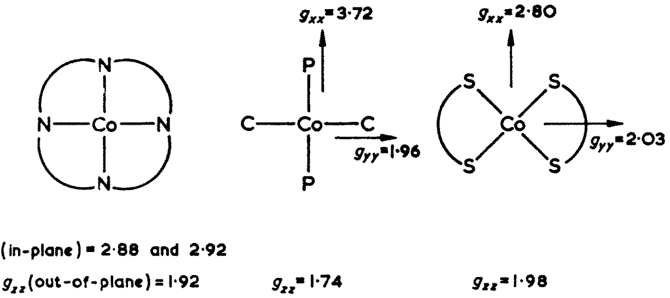
Single-crystal Magnetic Properties of *trans*-Dimesitylbis-(diethylphenylphosphine)cobalt(II)

R. B. BENTLEY, F. E. MABBS, and W. R. SMAIL
(*Chemistry Department, University of Manchester, Manchester,* 13)
and M. GERLOCH* and J. LEWIS
(*Chemistry Department, University College, Gower Street, London, W.C.*1)

AN X-ray structural analysis[1] of *trans*-dimesitylbis-(diethylphenylphosphine)cobalt(II) (I) has described the centrosymmetric, planar co-ordination of the metal atom as resulting from the steric blocking of the fifth and sixth octahedral co-ordination sites by the *ortho*-methyl groups of the mesityl ligands. E.s.r. work at Q-band frequencies at *ca* 80° K on single crystals of the pure compound, and of the cobalt-doped, diamagnetic, nickel(II) analogue, has defined the g- and A-tensors as approximately coincident with the co-ordination shell: x-axis (phosphine–Co–phosphine) A_{xx} = 0·0391 cm.$^{-1}$ (g_{xx} = 3·72), y-axis (mesityl-Co-mesityl) A_{yy} = 0·0045 cm.$^{-1}$ (g_{yy} = 1·96) and z-axis (perpendicular to co-ordination plane) A_{zz} = 0·0137 cm.$^{-1}$ (g_{zz} = 1·74). The large ansiotropy in the co-ordination plane of this complex may be contrasted with the essential in-plane isotropy of cobalt phthalocyanine (II).[2] The g-tensor is similar, however, to that reported for the planar molecule bis(maleonitriledithiolate)cobalt(II) (III)[3] as represented in Figure 1.



(II) (I) (III)

FIGURE 1. *The principal g-values of three square-planar cobalt*(II) *complexes.*

The electronic spectrum of the complex is characterised by a band at 8500 cm.$^{-1}$ ($\epsilon_{\max}$ *ca.* 8·5) which in the crystal at 20° K reveals a greater transition probability in the xy plane than parallel to z. The complex is transparent from 10,000 to *ca.* 20,000 cm.$^{-1}$, whilst structure on the edge of the charge-transfer spectrum at *ca.* 20,000 cm.$^{-1}$ has not yet been assigned with certainty.

If we assume a spin-paired d^7 configuration for the molecule and include spin–orbit coupling to second-order we have shown that the observed g and A tensors are compatible only with the ground state $(xz)^2(yz)^2(yx)^2(z^2)$.[1] (with the assumption that the $d_{x^2-y^2}$ orbital, which is directed at the ligand donor atoms, is energetically unfavourable for electron occupation). This interpretation leads to $\zeta/\Delta_{xz} = -0{\cdot}044$ and $\zeta/\Delta_{yz} = -0{\cdot}325$, with P reduced to 84% of the free-ion value. If the spin–orbit coupling constant ζ is reduced in the same proportion as P, we calculate the transfer energies Δ_{yz} and Δ_{xz}, of the odd electron from the $(xz)^2(yz)^2(xy)^2(z^2)^1 \rightarrow (xz)^2(yz)^1(xy)^2(z^2)^2$ and $(xz)^1(yz)^2(xy)^2(z^2)^2$ configurations to be 1350 and 9950 cm.$^{-1}$ respectively. However, if the absorption at 8500 cm.$^{-1}$ is taken to represent Δ_{xz} then $\zeta = -375$ cm.$^{-1}$, a reduction of 27% below the free-ion value. Such an assignment is not incompatible with the single-crystal electronic spectrum. By using this value for the spin–orbit coupling constant in the complex we calculate Δ_{yz} = 1150 cm.$^{-1}$.

Powder susceptibilities and single-crystal magnetic anisotropies of the mesityl complex have been measured over the range 90—300° K. Principal molecular magnetic susceptibilities and moments were calculated on the basis of the orientation of the g-tensor. The results may be represented briefly by:

	300° K		90° K
μ_x	3·55	B.M.	3·41
μ_y	1·84		1·31
μ_z	1·62		1·36

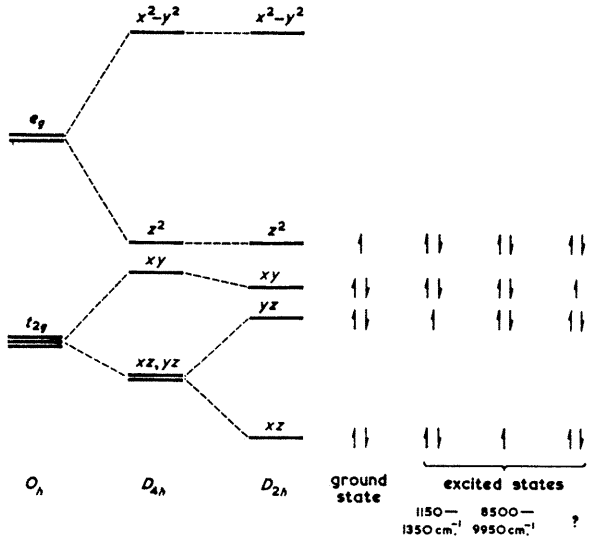


FIGURE 2. *Proposed energy level diagram for* trans-*dimesitylbis*(*diethylphenylphosphine*)*cobalt*(II).

If we assume that there is thermal population of the ground state only, the average magnetic moment calculated in first-order from the average g-value is 2·26 B.M.; this agrees well with the observed value of 2·26 B.M. at 90° K when the second-order Zeeman effects are relatively small.

The g and χ-tensors both show approximately axial symmetry with the unique direction being along the metal–phosphorus bonds. The approximate isotropy in the yz

plane need not, however, imply either a circularly symmetric ligand field in that plane or a unique role for the *P*–Co–P axis. This point has been demonstrated recently for tetrahedral copper(II)[4] and nickel(II)[5] complexes. In Figure 2 we show how the large in-plane magnetic anisotropies are compatible with a planar ligand-field. From left to right are shown the orbital splitting patterns under the octahedral field, the predominant tetragonal distortion, and the full D_{2h} symmetry in the molecule. The configuration $(xz)^2(yz)^2(xy)^1(z^2)^2$ does not mix into the ground state by spin–orbit coupling and so cannot be placed energetically by our calculations. The magnitudes of g_{xx} and of the in-plane anisotropy derive essentially from the proximity to the d_{z^2} of the d_{yz} relative to the d_{xz} orbital. This ordering of levels may result in two ways: (i) a stronger crystal field set up by the mesitylene groups relative to the phosphines would destabilise d_{yz} relative to d_{xz}, and (ii) π-bonding with the acceptor phosphine ligands may stabilise d_{xz} and d_{xy} relative to d_{yz}.

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