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EPR Studies of the Cobalt(II)-(N_2S_2)-Schiff Base Complex with Lewis Bases and CO

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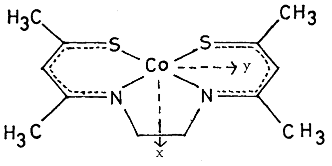
Synopsis. The EPR and optical spectra of *N,N'*-bis-3-thioxo-1-methylbutylidene)ethylenediaminatocobalt(II) in the presence of Lewis bases and CO were measured. The cobalt(II) complex formed five-coordinate adducts with Lewis bases and CO, which had a rhombic symmetry with a $(d_{x^2-y^2}, d_{xz}, d_{yz})^6(d_{z^2})^1$ ground configuration.

Basolo *et al.* have reported that several cobalt(II)-Schiff base complexes (N_2O_2 type) from monomeric oxygen adducts reversibly in the presence of nitrogen donors at a low temperature.[1,2] Recently, Corrigan *et al.* has demonstrated that *N, N'*-bis(2-mercaptobenzylidene)ethylenediaminatocobalt(II) (N_2S_2 type) reacts with molecular oxygen in the presence of pyridine at low temperatures.[3] We have found ourselves that *N, N'*-bis(3-thioxo-1-methyl-butylidene)ethylenediaminatocobalt(II) (N_2S_2 type) is capable of forming monomeric oxygen adducts in the presence of Lewis bases.[4] Here we will report the axial ligation of the cobalt(II) complex with Lewis bases and CO, as studied by the EPR method.



N,N'-bis(3-thioxo-1-methylbutylidene)ethylenediaminatocobalt(II), Co(tacacen).

Experimental

N,N'-Bis(3-thioxo-1-methylbutylidene)ethylenediaminatocobalt(II), Co(tacacen), was prepared according to the literature.[5] (Found: C, 45.90; H, 6.06; N, 8.73%. Calcd for $C_{12}H_{18}N_2S_2Co$: C, 46.00; H, 5.79; N, 8.94%). Pyridine, piperidine, and *N*-methylimidazole obtained commercially were purified by distillation, but triphenylphosphine, tributyl phosphine, tributyl phosphite, and trimethyl phosphite were used without further purification. All the EPR samples except the CO sample were prepared by dissolving Co(tacacen) in a toluene solution containing a proper quantity of the Lewis base. Prior to measurements, the samples were degassed thoroughly. The CO sample was prepared by exposing a degassed Co(tacacen) toluene solution to CO gas (500 Torr) at room temperature for three days. The EPR spectra were measured with a JEOL-ME-3X EPR spectrometer at X-band frequencies and calibrated with Mn^{2+} in MgO and DPPH. The optical spectra were measured in dichloromethane with a Hitachi 323 automatic recording spectrophotometer.

Results and Discussion

The EPR spectra for Co(tacacen) with pyridine, CO, and triphenylphosphine are shown in Fig. 1. The EPR parameters are tabulated in Table 1. The nitrogen-14 ($I=1$) superhyperfine structure, split into a triplet component, appears in the EPR spectrum for the pyridine system; this indicates that only one pyridine molecule coordinates to Co(tacacen). The phosphorus-31 ($I=1/2$) superhyperfine splitting similarly demonstrates that one triphenylphosphine molecule coordinates to Co(tacacen). Though we measured the EPR spectra of Co(tacacen) toluene solutions containing higher concentrations of these Lewis bases, no evidence for six-coordinate complexes, Co(tacacen)$(LB)_2$, was obtained. The CO adduct was obtained by exposing a Co(tacacen) toluene solution to CO gas, but it did not form in the presence of the Lewis bases.

When the $\boldsymbol{g}$- and $\boldsymbol{A}$-tensors have the same principal axes, the first-order relationships between an electronic structure for the $(d_{z^2})^1$ ground state and the EPR parameters are given according to the following equations:[6]

$$\begin{aligned}
g_{xx} &= 2.002 - 6\lambda/\Delta E_{yz} \\
g_{yy} &= 2.002 - 6\lambda/\Delta E_{xz} \\
g_{zz} &= 2.002 \\
A_{xx} &= P[-K-2/7+(g_{xx}-2.002) \\
&\quad +(1/14)(g_{yy}-2.002)] \\
A_{yy} &= P[-K-2/7+(g_{yy}-2.002) \\
&\quad +(1/14)(g_{xx}-2.002)] \\
A_{zz} &= P[-K+4/7+(1/14)\{(g_{xx}-2.002) \\
&\quad +(g_{yy}-2.002)\}]
\end{aligned} \tag{1}$$

TABLE 1. EPR PARAMETERS FOR Co(tacacen)(LB) COMPLEXES

LB	g_1	g_2	g_3	$-A_1$	$-A_2$	A_3	A_3^N	A_1^P	A_3^P	ΔE_{xz}	ΔE_{yz}	$P(cm^{-1})$	K
N-Methylimidazole	2.421	2.219	1.993	3.6	37.8	65.0	16.3			10.2	5.1	0.0169	0.169
Pyridine	2.444	2.207	1.993	−16.2	21.6	77.2	15.3			10.2	5.1	0.0173	0.077
Piperidine	2.432	2.189	2.004	−9.1	26.3	67.1	7.5			10.2	5.1	0.0157	0.099
Carbon monoxide	2.290	2.070	2.029	25.6	58.7	62.0						0.0162	0.165
Triphenylphosphine	2.320	2.161	2.014	8.8	28.9	67.7		149	175	10.4	5.2	0.0136	0.108
Tributylphosphine	2.348	2.175	2.012	8.9	32.6	61.3		140	162	10.4	5.2	0.0148	0.133
Trimethyl phosphite	2.364	2.185	2.012	7.8	33.6	65.1		124	211	10.4	5.2	0.0155	0.140
Tributyl phosphite	2.376	2.189	1.998	12.7	40.4	59.6		126	199	10.4	5.2	0.0160	0.181

A: 10^{-4} cm^{-1}. ΔE: 10^3 cm^{-1} (in dichloromethane solvent).

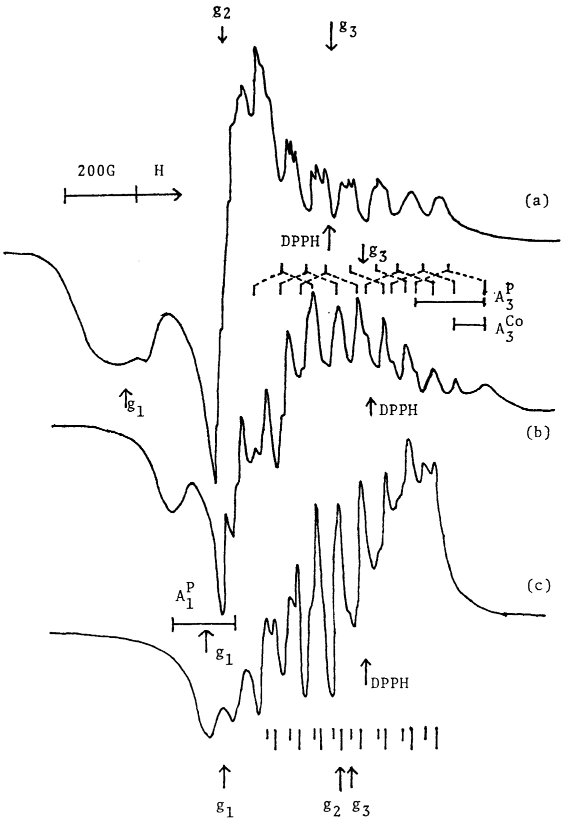


Fig. 1. EPR spectra of Co(tacacen) in the presence of Lewis bases at 77 K. (a) 10 % Pyridine; (b) 10^{-1} M triphenylphosphine; (c) CO gas (500 Torr).

where λ is the effective spin-orbit coupling constant, and where ΔE_{xz} and ΔE_{yz} are the energy separations for the $d_{z^2}\rightarrow d_{xz}$ and $d_{z^2}\rightarrow d_{yz}$ states respectively. $P=gg_n\beta\beta_n\langle r^{-3}\rangle_{3d}$ and PK is the Fermi contact term. The second-order contribution has little significance where $\Delta E \gg \lambda$. The g_3 values in the five-coordinate Co(tacacen)(LB) complexes we studied are nearly 2.002. This implies that the five-coordinate complexes have the $(d_{x^2-y^2}, d_{xz}, d_{yz})^6(d_{z^2})^1$ ground configuration.

The optical spectra for Co(tacacen) with N-donors and P-donors were measured in order to estimate the energy separations. The absorption bands were observed at 10200 cm^{-1} ($\varepsilon \simeq 80$) and 5,100 cm^{-1} ($\varepsilon \simeq 40$) for the N-donors, and at 10400 cm^{-1} ($\varepsilon \simeq 40$) and 5,200 cm^{-1} ($\varepsilon \simeq 10$) for the P-donors. Wayland *et al.* reported that the effective spin-orbit coupling constants for five-coordinate complexes of *N*,*N'*-disalicylideneethylenediaminato cobalt(II), Co(salen), with Lewis bases, which have the $(d_{z^2})^1$ ground state, are 20—30% less than the free-ion value.[7)] In Co(tacacen)(pyridine), when it is assumed that $\Delta E_{xz}=10200\ cm^{-1}$, that $\Delta E_{yz}=5100\ cm^{-1}$, and that the spin-orbit coupling constant is less than the free-ion value by the same degree as in Co(salen)(pyridine), g_{xx}, g_{yy}, and g_{zz} for $(d_{z^2})^1$ ground state are equal to 2.425, 2.214, and 2.002 respectively. These values are in good agreement with the g values observed. No such consistency is found for the other ground states. Therefore, it is concluded that the five-coordinate complexes in this study have the $(d_{x^2-y^2}, d_{xz}, d_{yz})^6\ (d_{z^2})^1$ ground configuration.

Table 2. Cobalt-59 spin densities for Co(tacacen)(LB) complexes

LB	$-A_c$	A_d	ρ_{3d}	ρ_{4s}	ρ_{Co}	%4s
N-Methylimidazole	30.7	104.0	0.717	0.024	0.740	3.24
Pyridine	13.2	98.3	0.678	0.036	0.714	5.04
Piperidine	15.6	89.6	0.617	0.029	0.647	4.48
Carbon monoxide	26.8	89.0	0.639	0.022	0.661	3.33
Triphenylphosphine	14.7	77.8	0.536	0.025	0.561	4.46
Tributylphosphine	19.6	84.6	0.583	0.024	0.607	3.95
Trimethyl phosphite	21.7	88.5	0.610	0.024	0.634	3.79
Tributyl phosphite	28.9	91.4	0.630	0.020	0.650	3.08

A: $10^{-4}\ cm^{-1}$. $A_c=-PK$. $A_d=(4/7)P$.
$\%4s=(\rho_{4s}/\rho_{Co})\times 100$.

The cobalt-59 spin densities can be evaluated from the EPR parameters. The Fermi term has two main factors: (1) the polarization of filled 1s, 2s, and 3s orbitals, which causes a negative spin on the cobalt nucleus because of the unpaired electron in the 3d orbital, and (2) the admixture of the $3d_{z^2}$ orbital into the 4s orbital, which causes a positive spin. Thus, $A_{contact}$ is written as follows:

$$A_{contact} = -PK = \rho_{4s}[A(Co4s)]+\rho_{3d}[A(Co3d)] \qquad (2)$$

where $A(Co4s)=0.1232\ cm^{-1}$ and $A(Co3d)=0.00840\ cm^{-1}$.[8)] ρ_{3d} and ρ_{4s} are the spin densities of the cobalt $3d_{z^2}$ and 4s orbitals respectively. The cobalt $3d_{z^2}$ spin density is estimated by comparing the observed dipolar coupling constant with the theoretical value ($A_d=(4/7)P_0=0.0145\ cm^{-1}$) according to this equation: $\rho_{3d}=(A_d)_{obsd}/(A_d)_{obsd}$. The results for the cobalt-spin density are given in Table 2. The total cobalt-spin densities increase in the order of: N-donors>CO>P-donors. This suggests that the N-donors have a smaller mixing between the cobalt $3d_{z^2}$ and the ligand σ-donor orbitals than do CO and the P-donors. This order also agrees with the tendency of the electronegativity of the ligand-donor atoms.

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