BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 2406—2410 (1973) Vol. 46, No. 8

Investigation on Low-spin Cobalt(II) Complexes. III. Structural, Optical and Magnetic Properties of Five-coordinate Complexes

Yuzo Nishida and Hideharu Shimohori

Department of Chemistry, Faculty of Science, Kyushu University, Fukuoka 812

(Received December 18, 1972)

ESR and reflectance spectra of low-spin five-coordinate cobalt(II) complexes [CoXdpe$_2$]Y, where dpe represents 1,2-bis(diphenylphosphino)ethane and X,Y are Cl$^-$, Br$^-$, NCS$^-$, NO$_3{}^-$ and ClO$_4{}^-$ anions, were measured. From the results it was inferred that the structures of [CoCldpe$_2$]ClO$_4$ and [CoBrdpe$_2$]ClO$_4$ are distorted trigonal bipyramids whereas those [CoNCSdpe$_2$]ClO$_4$ and [CoNO$_3$dpe$_2$]NO$_3$ are square pyramids.

In the last few years several papers have appeared on the low-spin five-coordinate cobalt(II) complexes,[1–3] the syntheses, electronic spectra and magnetic data of which have increased. However, ESR data are considered to be most reliable for understanding the relation between structure, electronic spectrum and magnetic moment of these complexes. We measured the ESR and reflectance spectra of low-spin five-coordinate cobalt(II) complexes [CoXdpe$_2$]Y, where dpe represents 1,2-bis(diphenylphosphino)ethane and X,Y are Cl$^-$, Br$^-$, NCS$^-$, NO$_3{}^-$ and ClO$_4{}^-$ anions. From results we discussed their structural, optical and magnetic properties.

Experimental

1,2-bis(diphenylphosphino)ethane, dpe, was prepared by the method of Hewertson and Watson.[4]

[CoXdpe$_2$]Y (X=Cl$^-$, Br$^-$, NCS$^-$, Y=ClO$_4{}^-$ and X=NO$_3{}^-$, Y=NO$_3{}^-$) were prepared by the method of Sacco and Gorieri.[5] They reported a brown crystal for [CoNCSdpe$_2$]ClO$_4$ but we obtained a green one. (Found: C, 62.94; H, 5.18; N, 1.44. Calcd for [CoNCSdpe$_2$]ClO$_4$: C, 62.80; H, 4.78; N, 1.38) [CoBrdpe$_2$]ClO$_4$·2CHCl$_3$ was obtained as a red prism by recrystallization of green [CoBrdpe$_2$]ClO$_4$ from a hot chloroform solution. (Found: C, 50.88; H, 4.10%. Calcd for [CoBrdpe$_2$]ClO$_4$·2CHCl$_3$: C, 50.92; H, 3.96%).

The ESR spectra were measured with a JEOL ESR-apparatus model JES-MX-3X at various temperatures using X- and K-bands. Manganese(II) doped in MgO was used as a standard marker. The infrared spectra were recorded with a Hitachi EPI-S2 spectrophotometer in the region 4000~650 cm^{-1} on a KBr disk. The reflectance spectra were measured with a Hitachi EPS-3T recording photometer at room temperature.

Theoretical

For the five-coordinate metal complexes, the two geometries of the highest symmetry are (a) trigonal bipyramid(D$_{3h}$) and (b) square pyramid(C$_{4v}$). For (a) the chromophore has C$_{3v}$ symmetry if the axial ligands are not the same and/or the metal lies in the plane of equatorial ligands. For (b) the chromophore naturally retains C$_{4v}$ symmetry, even when the metal lies out of the plane of four basal ligands (it generally lies above it).

Splittings of 3d orbitals in both five-coordinate chromophores have been studied experimentally and theoretically.[6–8] Application of the angular overlap model to MX$_5$ chromophores of trigonal bipyramidal and square pyramidal geometries gives the pattern shown in Fig. 1 for the energy of antibonding "d" molecular orbital.[9] The crystal field model gives a similar pattern.

Since the electronic structure of a cobalt(II) ion is 3d^7, low-spin trigonal bipyramidal cobalt(II) complexes should be more or less distorted from a perfect D$_{3h}$ symmetry, because of the Jahn-Teller effect on the degenerate ground state.

The probable ground state of low-spin cobalt(II) complex with a distorted trigonal bipyramidal geometry

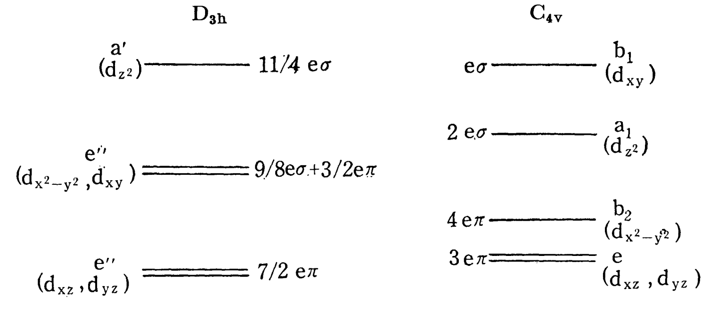

Fig. 1. The splittings of 3d orbitals in five-coordinate chromophores. (According to Jørgensen[9])

---

[1] G. Dyer and D. W. Meek, *J. Amer. Chem. Soc.*, **89**, 3983 (1967).

[2] J. P. Maher, *J. Chem. Soc.*, *A*, **1968**, 2918.

[3] F. Tsay, H. B. Gray, and J. Danon, *J. Chem. Phys.*, **54**, 3760 (1971).

[4] H. Hewertson and H. R. Watson, *J. Chem. Soc.*, **1962**, 1490.

[5] A. Sacco and F. Gorieri, *Gazz. Chim. Ital.*, **93**, 637 (1963).

[6] C. Furlani, *Coord. Chem. Rev.*, **3**, 141 (1967).

[7] M. Ciampolini, Structure and Bonding, **6**, 52 (1969).

[8] P. L. Orioli, *Coord. Chem. Rev.*, **6**, 285 (1971).

[9] C. K. Jørgensen, *J. Phys. Radium*, **26**, 825 (1965).

Table 1. Electronic repulsion energy of low-spin five-coordinate cobalt(II) complexes

$\mid(z^2)^+(z^2)^-(xy)^+\mid$	$3F_0-8F_2+33F_4$
$\mid(z^2)^+(z^2)^-(x^2-y^2)^+\mid$	$3F_0-8F_2+33F_4$
$\mid(z^2)^+(z^2)^-(yz)^+\mid$	$3F_0+7F_2-42F_4$
$\mid(z^2)^+(z^2)^-(xz)^+\mid$	$3F_0+7F_2-42F_4$
$\mid(x^2-y^2)^+(x^2-y^2)^-(z^2)^+\mid$	$3F_0-8F_2+33F_4$
$\mid(x^2-y^2)^+(x^2-y^2)^-(xy)^+\mid$	$3F_0+12F_2-67F_4$
$\mid(x^2-y^2)^+(x^2-y^2)^-(yz)^+\mid$	$3F_0-3F_2+8F_4$
$\mid(x^2-y^2)^+(x^2-y^2)^-(xz)^+\mid$	$3F_0-3F_2+8F_4$

is $(d_{z^2})^2(d_{x^2-y^2})^1$ or $(d_{z^2})^2(d_{xy})^1$, if we assume that in the d^3 configurations d_{z^2} remains the lowest orbital for the vacancies and consequently in a $S=1/2$ configuration is doubly occupied.

On the other hand in the case of a square pyramidal cobalt(II) complex, the predicted ground state is only $(d_{xy})^2(d_{z^2})^1$. No other states are likely for the ground state, even though the electronic repulsion energy is taken into account.

We calculated theoretical three g-values for both predicted ground states according to the methods given previously.[10] For a trigonal bipyramidal complex, we tentatively assumed the ground state to be $(d_{z^2})^2(d_{x^2-y^2})^1$, but found that the same results were also obtained for $(d_{z^2})^2(d_{xy})^1$.

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

By applying the spin-orbit interaction Hamiltonian $k\zeta ls$ to the zeroth-order Kramers doublet $(d_{z^2})^2(d_{x^2-y^2}^{+})^1$ and $(d_{z^2})^2(d_{x^2-y^2}^{-})^1$ as a perturbation, the ground state doublets are written by means of perturbation theory as follows.

$$\left.\begin{aligned}\Psi_a^+ &= N_a\{|(d_{z^2})^2(d_{x^2-y^2}^{+})^1| - ika_1|(d_{z^2})^2(d_{xy}^{+})^1| \\ &\quad + \frac{1}{2}ika_2|(d_{z^2})^2(d_{yz}^{-})^1| - \frac{1}{2}ka_3|(d_{z^2})^2(d_{xz}^{-})^1|\} \\ \Psi_a^- &= N_a\{|(d_{z^2})^2(d_{x^2-y^2}^{-})^1| + ika_1|(d_{z^2})^2(d_{xy}^{-})^1| \\ &\quad + \frac{1}{2}ika_2|(d_{z^2})^2(d_{yz}^{+})^1| + \frac{1}{2}ka_3|(d_{z^2})^2(d_{xz}^{+})^1|\}\end{aligned}\right\} \quad (1)$$

where N_a, ζ and k represent normalization constant, one-electron spin-orbit coupling constant for 3d orbitals and orbital reduction factor, respectively. Coefficients a_1, a_2 and a_3 denote $\zeta/\varDelta[(x^2-y^2)-xy]$, $\zeta/\varDelta[(x^2-y^2)-yz]$ and $\zeta/\varDelta[(x^2-y^2)-xz]$, respectively, where $\varDelta[(x^2-y^2)-xy]$ denotes the energy difference between the states $(d_{z^2})^2(d_{x^2-y^2})^1$ and $(d_{z^2})^2(d_{xy})^1$. Configurations which do not contribute to g-values were neglected. By means of the usual methods,[10] we obtain the following results in the first order.

$$\left.\begin{aligned}g_z &= 2N_a^2[1-4k^2a_1] \\ g_x &= 2N_a^2[1-k^2a_2] \\ g_y &= 2N_a^2[1-k^2a_3]\end{aligned}\right\} \quad (2)$$

This indicates that $g_z>g_x\approx g_y>2$, since a_1, a_2 and a_3 have negative values.

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

By the same procedure we obtained the perturbed ground state wave functions

$$\left.\begin{aligned}\Psi_b^+ &= N_b\Big\{|(d_{xy})^2(d_{z^2}^{+})^1| + \frac{\sqrt{3}}{2}ikb_1|(d_{xy})^2(d_{yz}^{-})^1| \\ &\quad + \frac{\sqrt{3}}{2}ikb_2|(d_{xy})^2(d_{xz}^{-})^1|\Big\} \\ \Psi_b^- &= N_b\Big\{|(d_{xy})^2(d_{z^2}^{-})^1| + \frac{\sqrt{3}}{2}ikb_1|(d_{xy})^2(d_{yz}^{+})^1| \\ &\quad - \frac{\sqrt{3}}{2}ikb_2|(d_{xy})^2(d_{xz}^{+})^1|\Big\}\end{aligned}\right\} \quad (3)$$

which include only terms which contribute to g-values. Three g-values are calculated as follows.

$$\left.\begin{aligned}g_z &= 2N_b^2 \\ g_x &= 2N_b^2[1-3k^2b_1] \\ g_y &= 2N_b^2[1-3k^2b_2]\end{aligned}\right\} \quad (4)$$

where N_b, b_1 and b_2 represent normalization constant, $\zeta/\varDelta[z^2-yz]$ and $\zeta/\varDelta[z^2-xz]$, respectively. g_z is shown to be nearly equal to 2, and g_x and g_y greater than 2.

It is thus predicted that the two possible geometries of low-spin five-coordinate cobalt(II) complexes can be discriminated by means of ESR spectroscopy.

Results and Discussion

Structures and ESR Spectra. Figure 2 shows the ESR spectra of polycrystalline samples of [CoCldpe$_2$]ClO$_4$ and [CoNCSdpe$_2$]ClO$_4$, obtained at room temperature using the K-band. For [CoCldpe$_2$]ClO$_4$, $g_{\parallel}=2.345$, $g_{\perp}=2.097$, for [CoNCSdpe$_2$]ClO$_4$, $g_{\parallel}=1.998$, $g_{\perp}=2.225$ are calculated according to the methods of Kneubühl[11] and Sands.[12] The ESR data [CoXdpe$_2$]Y are summarized in Table 2. It is evident that the ESR patterns can be divided into two classes, (A) complexes with the relation $g_{\parallel}>g_{\perp}$ and (B) those with the relation $g_{\parallel}<g_{\perp}$.

We see from Eqs. (2) and (4) that the structures of (A) [CoCldpe$_2$]ClO$_4$ and [CoBrdpe$_2$]ClO$_4$ are distorted trigonal bipyramids, whereas those (B) [CoNCSdpe$_2$]ClO$_4$ and [CoNO$_3$dpe$_2$]NO$_3$ are square py-

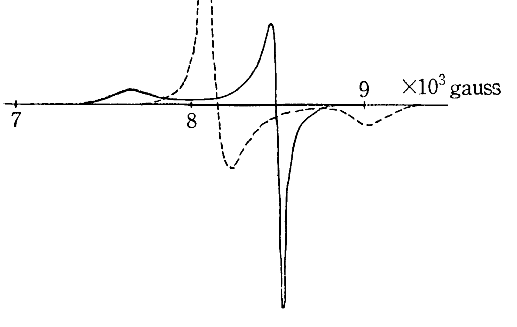

Fig. 2. ESR spectra of [CoCldpe$_2$]ClO$_4$ and [CoNCSdpe$_2$]ClO$_4$ polycrystalline samples at room temperature (K-band).

---

[10] Y. Nishida and S. Kida, *This Bulletin*, **45**, 461 (1972); *Chem. Lett.*, **1973**, 57.

[11] F. K. Kneubühl, *J. Chem. Phys.*, **33**, 1074 (1960).

[12] R. H. Sands, *Phys. Rev.*, **99**, 1222 (1955).

Table 2. ESR data of low-spin five-coordinate cobalt(II) complexes $[CoXdpe_2]Y$

	$g_\parallel$		$g_\perp$
The powder samples by K-band at 295 K			
$[CoCldpe_2]ClO_4$	2.345		2.097
$[CoNCSdpe_2]ClO_4$	1.998		2.225
The powder samples by X-band at 295 K			
$[CoCldpe_2]ClO_4$	2.26		2.06
$[CoBrdpe_2ClO_4$	2.26		2.07
$[CoNCSdpe_2]ClO_4$	2.01		2.25
$[CoNO_3dpe_2]$	*		2.44
$[CoBrdpe_2]ClO_4\cdot 2CHCl_3$	1.99	2.19	2.27
The CH_2Cl_2 glasses by X-band at 150 K			
$[CoCldpe_2]ClO_4$	2.30		2.02
$[CoBrdpe_2]ClO_4$	2.27	2.11	2.04
$[CoNCSdpe_2]ClO_4$	2.03		2.28
$[CoNO_3dpe_2]NO_3$	2.00		2.34

* The precise $g_\parallel$ value can not be calculated because of the overlapping of two absorptions.

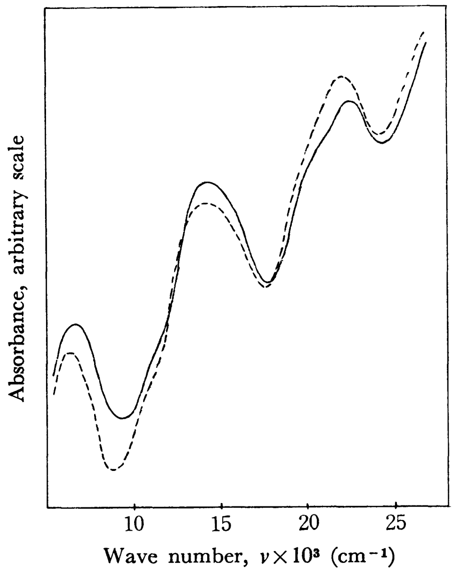

Fig. 3. Reflectance spectra of $[CoCldpe_2]ClO_4$ (——) and $[CoBrdpe_2]ClO_4$ (----).

ramids. This seems to be in line with the results of electronic spectra. The reflectance spectra of A and B complexes shown in Figs. 3 and 4, respectively, are seen to differ completely. The reflectance spectra of A complexes are very similar to the spectrum of $[CoClQP]BPh_4$,[13] whose structure has been determined by X-ray analysis[14] to be trigonal bipyramid, while those of B complexes are similar to that of $[CoBrPNNP]BPh_4$[15] with a square pyramidal geometry. A good agreement was observed between the results of ESR, electronic spectra and the structures of low-spin five-coordinate cobalt(II) complexes.

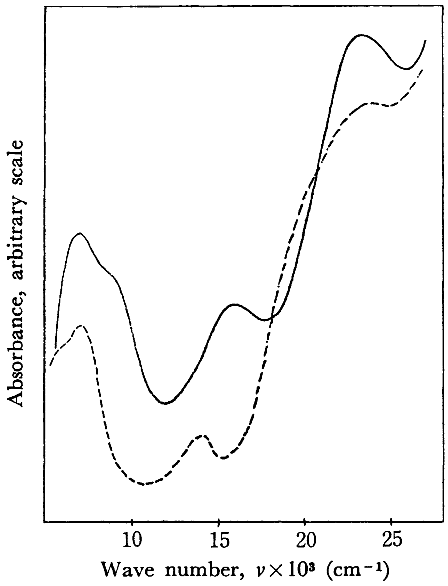

Fig. 4. Reflectance spectra of $[CoNCSdpe_2]ClO_4$ (——) and $[CoNO_3dpe_2]NO_3$ (----).

Although ESR studies of low-spin square pyramidal cobalt(II) complexes have been published, this is the first report on an ESR spectrum of a distorted trigonal bipyramidal cobalt(II) complex. Our ESR data of $[CoCldpe_2]ClO_4$ and $[CoBrdpe_2]ClO_4$ are similar to those of $[CoCldpe_2]Cl$ and $[CoBrdpe_2]Br$, by Horrocks, Van Vecke and Hall,[16] who discussed them on the assumption that the ground state of the latter complexes is $(d_{xy})^2(d_{x^2-y^2})^1$.

Electronic Spectra. In order to interpret the electronic spectra A complexes, the energy difference between the d_{xy} and the $d_{x^2-y^2}$ orbitals, degenerate in the perfect D_{3h} symmetry should be determined. This can be estimated from the results of ESR spectra.

From Eq. (2) we obtain the following result for $[CoCldpe_2]ClO_4$.

$$8N_a^2k^2\zeta/\Delta[(x^2-y^2)-xy]\simeq 0.345$$

If we assume N_a^2, $k^2\approx 1$ and use the value of free ion, $-515\ \mathrm{cm^{-1}}$ for ζ, $\Delta[x^2-y^2)-xy]$ is calculated to be $11800\ \mathrm{cm^{-1}}$. However, as it is known that k is reduced from unity in the metal complexes[17] and also ζ is reduced from free ion value, it is reasonable to assign the peak at $6500\ \mathrm{cm^{-1}}$ and the shoulder at

Table 3. Selection rules for electric dipole

		a_1'	e'	e''	
D_{3h} symmetry	a_1'	f	a	f	
	e'	a	a	a	
	e''	f	a	a	
		b_1	a_1	b_2	e
C_{4v} symmetry	b_2	a	f	f	a
	a_1	f	a	f	a
	b_2	f	f	a	a
	e	a	a	a	a

a : allowed, f : forbidden

---

[13] QP: tris(o-diphenylphosphinophenyl)phosphine, BPh_4^-: tetraphenylborate anion.

[14] T. L. Blundell, H. M. Powell, and L. M. Venanzi, *Chem. Commun.*, **1967**, 763.

[15] PNNP: tris(2-diphenylphosphinoethyl)amine, L. Sacconi and A. Dei, *J. Coord. Chem.*, **1**, 229 (1971).

[16] W. D. Horrocks, Jr, G. Van Vecke, and D-D. Hall, *Inorg. Chem.*, **6**, 694 (1967).

10000 cm^{-1} for the electronic transitions, $d_{xy} \rightarrow d_{x^2-y^2}$ and $d_{yz}, d_{xz} \rightarrow d_{x^2-y^2}$, respectively, on the basis of the results of ESR, the splittings of 3d orbitals and the selection rules of the electric dipole transition in D_{3h} symmetry (Table 3).

The electronic spectra of a low-spin trigonal bipyramidal nickel(II) complex show two peaks in the range 15000—25000 cm^{-1}. One peak of large intensity ($\log \varepsilon \sim 3$) in the lower energy region and the another peak of small intensity($\log \varepsilon \sim 2$) in the higher energy region have been assigned to the electronic transitions d_{xy}, $d_{x^2-y^2} \rightarrow d_{z^2}$ and d_{yz}, $d_{xz} \rightarrow d_{z^2}$, respectively.[18] This remarkable difference in the transition probability of two peaks can be explained in terms of selection rules for these electric dipole transitions (Table 3). Using the above results, two peaks at 14000 and 20000 cm^{-1} observed for A complexes can be assigned to the electronic transitions $d_{x^2-y^2} \rightarrow d_{z^2}$ and $d_{xy} \rightarrow d_{z^2}$, respectively. The energy difference between two peaks (14000 and 20000 cm^{-1}) is about 6000 cm^{-1}, which is consistent with the conclusion that the peak at 6500 cm^{-1} can be assigned to the electronic transition $d_{xy} \rightarrow d_{x^2-y^2}$. The peaks due to the electronic transitions $d_{yz}, d_{xz} \rightarrow d_{z^2}$ are observed at 23000 cm^{-1}. Our assignment is partially the same as that of Norgett *et al.*[19] for the complex $[CoNO_3QP]^+$, but they did not observe the electronic transition $d_{xy} \rightarrow d_{x^2-y^2}$.

In order to interpret the electronic spectra of B complexes, we used the results of the electronic spectra of square planar complex $[Codpe_2](ClO_4)_2$ and distorted octahedral complex $[Codgm_2(Ph_3P)_2]$,[20] since the assumed ground state of the latter two complexes is $(d_{xy})^2(d_{z^2})^1$.[21] The absorption peak due to the electronic transition $d_{z^2} \rightarrow d_{xy}$ is observed at 22000 cm^{-1} and 10500 cm^{-1} for $[Codpe_2](ClO_4)_2$ and $[Codgm_2(Ph_3P)_2]$, respectively. It is therefore reasonable to assign the peaks at 16000 cm^{-1} of $[CoNCSdpe_2]ClO_4$ and 14000 cm^{-1} of $[CoNO_3dpe_2]NO_3$ to the electronic transition $d_{z^2} \rightarrow d_{xy}$. Other peaks at 7000, 9000 and 23000 cm^{-1} of $[CoNCSdpe_2]ClO_4$ are assigned to the electronic transitions $d_{yz}, d_{xz} \rightarrow d_{z^2}$, $d_{x^2-y^2} \rightarrow d_{z^2}$ and $d_{yz}, d_{xz}, d_{x^2-y^2} \rightarrow d_{xy}$, respectively. The intensities of these peaks are also elucidated in terms of selection rules of electric dipole transitions in C_{4v} symmetry (Table 3).

Novel Configurational Change. We found a novel configurational change by adduct formation of chloroform for the complex $[CoBrdpe_2]ClO_4$. From the results of ESR and electronic spectra, the structure of green $[CoBrdpe_2]ClO_4$ is assumed to be a distorted trigonal bipyramid. When this green complex was recrystallized from a hot chloroform solution, red prisms were obtained. The result of elemental analysis is compatible with that of the adduct of chloroform of the parent complex $[CoBrdpe_2]ClO_4 \cdot 2CHCl_3$. The results of infrared spectra of the green and the red complexes also support the empirical formula. Two molecules of chloroform of the red complex can be removed at 110 °C in a vacuum, the color turning green. The ESR and reflectance spectra are shown in Figs. 5 and 6, respectively. It is estimated that the structure of the red complex is a distorted square pyramid and ground state is $(d_{xy})^2(d_{z^2})^1$, since the reflectance spectrum is quite similar to the spectra of B complexes and the ESR spectrum shows a small in-plane anisotropy.

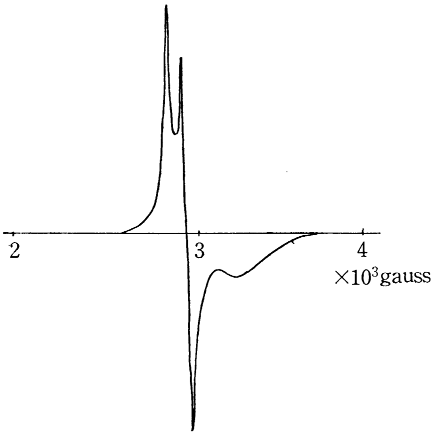

Fig. 5. ESR spectrum of $[CoBrdpe_2]ClO_4 \cdot 2CHCl_3$ polycrystalline sample at room temperature (X-band).

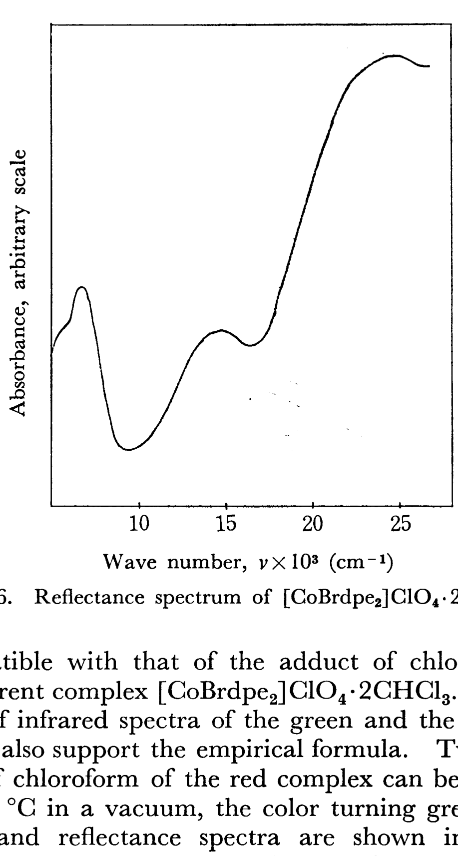

Fig. 6. Reflectance spectrum of $[CoBrdpe_2]ClO_4 \cdot 2CHCl_3$.

ESR Spectra of Glasses. The ESR spectra of $[CoCldpe_2]ClO_4$, $[CoNCSdpe_2]ClO_4$ and $[CoNO_3dpe_2]NO_3$ in CH_2Cl_2 glasses at 150 K are similar to those of polycrystalline samples. However, the situation differs for $[CoBrdpe_2]ClO_4$. The ESR spectrum of green $[CoBrdpe_2]ClO_4$ in CH_2Cl_2 glass at 150 K shows a typical rhombic symmetry, very similar to that of red $[CoBrdpe_2]ClO_4 \cdot 2CHCl_3$ in CH_2Cl_2 glass at 150 K (Fig. 7). This might be attributed to the existence of both, the trigonal bipyramid and the square pyramid in a solution.

---

17) M. Gerloch and J. R. Miller, *Progr. Inorg. Chem.*, **10**, 1 (1968).

18) O. St. C. Headley, R. S. Nyholm, C. A. McAuliffe, L. Sindellari, M. L. Tobe, and L. M. Venanzi, *Inorg. Chim. Acta.*, **4**, 93 (1970).

19) M. J. Norgett, L. H. M. Thornley, and L. M. Venanzi, *J. Chem. Soc.*, *A*, **1967**, 540.

20) dgm: dimethylglyoximato anion, Ph_3P: triphenylphosphine, G. N. Schrauzer and R. J. Windgassen, *Chem. Ber.*, **99**, 602 (1966).

21) Y. Nishida, unpublished work.

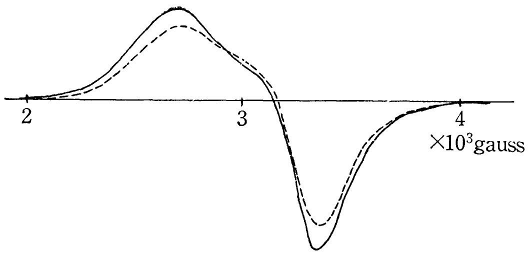

Fig. 7. ESR spectra of [$CoBrdpe_2$]ClO_4 (——) and [$CoBrdpe_2$]$ClO_4 \cdot 2CHCl_3$ in CH_2Cl_2 glasses at 150 K (X-band).

Magnetic Moments. The magnetic moments of these low-spin five-coordinate cobalt(II) complexes [$CoXdpe_2$]Y fluctuate in the range 2.0—2.3 B.M., which is lower than that of square planar complexes, and higher than that of the octahedral complexes.$^{10)}$ This can be elucidated according to the equation of Van Vleck, using the results of ESR and electronic spectra.

Conclusion

It was confirmed that two possible geometries, the trigonal bipyramid and the square pyramid, of low-spin five-coordinate cobalt(II) complexes can be discriminated by means of ESR spectroscopy.

The electronic spectra of both geometries have been characterized by means of ESR spectra and selection rules for electric dipole transitions. The absorption peak due to the electronic transition $d_{xy} \rightarrow d_{x^2-y^2}$ of a trigonal bipyramidal complex has been identified from the result of an ESR spectrum.

Acknowledgment: We wish to express our sincere thanks to Professor S. Kida for his valuable discussion. We also thank Professor S. Misumi and Dr. T. Isobe for use of the ESR apparatus and Professor Y. Murakami and Dr. Y. Matsuda for ESR measurement by the K-band.