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Magnetic Moments and Electronic Spectra of Low-spin Cobalt(II) Complexes

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Comprehensive elucidation of optical and magnetic properties of low-spin cobalt(II) complexes of various types has been attempted. The g-values and magnetic susceptibilities of the complexes have been calculated, the necessary numerical data being obtained from the spectral data and reasonable assumptions. Fairly good agreement has been obtained between the calculated and experimental values.

As is known, values of magnetic moments of low-spin cobalt(II) complexes fluctuate in a wide range (1.9~2.8 BM., see Table I)[1] higher than the spin-only value (1.73 BM.) for one unpaired electron. High magnetic moments compared to the spin-only value have been attributed to the orbital contribution to the ground state.[2] Theoretical approach to the elucidation of the magnetic properties of phthallocyanine cobalt(II) was reported by Griffith.[3] Recently Martin and Mitra[4] carried out cryomagnetic measurements of the single crystal of the same compound, and were successful in explaining the magnetic anisotropy of the crystal in terms of the ligand field theory. However, such studies were restricted to a few specific compounds, and no comprehensive elucidation of the large variation of the orbital contribution in low-spin cobalt(II) complexes has been given. In order to achieve this, it is necessary to discuss optical spectra and magnetic properties simultaneously, since the orbital contribution is mainly due to mixing of higher ligand-field terms into the ground term through spin-orbit coupling. The theoretical interpretation of electronic spectra of low-spin cobalt(II) complexes does not seem to be satisfactory. In the present study, therefore, we have attempted to elucidate the magnetic and optical properties of various types of low-spin cobalt(II) complexes in terms of ligand field theory.

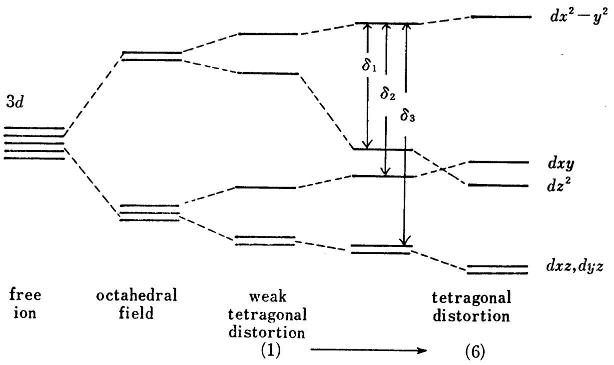

Fig. 1. Assumed *d*-orbital splitting for tetragonal distortion.

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[1] B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, **1954**, 12.

[2] B. N. Figgis, "Introduction to the Ligand Field" John Wiley & Sons, New York, (1964), p. 318.

[3] J. S. Griffith, *Disc. Faraday Soc.*, **26**, 81 (1958).

[4] R. L. Martin and S. Mitra, *Chem. Phys. Letters*, **3**, 183 (1969).

Table 1. The magnetic moment of the low-spin cobalt(II) complexes

	Complex	Coordination number	$\mu_{\text{eff.}}$(r. t.)
(1)	$[Co(NO_2)_6]^{4-}$	6	1.88[20]
(2)	$[Co\ diars_3](ClO_4)_2$[a]	6	1.92[21]
(3)	$[Co\ BrAP_2]ClO_4$[b]	5	2.18[19]
(4)	$[Co\ en_2](AgI_2)_2$[d]	4	2.46[5]
(5)	[Co pc][e]	4	2.72[14]
(6)	[Co sals][c]	4	2.30

a) diars=diarsine
b) AP=Diphenyl(*o*-diphenylarsinophenyl)phosphine
c) sals=Bis(salicylaldehyde)-meso-stilbenediimine
d) en=ethylenediamine
e) pc=phthallocyanine

Some spectral and magnetic measurements were carried out to obtain numerical data necessary for the calculations.

Experimental

$[Co\ en_2](AgI_2)_2$ and [Co sals] were prepared by the methods of Lever, Lewis and Nyholm[5], and Nishikawa and Yamada,[6] respectively, where sals represents bis(Salicylaldehyde)stilbenediimine.

The ESR spectra of polycrystalline sample of $[Co\ en_2](AgI_2)_2$ were measured with a JEOL ESR-apparatus model JES-ME-3X at room temperature using an X-band. Manganese(II) doped in MgO powder was used as a standard marker.

The reflection spectra of $[Co\ en_2](AgI_2)_2$ and [Co sals] were measured with a Shimadzu Multipurpose Spectrophotometer model MPS-50L at room temperature.

The magnetic moment of [Co sals] was determined by the Gouy method at room temperature.

The Theoretical Basis for Calculation

Generally, low-spin cobalt(II) complexes are under the effect of the Jahn-Teller distortion to form complexes of axial symmetry changing from a slightly distorted octahedron to a square-planar configuration. The axial symmetry being assumed, the qualitative one-electron energy diagram as shown in Fig. 1 may be drawn from the energy level splitting of copper(II) complexes of similar geometry.[7,8] The qualitative energy-level splitting for the $3d^7$ system of D_{4h} symmetry can be described as the functions of energy differences between *d*-orbitals, δ_1, δ_2 and δ_3 (Fig. 1) and of Slater-Condon parameters, F_2 and F_4, according to the strong field approximation scheme for the d^3 configuration[9] (see Table 11 and Fig. 4). When F_2 and F_4 are estimated as usual at 1000~1200 cm^{-1} and 90~100 cm^{-1}, respectively.[10,11] The relative energy levels of the states might be as given in Fig. 4.

As a result of the above consideration, the case in which an unpaired electron lies in d_{z^2} orbital appears to be most probable for the ground state.[12] Thus, the ground state ($S=1/2$) can be represented by

$$\Psi_{z^2}{}^{+} = |((x^2-y^2)^+(x^2-y^2)^-(z^2)^+|$$
$$\Psi_{z^2}{}^{-} = |(x^2-y^2)^+(x^2-y^2)^-(z^2)^-|.$$

The spin-orbit interaction gives rise to the mixing of some Russell Saunders states. Following the perturbation theory, the ground state is written as

$$\Psi_0{}^{+} = N\left(\Psi_{z^2}{}^{+} + \sum_i \frac{\langle \Psi_i | \zeta\kappa \boldsymbol{LS} | \Psi_{z^2}{}^{+} \rangle}{\Delta E} \Psi_i\right), \tag{1}$$

where N, ζ, and κ represent normalization constant, one-electron spin-orbit coupling constant for 3d orbitals and the orbital reduction factor, respectively, and $\Psi_o{}^{+}$, $\Psi_{z^2}{}^{+}$, Ψ_i are the wave functions of the perturbed ground state, unperturbed ground state, and the excited states respectively. The *g*-values can be calculated according to the equations,

$$\begin{aligned} g_{\parallel} &= 2\langle \Psi_0{}^{+} | \kappa \boldsymbol{L}_z + 2\boldsymbol{S}_z | \Psi_0{}^{+} \rangle \\ g_{\perp} &= 2\langle \Psi_0{}^{+} | \kappa \boldsymbol{L}_x + 2\boldsymbol{S}_x | \Psi_0{}^{-} \rangle. \end{aligned} \tag{2}$$

Neglecting the second order terms we finally obtain the results.

$$\begin{aligned} g_{\parallel} &= 2N, \\ g_{\perp} &= N\left(2 - \frac{6\kappa^2}{\Delta_1}\right), \end{aligned} \tag{3}$$

where Δ_1 is the energy difference between the states $|(x^2-y^2)^+(x^2-y^2)^-(z^2)^+|$ and $|(x^2-y^2)^+(x^2-y^2)^-(xy)^+|$.

According to Van Vleck's theory,[13,14] and assuming a metal complex where the separation between the levels of the ground term is small compared to $\boldsymbol{k}T$, and the next excited level has an energy large compared to $\boldsymbol{k}T$ (we believe that this is true for the low spin cobalt(II) complexes), the magnetic susceptibility is found to be given by

$$\chi_i = \frac{\boldsymbol{N}\beta^2 g_i{}^2}{3\boldsymbol{k}T} S(S+1) + N\alpha_i \quad (i=x, y, z), \tag{4}$$

where $\boldsymbol{N}$ and $\boldsymbol{k}$ denote the Avogadro number and the Boltzmann constant, respectively, and $N\alpha_i$ is the temperature-independent term of the susceptibility which is often called the high-frequency term of the susceptibility. α_i can be calculated by the equation

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[5] A. B. P. Lever, J. Lewis, and R. S. Nyholm, *J. Chem. Soc.*, **1963**, 2552.

[6] H. Nishikawa and S. Yamada, This Bulletin, **37**, 8 (1964).

[7] Y. Nishida and S. Kida, This Bulletin, **43**, 3814 (1970).

[8] B. J. Hathaway and D. E. Billing, *Coord. Chem. Rev.*, **5**, 143 (1970).

[9] C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill, New York, (1962), pp. 57—97.

[10] C. J. Ballhausen and A. D. Lieher, *J. Am. Chem. Soc.*, **81**, 538 (1958).

[11] H. Kamimura, S. Sugano, and Y. Tanabe, "Ligand Field Theory and its Application" (in Japanese) Shokabo, Tokyo, (1970), p. 222.

[12] Other possibilities for the ground state are where an unpaired electron is (1) in d_{xy} orbital and (2) in d_{xz} (or d_{yz}) orbital. these cases, we could give equations corresponding to equations (2) and (3) on the basis of the same principle. However, it has been found in many compounds that the calculation according to these equation gives results considerably deviating from experimental values, as long as we have assumed reasonable values for the energies of excited states, in contrast to the nice agreement when an unpaired electron is assumed to lie in d_{z^2} orbital.

[13] C. J. Ballhausen "Introduction to Ligand Field Theory," MaGraw-Hill, New York, (1962), pp. 139—141.

[14] J. H. Van Vleck, "The Theory of Electric and Magnetic Susceptibilities," Oxford University Press, Oxford (1932).

$$\alpha_i = 2\sum_{n,m}\frac{\{\langle\Psi_{0,m}|\beta(\boldsymbol{L}_i+2\boldsymbol{S}_i)|\Psi_{n,m}\rangle\}^2}{j_m(E_0-E_n)}$$

where n and m specify the electronic excited states and the magnetic sub-levels, respectively, and j_m and E_o are the multiplicity and the energy of the ground state.

In the case of low-spin cobalt(II) complexes, the integrals in equation (5) can be evaluated on the assumption of the energy-level splitting similar to that shown in Fig. 4. Thus we obtain

$$\alpha_z = \alpha_\parallel = \frac{16}{\Delta_3}\beta^2, \tag{6}$$

$$\alpha_x = \alpha_y = \alpha_\perp = \frac{4}{\Delta_2}\beta^2 + \frac{6}{\Delta_1}\beta^2. \tag{7}$$

By combining (4), (6), and (7), we find that χ is expressed by

$$\chi = \frac{\boldsymbol{N}\beta^2}{12\boldsymbol{kT}}(g_\parallel{}^2+2g_\perp{}^2) + \frac{N\beta^2}{3}\left(\frac{12}{\Delta_1}+\frac{8}{\Delta_2}+\frac{16}{\Delta_3}\right), \tag{8}$$

where Δ_1, Δ_2, and Δ_3 are the energy differences between the states ${}^2A_{1g}$ and ${}^2E_g$, ${}^2A_{1g}$ and ${}^2E_g{}'$, and ${}^2A_{1g}$ and ${}^2A_{2g}$, respectively (see Fig. 4 and Table II).

Results and Discussion

Phthalocyanine cobalt(II): The magnetic moment of this complex was reported to be 2.72 BM. at room temperature and 2.22 BM. at 90°K.[15] It is known that this compound has a square-planar structure,[16] and $g_\parallel$ and $g_\perp$ were determined by ESR study[17] to be 1.92 and 2.92, respectively. Substituting the experimental g- and ζ-values ($\zeta=-515\ \mathrm{cm}^{-1}$) into equations (2) and (3), and assuming $k^2=0.8$ as usual,[18] we obtain $\Delta_1=2373\ \mathrm{cm}^{-1}\approx 2.4$ kK, which seems to be a reasonable value for the separation of the states ${}^2A_{1g}$ and ${}^2E_g$.

We can now calculate the low frequency term of equation (8),

$$\chi_l = \frac{\boldsymbol{N}\beta^2}{12\boldsymbol{kT}}(g_\parallel{}^2+2g_\perp{}^2) \approx \frac{\boldsymbol{N}\beta^2}{12\boldsymbol{kT}} \times 20.74. \tag{9}$$

If we neglect the high frequency term of equation (8), the magnetic moment μ would be given by

$$\mu = \sqrt{\frac{3\boldsymbol{kT}}{\boldsymbol{N}\beta^2}\chi_l} = 2.28\,BM.$$

The result is not satisfactory when compared with the experimental value 2.72 BM. Thus, it is evident that we can not neglect the high-frequency term of equation (8). Since it is difficult in this case to estimate the energy differences experimentally, we estimate[19] the probable values of Δ_2 and Δ_3 both at 15 kK on the basis of the estimated energy diagram for a planar Co(II) complex in Fig. 4 (Δ_1 was already estimated at 2.4 kK). Then, we obtain

$$\chi = \frac{20.74\boldsymbol{N}\beta^2}{4\boldsymbol{kT}} + 2.20\boldsymbol{N}\beta^2 \times 10^{-3}.$$

This leads to the results

$$\mu_{300^\circ\mathrm{K}} = 2.56\,BM$$

$$\mu_{90^\circ\mathrm{K}} = 2.37\ \mathrm{BM},$$

which show a fairly good agreement with experimental values.

From this result we may conclude that the remarkably high magnetic moment of the phthalocyaninecobalt(II) relative to the spin-only value is attributable to the orbital contribution through spin-orbit coupling and also to the so called Van Vleck's high frequency term. This conclusion agrees with the result of the recent cryomagnetic measurements by Martin and Mitra.[4] It should be noted that our final formulation for χ_l with the assumption of the above numerical values is essentially the same as that of Martin and Mitra[4], their formulation giving a successful explanation for their results which show that the relation $\mu_\perp > \mu_\parallel$ and $\mu_\parallel$ is nearly independent of temperature whereas $\mu_\perp$ decreases considerably with the lowering of temperature.

Bis(ethylenediamine)cobalt(II)diiodo argentate(I) [Co en$_2$](AgI$_2$)$_2$: This compound is known to have the magnetic moment of 2.46 BM[5] and the structure of its cation is thus expected to be square planar. We have measured the optical and the ESR spectra. The results are shown in Figs. 2 and 3. From the latter g-values were obtained to be as follows according to the usual method for the case of $S=1/2$.

$$g_\parallel = 2.00 \text{ and } g_\perp = 2.58. \tag{11}$$

Assuming the energy level splitting similar to that of Fig. 4, we may tentatively assign the bands observed at 7.2 kK and at about 21 kK to the transitions ${}^2A_{1g}\rightarrow{}^2\mathrm{B}_{2g}$ and ${}^2A_{1g}\rightarrow{}^2E_g{}'$ (Δ_2) respectively. The transition ${}^2A_{1g}\rightarrow{}^2E_g$ (Δ_1) can then be estimated at 4~5 kK. The same g-values as the experimental ones (11) were obtained by the calculation according to equation (3) with $\Delta_1=4.8$.

Thus we can calculate the susceptibility by use of equation (8), substituting 4.8, 20, and 20 kK into Δ_1, Δ_2, and Δ_3, we get

$$\chi = \frac{0.54}{T} + 320\times 10^{-6}.$$

Hence

$$\mu_{300^\circ\mathrm{K}} = 2.26\ \mathrm{BM}\ (\mathrm{exp.}\ 2.46\ \mathrm{BM}).$$

This is a fairly satisfactory results, considering the degree of the present approximation.

Bis(salicylaldehyde)stilbenediiminatocobalt(II) [Co sals]: Among the derivatives of so-called "Salcomine type" complexes, this compound seems to be the most suitable for the purpose of the present study, since it is known to be unreactive with atmospheric oxygen,[6] and accessible with the usual techniques of optical and magnetic measurements.

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15) R. L. Carlin, "Transition Metal Chemistry," ed. by R. L. Carlin, Vol. I, Marcell Decker, New York, (1965), pp. 1—32.

16) A. B. P. Lever, "Advances in Inorganic Chemistry and Radiochemistry," ed. by H. J. Emeleus and A. G. Sharpe, Vol. 7, pp. 27—114.

17) J. F. Gibson, D. J. E. Ingram, and D. Shonland, *Discuss. Faraday Soc.*, **26**, 72 (1958).

18) B. N. Figgis, "Introduction to the Ligand Field", John Wiley & Sons, New York, (1964), pp. 278—291.

19) Since Δ_2 and Δ_3 are much larger than Δ_1, the high-frequency term of (8) will be only sensitive to Δ_1 as readily seen from Eq. (8). Thus, a rough estimation of the values of Δ_2 and Δ_3 is enough for the present purpose.

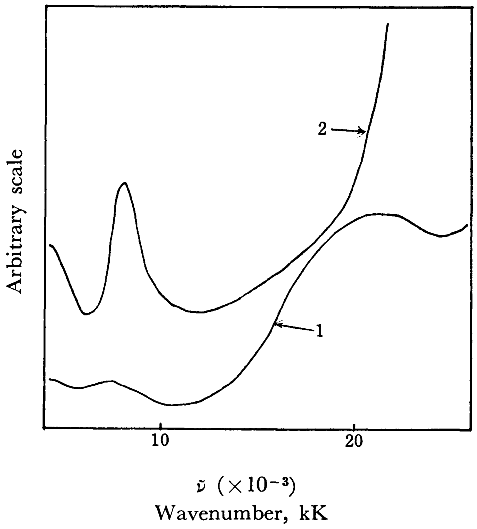

Fig. 2. Reflection spectra of
1—[Co en_2]$(AgI_2)_2$
2—[Co sals]

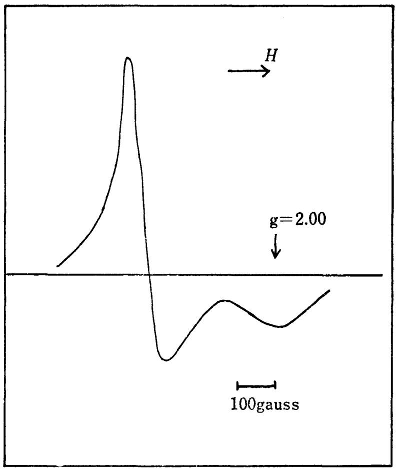

Fig. 3. ESR spectra of [Co en_2]$(AgI_2)_2$ polycrystalline sample at room temperature.

TABLE 2. ELECTRONIC REPULSION ENERGY OF THE LOW-SPIN COBALT(II) COMPLEX

$^2A_{1g}$	$\lvert (x^2-y^2)^+(x^2-y^2)^-(z^2)^+ \rvert$	$3F_0-8F_2+33F_4$
$^2B_{2g}$	$\lvert (x^2-y^2)^+(x^2-y^2)^-(xy)^+ \rvert$	$3F_0+12F_2-67F_4$
^2E_g	$\lvert (x^2-y^2)^+(x^2-y^2)^-(xz)^+ \rvert$	$3F_0-3F_2+8F_4$
$^2B_{1g}$	$\lvert (x^2-y^2)^+(z^2)^-(z^2)^+ \rvert$	$3F_0-8F_2+33F_4$
$^2A_{2g}$	$\lvert (x^2-y^2)^+(xy)^-(z^2)^+ \rvert$	$3F_0-8F_2-37F_4$
$^2E_g'$	$\lvert (x^2-y^2)^+(xz)^-(z^2)^+ \rvert$	$3F_0-8F_2-37F_4$
$^4A_{2g}$	$\lvert (x^2-y^2)^+(xy)^+(z^2)^+ \rvert$	$3F_0-4F_2-120F_4$
^4E_g	$\lvert (x^2-y^2)^+(xz)^+(z^2)^+ \rvert$	$3F_0-4F_2-120F_4$

In this case, we again assume an energy level splitting similar to that given in Fig. 4-b. Then, the band observed at ~8 kK pointed out by Nishikawa *et al.*[6] as characteristic of the square planar low-spin cobalt(II) complexes and tentatively assigned to the spin-forbidden transition ($^2B_{2g}\rightarrow{}^4A_{2g}$ or ^4E_g), should be assigned to the $^2A_{1g}\rightarrow{}^2B_{1g}$ transition. Accordingly, the transition $^2A_{1g}\rightarrow{}^2A_{2g}$ can be assigned to the shoulder at ~20 kK, and the transition $^2A_{1g}\rightarrow{}^2E_g$ will appear at 5 kK or the lower wave number. Thus, the *g*-values and magnetic susceptibility can be calculated with the use of equations (2), (3) and (8) with the numerical values $\Delta_1=5$, $\Delta_2=20$, and $\Delta_3=20$ kK as follows.

$$g_{\parallel} = 2.0,\ g_{\perp} = 2.5$$

$$\chi = \frac{0.52}{T} + 310 \times 10^{-6},$$

and this leads to

$$\mu_{300^\circ\mathrm{K}} = 2.21\ \mathrm{BM}$$

which is in good agreement with the experimental value 2.30 BM.

Dipotassium barium hexanitrocobaltate(II). $K_2Ba[Co(NO_2)_6]$: This complex has been known to show the lowest magnetic moment (1.88 BM) among the low-spin cobalt(II) complexes. Since the nearly isotropic *g*-value was observed in the ESR measurements,[21] it is almost evident that this compound has a nearly octahedral structure. Thus, the energy level splitting will be similar to that given Fig. 4-a. We can assign the band observed at 15.5 kK to the $^2A_{1g}\rightarrow{}^2E_g$ transition. The transitions $^2A_{1g}\rightarrow{}^2E_g'$ and $^2A_{1g}\rightarrow{}^2A_{2g}$ would then, correspond to the absorption around 18 kK. Accordingly, we can evaluate the susceptibility using equation (8) with $\Delta_1=15.5$ kK, $\Delta_2=18$ kK and $\Delta_3=18$ kK.

$$\chi = \frac{0.41}{T} + 180\times10^{-6}.$$

This leads to

$$\mu_{300^\circ\mathrm{K}} = 1.92\ \mathrm{BM}.$$

This is in fairly good agreement with the experimental value 1.88 BM.

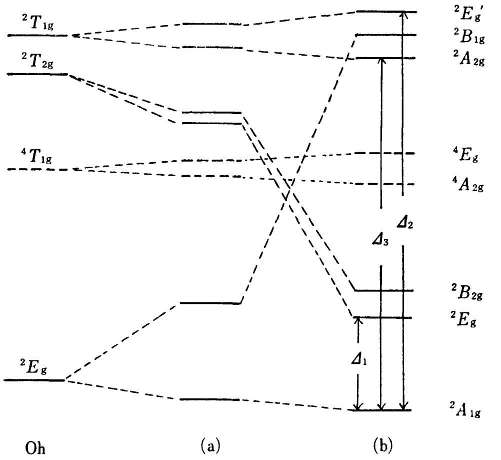

Fig. 4. Energy levels of low-spin cobalt(II) complexes with ground state, $^2A_{1g}$ in D_{4h}-symmetry.

*Bromo-bis-diphenyl(*o*-diphenylarsinophenyl)phosphine cobalt(II) perchlorate* $[CoBr(Ap)_2]ClO_4$: Dyer and Meek[20] proposed a five-coordinated square pyramidal structure for this compound from the results of spectral and magnetic measurements. In the optical spectrum they found three peaks at 7 kK, 13 kK, and 22 kK, and have assigned them to the transitions $d_{xy}\rightarrow d_{z^2}$, d_{xz},

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

$d_{yz} \rightarrow d_{z^2}$ and $d_{z^2} \rightarrow d_{x^2-y^2}$, assuming that an unpaired electron lies in d_{z^2} orbital in the ground state. Granted this assignment, we might deduce that $\Delta_1 = 13$ kK, $\Delta_2 = 22$ kK, and $\Delta_3 = 22$ kK. Using these numerical values and following equation (8), we obtain

$$\chi = \frac{0.42}{T} + 180 \times 10^{-6}$$

$$\mu_{300^\circ\mathrm{K}} = 1.95\ \mathrm{BM}$$

whereas the experimental value is 2.18 BM.

The alternative assignment for the electronic transitions is possible on the assumption of the energy level splitting similar to that given in Fig. 4-b, and this leads to a better agreement between the calculated and experimental values, *viz.*, the bands at 7 kK and 13 kK are assigned to the transitions d_{xz}, $d_{zy} \rightarrow d_{z^2}$ $({}^2A_{1g} \rightarrow {}^2E_g)$ and $d_{xy} \rightarrow d_{z^2}$ $({}^2A_{1g} \rightarrow {}^2B_{2g})$ respectively, and Δ_1, Δ_2, and Δ_3 are evaluated to be 7 kK, 22 kK, and 22 kK. By use of equation (8) and the above numerical values, we obtain a better accordance with the experimental value.

$$\chi = \frac{0.47}{T} + 240 \times 10^{-6}$$

$$\mu_{300^\circ\mathrm{K}} = 2.08\ \mathrm{BM}.$$

Conclusion

A quantitative knowledge of the energy-level splittings of the complexes was necessary for the calculation of the magnetic quantities such as *g*-values and susceptibilities. Although we tried to avoid arbitrary methods for obtaining the numerical values necessary for the calculations, some assumptions had to be made. However, it should be noted that (1) all the assumptions are reasonable and probable ones, drawn from other experimental data as well as theoretical considerations, (2) consistency between the calculated results, experimental data and starting assumption is satisfactory throughout this work, and (3) any alternative choice for the energy level splitting of the complexes would not lead to reasonable and consistent results. This implies that our energy level diagrams and assignments of the electronic spectra are correct.

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21) H. Elliott, B. J. Hathaway, and R. C. Slade, *Inorg. Chem.*, **5**, 669 (1966).

22) F. Burstall and R. S. Nyholm, *J. Chem. Soc.*, **1952**, 3570.