of vitamin B_{12a} to air. Vitamin B_{12a} for this reason was regarded to be the only known Co(III) oxygen carrier.[14] We have recently shown, however, that the apparent anomalous behavior of vitamin B_{12a} is a consequence of its tendency to undergo self-reduction to Co(II) corrin derivatives.[15] The esr spectrum of a solution of vitamin B_{12a} in water under anaerobic conditions accordingly resembles that of vitamin B_{12r}. In the presence of air the spectra often exhibit a superimposed free-radical signal around $\langle g \rangle$

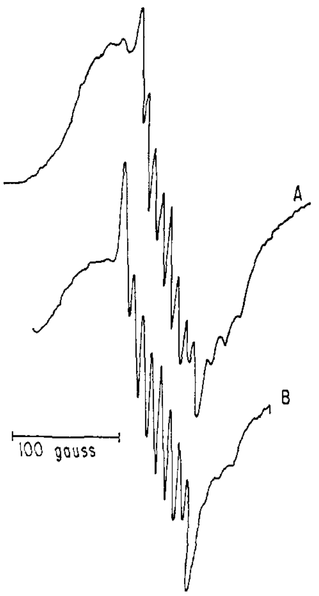

Figure 5. Esr spectra of oxygenated triphenylphosphinecobaloxime(II): A, signal immediately after oxygenation; B, after 80 min, in CH_2Cl_2 at 298°K.

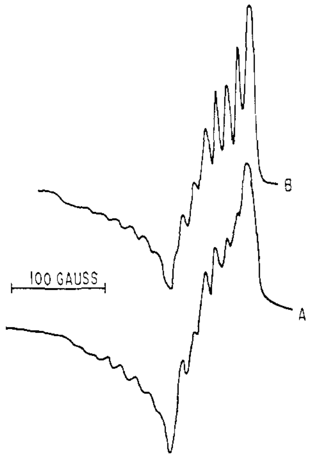

Figure 6. Esr spectra of Py-Co(D_2H_2)-O_2· (B) and of peroxocobalamin (A), both in methanol glass at 110°K.

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(10) J. H. Bayston, N. K. King, F. D. Looney, and M. E. Winfield, *J. Amer. Chem. Soc.*, **91**, 2775 (1969).

(11) G. N. Schrauzer and L. P. Lee, unpublished experiments.

(12) B. M. Babior, H. Kon, and H. Lecar, *Biochemistry*, **8**, 2662 (1969).

(13) Unpublished experiments.

(14) B. Jaselskis and H. Diehl, *J. Amer. Chem. Soc.*, **80**, 2147 (1958).

(15) L. P. Lee and G. N. Schrauzer, *ibid.*, **90**, 5274 (1968).

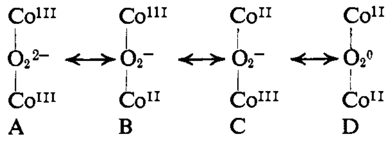
= 2.0029,[15] which we have identified to be due to peroxocobalamin on the basis of its g value and the magnitude of the ^{59}Co hf interaction. The esr parameters of peroxocobalamin are summarized together with those of cobaloxime derivatives in Table III. The signals shown in Figure 6 are consistent with an axially symmetric g tensor. The unpaired electron thus could occupy a MO composed of the $3d_{z^2}$ cobalt orbital and a $\pi_g{}^*$ MO of oxygen. The interaction with oxygen lowers the electron density on cobalt and is probably responsible for the smaller value of $\langle g \rangle$ (isotropic) in the peroxo complexes as compared to the parent Co(II) chelates. For similar reasons $\langle g_{\parallel} \rangle > \langle g_{\perp} \rangle$ in the peroxo species, whereas $\langle g_{\parallel} \rangle < \langle g_{\perp} \rangle$ in cobaloximes(II) and in vitamin B_{12r}.[6] Ideally, this orbital assignment would be proved by the observation of shf splitting due to the coordinated axial nitrogen base. However, the splitting should only be about 1–1.5 G, and hence is not resolved.

Discussion

There now appears to be general agreement that the ability of a Co(II) chelate to function as an oxygen carrier is linkd to the ease with which electron transfer occurs from the Co(II) ion to oxygen.[16] Most cobalt(II) chelates react with oxygen in two steps (eq 5 and 6), yielding the binuclear diamagnetic μ-peroxides. Equation 6 appears to be sufficiently slow in some cases recently reported by Basolo[17] and Calderazzo,[18] causing the oxygenation to terminate with the formation of the mononuclear peroxo radicals. This is also observed in the oxygenation of vitamin B_{12r}, where eq 6 cannot occur for steric reasons.[10] In the diamagnetic, binuclear μ-peroxides the coordinated oxygen molecule could simply be considered as $O_2{}^{2-}$ and the metal ions as Co(III), but this formulation is not entirely satisfactory as covalent contributions to the bonding are neglected. The inadequacy of the classical description becomes obvious from the results of the X-ray structure determination of the 1:2 adduct of oxygen with N,N′-ethylenebis(salicylaldehydeiminato)cobalt(II) containing dimethylformamide.[19] Although the Co–O–O–Co grouping is twisted as in a peroxide, the observed O–O bond length of 1.35 Å is much shorter than expected for a true peroxide (1.48 Å), suggesting only partial rather than complete transfer of electrons from cobalt to oxygen. Although the structure of the oxygen-carrying cobaloximes is unknown, their intense color and chemical lability similarly suggest a considerable deviation from the conventional peroxide type structure. Before discussing some aspects of the bonding in these complexes it must be emphasized that in any detailed description of the electronic structure the possible structural nonrigidity of the species in solution would have to be considered, which in the case of the μ-peroxo radicals could be responsible for considerable motional averaging and other anisotropy and relaxation effects. There can be little doubt, however, that the principal bonding orbital interactions involve the $\pi_g{}^*$ MO's of oxygen and the singly occupied $3d_{z^2}$ orbitals of the Co(II) chelates. An estimate[20] of the ionization potential of cobaloximes(II) suggests the energy of the $3d_{z^2}$ orbital to be between −8.0 and −10.0 eV, the value depending, in part, on the nature of the axial base component. Since the energy of the $\pi_g{}^*$ orbital of oxygen must be close to its first ionization potential of −12.5 eV, the resulting bonding MO of the Co–O–O–Co unit must show greater electron density on oxygen than cobalt; its metal character would also be significant, however. In terms of a simple valence bond description the ground state electronic configuration therefore would have to be represented as a hybrid of the limiting structures A–D in eq 7. Although structure A makes the most significant contribution in the ground state the oxygen adducts would still be best described as containing cobalt in a fractional valence state between 3+ and 2+. The participation of structures B–D in the ground state of the oxygen carrying cobaloximes is presumably responsible for the remarkably low energy of the observed CT transitions in the optical spectra. In contrast, the ion $(CN)_5Co\text{–}O_2\text{–}Co(CN)_5{}^{-6}$ [21] absorbs at 327 mμ. Due to the greater stability of the Co(III) valence state in the cyanide complexes of cobalt the μ-peroxide hexaanion must have greater "peroxide character" than the oxygen adducts of the cobaloximes.

$$Co^{II} + O_2 \rightleftharpoons Co\text{–}O_2\cdot \quad (5)$$

$$Co\text{–}O_2\cdot + Co^{II} \longrightarrow Co\text{–}O_2\text{–}Co \quad (6)$$



$$\begin{array}{ccccccc} Co^{III} & & Co^{III} & & Co^{II} & & Co^{II} \\ | & & | & & | & & | \\ O_2{}^{2-} & \longleftrightarrow & O_2{}^{-} & \longleftrightarrow & O_2{}^{-} & \longleftrightarrow & O_2{}^{0} \\ | & & | & & | & & | \\ Co^{III} & & Co^{II} & & Co^{III} & & Co^{II} \\ A & & B & & C & & D \end{array} \quad (7)$$

The μ-superoxo radicals formed by the oxidation of the binuclear μ-peroxides may be written classically as Co(III) superoxides,[22] *i.e.*, $Co^{III}\text{–}O_2{}^{-}\text{–}Co^{III}$, a structure which is expected to be dominant in a simple valence bond description. Since the unpaired electron is delocalized symmetrically over both cobalt ions, however, limiting structures such as $Co^{II}\text{–}O_2{}^{0}\text{–}Co^{III}$ are also contributing. The greater weight of the latter structures in the cobaloxime peroxo radicals is indicated by the magnitude of the observed ^{59}Co hf splitting (Table III). The binuclear cobaloxime μ-superoxides thus are again most realistically regarded as cobalt complexes with fractional metal valence states of between 3+ and 2+.

The mononuclear cobaloxime peroxo radicals contain the unpaired electron in a MO with approximately 10–20% metal character. This renders the classical formula A of eq 8 inadequate and suggests that structures such as B make a significant contribution. The

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[16] See, *e.g.*, F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1968, pp 641–648.

[17] A. L. Crumbliss and F. Basolo, *Science*, **164**, 1168 (1969).

[18] F. Calderazzo and C. Floriani, *J. Chem. Soc., A*, in press.

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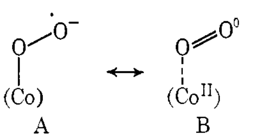
[22] J. D. Dunitz and L. E. Orgel, *J. Chem. Soc.*, 2594 (1954).

Table IV. Analyses of Cobaloxime(II) Base Adducts[a]

Compd no.	Empirical formula	Calcd % C	Calcd % H	Calcd % N	Found % C	Found % H	Found % N
I	$C_{18}H_{24}N_6O_4Co$	48.32	5.41	18.79	48.31	5.32	19.09
II	$C_{44}H_{43}N_4O_4CoP_2$	65.01	5.53	6.89	64.78	5.44	6.69
III	$C_{32}H_{68}N_4O_4CoP_2$			8.08			8.15
IV	$C_{13}H_{19}N_5O_4Co$	42.40	5.20	19.02	42.62	5.40	18.89
V	$C_{33}H_{27}N_5O_4Co$	64.48	4.39		64.75	4.66	
VI	$C_{26}H_{29}N_4O_4CoP$	56.62	5.32	10.16	56.59	5.38	10.0
VII	$C_{26}H_{29}N_4O_4CoAs$	52.53	4.90	9.39	52.66	5.00	9.28
VIII	$C_{26}H_{29}N_4O_4CoSb$	48.70	4.74	8.71	48.70	4.82	8.52
IX	$C_{15}H_{25}N_5O_4Co$	45.60	6.33		45.92	6.58	

[a] Numbering of complexes is as in Table I.



(8)

temperature dependence of the ^{59}Co hf splitting parameter, *a* (Table III), may have several reasons, among which we consider a possible sterical nonrigidity to be the most appealing, but the detailed nature of the conformational lability of the Co–O–O system is not yet understood.

In summary, the present work demonstrates that cobaloximes(II) possess oxygen-carrying properties similar to those of other Co(II) chelates. They are more labile than, *e.g.*, peroxopentacyanocobaltates, however, due to the greater electron affinity of cobaloximes(III) as compared to the $Co(CN)_5^{3-}$ ion. This in turn is responsible for the greater metal character of the constituent MO's of the cobaloxime peroxides and the unusually low energy of the CT transitions of the binuclear μ-peroxo-cobaloximes. We assign intermediate oxidation states of cobalt to all peroxo and superoxo species to stress the close relation of these compounds to electron-donor–acceptor complexes, a description which appears to be more consistent with their chemical properties than the classical Co(III) formalism.

Experimental Section

Synthesis of the Cobaloxime(II) Base Adducts. Cobalt acetate tetrahydrate, 24.9 g (0.1 mol), dimethylglyoxime, 23.2 g (or the equivalent amount of diphenylglyoxime), and the corresponding base (0.1 mol for the synthesis of the 1:1 adducts, 0.2 mol or more if the preparation of the 1:2 complexes is desired) are added successively into 400 ml of absolute methanol. The mixture is stirred under nitrogen for 1 hr. During this period the formation of the adducts is complete. The products are collected by filtration, washed with absolute methanol, and dried at room temperature at 1 mm. The dry complexes are relatively stable on storage if protected against humidity. Analyses of the complexes are given in Table IV.

Measurement of Oxygen Uptake. The absorption of oxygen by the cobaloxime(II) chelates was measured by using 3.0 g of the complexes suspended in 30–50 ml of absolute CH_2Cl_2 at 0°. All chelates absorbed not more than 0.5 mol of oxygen per mol of cobaloxime over the period of 10–20 min. On further standing approximately $^1/_8$ mol of O_2 was evolved in each case, with concomitant color change of the solutions to brown.

Isolation of the Oxygen Adducts. Solutions of pyridine–cobaloxime(II) and of triphenylphosphinecobaloxime(II) in dry CH_2Cl_2 were exposed to dry oxygen gas at −20° for 10 min. Dry *n*-hexane was added until a precipitate formed, while maintaining the reaction solution at −20°. Removal of the solvent mixture through decantation followed by drying of the solid adducts at −20° in a stream of dry oxygen afforded purple $Py\text{–}Co(D_2H_2)\text{–}O_2\text{–}Co(D_2H_2)\text{–}Py$ and blue $(C_6H_5)_3P\text{–}Co(D_2H_2)\text{–}O_2\text{–}Co(D_2H_2)\text{–}P(C_6H_5)_3$. The dry solids decomposed slowly at 0°, rapidly at 27°, or on heating to about 50°. The amount of oxygen evolved corresponded to about 0.5 mol of oxygen per mol of cobalt.

Physical Measurements. For details concerning the molecular weight determinations see Table I, footnote *a*. ^1H nmr spectra of py-$Co(D_2H_2)$ and Py-$Co(Dpg_2H_2)$ were carried out in CD_2Cl_2 solution under nitrogen. The signal of the dimethylglyoxime methyl protons was observed as a single peak at τ 1.43 ppm, confirming the diamagnetism of the solution. The signal broadened out almost completely upon the addition of pyridine. Similarly, the signal of the phenyl protons in Py-$Co(Dpg_2H_2)$ was observed at τ 7.30 ppm; the peak was slightly broadened due to the presence of a paramagnetic species and disappeared almost completely upon the addition of pyridine. The esr spectra were obtained using a Varian E 3 epr spectrometer with 100-kc field modulation, and under the conditions outlined in the text. The magnetic measurements were carried out by Dr. D. Wohlleben, Department of Physics, UCSD, by the Faraday method.

Acknowledgment. This research was supported by Grant 1-RO1-ES 00325-01 of the Department of Health, Education, and Welfare. The esr measurements were performed on a Departmental Instrument obtained through National Science Foundation Grant GP 5208.