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INVESTIGATION ON LOW-SPIN COBALT(II) COMPLEXES. II. AN ESR STUDY OF THE SCHIFF BASE COMPLEXES OF THE PLANAR cis-[CoN_2O_2] TYPE

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ESR spectra of nine Schiff base complexes of the planar cis-[CoN_2O_2] type were measured in host crystals of the nickel(II) homologues. The spectra showed rhombic patterns, the three eight-lined hyperfine structures due to ^{59}Co being resolved. The theoretical discussion on these data led to the conclusion that in the ground state an unpaired electron hauses in d_{yz}(or d_{xz}) orbital.

In the preceding paper of this series$^{1)}$, we have tried to make a comprehensive elucidation of magnetic and optical properties of low-spin cobalt(II) complexes on the basis of the ground state, $(d_{x^2-y^2})^2(d_{z^2})^1$ (described in terms of the electron-hole formulism). In that study, the symmetry of the complexes were all approximated by the point group D_{4h}, and the $g_{/\!/}$ and $g_{\perp}$ of N,N'-stilbenbis(salicylaldehydato)-cobalt(II) (compound H in Table 1), one of the complexes of the planar cis-[CoN_2O_2] type, were calculated to be 2.0 and 2.5, respectively, giving the calculated magnetic moment $\mu_{300°}$= 2.21 BM which is in good agreement with the experimental value 2.30 BM. Very recently, Engelhardt et al.$^{2)}$ also discussed the ESR spectrum of the compound C (in Table 1) on the basis of the ground state $(d_{x^2-y^2})^2(d_{z^2})^1$. However, those discussions$^{1),2)}$were not based on the precise g-values of the compounds. In the present study, well resolved ESR spectra were obtained for complexes of the planar cis-[CoN_2O_2] type diluted in crystals of the nickel(II) complexes, giving three different values of g-tensor, which are shown in Table 2, quite different from the values predicted theoretically in the preceding investigation$^{1)}$. Therefore, we have to change the part of the previous conclusion concerning with the complexes of the present paper. In this investigation, we have made an alternative assumption for the ground state which can account for the experimental g-values as well as the optical spectra of those compounds.

The powder ESR spectrum of the compound H is shown in Fig. 1 as a representative of the series of the complexes. The spectrum shows a typical rhombic pattern, three eight-lined hyperfine structures due to $^{59}Co(I = \frac{7}{2})$ being observed to give three precise g-values, 3.289, 2.337 and 1.987. The additional small bands observed in the $2\sim3 \times 10^3$gauss region may be attributable to higher order effect of ^{59}Co nuclear quadrupole and/or nuclear spin$^{3)}$.

For the ground state of low-spin cobalt(II), there are three possibilities that is, $(d_{xy})^2(d_{z^2})^1$, $(d_{xy})^2(d_{x^2-y^2})^1$ and $(d_{xy})^2(d_{yz})^1$, following the electron-hole formulism; (here and hereafter we adopt the coordinate axes as shown in Fig. 2 and assume, for convenience, that d_{yz} is higher in energy than d_{xz}). Before starting a theoretical approach for each case, we made a basic assumption that the splitting between d_{xz} and d_{yz} orbitals is small, (say, a few hundred kaysers at the

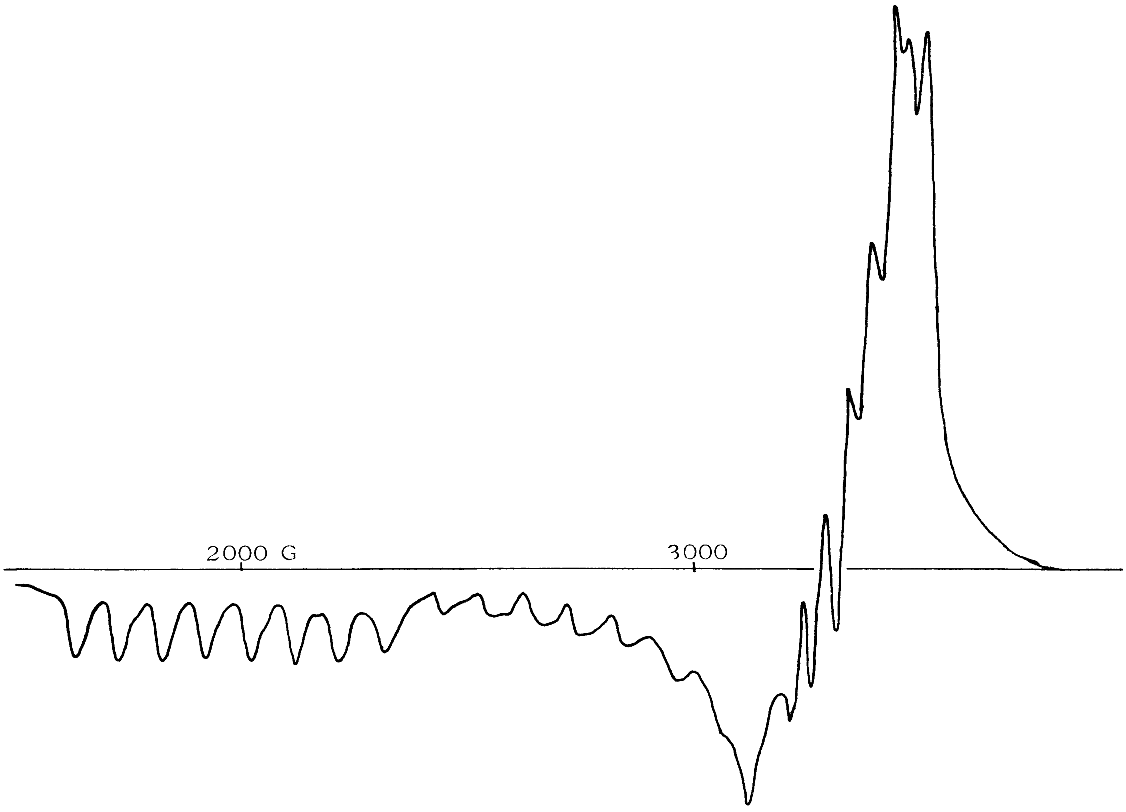

Fig.1. Powder ESR spectrum of the compound H diluted in the nickel(II) complex

Table 1. The list of the compounds

complex([Co L])	ligand(LH_2)
A	bis(5-bromosalicylaldehyde)-1,2-phenylenediimine
B	bis(salicylaldehyde)-1,2-phenylenediamine
C	bis(salicylaldehyde)ethylenediimine
D	bis(5-bromosalicylaldehyde)ethylenediimine
E	bis(5-bromosalicylaldehyde)-2,3-butylenediimine (racemic)
F	bis(2-hydroxyacetophenone)ethylenediimine
G	bis(salicylaldehyde)-2,3-butylenediimine (meso)
H	bis(salicylaldehyde)**stilbenediimine** (meso)
I	bis(acetylacetone)ethylenediimine

Table 2. ESR data of the complexes

complexes	g_1	g_2	g_3	A_1 (gauss)
A	4.010	——	1.690	179
B	3.891	——	1.776	163
C	3.879	2.07*	1.743	167
D	3.834	2.12*	1.758	167
E	3.684	——	1.806	153*
F	3.564	——	1.863	133
G	3.399	2.22*	1.91*	114*
H	3.289	2.337	1.987	90
I	3.268	——	1.98*	86

* less precise because of overlapping of superhyperfine structure due to ^{14}N.

The symbols, * and ——, indicate "less precise" and difficult to obtain a numerical datum, respectively, because of overlapping of superhyperfine structure due to ^{14}N.

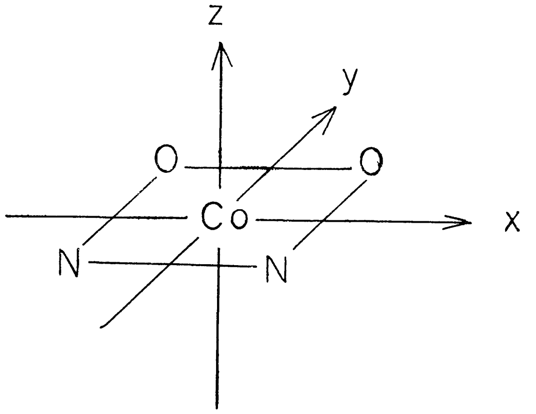

Fig.2. Coordinate axes for cis-[Co N_2O_2]

largest) in the complexes of the planar cis-[CoN_2O_2] type. This assumption is quite reasonable from the theoretical4),5) and experimantal stand points6),7),8).

1) The case where the ground state, $(d_{xy})^2(d_{z^2})^1$ is assumed.....

Starting with the non-perturbed wave functions,

$$\Psi_0^+ = \left|(x\overset{+}{y})(x\bar{y})(\overset{+}{z}{}^2)\right| \quad \text{and} \quad \Psi_0^- = \left|(x\overset{+}{y})(x\bar{y})(\bar{z}{}^2)\right| \qquad (1)$$

we obtained the following wave functions allowing for the spin-orbit coupling.

$$\begin{aligned} \Psi^{+} &= N_b\left\{ \left|(x\overset{+}{y})(x\bar{y})(\overset{+}{z^2})\right| + i\frac{\sqrt{3}}{2}b_1\left|(x\overset{+}{y})(x\bar{y})(y\bar{z})\right| + \frac{\sqrt{3}}{2}b_2\left|(x\overset{+}{y})(x\bar{y})(x\bar{z})\right|\right\} \\ \Psi^{-} &= N_b\left\{ \left|(x\overset{+}{y})(x\bar{y})(\bar{z}^2)\right| + i\frac{\sqrt{3}}{2}b_1\left|(x\overset{+}{y})(x\bar{y})(y\overset{+}{z})\right| - \frac{\sqrt{3}}{2}b_2\left|(x\overset{+}{y})(x\bar{y})(x\overset{+}{z})\right|\right\} \end{aligned} \qquad (2)$$

where N_b is the normalization constant, and $b_1 = k\zeta/\Delta[z^2\text{-}yz]$, $b_2 = k\zeta/\Delta[z^2\text{-}xz]$ in which k, ζ and $\Delta[z^2\text{-}yz]$ denote the orbital reduction factor, spin-orbit coupling constant and tne energy difference between the states, $(d_{xy})^2(d_{z^2})^1$ and $(d_{xy})^2(d_{yz})^1$.

The g-values are expressed as follows.

$$\begin{aligned} g_z &= 2\langle\Psi^{+}|L_z + 2S_z|\Psi^{+}\rangle \\ g_x &= 2\langle\Psi^{+}|L_x + 2S_x|\Psi^{-}\rangle \\ g_y &= 2i\langle\Psi^{+}|L_y + 2S_y|\Psi^{-}\rangle \end{aligned} \qquad (3)$$

and are calculated as

$$\begin{aligned} g_z &= 2N_b^2[1 - \tfrac{3}{4}(b_1 - b_2)^2] \\ g_x &= 2N_b^2[1 - 3b_1 + \tfrac{3}{4}(b_1^2 - b_2^2)] \\ g_y &= 2N_b^2[1 - 3b_2 + \tfrac{3}{4}(b_2^2 - b_1^2)] \end{aligned} \qquad (4)$$

Since we are assuming a very small splitting for the d_{xz} and the d_{yz} orbitals, $(b_1 - b_2)^2$ and $b_1^2 - b_2^2$ will be small compared to unity, and may be neglected.

Thus, $g_z = 2N_b^2$, $g_x = 2N_b^2(1 - 3b_1) \approx 2N_b^2(1 - 3b_2) = g_y$. (5)

These equations are not compatible by any means with the experimental results in which g_x and g_y are remarkably different.

2) The case where the ground state, $(d_{xy})^2(x^2\text{-}y^2)^1$ is assumed.....

By use of the same principle as for the above case, g-values were calculated as:

$$\begin{aligned} g_z &= 2N_a^2[1 + 4a_3 + a_3^2 - \tfrac{1}{4}(a_1 + a_2)^2] \\ g_x &= 2N_a^2[1 - a_1 - a_3^2 + \tfrac{1}{4}(a_1^2 - a_2^2)] \\ g_y &= 2N_a^2[1 - a_2 - a_3^2 - \tfrac{1}{4}(a_1^2 - a_2^2)] \end{aligned} \qquad (6)$$

where, N_a is the normalization constant and $a_1 = k\zeta/\Delta[(x^2\text{-}y^2)\text{-}yz]$, $a_2 = k\zeta/\Delta[(x^2\text{-}y^2)\text{-}xz]$ and $a_3 = k\zeta/\Delta[xy\text{-}(x^2\text{-}y^2)]$.

Considered from the absorption spectra, $\Delta[xy\text{-}(x^2\text{-}y^2)]$ can not be less than 20 kK, so that a_3^2 should be very small compared to unity and may be neglected in the equations (6). Since a very small splitting is assumed for the d_{xz} and d_{yz} orbitals, $\frac{1}{4}|a_1^2 - a_2^2|$ is small compared to $|a_1|$ and $|a_2|$ and may be neglected.

Therefore,

$$\begin{aligned} g_z &= 2N_a^2[1 + 4a_3 - \tfrac{1}{4}(a_1 + a_2)^2] \\ g_x &= 2N_a^2(1 - a_1) \\ g_y &= 2N_a^2(1 - a_2) \end{aligned} \qquad (7)$$

Accordingly, $g_z < 2$, $g_x > 2$ and $g_y > 2$, because a_1, a_2 and a_3 have negative sign from the definition. The above equations are not compatible with the experimental results by any means, because 1) in order to fit the g_x and g_y of the above equations for the experimentally obtained g_1 and g_2 (see Table 2), we have to assume an unreasonably large energy difference, say 6~7 kK, between the d_{xz} and d_{yz} orbitals, and 2) assuming appropriate values for a_1 and a_2, the equations (7) would not give a value less than 0.4 for $2 - g_z$, for which 0.013 were obtained experimentally in the case of the compound H.

3) The case where the ground state, $(d_{xy})^2(d_{yz})^1$ is assumed..... The calculation based on the same principle as for the above cases led to the following equations.

$$\begin{aligned} g_z &= 2N_c^2[1 - c_2 + \tfrac{1}{4}(-3c_1^2 + c_2^2 - c_3^2 - c_4^2)] \\ g_x &= 2N_c^2[1 - 3c_1 - c_3 + \tfrac{1}{4}(3c_1^2 - c_2^2 + c_3^2 - c_4^2)] \\ g_y &= 2N_c^2[1 - c_4 + \tfrac{1}{2}(c_1c_2 - c_2c_3) + \tfrac{1}{4}(-3c_1^2 - c_3^2 - c_2^2 + c_4^2)] \end{aligned} \qquad (8)$$

where, c_1, c_2, c_3 and c_4 are $\kappa\zeta/\Delta[yz-z^2]$, $\kappa\zeta/\Delta[yz-xz]$, $\kappa\zeta/\Delta[yz-(x^2-y^2)]$ and $\kappa\zeta/\Delta[xy-yz]$, respectively. From the energy levels we have assumed, the relation, $c_2 \gg c_1 \approx c_3 \gg c_4$, are deduced. With this relation the equations (8) bring on $g_z > g_x > 2 \gtrsim g_y$. This result is well compatible with the experimental values cited in Table 2.

As shown in Fig. 3, there is a trend that the values of g_2 and g_3 decrease with increasing value of g_1. This may be explained in terms of the equations (8), i.e., since we have assumed that c_2 is much larger than any other c_i's (i = 1, 3, 4), g-values will be affected most sensitively by a change of c_2, and, accordingly, increasing value of c_2 brings about increasing g_1 and decreasing g_2 and g_3 according to the equations (8).

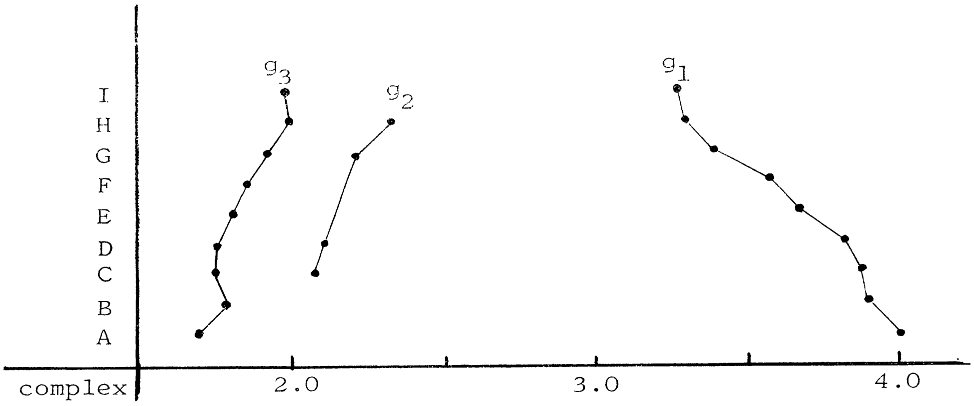

Fig.3. Diagramatic representation of g_i-values(i=1,2,3)

From the above discussion we conclude that unlike the general case for low-spin Co(II) complexes, those of the planar cis-[CoN_2O_2] type have the ground state $(d_{xy})^2(d_{yz})^1$. This is probably due to the anti-π-bonding effect of coordinated oxygen atoms on metal dπ-orbitals and also to a small interelectronic repulsion in the $(d_{xy})^2(d_{yz})^1$ state relative to that in the $(d_{xy})^2(d_{x^2-y^2})^1$ state$^{1)}$.

The optical spectra of the complexes of this type show a peak at ~8 kK and a shoulder at ~13 kK9). Considered from the above discussion, the former may be assigned to the $d_{z^2} \longrightarrow d_{yz}$ transition and the latter to the $d_{x^2-y^2} \longrightarrow d_{yz}$ transition. The other d-d transitions are of much higher energy and are masked by intense absorptions probably due to charge transfer transitions.

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