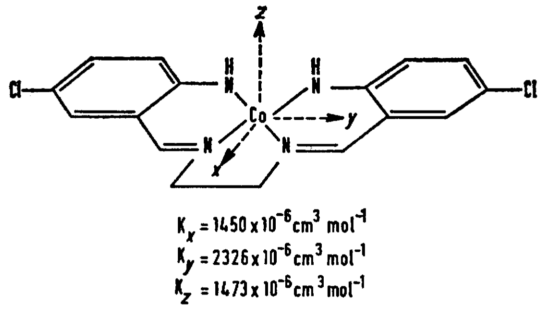
Ground State of Low-spin Cobalt(II) Chelate Complexes

By KEITH S. MURRAY* and ROBERT M. SHEAHAN
(*Department of Chemistry, Monash University, Clayton, Victoria* 3168, *Australia*)

Summary Calculations of the correct g and A expressions for low-spin cobalt(II) remove the confusion and ambiguities often encountered in postulating orbital ground states by use of the usual Griffith model; experimental susceptibility tensors for [Co(5-Cl-amben)] support a d_{z^2} ground state and not $d_{x^2-y^2}$ as proposed previously.

THERE has been considerable interest in the electronic ground states[1–7] of cobalt(II) compounds of the type Co(salen)], [Co(amben)], [Co(pc)], [Co(corrin)];† particularly with regard to the large differences in chemical behaviour of seemingly not-too-different chemical units. There is some confusion and controversy in the literature over the electronic structures of such complexes owing to a lack of single crystal magnetic and spectral data, together with the use,[1–5] and misuse,‡ of the over-simplified Griffith method[6]. We shall illustrate the problem with the literature example of [Co(5-Cl-amben)][4,8] for which we have determined the room temperature magnetic susceptibility tensors, (Figure) as described previously.[7]



Green *et al.*[4] deduced that $g_z >> g_x$, g_y for [Co(5-Cl-amben)], and hence postulated a d_{x^2-y} ground state for the molecule, because of the unreasonable parameters deduced on the assumption of the more normal d_{z2} ground state. However, the single-crystal measurements presented here show the incorrectness of their assignment, and that in fact the ground state is d_{z^2}, pointing out a general inadequacy of the Griffith method for divalent cobalt.[9]

TABLE

Magnetic parameters for [Co(5-Cl-amben)]

	Observed[a]	Calculated[b]
g_x	*ca.* 2·01	2·01
g_y	2·67	2·67
g_z	1·975	1·975[c]
A_x/cm^{-1}	?	−0·0073
A_y/cm^{-1}	<0·001	0·001
A_z/cm^{-1}	0·0028	0·0028[c]

[a] Ref. 4. The directions of the observed g values were assigned using the magnetic anisotropy data. [b] $\alpha_1 = 0{\cdot}065$; $\alpha_2 = 0{\cdot}15$; $\beta_1 = 0{\cdot}02$; $\beta_2 = 0{\cdot}175$; $\gamma_1 = 0{\cdot}49$; $\gamma_2 = 0{\cdot}05$; $\delta_1 = 0{\cdot}05$; $\delta_2 = 0{\cdot}1$; $P = 0{\cdot}014$ cm^{-1}; $\kappa = +\,0{\cdot}30$. [c] These were set at the observed values, yielding $4\tau_1 - 4\tau_2 = 0{\cdot}025$.

The Griffith method, used extensively in the treatment of the e.s.r.[1–5,10] and magnetic properties[11,12] of Co^{II}, suffers from the defect that the Co^{II} excited states are not analogous to those of Cu^{II} but consist of various linear combinations of orbitals. Although the correct treatment, which we shall now outline, involves many additional parameters, it is now possible to describe the electronic structures of many low-spin cobalt(II) complexes in a qualitatively simple manner without resorting to the convolutions that the incorrect model sometimes requires.

We have derived expressions for the g- and A-tensors of the low-spin Co^{II} ion, with a d_{z^2} ground state ($^2A_1$ in C_{2v}) based on the electronic configurations $t_2{}^6e$, $t_2{}^5e^2$ [Griffith:[13] Tables A20, A24; Golding:[14] Table 7.1; Ballhausen:[15] Appendices I, II (ch. 6)]. We have assumed that the zero-order energy differences between states are diagonal and have taken the spin–orbit coupling perturbation to first order, although we have included some important second-order corrections to the g-tensors. The octahedral symmetry notation of states is used for clarity, as the low symmetry of these complexes ($\sim C_s$, C_{2v}) makes symmetry labels cumbersome and confusing. The electronic configurations $t_2{}^6e$, $t_2{}^5e^2$ give rise to the octahedral states ^2E, $^4T_1$ ($^3A_2$), $^2T_1$ ($^3A_2$), $^2T_1$ (^1E), $^2T_2$ (^1E), $^2T_2$($^1A_1$). The g and A expressions are as follows:

$$g_x = 2-\alpha_1+\alpha_2+3\beta_1+3\beta_2+8\phi_3{}^2/3$$

$$g_y = 2-\gamma_1+\gamma_2+3\delta_1+3\delta_2+8\phi_3{}^2/3$$

$$g_z = 2-4\tau_1+4\tau_2+8\phi_3{}^2/3$$

$$A_x = P[-\kappa-\frac{2}{7}-\alpha_1+\alpha_2+3\beta_1+3\beta_2+\frac{1}{7}(-\delta_1/2+3\delta_2/2 \\ +3\gamma_2/2-\gamma_1/2+2\phi_2)]$$

$$A_y = P[-\kappa-\frac{2}{7}-\gamma_1+\gamma_2+3\delta_1+3\delta_2+\frac{1}{7}(-3\beta_1/2+3\beta_2/2 \\ +3\alpha_2/2-\alpha_1/2+2\phi_1)]$$

$$A_z = P[-\kappa+\frac{4}{7}-4\tau_1+4\tau_2+\frac{1}{7}(\alpha_1/2-3\alpha_2/2+3\beta_1/2-3\beta_2/2 \\ -3\gamma_2/2+\gamma_1/2+3\delta_1/2-3\delta_2/2-2\phi_1-2\phi_2)]$$

$$\text{where } \alpha_1 = \frac{\zeta(^3A_2)}{\Delta^2T_1x},\ \alpha_2 = \frac{\zeta(^1E)}{\Delta^2T_1x};\ \beta_1 = \frac{\zeta(^1E)}{\Delta^2T_2\xi},\ \beta_2 = \frac{\zeta(^1A_1)}{\Delta^2T_2\xi}$$

$$\gamma_1 = \frac{\zeta(^3A_2)}{\Delta^2T_1y},\ \gamma_2 = \frac{\zeta(^1E)}{\Delta^2T_1y};\ \delta_1 = \frac{\zeta(^1E)}{\Delta^2T_2\eta},\ \delta_2 = \frac{\zeta(^1A_1)}{\Delta^2T_2\eta};$$

$$\tau_1 = \frac{\zeta(^3A_2)}{\Delta^2T_1z},\ \tau_2 = \frac{\zeta(^1E)}{\Delta^2T_1z};\ \phi_1 = \frac{\zeta(^3A_2)}{\Delta^4T_1x},\ \phi_2 = \frac{\zeta(^3A_2)}{\Delta^4T_1y},$$

$$\phi_3 = \frac{\zeta(^3A_2)}{\Delta^4T_1z}$$

ζ is the spin–orbit coupling constant
P and κ have their usual meaning.

With these expressions, the impossibility of fitting the e.s.r. data[4] to the correct d_z ground state is immediately removed.

---

† salen ≡ *NN′*-ethylenebis(salicylaldiminato); amben ≡ *NN′*-ethylenebis(2-aminobenzylideneiminato); pc ≡ phthalocyaninato.

‡ In ref. 1 a ground state of $d_{x^2-y^2}$ is postulated to result from a g_z value of 1·8. Correct use of the approximate Griffith method shows that $g_z > 2$ for such a ground state.

A good fit to the experimental g and A values is obtained using the parameters given in the Table. In obtaining a fit the values of the mixing coefficients α, β, γ, *etc.* are restricted on account of their interdependence within the g and A expressions. Small changes from the best-fit values cause quite large changes in g and A. The values of the coefficients and P and κ are reasonable for low-spin cobalt(II).[4,10,12] Quartet-state interactions have been ignored since variable-temperature susceptibility measurements show no marked increase in μ_{eff} at higher temperatures.[7]

An obvious difference between [Co(5-Cl-amben)] and other planar, low-spin Co^{II} complexes of a similar type is the reversal of the normal patterns K_x, $K_y >> K_z$ or $K_x >> K_y$, K_z to yield $K_y >> K_z$, K_x which appears to be unique, and may be related to the noted lack of reactivity of Co(amben) chelates. Further single-crystal measurements will establish whether this is a general rule for such complexes.

We thank the Australian Research Grants Committee for financial support, and Dr. A. Hartshorn for experimental assistance.

(*Received, 24th February* 1975; *Com.* 234.)

[1] E. Ochiai, *J. Inorg. Nuclear Chem.*, 1973, **35**, 1727.
[2] B. M. Hoffman, F. Basolo, and D. L. Diemente, *J. Amer. Chem. Soc.*, 1973, **95**, 6497.
[3] C. Busetto, F. Cariati, P. Fantucci, D. Galizioli, and F. Morazzoni, *J.C.S. Dalton*, 1973, 1712.
[4] L. M. Engelhardt, J. D. Duncan, and M. Green, *Inorg. Nuclear Chem. Letters*, 1972, **8**, 725.
[5] N. S. Hush and I. S. Woolsey, *J.C.S. Dalton*, 1974, 24.
[6] J. S. Griffith, *Discus. Faraday Soc.*, 1958, **26**, 81.
[7] K. S. Murray and R. M. Sheahan, *Chem. Phys. Letters*, 1973, **22**, 406.
[8] R. Karlsson, L. M. Engelhardt, and M. Green, *J.C.S. Dalton*, 1972, 2463.
[9] The limitations of the Griffith model have recently been recognised in an e.s.r. study of vitamin B_{12r}; J. R. Pilbrow and M. E. Winfield, *Mol. Phys.*, 1973, **25**, 1073.
[10] A. H. Maki, N. Edelstein, A. Davidson, and R. H. Holm, *J. Amer. Chem. Soc.*, 1964, **84**, 4580.
[11] R. L. Martin and S. Mitra, *Chem. Phys. Letters*, 1969, **3**, 183.
[12] R. B. Bentley, F. E. Mabbs, W. R. Smail, M. Gerloch, and J. Lewis, *J. Chem. Soc.* (*A*), 1970, 3003.
[13] J. S. Griffith, 'The Theory of Transition-Metal Ions,' Cambridge University Press, 1961.
[14] R. M. Golding, 'Applied Wave Mechanics,' Van Nostrand, Amsterdam, 1969.
[15] C. J. Ballhausen, 'Introduction to Ligand Field Theory,' McGraw-Hill, New York, 1962.