Electron Spin Resonance of Bis(1-phenylborabenzene)cobalt(II)

By **G. E. Herberich,** Institut für Anorganische Chemie der Technischen Hochschule Aachen, 51 Aachen, Germany
Trevor Lund and **J. Barrie Raynor,*** Department of Chemistry, University of Leicester, Leicester LE17 RH

Electron spin resonance measurements of bis(1-phenylborabenzene)cobalt(II) in toluene–ether solution at 77 K yields the following parameters: $g_x = 2{\cdot}130$, $g_y = 1{\cdot}915$, $g_z = 1{\cdot}990$, $A_x = 142$, $A_y = 62$, $A_z = 34$ ($\times 10^{-4}$ cm^{-1}), and $|Q'| = 0{\cdot}0003$ cm^{-1}. The sign of Q' is deduced to be positive. The nominal electron configuration is $(d_{x^2-y^2})^2$, $(d_{xy})^2$, $(d_{yz})^2$, $(d_{z^2})^1$. The unpaired electron is in a $d_{z^2} - d_{x^2-y^2}$ hybrid orbital with 66% in d_{z^2} and 13% in $d_{x^2-y^2}$. Analysis of the quadrupole coupling constant suggests that the bonding is very similar to that in ferrocene with 0·7 electron back donated to each borabenzene ring.

BIS-h^6-BENZENE and bis-h^5-cyclopentadiene complexes with metals are well established as also is an understanding of the bonding and molecular orbital energy levels in such compounds. Recently,[1] a new class of 'sandwich' complexes has been prepared involving the borabenzene ring system. So far, only cobalt complexes have been prepared of a variety of substituted borabenzenes $[Co(C_5H_5BR)_2]$ and of the mixed complex with cyclopentadienyl $[Co(C_5H_5BR)(C_5H_5)]$. The cobalt(II) complexes are paramagnetic with an effective magnetic moment $\mu = 1{\cdot}8$ B.M. suggesting one unpaired electron in a nominal d^7 spin-paired configuration. Evidence from X-ray data[2] on the methyl and methoxy derivatives and

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[1] G. E. Herberich, G. Greiss, H. F. Heil, and J. Müller, *Chem. Comm.*, **1971**, 1328; G. E. Herberich and G. Greiss, *Chem. Ber.*, 1972, **105**, 3413.

[2] G. Huttner, B. Krieg, and W. Gartzke, *Chem. Ber.*, **1972**, **105**, 3424.

from ^1H and ^{11}B n.m.r. measurements[3] on $[Co(C_5H_5BC_6H_5)(C_5H_5)]^+$ salts show that the borabenzene acts as a hexahapto-ligand. The cobalt atom is centred between the two rings which are in the centrosymmetric *trans*-conformation. The rings are laterally displaced such that the C_4 carbon atoms are nearer the cobalt than the borons. This paper describes e.s.r. measurements on bis(1-phenylborabenzene)cobalt(II), which is the least air-sensitive of the cobalt(II) derivatives so far prepared.

EXPERIMENTAL AND RESULTS

E.s.r. measurements were carried out on toluene–ether solutions of the complex at temperatures down to 77 K using a Varian E3 spectrometer. In fluid solution, resolution was best at *ca.* 230 K where only four equally spaced and well resolved lines were detected. A broad feature at lower field obscured what was presumably an octet of lines from an electron interacting with a nucleus of $I = 7/2$. The four resolved lines broadened very considerably towards low field. Their spacing was 80 ± 5 G and assuming that they were the four high-field lines of an octet, were centred on $g = 2{\cdot}006 \pm 0{\cdot}001$. At 77 K, a very well resolved spectrum exhibiting three sets of octets was observed (Figure 1a), which exhibited considerable second-order and quadrupole effects. The spectrum was analysed by comparison with spectra simulated on an ICL 4130 computer using methods similar to those described earlier.[4] The resulting parameters were $g_z = 1{\cdot}990$, $g_x = 2{\cdot}130$, $g_y = 1{\cdot}915$; $A_z = 34$, $A_x = 142$, $A_y = 62$ ($\times$ 10^{-4} cm^{-1}), and $|Q'| = 0{\cdot}00030$ cm^{-1}. The error in the g-parameters was $\pm 0{\cdot}002$; in A, $\pm 1 \times 10^{-4}$ cm^{-1}; and in Q', $\pm 0{\cdot}2 \times 10^{-4}$ cm^{-1}. Optical spectra were measured on a Unicam SP 800 spectrophotometer. The spectrum consisted of a peak at 23 350 cm^{-1} (ε = 6 110) and a shoulder at 29 400 cm^{-1} (ε = 3 300).

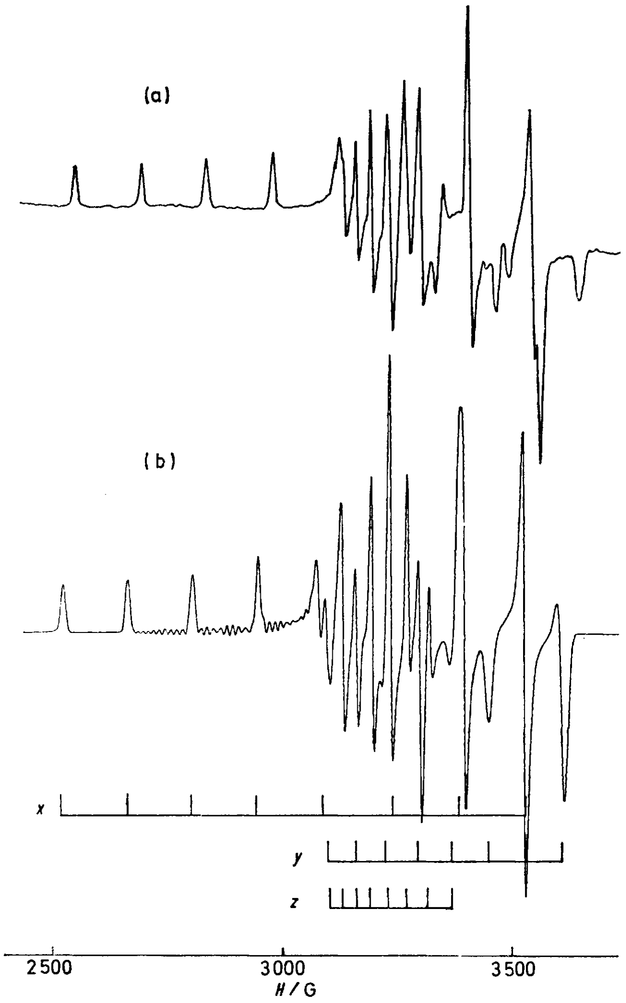

FIGURE 1 (a) E.s.r. spectrum of bis(1-phenylborabenzene)-cobalt(II) in toluene–ether at 77 K; (b) computer simulation of spectrum showing the assignments of the lines

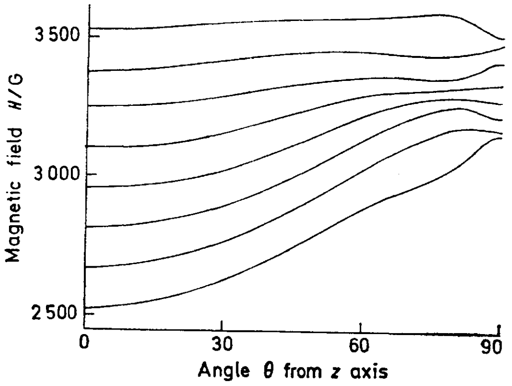

FIGURE 2 Plot of H vs. θ for the eight ^{59}Co lines showing the additional turning points between $\theta = 0$ and $\theta = 90°$ arising from an introduction of the quadrupole term

Interpretation of the E.s.r. Spectrum.—Attempts to simulate the spectrum were initiated before a program capable of coping with low-symmetry situations was available. The programs then in use depended on the formulae given by Bleaney[5,6] for transition field as a function of orientation angle of the magnetic field, when the paramagnetic centre is supposed to have an axially symmetric spin Hamiltonian of the form:

$$\mathscr{H} = \beta\{g_{\|}H_zS_z + g_{\perp}(H_xS_x + H_yS_y)\} + AS_zI_z + B(S_xI_x + S_yI_y) + Q'\{I_z^2 - \tfrac{1}{3}I(I+1)\} \quad (1)$$

This approximation produced encouraging results since the simulated spectra showed more lines than just those attributable primarily to contributions from magnetic field orientations close to the principal axes of the g-tensor. These off-axis contributions (Figure 2) resulted from turning points in the H vs. θ plot between the ' parallel ' axis and ' perpendicular ' plane, caused by the inclusion of the quadrupole coupling *via* the term in Q. Under these conditions the line found at 3 615 G in the experimental spectrum is attributed to an off-axis extremum of the $m = -7/2$ transition. Plots similar to Figure 2 showed, however, that it was impossible under conditions of axial symmetry to produce an extremum high enough in field without also producing a turning point below 3 090 G, from which no contribution is observed experimentally.

A program was therefore written to simulate spectra from

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[3] G. E. Herberich, G. Greiss, and H. F. Heil, *Angew. Chem.*, 1970, **82**, 838.

[4] J. F. Boas, R. H. Dunhill, J. R. Pilbrow, R. C. Srivastava, and T. D. Smith, *J. Chem. Soc.* (*A*), 1969, 94; T. Lund and W. E. Hatfield, *J. Chem. Phys.*, 1973, **59**, 885.

[5] B. Bleaney, *Phil. Mag.*, 1951, **42**, 441.

[6] A. Abragam and B. Bleaney, ' Electron Paramagnetic Resonance of Transition Ions,' Clarendon Press, Oxford, 1970.

a paramagnetic centre with C_2 symmetry, using the formulae given by Pilbrow [7] where the starting point is the spin Hamiltonian

$$\mathscr{H} = \beta \mathbf{S} \cdot \mathbf{g} \cdot \mathbf{H} + \mathbf{S} \cdot \mathbf{A} \cdot \mathbf{I} \qquad (2)$$

where **g** and **A** have a common z axis but may have different x and y axes. Even when α (the angle through which the axes of **A** are rotated compared with those of **g**) was varied, a satisfactory agreement between the experimental and theoretical spectra was not obtained. The effect of quadrupole coupling was therefore added to Pilbrow's formulae. It can be shown that the effect of the term $Q'[I_z^2 - \frac{1}{3}I(I+1)]$ is given by Bleaney's expressions even in this low symmetry situation provided that for Bleaney's B, K, and $g_\perp$ we use the expressions given by Pilbrow for $A_\perp$, A, and $g_\perp$. In view of the great asymmetry in the x,y plane, an extra quadrupole coupling term was included in the spin Hamiltonian. Following Abragam and Bleaney,[6] the extra term is $\frac{1}{3}Q'\eta(I_x^2 - I_y^2)$, where Q' is equivalent to the $P_\parallel$ of the later Bleaney reference.[6] The inclusion of this last term changes the magnetic field previously calculated for the e.s.r. transition by an amount:

$$\begin{aligned}\Delta H = \frac{(\frac{1}{3}Q'\eta)^2}{\beta K^3 g^3 B^2 g_\perp^2}\Bigg\{\Bigg[&\frac{(A_z g_z \cos\theta \,.\, \sin\theta)^2 (A_x^2 g_x^2 \cos^2\phi - A_y^2 g_y^2 \sin^2\phi)^2}{K^2 g^2} - 4(A_x A_y g_x g_y \sin\theta \,.\, \cos\phi \,.\, \sin\phi)^2\Bigg] \\ &\times 2m[4I(I+1) - 8m^2 - 1] - \frac{1}{2Bg_\perp}\Bigg[\frac{(A_z g_z \cos\theta)^4 + K^4 g^4}{K^2 g^2}(A_x^2 g_x^2 \cos^2\phi - A_y^2 g_y^2 \sin^2\phi)^2 + \\ &16(A_x A_y A_z g_x g_y g_z \cos\theta \,.\, \cos\phi \,.\, \sin\phi)^2\Bigg] \times m[2I(I+1) - 2m^2 - \Bigg\} \qquad (3)\end{aligned}$$

In fact η has only a minor effect on the spectrum but its inclusion was felt necessary for completeness. The inclusion of ligand hyperfine coupling is considered unwarranted, as is the inclusion of the $\Delta m \neq 0$ transitions, forbidden in first order. The substantial increase in computer time required would not seem justified by the small improvement in quality of the fit produced. The best result obtained is shown in Figure 1(b).

DISCUSSION

The Molecular Orbital Energy Levels in Sandwich Molecules.—The nature of the molecular orbitals and the bonding in numerous ' sandwich ' compounds has been considered by many workers ever since ferrocene was discovered.[8] It is now established that in ferrocene the three highest filled orbitals are a_{1g} and e_{2g} and the two lowest empty orbitals are e_{1g} (in D_{5d} symmetry). In all these, the orbitals have considerable metal character. The relative order of the a_{1g} and e_{2g} orbitals varies with the metal and has been a source of some confusion and controversy. However, for d^7 complexes of Co^{II}, the electron configuration would be predicted to be a_{1g}^2, e_{2g}^4, e_{1g}^1 and this is established for cobaltocene.[9] It is a straightforward matter for this configuration to be confirmed by e.s.r. On going to D_{6h} symmetry, the qualitative nature of the energy levels remains essentially unaltered. Likewise in mixed C_5H_5/C_6H_6 complexes or in substituted systems like the bisborabenzene complexes the above molecular orbital description would not be an unreasonable first approximation.[10]

The Ground-state Configuration.—The unambiguous observation of three well-separated g-features in frozen solutions of the complex allows us to eliminate the 90° staggered arrangement of the borabenzene rings. For steric reasons, an eclipsed *cis*-conformation is unlikely, but a centrosymmetric *trans*-conformation would be energetically very favourable. The centrosymmetric *trans*-conformation is found [2] in the crystal and we will assume that in solution the same configuration occurs.

The experimental magnetic moment [1] confirms a doublet ground state like cobaltocene. If we use the molecular orbital scheme derived for cobaltocene, then the $^2E_{1g}$ ground state would be split because of the presence of the very electropositive boron atom. The magnitude of the splitting will be crucial, since one component may be stabilised so much as to become lower than the a_{1g} level with the result that the ground state is $^2A_{1g}$.

The symmetry of the molecule may be considered as distorted D_{6h}, although the effect of the boron group is to reduce the symmetry in practice to C_i. We will consider how the two configurations, which depend upon the differing magnitudes of the splitting of the d_{xz} and d_{yz} orbitals, can be characterised from a qualitative analysis of the experimental g-tensor. The axis notation is given in Figure 3.

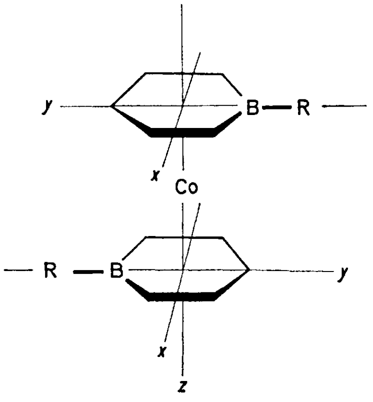

FIGURE 3 Axis notation for bis(borabenzene)cobalt(II)

(i) Electron in d_{yz}. If we take the electron configuration as $(d_{x^2-y^2})^2$, $(d_{xy})^2$, $(d_{z^2})^2$, $(d_{yz})^1$, then spin-orbit coupling about the z-axes will mix the d_{yz} orbital with the empty d_{xz} orbital with the result that $g_z < 2$. Coupling

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[7] J. R. Pilbrow and M. E. Winfield, *Mol. Phys.*, 1973, **25**, 1073.

[8] Y. S. Sohn, D. N. Hendrickson, and H. B. Gray, *J. Amer. Chem. Soc.*, 1971, **93**, 3603 and refs. therein.

[9] R. Krieger and J. Voitländer, *Z. Naturforsch.*, 1972, **27a**, 1444.

[10] A. H. Maki and T. E. Berry, *J. Amer. Chem. Soc.*, 1965, **87**, 4437.

about the x- and y-axes will mix d_{yz} with filled d_{z^2} and d_{xy} orbitals respectively with the result that g_x and g_y will be both >2. This does not fit the observed e.s.r. data. Alternatively, if the electron is considered to be in d_{xz}, the result is the same.

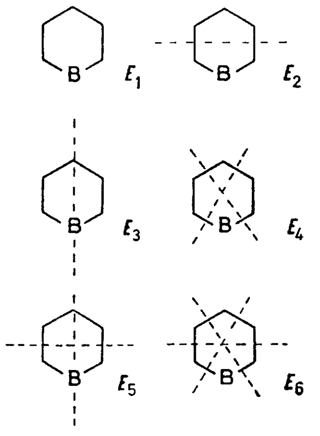

FIGURE 4 The six molecular orbitals for borabenzene showing the nodal planes

(ii) Electron in d_{z^2}. If we take the electron configuration as $(d_{x^2-y^2})^2$, $(d_{xy})^2$, $(d_{yz})^2$, $(d_{z^2})^1$, then spin-orbit coupling about the z-axis will not mix the d_{z^2} orbital with any other, and so $g_z = 2$. Coupling about the x- and y-axes will mix d_{z^2} with the filled d_{yz} and with the empty d_{xz} orbitals respectively so that $g_x > 2$ and $g_y < 2$. This now fits qualitatively the e.s.r. data.

The Molecular Orbital Energy Levels.—The π-molecular orbitals in borabenzene may be described (Figure 4) by analogy to those previously deduced for pyridine by Wheland and Pauling.[11] The main difference is the destabilisation of orbitals E_1, E_2, E_4, and E_6 relative to benzene and pyridine (see Figure 5) caused by the electropositive character of the boron. The presence of the phenyl substituent will alleviate some of the destabilisation. The relative energies of the relevant molecular orbitals in bis(borabenzene)cobalt(II) are given in the qualitative molecular-orbital energy-level diagram shown in Figure 6. Here, the molecular orbitals of cobaltocene are given for comparison. Inspection of the borabenzene orbital E_2 shows that it has the right symmetry for overlapping with the metal d_{yz} orbital while the E_3 orbital will interact with the metal d_{xz} orbital. Because of the electropositive character of the boron, the d_{yz} orbital will be stabilised relative to the d_{xz} orbital. This now allows us to describe the order of the metal d orbitals as $(d_{xy}, d_{x^2-y^2}) < d_{yz} < d_{z^2} < d_{xz}$. We are not concerned with the small splitting of the d_{xy} and $d_{x^2-y^2}$ orbitals nor their relative order since the energy of the $d_{x^2-y^2}$ orbital does not feature in the calculations.

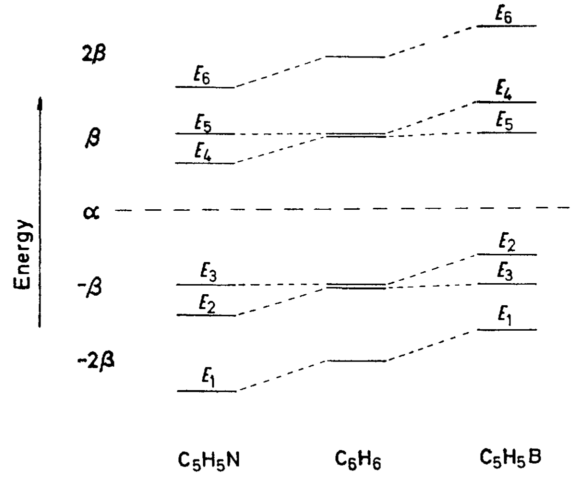

FIGURE 5 The energies of the π-molecular orbitals of borabenzene relative to those for benzene and pyridine. β Is the resonance integral for benzene

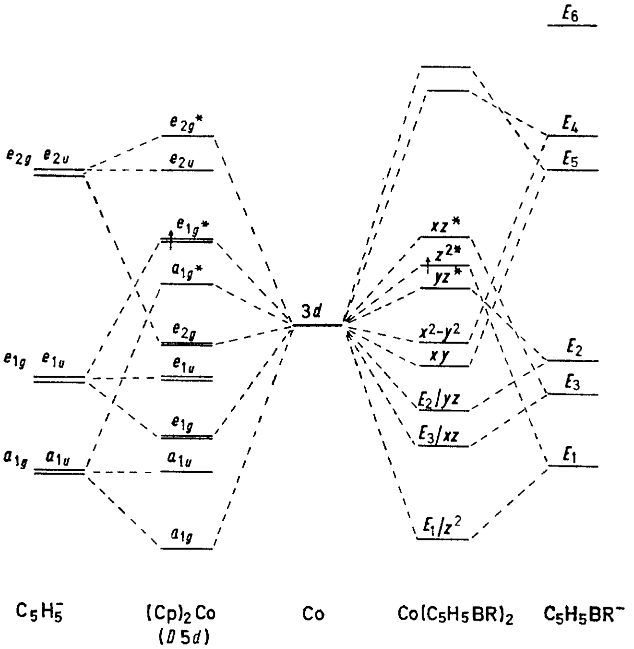

FIGURE 6 Qualitative energy-level diagram for some of the molecular orbitals of cobaltocene (left) and bis(borabenzene)-cobalt(II) (right)

Bonding Parameters.—The large distortion in the xy plane of the molecule, in contrast with cobaltocene, arises because of the presence of the boron atom. The effect is to distort the orbital containing the unpaired electron in such a way as to make it have more electron density in one plane (yz) than the other (xz). In quantum mechanical terms, the d_{z^2} orbital has some $d_{x^2-y^2}$ orbital mixed with it such that the ground-state wavefunction of the cobalt may be written as:

$$\psi_{gs} = \alpha(d_{z^2} + \beta d_{x^2-y^2}) \qquad (4)$$

Maki *et al.*[12] have derived expressions for the parameters of the spin Hamiltonian for various ground-state configurations. We combine those of his derived for the

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[11] G. W. Wheland and L. Pauling, *J. Amer. Chem. Soc.*, 1935, **57**, 2086.

[12] A. H. Maki, N. Edelstein, A. Davidson, and R. H. Holm, *J. Amer. Chem. Soc.*, 1964, **86**, 4580.

$d_{x^2-y^2}$ and d_{z^2} orbitals to account for the hybridisation (4). The resulting expressions are

$$\begin{aligned} g_x &= 2 - \frac{6\alpha^2\lambda + 2\alpha^2\beta^2\lambda}{\Delta E(d_{z^2} - d_{yz})} \\ g_y &= 2 - \frac{6\alpha^2\lambda + 2\alpha^2\beta^2\lambda}{\Delta E(d_{z^2} - d_{xz})} \qquad (5) \\ g_z &= 2 + \frac{8\alpha^2\beta^2\lambda}{\Delta E(d_{z^2} - d_{xy})} \end{aligned}$$

where λ is the spin–orbit coupling constant of the Co^{2+} ion (515 cm^{-1}).[13] The expressions for the metal hyperfine coupling are as follows[14]

$$\begin{aligned} A_x &= P(-\alpha^2\kappa + \Delta g_x + \tfrac{1}{14}\Delta g_y - \alpha^2\tfrac{2}{7} - \alpha^2\tfrac{4}{7}\sqrt{3}\beta) \\ A_y &= P(-\alpha^2\kappa + \Delta g_y + \tfrac{1}{14}\Delta g_x - \alpha^2\tfrac{2}{7} + \alpha^2\tfrac{4}{7}\sqrt{3}\beta) \qquad (6) \\ A_z &= P(-\alpha^2\kappa + \Delta g_z - \tfrac{1}{14}\Delta g_x - \tfrac{1}{14}\Delta g_y + \alpha^2\tfrac{4}{7}) \end{aligned}$$

where $\Delta g = g_{\text{expt}} - 2{\cdot}0023$, $P = g_e\beta_e g_N\beta_N\langle r^{-3}\rangle$ for the free ion (= 0·0255 cm^{-1}),[15] and κ is the Fermi contact interaction term. The signs of A are not known with certainty, although the most likely combinations are all negative or all negative except A_y since they must average to a number close to the experimental A_{iso} which is almost certainly negative. All combinations of signs were in fact taken, but the only one to give sensible values for α and β (*i.e.* between 0 and 1) was with A_x and A_y negative and A_z positive. The resulting bonding parameters are $\alpha = 0{\cdot}81$, $\beta = 0{\cdot}45$, and $\kappa = 0{\cdot}344$. These orbital coefficients show that the unpaired electron is in an orbital made up of 66% d_{z^2} and 13% $d_{x^2-y^2}$.

The two optical absorptions may be assigned to the $d_{yz} \longrightarrow d_{z^2}$ and $d_{z^2} \longrightarrow d_{xz}$ transitions respectively. Substitutions of the energies in equations (5) yields a value for $g_x = 2{\cdot}093$ and $g_y = 1{\cdot}926$ compared with the experimental 2·193 and 1·915 respectively. The similarity with the experimental values is encouraging and lends substance to the assignments. The extinction coefficients are larger than usual for dicyclopentadienyl complexes and arise from the lower symmetry of the molecule and the admixture of ligand orbitals with the metal *d*-orbitals.

The Quadrupole Coupling.—Quadrupole couplings of paramagnetic molecules cannot normally be determined by nuclear quadrupole resonance measurements. It is fortunate that in molecules amenable to study by e.s.r. the absolute value of the quadrupole coupling can usually be determined. The only drawback is that the sign cannot readily be determined since the formulae for transition fields contain only Q'^2, the e.s.r. resonances being shifted by second, but not first, order effects of the quadrupole interaction.

In the present study, the electric field gradient, q, and the asymmetry parameter, η, defined in terms of the irreducible tensor components (7), were calculated:

$$\eta = (q_{xx} - q_{yy})/q_{zz} \qquad (7)$$

In this work, we will assume η is zero. This is reasonable, since in the related compound $Cs[Co(1,2\text{-}B_9C_2H_{11})]$,[16] η is found to be 0·03, and a value this small would not significantly affect the e.s.r. spectrum. Since the principal value of the field gradient tensor is primarily governed by the molecular symmetry then it is reasonable to define the z direction as before.

The interpretation of the electric field gradient is straightforward. In either the valence bond or molecular orbital approach, q_{zz} arises from an imbalance of valence electrons. In first-row transition-metal complexes, there is the possibility of having 3*d*, 4*s*, and 4*p* electrons participating in the metal-to-ligand bond. Since *s*-electrons do not contribute to the electric field gradient, we need only directly consider 3*d* and 4*p* electrons. The indirect effects of 4*s* populations can safely be ignored since it has been shown that the mixing of the 4*s* and $3d_{z^2}$ is less than 1% in vanadocene.[17]

Utilizing the relation of the field gradient to angular momentum,[18]

$$q_{n,l,m} = q_{n,l,0}[1 - 3m^2/l(l+1)] \qquad (8)$$

where n, l, and m are the principal angular momentum and magnetic quantum numbers respectively, we can write an expression for q_{zz} in terms of the number of various types of d and p electrons:

$$\begin{aligned} q_{zz} = q_{3,2,0}[3d_{z^2} + \tfrac{1}{2}(3d_{xz,yz}) - (3d_{x^2-y^2,xy})] &+ \\ q_{4,1,0}[4p_z - \tfrac{1}{2}4p_{x,y}] & \qquad (9) \end{aligned}$$

It follows from this equation that the experimental electric field gradient, q_{expt}, is related to the populations of the *d*-orbitals by the more useful expression

$$\frac{eQq_{\text{expt}}}{h} = \frac{eQq_{\text{atom}}}{h}(n_{z^2} + \tfrac{1}{2}n_{xz,yz} - n_{x^2-y^2,xy}) \qquad (10)$$

where the unit of eQq/h is Hz. n Is here defined as the fraction of each electron localised in each orbital. The magnitude of the term involving *p*-orbitals is likely to be small, and Harris[16] has estimated it as *ca.* 0·02. In this work we shall ignore it.

The value for the field gradient contribution of one cobalt $3d_{z^2}$ electron can be calculated using the quadrupole coupling constant and the magnetic hyperfine interaction obtained from the $^4F_{9/2}$ state measured by cobalt atomic-beam spectroscopy.[19] Using equation (8) the known nuclear quadrupole moment Q for ^{59}Co ($0{\cdot}5 \times 10^{-24}$ cm^2)[20] and $q_{\text{atom}} = q_{zz}(3d_{z^2}) = (-9{\cdot}53 \times 10^{15}$ e.s.u. cm^{-1}), then $\frac{eQq_{\text{atom}}}{h} = -343$ MHz. This is only a working number since it neglects the Sternheimer correction[21]

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[13] T. M. Dunn, *Trans. Faraday Soc.*, 1961, **57**, 1441.

[14] Z. Sroubek and K. Zdansky, *J. Chem. Phys.*, 1966, **44**, 3078.

[15] B. A. Goodman and J. B. Raynor, *J. Inorg. Nuclear Chem.*, 1970, **32**, 3406.

[16] C. B. Harris, *Inorg. Chem.*, 1968, **7**, 1517.

[17] H. M. McConnell, W. W. Porterfield, and R. E. Robertson, *J. Chem. Phys.*, 1959, **30**, 442.

[18] C. H. Townes and A. L. Schawlaw, 'Microwave Spectroscopy,' McGraw-Hill, New York, 1955.

[19] D. von Ehrenstein, H. Kopfermann, and S. Reuselin, *Z. Physik*. 1960, **159**, 230.

[20] J. Michielsen-Effinger, *J. Chim. phys.*, 1961, **58**, 533.

[21] R. M. Sternheimer, *Phys. Rev.*, 1951, **84**, 244; 1952, **86**, 316; 1954, **95**, 736.

$(1 - R)$ and a small contribution from spin–orbit coupling.[22] For comparative purposes and for estimating relative electron distribution changes in cobalt complexes, it is more than adequate.

The parameter Q' used in the spin Hamiltonian is related to Q by the expression:

$$Q' = \frac{3eQq}{4I(2I - 1)} \qquad (11)$$

Hence our experimental value of Q' (0·0003 cm^{-1}) is equivalent to a value for eQq/h of ± 252 MHz (since we do not know the sign of Q'). The nomenclature and units of quadrupole couplings are notoriously varied;[23] we will use frequency for the energy unit for consistency with pure n.q.r. measurements.

To a first approximation which assumes no metal–ligand covalency, the complex can be considered as having electrons entirely in the *d*-orbitals, *viz.* $(d_{xy})^2$, $(d_{x^2-y^2})^2$, $(d_{yz})^2$, $(d_{z^2})^1$. By using equation (9), an expected experimental value of eQq/h would be -686 MHz. This is so different from our experimental value that considerable covalency needs to be invoked. The following metal populations may be deduced for various orbitals and substituted into equation (10): $d_{z^2}{}^* = 0{\cdot}66$ (e.s.r. evidence); $d_{x^2-y^2}{}^* = 0{\cdot}13$ (e.s.r. evidence); $d_{z^2}(E_1) = 2 \times (1 - 0{\cdot}66 - 0{\cdot}13)$ (ignoring the small $d_{x^2-y^2}$ contribution to this orbital); d_{yz} and $d_{yz}{}^* = 2 \times 1$ (total population in bonding and antibonding orbitals equals 1); $d_{xz}(E_3) = 2 \times 0{\cdot}21$ [not unreasonably assumed the same as $d_{z^2}(E_1)$]. The only unknowns left in equation (10) are the metal populations of the $d_{x^2-y^2}, d_{xy}$ bonding pair of orbitals. Since these are likely to have very similar populations, then the average population may be deduced by solving equation (10), whence the population is found to be 0·71, assuming $eQq/h_{\text{expt.}}$ is positive. A negative value of $eQq/h_{\text{expt.}}$ gives meaningless results.

We can summarise by saying that the bonding in bis(borabenzene)cobalt(II) is very similar to that in ferrocene and the cobaltocinium cation. Ligand electrons are donated into metal d_{z^2}, d_{xz}, and d_{yz} orbitals with the populations in d_{z^2} and d_{xz} (*ca.* 0·21) only slightly greater than that found in ferrocene (ranges from 0·11 to 0·20 for d_{yz} depending upon author [16]). On the other hand, there is considerable back bonding from filled metal $d_{x^2-y^2}$ and d_{xy} orbitals to the ligands amounting to $4 \times (1 - 0{\cdot}71)$ electrons overall, *i.e. ca.* 0·6 electrons back bonded to each ring of the borabenzene. This value is identical to that found in $[\mathrm{Co}(1{,}2\text{-}\mathrm{B_9C_2H_{11}})_2]^-$ and slightly less than that found in ferrocene (ranges from 0·60 to 0·80 depending upon author [16]).

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[22] R. Ingalls, *Phys. Rev.*, 1964, **133**, A787.
[23] H. B. G. Casimir, *Helv. Phys. Acta*, 1968, **41**, 741.