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An Electron Paramagnetic Resonance Study of Low-Spin Five-coordinate Cobalt(II) Complexes[1]

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Synopsis. EPR spectra were measured for the five-coordinate cobalt(II) complexes, $[CoCldpe_2]SnCl_3$ and $[CoCldpe_2]SnCl_3 \cdot C_6H_5Cl$, which had been determined by X-ray analyses to have a tetragonal pyramidal and trigonal bipyramidal structures, respectively. The observed *g*-values showed a satisfactory agreement with the previously reported prediction.[6]

Recently, several EPR studies were reported on five-coordinate low-spin cobalt(II) complexes.[1–6] In all those studies EPR spectra of tetragonal pyramidal complexes were interpreted on the basis of the ground state configuration $(d_{xz})^2(d_{yz})^2(d_{x^2-y^2})^2(d_{z^2})^1$, where the Z-axis conincides with the tetragonal axis and X-axis divides the planar P–Co–P bond angle. On the other hand, the ground state configuration for the trigonal bipyramidal complexes has been assumed to be $(d_{xz})^2(d_{yz})^2(d_{x^2-y^2})^2(d_{xy})^1$. On this basis Maher[2] and Kimball *et al.*[4] theoretically calculated $g_{//}$ and $g_{\perp}$ values to be 4.0 and 0, respectively. However, no EPR data to support their conclusion have yet been reported. Nishida and Shimohori investigated a series of penta-coordinated low-spin cobalt(II) complexes, $[CoXdpe]_2Y$ ($X=Cl^-$, Br^-, NCS^-, NO_3^- and $Y=ClO_4^-$, NO_3^-) and reached a different conclusion for *g*-values ($g_z > g_x \approx g_y > 2$) for trigonal bipyramidal complexes, assuming that the orbital degeneracy is removed by the distortion from regular trigonal symmetry, (probably due to, *e.g.*, the Jahn-Teller effect or a steric requirement of the crystal, *etc.*). On this basis they showed that the two possible geometries, *i.e.*, tetragonal pyramid and trigonal bipyramid, can be discriminated by the use of EPR data. Recently, it was demonstrated by X-ray analyses that $[CoCldpe_2]SnCl_3$ and $[CoCldpe_2]SnCl_3 \cdot C_6H_5Cl$ have tetragonal pyramidal and trigonal bipyramidal structures, respectively,[7] where dpe denotes 1,2-bis(diphenylphosphino)ethane. Accordingly, we have carried out an EPR study on these compounds in order to confirm the previously derived criterion for the discrimination of the geometrical isomers.[6]

Experimental

Preparation. 1,2-Bis(diphenylphosphino)ethane(=dpe) was prepared according to Hewertson's method.[8] The complexes, $[CoCldpe_2]SnCl_3$ and $[CoCldpe_2]SnCl_3 \cdot C_6H_5Cl$ were prepared by the method described in the literature.[7]

EPR Measurements. EPR spectra were measured using X-band at room temperature with a JEOL ESR apparatus model JES-ME-3X, DPPH being used as a standard for magnetic field strength.

Results and Discussion

Powder EPR spectra of $[CoCldpe_2]SnCl_3 \cdot C_6H_5Cl$ and $[CoCldpe_2]SnCl_3$ were shown in Figs. 1 and 2, respectively. The former shows an axial symmetry, and $g_{//}$ and $g_{\perp}$ were evaluated from the spectra following Sands[9] and Kneubuhls'[10] method. On the other hand, the latter spectrum shows a rhombic symmetry, and g_1, g_2, and g_3 were evaluated at 2.357, 2.276, and 2.003, respectively, by the same method.

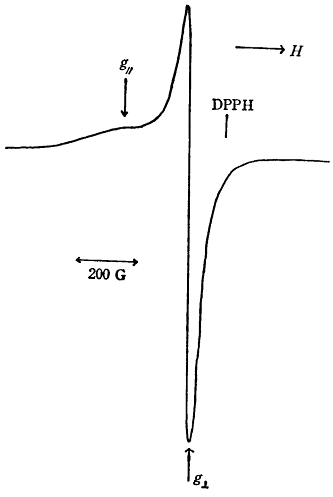

Fig. 1.

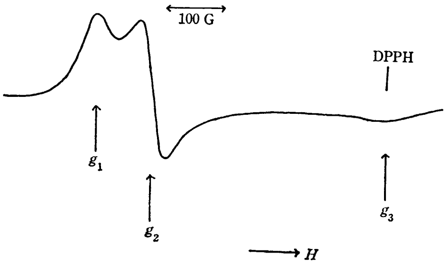

Fig. 2

As was shown in the preceeding paper,[6] *g*-values for the low-spin cobalt(II) complexes of a distorted trigonal bipyramidal symmetry* were calculated in the first order as,

$$g_z = 2(1-4a_1)$$
$$g_x = 2(1-a_2)$$
$$g_y = 2(1-a_3)$$

where

$$a_1 = \zeta/\Delta\{(x^2-y^2)-(xy)\}$$

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* In this model the d_{xy} and $d_{x^2-y^2}$ orbitals are not degenerate, $d_{x^2-y^2} > d_{xy}$ in energy being assumed.

$$a_2 = \zeta/\Delta\{(x^2-y^2)-(yz)\}$$

$$a_3 = \zeta/\Delta\{(x^2-y^2)-(xz)\}$$

ζ: one electron spin-orbit coupling const.

$\Delta\{(x^2-y^2)-(xy)\}$: the energy difference between the $(d_{z^2})^2(d_{x^2-y^2})^1$ and the $(d_{z^2})^2(d_{xy})^1$ states (in terms of electron-hole formulism), and so on.

From these equations the following relation was derived for this type of complexes.

$$g_z > g_x \approx g_y > 2.0 \tag{1}$$

For the complexes of tetragonal pyramidal symmetry,

$$g_z = 2.0$$

$$g_x = 2(1-3b_1)$$

$$g_y = 2(1-3b_2)$$

where

$$b_1 = \zeta/\{\Delta(z^2)-(yz)\}$$

$$b_2 = \zeta/\{\Delta(z^2)-(xz)\}$$

$\Delta\{(z_2)-(xz)\}$: the energy difference between the $(d_{xy})^2(d_{z^2})^1$ and the $(d_{xy})^2(d_{xz})^1$ states, and so on.

From these equations the relation

$$g_x \geqq g_y > g_z \approx 2.0 \tag{2}$$

was derived.

In fact, the present EPR data** show a satisfactory agreement with the above theoretical prediction. The trigonal bipyramidal complex, $[CoCldpe_2]SnCl_3 \cdot C_6H_5Cl$ gives the *g*-values ($g_{//}=2.258$, $g_{\perp}=2.062$) conforming to the relation (1), and the tetragonal pyramidal one, $[CoCldpe_2]SnCl_3$, gives the *g*-values ($g_1=2.357$, $g_2=2.276$, $g_3=2.003$) conforming to the relation (2). This result is also quite compatible with the previous conclusion for $[CoXdpe_2]Y$.

Thus, we can conclude that the assumption on which our theoretical calculation are based⁶⁾ is valid and the two possible geometries for low-spin five-coordinate cobalt(II) complexes can be discriminated on the criterion based on the relations (1) and (2) for which numerical values are obtainable from EPR spectra.

References

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** The effect of the intermolecular magnetic interaction on the observed *g*-values can be neglected in this discussion, since according to Stalick *et al.*,⁷⁾ the shortest Co–Co distance are 11.4 Å and 9.49 Å in $[CoCldpe_2]SnCl_3$ and $[CoCldpe_2]SnCl_3 \cdot C_6H_5Cl$, respectively.