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Five-Coordinate Dioxygen Adducts of Cobalt(II) Complexes

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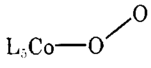
Abstract: A series of five-coordinate cobalt(II) trisphosphine complexes are reported and their electronic structures determined via EPR. Both distorted trigonal bipyramidal and tetragonal pyramidal geometries are obtained with ligand variation. Complexes with both geometries reversibly bind dioxygen but dissociate a phosphine in the process to form a novel series of five-coordinate terminally bound dioxygen complexes. The implication of this new type of adduct to the requirements for a ring-bonded mode of cobalt-dioxygen binding is discussed.

I. Introduction

Extensive research in recent years has enhanced our understanding of the binding of dioxygen to cobalt(II) complexes. However, many significant questions remain. For example, what properties of the cobalt determine the extent of electron transfer into and the nucleophilicity of the bound O_2? Several different geometries are possible for a bound dioxygen including end-on bonding[1] (I), bridging[1] (II), and a ring bonding[2] mode (III). The factors that determine the geometry which is obtained when dioxygen coordinates and the influences which these geometrical and electronic variations have on the reactivity of the bound O_2 remain as unanswered questions. A greater variety of systems need to be prepared and their electronic structures and chemical reactivity investigated before general patterns can be recognized. In this article the synthesis of a series of complexes in which rigid chelating structures are not attached to cobalt(II) is reported and their reactions with dioxygen are investigated. Five-coordinate complexes containing end-on bonded O_2, i.e., CoL_4O_2, are reported for the first time and the implications of this finding to the spin-pairing model of dioxygen binding are discussed.[3,4] Additional insight is provided regarding the requirements for forming structure III above.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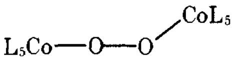
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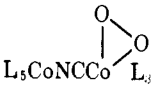
III

II. Experimental Section

A. General. All operations were carried out in oven-dried glassware in a dry N_2 atmosphere using Schlenk-type apparatus or in an inert atmosphere box, unless otherwise indicated. Heptane and medium petroleum ether were stirred vigorously over H_2SO_4 for 24 h, washed with dilute $NaHCO_3$ solution, and dried over $CaSO_4$. They were further purified before use by refluxing over $LiAlH_4$ for 24 h followed by distillation in a dry N_2 atmosphere. Toluene, benzene, and CH_2Cl_2 were refluxed over CaH_2 for 24 h and distilled under N_2 prior to use. Ethanol was treated with Na and distilled under N_2. Anhydrous $CoBr_2$ was prepared by heating $CoBr_2 \cdot 6H_2O$ in vacuo at 150 °C for 48 h. IR spectra were recorded on a Perkin-Elmer 467 grating infrared spectrophotometer. X-Band ESR spectra were recorded on a Varian Model E-9 spectrometer operating at ca. 9.1 GHz with a field sweep of 0-10 kG. A Varian E-15 Q band spectrometer was used to cover the range from 0 to 29 kG. Cooling was provided by a stream of cold (80 K) N_2 gas passing through the probe. Anisotropic EPR spectra were obtained in glasses formed from 3/2 (volume basis) toluene/CH_2Cl_2.

B. Preparation of Complexes. $Co(PMe_2Ph)_3Br_2$. Anhydrous $CoBr_2$ (2.2 g, 0.01 mol) was slurried in 50 mL of CH_2Cl_2 and PMe_2Ph (4.8 g, 0.035 mol) was added. The $CoBr_2$ slowly dissolved to yield a deep violet solution. The CH_2Cl_2 was removed in vacuo and the crude complex recrystallized from 50 mL of hot C_6H_6. The violet, crystalline solid was washed three times with 25-mL portions of heptane and dried in vacuo, yield 5.5 g (88%). The compound can be recrystallized from C_6H_6 in the presence of added phosphine.

Anal. Calcd for $CoC_{24}H_{33}P_3Br_2$: Co, 9.31; C, 45.52; H, 5.25; Br, 25.24. Found: Co, 9.19; C, 45.82; H, 5.30; Br, 25.54.

$Co(PMePh_2)_3Br_2$. An attempt to prepare this dibromotrisphosphine complex by the method used for $Co(PMe_2Ph)_3Br_2$ was unsuccessful. Only the green dibromobisphosphine complex, $Co(PMePh_2)_2Br_2$, was isolated.

Anal. Calcd for $CoC_{26}H_{26}P_2Br_2$: Co, 9.56; C, 50.43; H, 4.23; Br, 24.81. Found: Co, 9.52; C, 50.07; H, 4.14; Br, 25.76.

$Co(PMe_3)_3Br_2$. Anhydrous $CoBr_2$ (1.1 g, 5 mmol) was placed in a 50-mL round-bottom flask, and 25 mL of CH_2Cl_2 was added. The flask was attached to a vacuum line and the solution degassed. PMe_3 (2.5 g, 33 mmol) was vacuum transferred into the flask which had been cooled to liquid N_2 temperature. The solution was allowed to warm to ambient temperature and a dark violet solution resulted. The reaction was continued for 3 h, at which time the solvent and excess PMe_3 were vacuum transferred away, leaving a violet solid. This crude material was taken into an inert atmosphere box where it was dissolved in 10 mL of hot CH_2Cl_2 containing 1 equiv of PMe_3. Petroleum ether

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(60–68 °C), 30 mL, was added to induce crystallization. After the solution was allowed to stand for 2 h, a dark blue-violet, crystalline solid was isolated, washed three times with 10-mL portions of petroleum ether, and dried in vacuo, yield 1.6 g (72%). Attempted recrystallization of the compound in the absence of added PMe_3 often led to decomposition of the compound. This compound is sensitive to atmospheric conditions in the solid state and in solution.

Anal. Calcd for $CoC_9H_{27}P_3Br_2$: Co, 13.18; C, 24.18; H, 6.09. Found: Co, 13.18; C, 24.54; H, 6.01.

$Co(PMe_2Ph)_3(SCN)_2$. Anhydrous $Co(SCN)_2$ (2.63 g, 0.015 mol) was heated to reflux with 10 g of dimethylphenylphosphine (0.073 mol) in 100 mL of CH_2Cl_2 for 12 h in an inert atmosphere. A light green precipitate formed from the brown solution after about 2 h. The precipitate was recrystallized to forest-green crystals from benzene.

Anal. Calcd for $CoC_{26}H_{33}N_2S_2P_3$: C, 52.98; H, 5.60; N, 4.75; Co, 10.00. Found: C, 52.71; H, 5.55; N, 4.85; Co, 9.78.

A single infrared ν_{SCN} stretching vibration of 2095 cm^{-1} suggests that the thiocyanate groups are trans.

$Co(PMe_2Ph)_3Cl_2$. Anhydrous $CoCl_2$ (1.3 g, 0.01 mol) was slurried in 100 mL of CH_2Cl_2 and 5 g (0.036 mol) of dimethylphenylphosphine was added. After stirring under argon for 48 h a deep violet solution was observed. The CH_2Cl_2 was removed in vacuo. The crude complex was recrystallized from 50 mL of hot benzene. The violet, crystalline solid was washed three times with heptane and dried in vacuo, yield 5.0 g (92.4%).

Anal. Calcd for $CoC_{24}H_{33}P_3Cl_2$: C, 52.95; H, 6.07; Co, 10.82. Found: C, 53.16; H, 6.20; Co, 11.04.

$Co(PMe_2Ph)_3F_2$. Under argon, CoF_2 (1 g, 0.01 mol) was slurried in 100 mL of CH_2Cl_2 and 5 g (0.036 mol) of dimethylphenylphosphine was added. After stirring under argon for 48 h a deep violet solution was observed. The CH_2Cl_2 was removed in vacuo and the crude complex recrystallized from 50 mL of hot benzene containing a small amount (0.5 g) of PMe_2Ph. The blue-violet solid was washed three times with heptane and dried in vacuo. Decomposition of the product occurred when added phosphine was not used in the recrystallization.

Anal. Calcd for $CoC_{24}H_{33}P_3F_2$: C, 56.37; H, 6.46; Co, 11.53. Found: C, 55.98; H, 6.25; Co, 11.37.

Cyanide Anion-Exchange Resin. A procedure similar to that described by Solodar[5] was employed in the preparation of the CN^- anion-exchange resin. DOWEX 2-X8 strongly basic anion-exchange resin (275 g, 50–100 mesh) was used. (To avoid formation of channels and gas pockets the CN^- ion-exchange resin is allowed to swell in the solvent mixture used for the ion-exchange reaction for approximately 30 min prior to packing the column.)

$Co(PMe_2Ph)_3(CN)_2$. The preparation of this complex was carried out by a procedure similar to that previously described in the literature for analogous compounds.[6] $Co(PMe_2Ph)_3Br_2$ (2.5 g, 4 mmol) was dissolved in 70 mL of 1:1 (v/v) CH_2Cl_2/EtOH containing PMe_2Ph (0.55 g, 4 mmol). The deep violet solution was passed through a 3 × 20 cm column containing 25 g (100 mol equiv) of the DOWEX CN^- ion-exchange resin. The deep red solution which was eluted from the column was evaporated to dryness and the resulting reddish-brown solid redissolved in hot benzene and reprecipitated with an equivalent volume of heptane. The resulting red-brown, microcrystalline solid was isolated, washed with heptane, and dried in vacuo, yield 1.5 g (71%). The complex can be further purified by recrystallization from a benzene/ether mixture.

Anal. Calcd for $CoC_{26}H_{33}N_2P_3$: Co, 11.22; C, 59.44; H, 6.33; N, 5.33. Found: Co, 11.24; C, 59.50; H, 6.22; N, 5.24. IR: ν_{CN} 2085 cm^{-1}.

$Co(PMePh_2)_3(CN)_2$. The preparation of this complex was carried out in a manner similar to that described for $Co(PMe_2Ph)_3(CN)_2$. A red solid was isolated, washed three times with heptane, and dried in vacuo. In toluene or CH_2Cl_2 some added $PMePh_2$ was needed to prevent the appearance of a small amount of blue-green precipitate.

Anal. Calcd for $CoC_{41}H_{39}N_2P_3$: Co, 8.28; C, 69.20; H, 5.52; N, 3.94. Found: Co, 8.44; C, 68.24; H, 5.45; N, 4.23. IR: ν_{CN} 2085 cm^{-1}.

$Co(PMe_3)_3(CN)_2$. This complex was prepared from $Co(PMe_3)_3Br_2$ using the same procedure described for $Co(PMePh_2)_3(CN)_2$. However, attempts to isolate it using a similar workup procedure failed. Upon attempting to remove the solvent under vacuum or by evaporation with heating, the complex decomposed to an insoluble blue-green solid. This was attributed to the high volatility of PMe_3. It also could not be precipitated by the addition of petroleum ether. It was therefore only characterized in solution by ESR spectroscopy (vide infra).

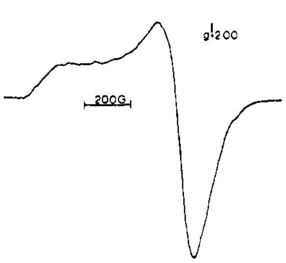


Figure 1. Frozen solution ESR spectra of $Co(PMePh_2)_3Br_2$ in 2:3 CH_2Cl_2/toluene at 80 K.

III. Results and Discussion

Chemical Properties and Characterization of the Pentacoordinate Cobalt(II) Phosphine Complexes. Halogen Derivatives. The dibromotrisphosphine cobalt(II) complexes were prepared by the reaction of a slight excess of the appropriate phosphine with anhydrous $CoBr_2$ dispersed in methylene chloride. $Co(PMe_3)_3Br_2$ was isolated as a dark, blue-violet, crystalline material which was sensitive to atmospheric conditions decomposing to a black, amorphous solid. $Co(PMe_2Ph)_3Br_2$ was isolated as a violet solid which was less sensitive to atmospheric conditions in the solid state but decomposed in exposed solutions to yield a blue solid. $Co(PMePh_2)_3Br_2$ could not be isolated as a stable solid material, but its existence in solution in the presence of excess methyldiphenylphosphine was confirmed via ESR spectroscopy (vide infra).

The dibromotrisphosphine complexes are all low-spin cobalt(II) complexes which exhibit broad, featureless ESR signals at room temperature in CH_2Cl_2/toluene solutions. Upon cooling to liquid N_2 temperatures axially symmetric spectra with $g_\parallel > g_\perp$ are observed in the CH_2Cl_2/toluene glass. The spectrum of $Co(PMePh_2)_3Br_2$ with excess phosphine (~1 equiv) at 80 K in a toluene/CH_2Cl_2 glass is illustrated in Figure 1. Simulation of this spectrum could be accomplished by using two g values ($g_\perp$ = 2.07 and $g_\parallel$ = 2.39) and an $A_\parallel$(Co) value of 57 × 10^{-4} cm^{-1}. This value of the cobalt hyperfine leads to the broad unresolved $g_\parallel$ peak which is illustrated in Figure 1. This broad feature could also be simulated with an $A_\parallel$(P) hyperfine splitting from one phosphorus ligand whose value is 170 × 10^{-4} cm^{-1}. The spectrum could not be simulated by using three g values (with or without unresolved hyperfine) nor could it be reproduced by the addition of hyperfine splitting from three equivalent phosphorus ligands. Since numerous combinations of unresolvable cobalt and phosphorus (one nucleus) hyperfine values allow spectral reproduction, only the $g_\parallel$ and $g_\perp$ values can be obtained for all the $Co(PR_3)_3Br_2$ complexes. The results, summarized in Table I, do permit a structural assignment.

Elemental analyses and the EPR spectra suggest five coordination about the cobalt(II). Trigonal-bipyramidal or tetragonal-pyramidal limiting structures can result. The g values enable one to distinguish between the two idealized limiting structures because of the different d-orbital occupations in the two cases; see Figure 2a,b. The spin-orbit coupling that exists in these systems mixes excited states into the ground states. This gives rise to g values that differ from the spin-only value of 2.0023 in accord with the following equation for a system with an $S = 1/2$ nondegenerate ground state:[8]

$$g = 2.0023 + \frac{n\xi}{E_{(0)} - E_{(n)}} \qquad (1)$$

where ξ represents the one-electron spin-orbital coupling

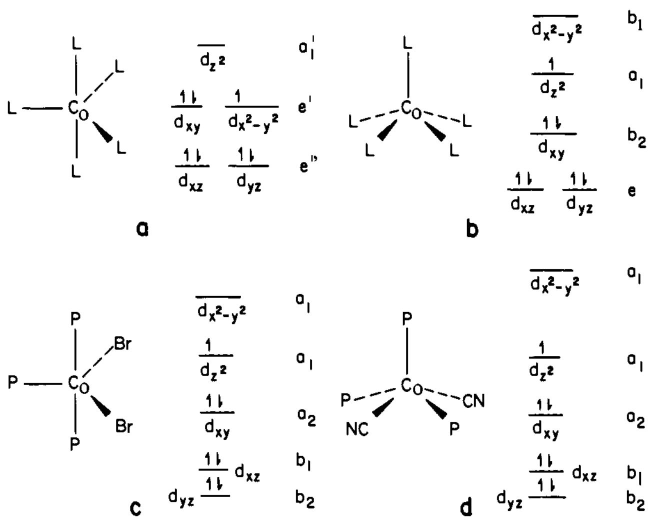


Figure 2. Idealized structures and electron configuration for the (a) trigonal-bipyramidal and (b) tetragonal-pyramidal structures. Actual structures and electron configurations for the (c) $Co(PR_3)_3Br_2$ and (d) $Co(PR_3)_3(CN)_2$ complexes.

constant, $E_{(0)} - E_{(n)}$ is the difference between the ground- and excited-state energies in the hole formalism, and n is an integer whose value arises from the evaluation of the matrix elements connecting the various states. For the trigonal bipyramidal structure we expect the electron configuration $e''^4\, e'^3\, a'^0$. A Jahn–Teller distortion is predicted to remove the degeneracy of the e′ orbitals. The g values which one would expect for the slightly distorted trigonal bipyramidal structure are given by

$$g_x \simeq g_y = 2.0023 + \frac{2\xi}{E_{yz}, E_{xz} - E_{xy}} \tag{2}$$

$$g_z = 2.0023 + \frac{8\xi}{E_{x^2-y^2} - E_{xy}} \tag{3}$$

where the z axis is the threefold axis of a regular trigonal bipyramid and the ground state is assumed to have the unpaired electron in the d_{xy} orbital after a Jahn–Teller distortion for the purpose of illustration. The expressions above result in

$$g_z > g_x \sim g_y > 2.002$$

A dynamic Jahn–Teller distortion would give rise to an axial spectrum.

For a tetragonal pyramidal complex, the g-value expressions are

$$g_x = g_y = 2.0023 + \frac{6\xi}{E_{yz}, E_{xz} - E_{z^2}} \tag{4}$$

$$g_z = 2.0023 \tag{5}$$

where the z axis is the fourfold rotation axis of a regular tetragonal pyramid. Thus the g values from EPR differentiate these two limiting structures and support the assignment of a trigonal bipyramidal geometry to the $Co(PR_3)_3Br_2$ complexes since $g_\parallel > g_\perp > 2.002$ (see Table I).

The arrangement of the phosphine ligands in the coordination sphere can also be deduced from the hyperfine splittings. A system with three equatorial phosphine ligands should have extensive delocalization of the unpaired electron in the d_{xy} or $d_{x^2-y^2}$ orbitals over all three equivalent phosphorus ligands giving rise to a significant hyperfine coupling. The spectra could not be simulated for these conditions. Accordingly we propose a structure comparable to that reported for $Co(PF_2Ph)_3Br_2$[9] with two axial phosphines and one equatorial phosphine. As mentioned earlier the EPR spectrum could be fit with hyperfine coupling from one phosphorus. In this distorted geometry, the molecule belongs to the C_{2v} point group. Picking the z axis so that it lies in the plane of equatorial atoms and passes through the cobalt and unique phosphorus, the ground-state electron configuration becomes $b_2{}^2b_1{}^2a_2{}^2a_1{}^1$. Both the d_{z^2} and $d_{x^2-y^2}$ orbitals have a_1 symmetry and contribute to the a_1 orbital. With $g_\parallel$ assigned to g_z the $x^2 - y^2$ contribution to a_1 provides nonzero matrix elements to give orbital angular momentum about the z axis. This geometry and ground state are illustrated in Figure 2c.

Table I. Spin Hamiltonian Parameters for the Dibromotrisphosphine Complexes

complex	$g_\parallel$	$g_\perp$
$Co(PMe_3)_3Br_2$	2.42	2.08
$Co(PMe_2Ph)_3Br_2$	2.52	2.09
$Co(PMePh_2)_3Br_2$	2.39	2.07

The g values are given by

$$g_\parallel = g_z = 2.0023 + \frac{8\xi}{E_{xy} - E_{A_1}} \tag{6}$$

$$g_\perp = g_x = g_y = 2.0023 + \frac{6\xi}{E_{yz,xz} - E_{A_1}} \tag{7}$$

where the A_1 ground state is a combination of the d_{z^2} and $d_{x^2-y^2}$ orbitals. The energy difference between the d_{xz} and d_{yz} orbitals must be small in these systems because an axial spectrum is observed. Also $g_\parallel$ is greater than $g_\perp$ owing to the smaller energy difference in the denominator of eq 6 than that of eq 7.

Subsequent to our completion of this research an ESR study and X-ray structure determination were reported on the complexes $Co(PPhF_2)_3Br_2$ and $Co(PPhF_2)_3I_2$.[9] In this case cobalt and phosphorus hyperfine was resolvable in the parallel region of the frozen solution ESR spectra and it was found that $A_\parallel(Co) = 102 \times 10^{-4}\ cm^{-1}$ and $A_\parallel(P) = 64.6 \times 10^{-4}\ cm^{-1}$ for both the bromide and iodide complexes with $g_\parallel > g_\perp > 2.00$. This was interpreted as being due to the complexes having a distorted trigonal-bipyramidal structure in which there are two axial and one equatorial phosphine ligands. The crystal structure shows a large distortion with the two axial cobalt–phosphine bonds being bent markedly away from the equatorial cobalt–phosphine bond and into the Br–Co–Br group. We expect similar distortions in the complexes reported here.

In order to investigate substituent variation on dioxygen binding, the analogous chloride and fluoride complexes were prepared. The EPR spectra in the absence of O_2 gave $g_\parallel$ values greater than $g_\perp$ for these systems, supporting a trigonal-bipyramidal geometry similar to that of the bromide complexes.

Cyano Complexes. The dicyanotrisphosphine cobalt(II) complexes were prepared[6] from the bromo analogues via cyanide ion-exchange column chromatography. Attempts to prepare $Co(PPh_3)_3(CN)_2$ using a similar procedure failed. The $Co(PMe_3)_3(CN)_2$ complex could not be isolated from solution, presumably owing to its high solubility in the solvents employed and to the volatility of trimethylphosphine; however, its presence was confirmed via ESR (vide infra). The room temperature ESR spectrum of $Co(PMe_2Ph)_3(CN)_2$ in a 1:1 (v/v) mixture of CH_2Cl_2/toluene appeared to be split into a doublet with $\langle g \rangle = 2.12$ and $\langle A \rangle = 90 \times 10^{-4}\ cm^{-1}$ (see Figure 3a).[10] Confirmation that this spectrum consisted of a doublet from phosphorus coupling and was not the superposition of the isotropic signals from two different species was obtained by comparing $\langle A \rangle$ from the Q-band spectrum with that at X-band. An identical splitting at $\langle g \rangle = 2.12$ was observed at both frequencies, establishing the assignment of this splitting to a hyperfine coupling. No cobalt hyperfine was observed in either

Table II. Spin Hamiltonian Parameters for the Dicyanotrisphosphine Complexes

complex	$\langle g \rangle$	g_1	g_2	g_z	$A_{1,2\mathrm{Co}}{}^a$	$Az_{\mathrm{Co}}{}^a$	$A_{1_\mathrm{P}}{}^a$	$A_{2_\mathrm{P}}{}^a$	$Az_\mathrm{P}{}^a$	$A_{1,2_{\mathrm{P'}}}{}^a$	$Az_{\mathrm{P'}}{}^a$	$\langle A_\mathrm{P} \rangle^a$
$Co(PMe_3)_3(CN)_2$	2.11	2.17	2.136	2.010	*b*	80	95	98	132	*b*	18	*b*
$Co(PMe_2Ph)_3(CN)_2$	2.12	2.17	2.138	2.012	*b*	78	78	95	126	*b*	13	90
$Co(PMePh_2)_3(CN)_2$	2.13	2.19	2.162	2.010	*b*	75	79	92	120	*b*	13	92

[a] Values in 10^{-4} cm^{-1}. [b] Not observed.

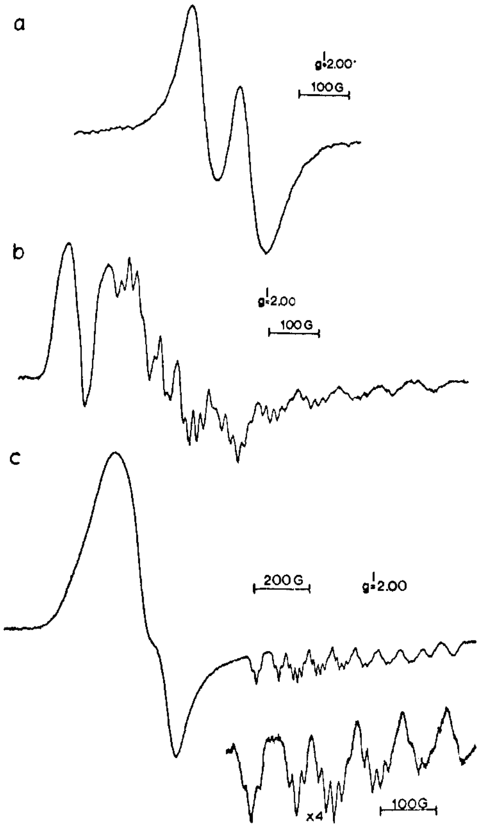


Figure 3. ESR spectra for $CO(PMe_2Ph)_3(CN)_2$ in CH_2Cl_2/toluene: (a) X-band, ambient temperature; (b) X-band, 80 K; (c) Q-band, 80 K.

the X-band or Q-band spectra at room temperature. Similar behavior was observed for $Co(PMePh_2)_3(CN)_2$ with $\langle g \rangle$ = 2.13 and $\langle A \rangle = 92 \times 10^{-4}$ cm^{-1}. The ESR spectrum of $Co(PMe_3)_3(CN)_2$ under similar conditions was only a broad, featureless signal at $\langle g \rangle = 2.16$. At −27 °C a doublet arising from a unique phosphorus ligand was resolved.

The frozen solution spectrum of $Co(PMe_2Ph)_3(CN)_2$ at X-band frequencies (Figure 3b) is quite complex owing to the overlap of the $g_\parallel$ and $g_\perp$ regions and the presence of extensive hyperfine interactions. Based on the relative intensities observed in this spectrum, it is readily apparent that g_x, $g_y > g_z$. Similar behavior was observed for both $Co(PMe_3)_3(CN)_2$ and $Co(PMePh_2)_3(CN)_2$.

An understanding of the electronic structure and ligand configuration for these complexes can be obtained from the detailed consideration of the frozen solution Q-band spectra. The spectrum of $Co(PMe_2Ph)_3(CN)_2$ at 80 K is shown in Figure 3c. The series of high-field resonances are attributed to the $g_\parallel$ signal. The reversal in g-value order, the appearance of ten distinct resonances in the parallel region, and the triplet structure on the outermost signals in the parallel region are readily accounted for by assigning a square-pyramidal structure to the complex with an apical phosphine and $d_{z^2}{}^1$ electronic configuration (Figure 2d). The hyperfine coupling to the apical phosphorus in the parallel region is large, 126×10^{-4} cm^{-1}. With the addition of Co hyperfine (78×10^{-4} cm^{-1}) one expects to see 16 resonances, but, owing to overlap of signals in this region and additional phosphorus superhyperfine coupling (13×10^{-4} cm^{-1}) of the two basal phosphines, the identity in the central area is lost. The line diagram shown in Figure 4, constructed by employing the observed coupling constants, adequately accounts for all the resonances observed in the parallel region. Both $Co(PMe_3)_3(CN)_2$ and $Co(PMePh_2)_3(CN)_2$ exhibit similar Q-band spectra and the spin Hamiltonian parameters used to computer simulate the spectra for all three complexes are reported in Table II.

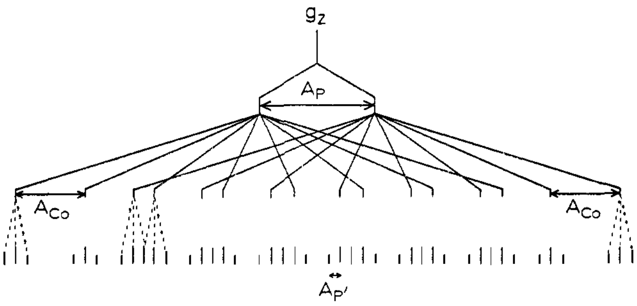


Figure 4. Calculated splitting diagram for the g_z region of the EPR spectrum of $Co(PMe_2Ph)_3(CN)_2$ using the parameters given in Table II.

The spectral assignments give strong support for the tetragonal-pyramidal ground state shown in Figure 2d. The apical phosphorus which interacts most strongly with the d_{z^2} orbital containing a single unpaired electron results in large phosphorus hyperfine splittings for all three g values. A much smaller phosphorus hyperfine splitting from the two equivalent phosphorus ligands in the basal plane is observed only in the g_z region.

The perpendicular region of the Q-band spectra of all the complexes is rather broad and featureless. However, two additional g values and phosphorus hyperfine were required to simulate this portion of the spectra. The appearance of the doublet structure in the room temperature spectra of $Co(PMe_2Ph)_3(CN)_2$ and $Co(PMePh_2)_3(CN)_2$ suggests that the molecule is not fluxional and the square-pyramidal structure (Figure 2d) is maintained on the ESR time scale at this temperature.

The appearance of a single, sharp cyanide stretch in the IR spectra (as solutions and/or Nujol mulls) of these complexes suggests that the configuration in the basal plane consists of trans cyanides and trans phosphines. The trans arrangement would be predicted on the basis of steric considerations. Thus, although IR data on similar cobalt compounds resulted in these being reported as low-spin complexes having a trigonal-bipyramidal structure with trans cyanides[6] and X-ray crystallography showed[11] that the analogous $Ni(PMe_2Ph)_3(CN)_2$ complex adopted this trigonal-bipyramidal structure, characterization of the dicyanotrisphosphine cobalt(II) complexes used in this study leads to their being assigned to a square-pyramidal geometry with trans cyanides and trans phosphines in the basal plane. With this geometry the tetragonal-pyramidal complexes belong to the point group C_{2v} with a ground state of $b_2{}^2b_1{}^2a_2{}^2a_1{}^1$ (see Figure 2d). However, in this case, the a_1 orbital is composed of essentially d_{z^2} ($g_z = 2.002$) because of the nature of the crystal field.

The thiocyanate derivative, $Co(PMe_2Ph)_3(SCN)_2$, was also

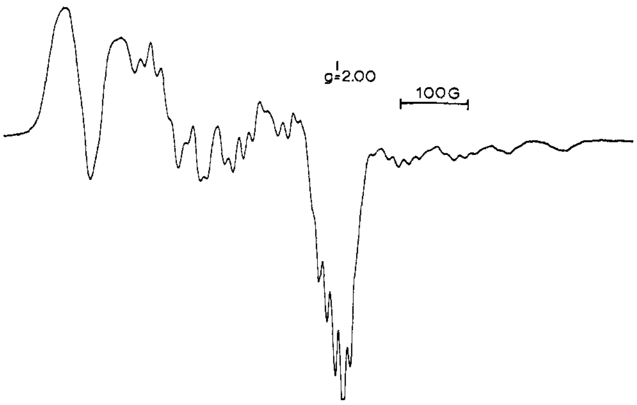


Figure 5. EPR spectrum of $Co(PMe_2Ph)_3(CN)_2$ and its dioxygen adduct.

prepared. As with the cyanides, the room temperature ESR spectrum in toluene/CH_2Cl_2 appeared to be split into a doublet with $\langle g \rangle = 2.15$. The Q-band spectrum shows the same splitting at $\langle g \rangle = 2.15$, thereby confirming that the signal is truly a doublet and not a superposition of the isotropic signals from two different species. No cobalt hyperfine was observed in either spectrum.

The frozen solution X-band ESR spectrum is quite complex owing to overlap of the parallel and perpendicular regions and the presence of hyperfine interactions. However, it is readily apparent from considerations of intensities that $g_x, g_y > g_z$. Comparison of the X-band spectra of this complex with that of $Co(PMe_2Ph)_3(CN)_2$ shows that the structures are nearly identical. Further evidence for this structure comes from the solution IR spectra where the appearance of a single sharp stretch at 2095 cm^{-1} implies that the thiocyanates are trans and S-bonded.

Our structural classification for these five-coordinate complexes has been based upon the relative magnitudes of the $g_\parallel$ and $g_\perp$ values. Two limiting geometries associated with these classes have been employed. In actual practice there is a continuum of geometries involving these extremes. Accordingly our preference is to classify these systems in terms of the similarity of the electronic ground states to the limiting forms. No information regarding the extent of deviation of the geometry from these limiting forms is implied.

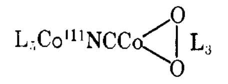
Reactivity of the Phosphine Complexes with Dioxygen. The reactivity of these complexes toward dioxygen was investigated. Solutions of all three phosphine–cyanide complexes when exposed to air noticeably darken upon cooling and return to the original color on warming. The EPR of frozen solutions of dicyanotris(dimethylphenylphosphine)cobalt(II) and dicyanotris(methyldiphenylphosphine)cobalt(II) exposed to dioxygen show a sharp signal near $g = 2.00$ which on the basis of intensity is attributed to the $g_\perp$ signal of the dioxygen adduct. The observed spectrum (Figure 5) consists of the O_2 adduct spectrum overlapping that of $Co(PMe_2Ph)_3(CN)_2$. The parallel region of the O_2 adduct signal is not observed owing to the overlap with resonances of the parent compound. Cobalt hyperfine coupling in the O_2 adduct, which has been related to electron transfer into the bound O_2,[3] is about 12×10^{-4} cm^{-1}, comparable to that observed for $Co(CN)_5O_2^{3-}$. The dicyanotris(trimethylphosphine)cobalt(II) complex does not yield a frozen solution EPR signal attributable to a dioxygen adduct in the presence of air. The $Co(PMe_3)_3(CN)_2$ complex begins to darken upon cooling to about −50 °C, and upon further cooling the color change reverses. The EPR spectrum observed at liquid nitrogen consists only of that of the $Co(PMe_3)_3(CN)_2$. The solution color of $Co(PMe_3)_3(CN)_2$ in the presence of O_2 at −50 °C is very similar to the characteristic dark brown solution color of the dioxygen adducts of $Co(PMe_2Ph)_3(CN)_2$ and $Co(PMePh_2)_3(CN)_2$ at liquid nitrogen.

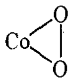
The ESR experiments were run in the presence of air in various ratios of excess phosphine to complex for all three complexes to demonstrate the necessity of phosphine dissociation for dioxygen adduct formation. At about a three to one excess of phosphine no color change was observed in solutions of $Co(PMe_3)_3(CN)_2$ upon cooling. At about a six to one excess phosphine for the PMe_2Ph and $PMePh_2$ complexes, no color change is observed upon cooling, and the liquid nitrogen frozen solution EPR spectra shows only the presence of the five-coordinate dicyanotrisphosphinecobalt(II) adduct. Increasing the metal complex to phosphine ratios in these solutions results in the observation of a color change and at liquid nitrogen an intense ESR signal at $g = 2.00$ indicative of the dioxygen adduct. These results provide good evidence for the loss of a phosphine as a requirement for complexation of dioxygen, and the existence of a five-coordinate dioxygen adduct:

$$Co(P)_3(CN)_2 + O_2 \rightarrow Co(P)_2(CN)_2 \cdot O_2 + P$$

The possibility that the bound O_2 is bidentate, via donation from an orbital with a lone pair of electrons on the terminal oxygen, cannot be excluded. In the absence of precedence for this type of bound O_2, we can only speculate about this possibility. A peroxo species would require that the unpaired electron be metal based and this can be eliminated by considering the g values (vide infra).

Our results are interesting when compared to those reported by Halpern et al.[2] When oxygen was bubbled through a benzene solution of $Co(PMe_2Ph)_3(CN)_2$ for 8 h, $Co_2(PMe_2Ph)_5(CN)_4O_2$ was crystallized out as a solid by the addition of hexane. A single-crystal X-ray structure indicated that both of the oxygen atoms were coordinated to the metal in a ring bonding type of interaction. It was proposed[2] that electron transfer occurred to produce a formal i (where L = CN or phosphines) bimetallomer.[12] The ii interaction is isoelectronic with the dioxygen adduct[13] of Ir(I), that is, iii.[14] This result


i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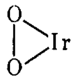
iii

is not inconsistent with our findings. Preliminary kinetic measurements on the reaction leading to the bimetallomer contained a term inverse in phosphine concentration. This suggested[2] a mechanism in which the five-coordinate O_2 complex reported here is a proposed intermediate. This species then reacts in a slow second step with another $Co(CN)_2(PMe_2Ph)_3$ molecule to form the bimetallomer.[15]

It is possible that the ground state of this bimetallomer could be described by an electronic configuration that arises by promotion of an electron out of the d_{xz}, d_{yz} set producing $d_{xy}{}^2$, $d_{xz}{}^2 d_{yz}{}^1 d_{z^2}{}^1 d_{x^2-y^2}{}^1$. A spin pairing interaction of the two orthogonal π^* electrons of O_2 with those unpaired electrons in two metal ion orbitals (d_{z^2} and $d_{x^2-y^2}$) would lead to a ring-bonded dioxygen adduct with an unpaired electron in an essentially metal orbital. The two cobalt centers in the bimetallomer could be antiferromagnetically coupled to produce a diamagnetic product. If this were the case, we might have expected that the 1:1 O_2 adduct $[Co(PMe_2Ph)_2(CN)_2O_2]$ would have a six-coordinate, ring-bonded geometry with a metal localized unpaired electron. However, the EPR spectra indicate that the unpaired electron in this system is essentially localized on dioxygen. If both oxygen atoms of the dioxygen molecule were spin paired to cobalt (i.e., a peroxo complex), the unpaired electron in the system would be essentially metal orbital based. Since the singly coordinated O_2 complexes reported here do have a vacant coordination position, evidently not enough energy is gained by spin pairing the second unpaired electron of dioxygen with cobalt to unpair electrons on the metal via promotion to the $d_{x^2-y^2}$ orbital. Thus, the d^8 configuration (or the potential to attain a formal oxidation state similar to d^8 by electron transfer) and not a vacant coordination position appears to be the requirement for the ring-bonded peroxo mode of dioxygen binding. This conclusion supports the electron-transfer step proposed by Halpern et al.[2] to account for the reported product isolated from the reaction of $Co(PMe_2Ph)_3(CN)_2$ with O_2.

Upon cooling solutions of the trigonal-bipyramidal chloride and bromide complexes (CoP_3Br_2) in the presence of dioxygen, no color change is observed, and the O_2 adduct signal is not detected in the EPR. On the other hand, the trigonal-bipyramidal complex, $Co(PMe_2Ph)_3F_2$, undergoes the characteristic color change for oxygenation upon cooling as does the square-pyramidal thiocyanate complex.

The experiments described above provide a substantial variation in the factors that could potentially influence dioxygen binding stability. Binding ability does not correlate with the initial geometrical configuration for both trigonal-bipyramidal and tetragonal-pyramidal complexes from adducts. The ligand field strength does not appear to be a determining factor inasmuch as the thiocyanate ion (N bonded) and chloride ion have comparable coordination tendencies. Based upon electronic arguments both the bromide and chloride systems should form dioxygen adducts if the fluoride and thiocyanate complexes do. These results suggest that steric factors could be contributing to the instability of the chloride and bromide adducts of dioxygen. The S-bonded thiocyanate system apparently contradicts this conclusion, but it is possible that this ion could be nitrogen bound in the O_2 adduct, even though it is sulfur bound in the five-coordinate complex. Though these studies do provide insight into the requirements for ring-bonded O_2 coordination, more quantitative work is needed to gain a better appreciation of the factors influencing the strength of binding of dioxygen to transition metals.

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(14) We would hasten to point out, in the event anyone is interested, that both cobalt and iridium have an oxidation state of three in these O_2 adducts.
(15) A referee has suggested that oxidation of the phosphine to phosphine oxide might have depleted the O_2 so no resonance for the O_2 adduct is observed. This is inconsistent with our observation of an O_2 adduct spectrum at low phosphine to cobalt ratios. More than enough phosphine was present to scavenge all the O_2 in those systems. It is also inconsistent with the stability of the phosphine on long standing in experiments by Halpern et al.[2]

Axial Ligation Constants of Iron(II) and Cobalt(II) "Capped" Porphyrins

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Abstract: Equilibrium constants for the addition of ligands to cobalt(II) and iron(II) complexes of the "capped" and "homologous capped" porphyrins are reported. For the equilibrium $Fe^{II}(Cap) + B \rightleftharpoons Fe^{II}(Cap)(B)$ (K^B), a plot of log K^B vs. the pK_a of the conjugate acid of the ligand shows a linear relationship among structurally similar base ligands. π-Bonding ligands form more stable complexes than predicted by their pK_a values. Sulfur base binding to $Co^{II}(Cap)$ shows a relative binding order for S-donor ligands of thiolates $\gg$ thioethers $>$ mercaptans. Unlike the Fe(Cap), which can bind only one axial base ligand, Fe(HmCap) can bind two small ligands axially in the usual manner. Intermediate-size ligands, such as 1-methylimidazole, however, weakly coordinate a second base leading to an unusual six-coordinate complex with an intermediate electronic spin of $S = 1$.

Introduction

Investigations on the variations in the biological role of the naturally occurring hemoproteins which are associated with changes in axial ligation of the heme moiety are necessary and desirable. This can best be done by means of metalloporphyrin model complexes owing to the versatility and relative simplicity of the binding of axial ligands to these complexes.

Although several research groups have reported on the axial ligation of cobalt(II) porphyrins[1-5]

$$Co^{II}(Por) + B \overset{K^B}{\rightleftharpoons} Co^{II}(Por)(B)^6 \qquad (1)$$

there is much less information on similar axial ligation to iron(II) porphyrins. This is largely because of the difficulty in obtaining direct experimental values for K^B and $K_B{}^B$, since the high-to-low electronic spin change of the iron(II) complexes causes the anomaly of $K_B{}^B > K^B$:

$$Fe(Por) + B \overset{K^B}{\rightleftharpoons} Fe(Por)(B) \qquad (2)$$

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