Optical and Electron Spin Resonance Spectra of Cobalt Complexes related to Vitamin B_{12}

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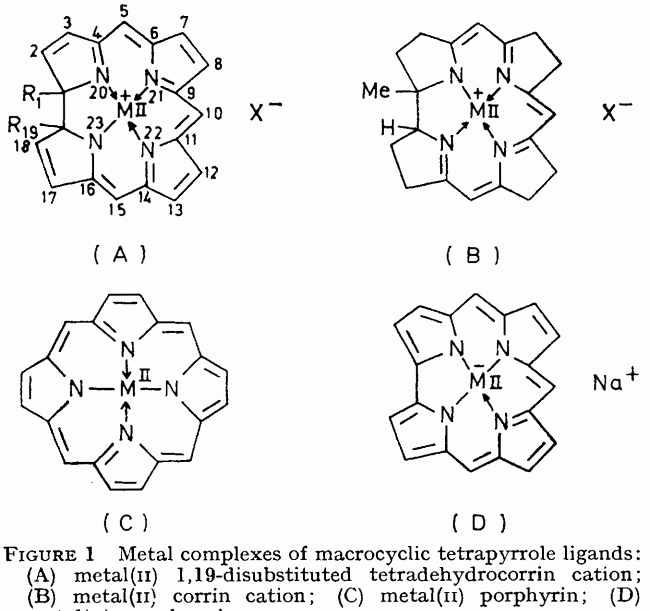
The optical spectra of the dipyridinecobalt(III) corrole, the cobalt(II) corrole anion, and the cobalt(II) 1,19-diethoxycarbonyltetradehydrocorrin cation have been measured in tetrahydrofuran and pyridine. Except for the cobalt(II) corrole anion, distinct differences in the optical spectra were observed in the two solvents, and have been interpreted in terms of the changes in the state of further co-ordination of the complex. E.p.r. studies of the cobalt(II) corrole anion and tetradehydrocorrin cation show the two complexes to have different electronic ground states for the central cobalt(II) ion, in spite of the similarity of the ligand moieties. This conclusion is supported by the optical studies, and is explained in terms of the changes in in-plane π-bonding and the difference in charge of the two species.

METAL CORROLES[1] and the related 1,19-disubstituted tetradehydrocorrins [2] are an interesting class of macrocyclic tetrapyrrole metal complexes which are closely related to both metal corrins and metal porphyrins. The structure of the ring systems of these complexes are shown in Figure 1. Of particular interest are the cobalt complexes, since these are the analogues of the vitamin B_{12} complexes. Indeed, cobalt corrole derivatives are believed to be formed as intermediates in the biosynthesis of vitamin B_{12}.[2] We have already shown that the nickel and cobalt complexes of 1,19-disubstituted tetradehydrocorrins exhibit interesting and unusual redox properties which may prove useful in understanding vitamin B_{12} chemistry.[3] Here we report the results of optical and e.s.r. studies of the cobalt 1,19-diethoxycarbonyltetradehydrocorrin and cobalt corrole complexes.



(A) (B) (C) (D)

FIGURE 1 Metal complexes of macrocyclic tetrapyrrole ligands: (A) metal(II) 1,19-disubstituted tetradehydrocorrin cation; (B) metal(II) corrin cation; (C) metal(II) porphyrin; (D) metal(II) corrole anion

EXPERIMENTAL

Materials.—The complexes used in the present investigation were the dipyridinecobalt(III) 8,12-diethyl-2,3,7,13,17,18-hexamethylcorrole, and the 1,19-diethoxycarbonyl-8,12-diethyl-2,3,7,13,17,18-hexamethylcobalt(II) tetradehydrocorrin perchlorate. The samples were kindly provided by Professor A. W. Johnson (University of Sussex). Their preparation has been described elsewhere [1,2] and the samples were used without further purification.

Tetrahydrofuran (THF) was used as the solvent for most of this work, and its purification has been described elsewhere.[3] The reduction technique, where used, has also been described previously.[3]

Pyridine (Hopkin and Williams) was purified by refluxing over potassium hydroxide pellets for several hours, followed by distillation. The fraction boiling at 115 ± 1 °C was collected and used immediately.

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[1] A. W. Johnson and I. T. Kay, *J. Chem. Soc.*, **1965**, 1620.

[2] D. Dolphin, R. L. N. Harris, J. L. Huppatz, A. W. Johnson, and I. T. Kay, *J. Chem. Soc.* (*C*), 1966, 30.

[3] N. S. Hush and I. S. Woolsey, *J. Amer. Chem. Soc.*, 1972, **94**, 4107.

Methanol (B.D.H. spectroscopy grade) was used without further purification.

Physical Measurements.—The e.s.r. spectra were recorded on a Varian 4502-15 E.S.R. spectrometer fitted with a dual sample cavity. All spectra were recorded at *X*-band frequency in the manner described previously.[3]

The visible and u.v. spectra were recorded using a Beckmann D.K.2A ratio recording spectrophotometer. All optical spectra were measured at room temperature.

RESULTS AND DISCUSSION

Electronic Spectra.—*Cobalt corroles.* The electronic absorption spectrum of the dipyridine cobalt(III) corrole in THF is shown in Figure 2.

The general features of the spectra are similar to those observed for metal porphyrins.[4] An extremely intense absorption is observed around 25 000 cm^{-1} analogous to the so-called Soret band of porphyrins, with a weaker series of bands in the visible region of the spectrum comparable with the *Q*-bands of metal porphyrins. It is now well established that the *Q* and Soret bands of metal porphyrins arise from $\pi \rightarrow \pi^*$ transitions of the ligand,[5] and we have established from PPP–SCF π-electron calculations that the absorption bands of metal corroles arise from the corresponding $\pi \rightarrow \pi^*$ transitions of the corrole ligand.[6] We are, therefore, essentially dealing with the absorption spectrum of the ligand rather than the central cobalt ion, although the relatively weak absorptions observed below 16 000 cm^{-1} may be attributed to *d–d* or charge-transfer transitions associated with the cobalt ion.

The spectrum of the dipyridinecobalt(III) corrole shows quite a marked concentration and solvent dependence (see Figure 2).

Controlled addition of pyridine to a solution of the complex at low concentration in THF gives spectra similar to that observed at higher concentrations (Figure 2a), whilst the spectrum in the presence of an excess of pyridine (Figure 2b) is almost identical to that observed in pure pyridine.

It is interesting to compare this behaviour with that of cobalt mesoporphyrins. Here, changes in solvent apparently change the oxidation state of the central cobalt ion. In strong donor solvents, such as pyridine, axial co-ordination takes place, and the cobalt(III) species is formed. In non-co-ordinating solvents, however, the cobalt(II) species is favoured. With solvents of intermediate co-ordinating power mixtures of the two are observed.[7] The cobalt(II) and cobalt(III) species of mesoporphyrins show quite markedly different spectra, with the Soret band shifting about 1 300 cm^{-1} to higher energy on going from cobalt(III) to cobalt(II), and the lowest-energy visible band by *ca.* 700 cm^{-1}. That the observed changes in spectra are due to species with different oxidation states for the central cobalt ion, rather than just due to different degrees of co-ordination of the cobalt ion has been established by magnetic susceptibility measurements.[8]

At first, it might be thought that the present cobalt corrole species are exhibiting a similar type of behaviour to that just described for the cobalt mesoporphyrins. Indeed, Johnson and Kay indicated that treatment of the dipyridinecobalt(III) corrole with hot methanol generates the cobalt(II) corrole with loss of pyridine.[1] This is not the case, however. When the dipyridinecobalt(III) corrole is treated with hot methanol, and the product recovered and washed with THF (the sample is now much less soluble in THF than previously), the sample gives a spectrum identical to that observed for the dipyridinecobalt(III) corrole at low concentration, throughout the available concentration range. Also, although the visible bands of the dipyridinecobalt(III) complex observed at intermediate concentrations (Figure 2b) are similar to a composite spectrum of the spectra observed at low concentrations and on addition of excess of pyridine, the Soret band is not, the peak maximum being clearly shifted to higher energy of either of the other two species. We have also shown that the species whose spectra are given in Figure 2b and c are diamagnetic, by observation of their n.m.r. spectra. We believe the explanation in the case of the cobalt corrole species is quite simple, but rather different from that of the cobalt mesoporphyrins.

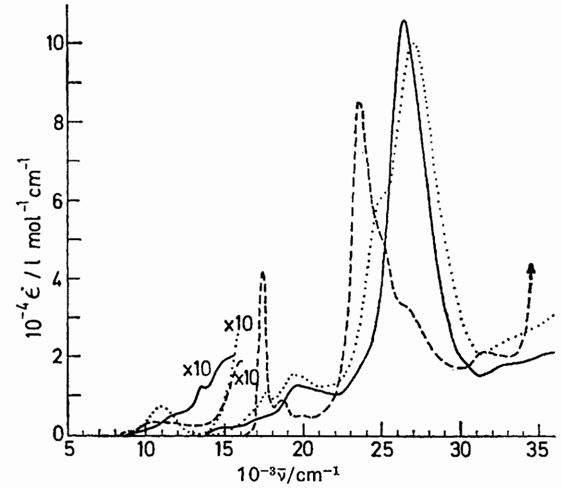

FIGURE 2 Electronic absorption spectrum of the dipyridinecobalt(III) corrole in THF. (a) —— Concentration 6·87 × 10^{-5}M; (b) ···· concentration 4 × 10^{-4}M; (c) — — — as for (a), but with excess of pyridine added

At low concentrations of dipyridinecobalt(III) corrole in solution the pyridine ligands dissociate, so that the spectrum given in Figure 2a corresponds to the uncomplexed cobalt(III) corrole. In the presence of an excess of pyridine, as in Figure 2c, the species present is again a cobalt(III) corrole, but with *both* axial positions being occupied by pyridine ligands. That two are

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[4] L. Edwards, D. H. Dolphin, and M. Gouterman, *J. Mol. Spectroscopy*, 1970, **35**, 90.

[5] C. Weiss, H. Kobayashi, and M. Gouterman, *J. Mol. Spectroscopy*, 1965, **16**, 415.

[6] N. S. Hush, J. M. Dyke, M. L. Williams, and I. S. Woolsey, *J.C.S. Dalton*, 1974, in the press.

[7] D. G. Whitten, E. W. Baker, and A. H. Corwin, *J. Org. Chem.*, 1963, **28**, 2363.

[8] M. Isutsui, R. A. Velapoldi, L. Hoffman, K. Suzuki, and A. Ferrari, *J. Amer. Chem. Soc.*, 1969, **91**, 3337.

present and not one is confirmed by the fact that the spectrum is identical with that of Figure 2c when determined in pyridine, the solvent from which the dipyridinecobalt(III) corrole was originally prepared.[1] Finally, we assign the spectrum given in Figure 2b as that of the mono-pyridine adduct, although a small percentage of the other two complexes may also be present. Thus all three species are cobalt(III) corrole derivatives, and the marked changes in spectra are due to the changes in co-ordination of the central cobalt ion.

This was further confirmed by the preparation of the cobalt(II) corrole anion by sodium film reduction in THF *in vacuo* of the cobalt(III) corrole with no co-ordinating pyridines. The spectrum of the cobalt(II) corrole anion is shown in Figure 3b, together with that of the parent cobalt(III) corrole. Its identity as a cobalt(II) complex was confirmed by the observation of a cobalt(II) e.s.r. signal for the species in solution (see subsequent discussion), and its absorption spectrum is quite distinct from all those of the cobalt(III) corrole species. It may also be generated by addition of tetra-n-butylammonium hydroxide or reducing agents such as $NaBH_4$ to a solution of the cobalt(III) corrole in dimethylformamide. The reaction is rather slow and incomplete in these cases, however, and these methods were much less satisfactory than the sodium film reduction. When prepared by sodium film reduction *in vacuo*, exposure of the cobalt(II) corrole anion to air results in immediate reoxidation to the cobalt(III) species in almost quantitative yields (>95%). When prepared by other methods, it is moderately air stable in the presence of the reducing agent. An attempt was made, therefore, to generate the neutral cobalt(II) corrole by protonation of the cobalt(II) corrole anion using perchloric acid. This simply resulted in oxidation to the cobalt(III) corrole, which implies that the neutral cobalt(II) corrole is rather unstable. It is interesting to note, however, that addition of perchloric acid to a solution of cobalt(III) corrole in THF produces a new species, which shows a broad main absorption peak at 28 170 cm^{-1} ($\varepsilon = 5{\cdot}5 \times 10^4$), with very little absorption in the visible region. Acid–base titrations in DMF show that this is the mono-protonated cobalt(III) corrole cation.[9] The spectrum is rather similar to that of the neutral nickel(II) corrole complex,[1] but since the location of the additional proton is uncertain it seems unwise to speculate too much about this species.

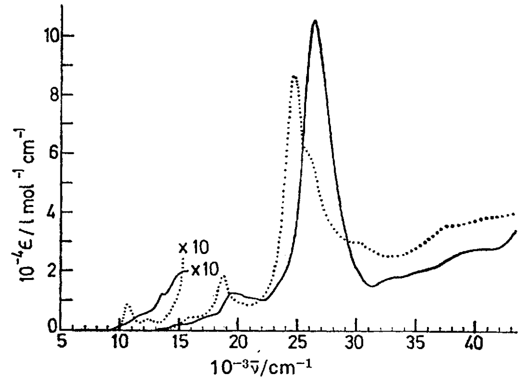

FIGURE 3 Electronic absorption spectrum of the cobalt(III) corrole and cobalt(II) corrole anion in THF. (a) —— Cobalt(III) corrole (1 × 10^{-4}M) and (b) ···· cobalt(II) corrole anion (1 × 10^{-4}M)

Addition of pyridine to a solution of the cobalt(II) corrole anion in THF *in vacuo* causes no change in the electronic spectrum, in marked contrast to the cobalt(III) species.* This indicates that the complex shows little or no tendency towards co-ordination in the axial positions, which is unusual for cobalt(II) complexes of this type. It is well known, for example, that cobalt(II) complexes of porphyrins and phthalocyanins and vitamin B_{12r} all show a fairly strong tendency to co-ordinate with pyridine-like ligands.[10-12] We will return to this point again later.

Finally, we note that the reduction potential of the cobalt(III) corrole to form the cobalt(II) species in DMF is $-0{\cdot}34$ V *vs.* S.C.E.[13] This shifts to $-0{\cdot}47$ V in the presence of pyridine, and reflects the stability of the cobalt(III) corrole with respect to the cobalt(II) corrole anion. These may be compared with the oxidation potential of cobalt(II) tetraphenylporphin to give the cobalt(III) species, which has been given as $+0{\cdot}32$ V in butyronitrile–$LiClO_4$ solution,[14] and $+0{\cdot}52$ V in benzonitrile–$Bu^n{}_4NClO_4$ solution.[15] Clearly, therefore, we expect the cobalt(III) corrole to be the more stable cobalt corrole species, whereas in the cobalt porphyrins, the cobalt(II) species tends to be the more stable. In the case of vitamin B_{12}, both cobalt(II) and cobalt(III) species are relatively stable, the redox potential for the cobalt(II) $\longrightarrow$ cobalt(III) process being *ca.* $-0{\cdot}06$ V in aqueous K_2SO_4 solution *vs.* S.C.E.[16]

Cobalt(II) 1,19-*Diethoxycarbonyltetradehydrocorrin Perchlorate*.—The electronic spectrum of this complex has been discussed briefly in our earlier paper.[3] The spectra in THF and pyridine are shown in Figure 4. No concentration dependence was observed for the spectrum in either solvent. The differences between the spectra observed in THF and pyridine may be attributed to the strong axial co-ordination of a single solvent molecule in the case of pyridine (see discussion of e.s.r. spectra). Co-ordination may also occur in the case of THF, but it is expected to be much weaker than for pyridine. The spectrum in solvents of intermediate co-ordinating strength, *e.g.* DMF and methanol, is intermediate between those observed in THF and pyridine. This behaviour is in marked contrast to the cobalt(II) corrole anion. However, as we have already noted, the cobalt corrole anion appears to be the exception in this respect.

The electronic spectrum of the cobalt(II) 1,19-diethoxycarbonyltetradehydrocorrin is rather different from those observed for the cobalt corroles. The band observed in the 28 000 to 31 000 cm^{-1} region of the spectrum for the tetradehydrocorrin complex has diminished in intensity quite considerably when compared with the corrole complexes, whilst a much stronger band appears in the 35 300 cm^{-1} region. The change in intensity of the former band is similar to that observed in the case of analogous corrin species when compared with porphyrins. This has been explained in terms of decreasing configuration interaction between the four lowest-energy electronic transitions of the ligand π-system.[17] PPP-SCF π-MO calculations on the present systems indicate that a similar explanation exists in this case.[6] The calculations also clearly indicate that the bands observed above 15 000 cm^{-1} arise from $\pi\rightarrow\pi^*$ transitions of the ligand as in the case of the cobalt corrole, the weak transitions below this being assigned as *d–d* and charge-transfer transitions associated with the central cobalt ion.

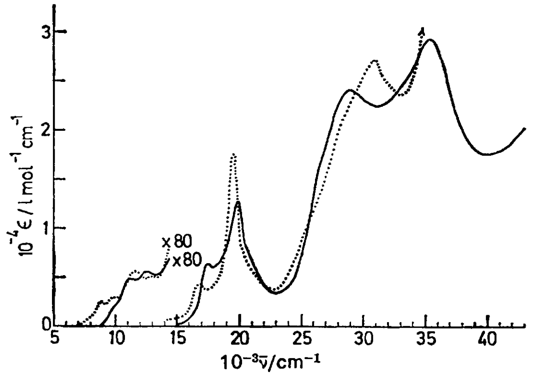

FIGURE 4 Electronic absorption spectrum of the cobalt(II) 1,19-diethoxycarbonyltetradehydrocorrin perchlorate. —— In THF (2×10^{-4}M) and ···· in pyridine (2×10^{-4}M)

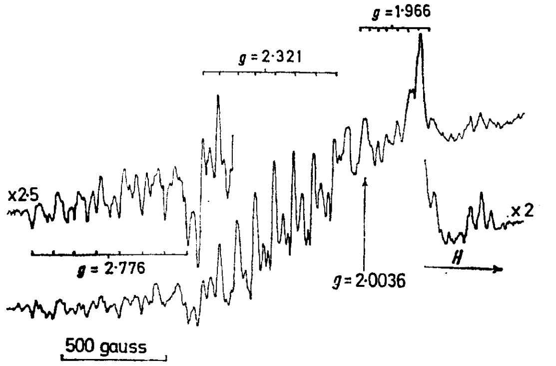

FIGURE 5 E.s.r. spectrum of the cobalt(II) corrole anion in THF at 77 K. Concentration 1×10^{-3}M. The room-temperature resonance was not observed. The hyperfine splittings indicated are for only one of the species observed (see text).

E.S.R. Spectra.—Cobalt(II) *corrole anion.* The e.s.r. spectrum of the cobalt corrole anion in THF at 77 K, generated by sodium film reduction *in vacuo* is shown in Figure 5. The spectrum at room temperature was unobservable, presumably owing to a short spin-lattice relaxation time, as in the case of cobalt(II) tetraphenylporphin.[18] Observation of the resonance at 77 K with a characteristic eight-line hyperfine splitting from the ^{59}Co nucleus ($I = \frac{7}{2}$) confirms the identity of the species as a low-spin cobalt(II) complex, for which $S = \frac{1}{2}$. It shows three principal *g*-tensor components, each with cobalt hyperfine coupling. The appropriate spin Hamiltonian to describe the spectrum is therefore:

$$\begin{aligned}\mathscr{H}_s = {} & \beta_e[g_{xx}H_xS_x + g_{yy}H_yS_y + g_{zz}H_zS_z] + \\ & A_{xx}S_xI_x + A_{yy}S_yI_y + A_{zz}S_zI_z + \\ & P[I_z^2 - \tfrac{1}{3}I(I+1)] + P^1[I_x^2 - I_y^2] - g_n\beta_nH\,.\,I \qquad (1)\end{aligned}$$

The experimental spectrum is complicated by the presence of more than one species in solution with slightly differing principal *g* and *A*-tensor components. By varying the concentration over the limited range available, owing to the low solubility of the complex (*ca.* 2×10^{-3}M), the relative intensities of the hyperfine lines could be altered, thus changing the appearance of the spectrum slightly. The dominant species at higher concentrations was observed to have the highest principal *g*-tensor values.

Similar effects have been observed in the case of cobalt(II) tetraphenylporphin in chloroform,[18] and as in that case, it seems most reasonable to attribute them to the existence of slightly different conformers of the molecule in the rigid solvent matrix. Certainly the parameters of the spin Hamiltonians of the various species are very similar, and those of low-spin cobalt(II) complexes are known to be very sensitive to their environment.[18,19] Attempts were made to record the spectrum of the cobalt(II) corrole anion in the presence of pyridine by addition of pyridine to the complex in THF under vacuum, and also by performing the reduction in pyridine itself *in vacuo*.* In neither case, however, were we able to observe the cobalt resonance, either at room temperature or 77 K. As noted earlier, though, the electronic spectrum of the complex is unchanged by the addition of pyridine, so that the species present is clearly still the cobalt(II) corrole anion.

It may be that this is an effect of the change in properties of the matrix formed on freezing the solution. Similar difficulties have been encountered with cobalt(II) *p*-methyltetraphenylporphin in toluene glasses.[10] However, as we shall see, other explanations are possible. The experimental spectrum observed for the cobalt(II) corrole anion in THF was analysed using the methods of Walker [10] and Kneubuhl [20] to yield the parameters of the spin Hamiltonian given in equation (1). To simplify

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* The latter case is complicated by reaction of the pyridine with the sodium, but could nevertheless be accomplished, electron transfer to the neutral cobalt(III) corrole occurring before reduction of the pyridine.

[17] P. O. Offenhartz, B. H. Offenhartz, and M. M. Fung, *J. Amer. Chem. Soc.*, 1970, **92**, 2966.

[18] J. M. Assour, *J. Chem. Phys.*, 1965, **43**, 2477.

[19] J. M. Assour and W. K. Kahn, *J. Amer. Chem. Soc.*, 1965, **87**, 207.

[20] F. K. Kneubuhl, *J. Chem. Phys.*, 1960, **33**, 1074.

analysis of the spectrum the quadrupolar terms were ignored. The g and A-tensor components derived in this manner are given in Table 1. The most difficult parameters to determine are g_{zz} and A_{zz}, since the high-field part of the spectrum is less well resolved than the rest. The weak triplet of hyperfine lines to high field of the main hyperfine lines of the lowest g-tensor component (g_{zz}) are of uncertain origin. They may arise from one of the secondary species present in solution, in which case they presumably correspond to the $m_I = \frac{3}{2}$, $\frac{5}{2}$, and $\frac{7}{2}$ hyperfine lines of the lowest g-tensor component. The slightly anomalous intensity of the $m_I = \frac{5}{2}$ hyperfine line of the main g_{zz} tensor component may well result from angular anomalies in the lineshape function similar to those discussed by Kivelson and Neiman [21] and Rollmann and Chan.[22]

TABLE 1

Parameters of the spin Hamiltonian for the cobalt(II) corrole anion in THF at 77 K

(i) For main species *

$g_{xx} = 2{\cdot}776 \pm 0{\cdot}003$
$g_{yy} = 2{\cdot}321 \pm 0{\cdot}003$
$g_{zz} = 1{\cdot}966 \pm 0{\cdot}003$
$A_{xx} = 108 \pm 5$ gauss $= 140 \pm 6 \times 10^{-4}$ cm^{-1}
$A_{yy} = 94 \pm 5$ gauss $= 102 \pm 5 \times 10^{-4}$ cm^{-1}
$A_{zz} = 51 \pm 5$ gauss $= 47 \pm 5 \times 10^{-4}$ cm^{-1}

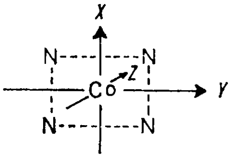
(ii) Second species

$g_{xx} = 2{\cdot}748 \pm 0{\cdot}003$
$g_{yy} = 2{\cdot}297 \pm 0{\cdot}003$
$g_{zz} = 1{\cdot}966 \pm 0{\cdot}003$ (assumed) †
$A_{xx} = 109 \pm 5$ gauss $= 140 \pm 6 \times 10^{-4}$ cm^{-1}
$A_{yy} = 94 \pm 5$ gauss $= 102 \pm 5 \times 10^{-4}$ cm^{-1}
$A_{zz} = 51 \pm 5$ gauss $= 47 \pm 5 \times 10^{-4}$ cm^{-1} (assumed) †

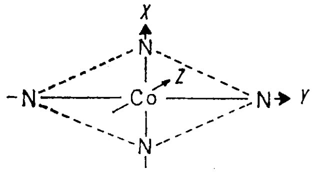
* Dominates at higher concentrations (see text). † It has been assumed that A_{zz} and g_{zz} differ very little from those of the main species, and hence have not been separately resolved. A third species may be assigned a value of $g_{yy} = 2{\cdot}283$ and $A_{yy} = 94 \pm 5$ gauss, but the other values of g and A were indeterminant.

We now proceed to interpret the experimentally determined parameters of the spin Hamiltonian in terms of the electronic structure of the central cobalt(II) ion of the complex.

The presence of three principal g-tensor components indicates that the complex has rhombic or lower symmetry. In this situation the $3d$-orbitals of the cobalt ion mix together, and the precise nature of the mixing is governed by the true geometry of the complex. Clearly this presents a considerable problem in any attempt to derive useful information about the electronic structure of the cobalt ion. However, as noted earlier, the e.s.r. spectra of low-spin cobalt(II) complexes are extremely sensitive to small changes in the geometry of the complex. Even cobalt(II) phthalocyanin shows a small rhombic splitting of the perpendicular g-tensor component.[19,23] Thus, although the splitting of the g_{xx} and g_{yy} components is rather larger in this case, corresponding to the $g_\perp$ component in D_{4h} symmetry, the deviation of the local symmetry of the central cobalt ion from D_{4h} is most likely still rather small. Indeed, we have been unable to detect any anisotropy of the perpendicular g-tensor component for the corresponding copper(II) corrole anion under identical experimental conditions.[24,25] We believe it is reasonable, therefore, to interpret the parameters of the spin Hamiltonian assuming the local symmetry of the cobalt ion to be D_{2h}, and the $3d$-orbitals to remain largely unmixed by the distortions, so that they may be considered as the real $d_{x^2-y^2}$, d_{z^2}, d_{xy}, d_{xz}, and d_{yz} basis orbitals. Two distortions from D_{4h} symmetry are possible for the local environment of the cobalt(II) ion which retain D_{2h} symmetry, as shown below. Of these two possibilities, the ligand geometry makes case A more likely, and we therefore assume that the principal g- and A-tensor components are along the three two-fold axes as shown in case (A). This is found to be the case in various planar paramagnetic bis(maleonitrile-dithiolate)metal complexes which have D_{2h} symmetry.[26] *



(A)



(B)

Z-axis is perpendicular to plane of paper.

Maki *et al.*[26] have derived expressions for the parameters of the spin Hamiltonian for various ground-state configurations of transition-metal ions, based on the method of Griffith; [28,29] and using these it is possible to deduce the electronic configuration of the cobalt ion in in the present complex. We may eliminate one possibility, however, from our studies of the e.s.r. spectra of the copper(II) corrole anion, which clearly show that the unpaired electron is in the d_{xy} orbital, and that this is much higher in energy than the other d-orbitals.[24,25] This may therefore be eliminated as a possibility for the cobalt(II) corrole anion. Indeed, it is intuitively acceptable that the unpaired electron is not in the d_{xy}

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* In fact the choice of either of the distortions (A) or (B) together with their appropriate principal axes does not affect the arguments or conclusions regarding the nature of the ground-state configuration of the complex. However, the value deduced for the Fermi contact interaction (see subsequent discussion) also suggests that distortion (A) is the more likely.

We also note that Bentley *et al.*[27] have demonstrated the equivalence of the spin-Hamiltonian parameters determined from single-crystal and powder e.s.r. spectra in the case of systems having D_{2h} symmetry.

[21] D. Kivelson and R. Neiman, *J. Chem. Phys.*, 1961, **35**, 156.

[22] L. D. Rollmann and S. I. Chan, *J. Chem. Phys.*, 1969, **50**, 3416.

[23] J. F. Gibson, D. J. E. Ingram, and D. Schonland, *Discuss. Faraday Soc.*, 1958, **26**, 72.

[24] I. S. Woolsey, Ph.D. Thesis, University of Bristol, 1970.

[25] N. S. Hush and I. S. Woolsey, unpublished work.

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

[27] R. B. Bentley, F. E. Mabbs, W. R. Small, M. Gerloch, and J. Lewis, *J. Chem. Soc.* (*A*), 1970, 3003.

[28] J. S. Griffith, *Discuss. Faraday Soc.*, 1958, **26**, 81.

[29] J. S. Griffith, 'The Theory of Transition Metal Ions,' Cambridge University Press, Cambridge, 1961.

orbital of the cobalt ion, since this is directed towards the ligating pyrrole nitrogens and should be highest in energy.

For the other possible locations of the unpaired electron it is necessary to consider whether the experimental parameters of the spin Hamiltonian are consistent with the theoretical expressions derived by Maki *et al.*[26] Our notation is basically the same as theirs, except we continue to refer to the $3d$ basis orbitals as the $d_{x^2-y^2}$, d_{z^2}, d_{xy}, d_{xz}, and d_{yz} orbitals. It should be pointed out in this context, that due to our choice of principal axes, our orbital notation differs from that usually used for phthalocyanins[19,23,28,30] and porphyrins.[18] This should be kept in mind when comparison is made with these complexes.

For the unpaired electron located in the $d_{x^2-y^2}$ orbital using 'hole formalism' (*i.e.* treating the system as d^3 for positive electrons or holes), the expressions are:[26]

(i) for the unpaired electron in the $d_{x^2-y^2}$ orbital

$$g_{xx} = 2 - 2a_1 \tag{2}$$

$$g_{yy} = 2 - 2a_2 \tag{3}$$

$$g_{zz} = 2 + 8a_3 \tag{4}$$

$$A_{xx} = P[-2a_1 - K + \tfrac{2}{7} + \tfrac{3}{7}\,a_2] \tag{5}$$

$$A_{yy} = P[-2a_2 - K + \tfrac{2}{7} + \tfrac{3}{7}\,a_1] \tag{6}$$

$$A_{zz} = P[8a_3 - K - \tfrac{4}{7} - \tfrac{3}{7}\,(a_1 + a_2)] \tag{7}$$

(ii) for the unpaired electron in the d_{z^2} orbital

$$g_{xx} = 2 - 6b_1 \tag{8}$$

$$g_{yy} = 2 - 6b_2 \tag{9}$$

$$g_{zz} = 2 \tag{10}$$

$$A_{xx} = P[-6b_1 - K - \tfrac{1}{7}\,(2 + 3b_2)] \tag{11}$$

$$A_{yy} = P[-6b_2 - K - \tfrac{1}{7}\,(2 + 3b_1)] \tag{12}$$

$$A_{zz} = P[-K + \tfrac{1}{7}\,(4 + 3b_1 + 3b_2)] \tag{13}$$

where

$$a_1 = \frac{\lambda}{\Delta_{x^2-y^2\rightarrow xz}}, \quad a_2 = \frac{\lambda}{\Delta_{x^2-y^2\rightarrow yz}}, \quad a_3 = \frac{\lambda}{\Delta_{x^2-y^2\rightarrow xy}}$$

$$b_1 = \frac{\lambda}{\Delta_{z^2\rightarrow xz}}, \quad b_2 = \frac{\lambda}{\Delta_{z^2\rightarrow yz}}$$

and λ = spin orbit coupling constant for Co^{2+}, which will be negative due to the use of hole configurations.

$P = g_e\beta_e g_n\beta_n \left\langle \frac{1}{r^3} \right\rangle_d$ where $\left\langle \frac{1}{r^3} \right\rangle_{3d}$ is the mean inverse cube of the unpaired electron nuclear distance. K = Fermi contact interaction term.

For these two possibilities only one of the g-tensor components, g_{zz}, may be less than 2,* which therefore assigns g_{xx} and g_{yy} of Table 1 as the two in-plane g-tensor components, and g_{zz} as the perpendicular component. Similarly the A-tensor components. These equations take no account of the effects of orbital overlap with the ligands. To do so would be very difficult, and is not justifiable in view of the approximations already made concerning mixing of the cobalt $3d$-orbitals. However, the effect of such ligand-field mixing may be taken into account by reducing the value of λ from the free-ion value. For the unpaired electron in the $d_{x^2-y^2}$ orbital, using the experimentally determined parameters of the spin Hamiltonian for the main species present in solution, equations (2)—(4) give $a_1 = -0{\cdot}387$, $a_2 = -0{\cdot}160$, and $a_3 = -0{\cdot}0045$, so that the hyperfine coupling constants may be expressed as $A_{xx} = P[-K + 0{\cdot}991]$, $A_{yy} = P[-K + 0{\cdot}439]$, and $A_{zz} = P[-K - 0{\cdot}373]$. The signs of the experimental hyperfine coupling constants are not known, but P is necessarily positive, thus any two of the three expressions for the hyperfine constants may be used to evaluate the various possible values of P, K, and the third coupling constant.

If A_{xx} and A_{yy} have the same sign, then since P is positive, both A_{xx} and A_{yy} are positive, and substitution of their experimental values in the expressions for the hyperfine constants gives $P = 69 \times 10^{-4}$ cm^{-1}, $K = -1{\cdot}04$, and $A_{zz} = +46 \times 10^{-4}$ cm^{-1}. The value for A_{zz} is in very good agreement with the experimental value (47×10^{-4} cm^{-1}), and assigns A_{zz} as being positive.

In contrast, if A_{xx} and A_{yy} are assumed to have opposite signs, A_{xx} is positive, A_{yy} negative, and they yield values of $K = +0{\cdot}672$, $P = 439 \times 10^{-4}$ cm^{-1}, and $A_{zz} = -459 \times 10^{-4}$ cm^{-1}. In this case A_{zz} is an order of magnitude too large compared with the experimentally determined value. Consideration of all the other possible combinations of signs of the hyperfine coupling constants showed that the *only* self consistent solution is the case given above with all the coupling constants being positive. For the unpaired electron in the d_{z^2} orbital, again using the spin Hamiltonian parameters for the main species present in solution, equations (8) and (9) give $b_1 = -0{\cdot}129$ and $b_2 = -0{\cdot}053$, and the hyperfine coupling constants may then be expressed as $A_{xx} = P[-K + 0{\cdot}511]$, $A_{yy} = P[-K + 0{\cdot}088]$, and $A_{zz} = P[-K + 0{\cdot}494]$. Inspection of these expressions shows that for *any* value of P and K, A_{xx} and A_{zz} should be almost identical, whereas experimentally $A_{xx} \sim 3A_{zz}$. Clearly therefore, no values of P and K are compatible with the experimental values of the hyperfine coupling constants, whatever their signs, and it may be concluded therefore that the unpaired electron cannot be located in the d_{z^2} orbital.

The situation in the case of the unpaired electron residing in the d_{yz} or d_{xz} orbitals is more complex. The lack of any detectable anisotropy in the in-plane g-tensor components ($g_\perp$) of the copper(II) corrole anion sets an upper limit to the energy separation of the d_{xz} and d_{yz} orbitals of *ca.* 2 000 cm^{-1}, but does not necessarily exclude them as possible locations for the unpaired electron in the cobalt(II) corrole anion.

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* For the unpaired electron in the d_{z^2} orbital, g_{zz} may become less than 2 by the inclusion of second-order terms.[28,29]

[30] S. E. Harrison and J. M. Assour, *J. Chem. Phys.*, 1964, **40**, 365.

The expressions for the parameters of the spin Hamiltonian for the unpaired electron in the d_{yz} orbital are: [26]

(iii)

$$g_{xx} = 2 - 6c_1 - 2c_3 \tag{14}$$

$$g_{yy} = 2 + 2c_4 \tag{15) *$$

$$g_{zz} = 2 - 2c_2 \tag{16}$$

$$A_{xx} = P[-6c_1 - 2c_3 - K - \tfrac{4}{7} - \tfrac{3}{7}(c_2 + c_4)] \tag{17}$$

$$A_{yy} = P[+2c_4 - K + \tfrac{2}{7} + \tfrac{3}{7}(c_1 + c_2 - c_3)] \tag{18}$$

$$A_{zz} = P[-2c_2 - K + \tfrac{2}{7} + \tfrac{3}{7}(c_3 - c_1 - c_4)] \tag{19}$$

where

$$c_1 = \frac{\lambda}{\Delta_{yz\rightarrow z^2}}, \quad c_2 = \frac{\lambda}{\Delta_{yz\rightarrow xz}}$$

$$c_3 = \frac{\lambda}{\Delta_{yz\rightarrow x^2-y^2}}, \quad c_4 = \frac{\lambda}{\Delta_{yz\rightarrow xy}}$$

Corresponding expressions for the d_{xz} case are obtained by interchange of the magnetic x and y axes, and with c_i referring to excitations from the d_{xz} orbital.

In (iii), only g_{yy} is less than 2, not g_{zz} as in (i) and (ii), and we cannot immediately assign the remaining g-tensor components given in Table 1. However, neither of the two possible assignments of g_{xx} or g_{zz} give physically reasonable values for K and P when equations (14) to (19) are solved, so that the unpaired electron cannot be located in the d_{yz} orbital. Similarly, it cannot be located in the d_{xz} orbital.

We have already shown that the values of $P = 69 \times 10^{-4}$ cm^{-1} and $K = -1{\cdot}04$ give very good agreement between the theoretical and experimental values for the hyperfine coupling constants with the unpaired electron located in the $d_{x^2-y^2}$ orbital, and since this is evidently a unique solution, we believe the unpaired electron of the cobalt(II) corrole anion is indeed located in the $d_{x^2-y^2}$ orbital of the central cobalt(II) ion. This is an in-plane orbital directed between the four pyrrole nitrogens, and is in contrast to the case of cobalt(II) phthalocyanin,[11,19,28] cobalt(II) porphyrins,[10,18] and vitamin B_{12r},[12] where the unpaired electron of the cobalt(II) ion is located in the out of plane d_{z^2} orbital. However, it would explain why the present complex shows little or no tendency towards axial co-ordination of ligands such as pyridine, which are fairly readily co-ordinated by the other cobalt complexes mentioned.[10-12] With the unpaired electron in the $d_{x^2-y^2}$ orbital, the d_{z^2} orbital should be doubly occupied, and hence further axial co-ordination of σ-donor ligands should be less favourable than in the case of a singly occupied d_{z^2} orbital. We will return to this point again later.

The values of a_1, a_2, and a_3 may be used to evaluate the energies of the excited-state configurations relative to the ground state, knowing the spin–orbit coupling constant for cobalt. Since the spin–orbit coupling constant has the same dependence on $\langle 1/r^3 \rangle 3d$ as does P,[27,31] we choose a value of λ such that $P/P_0 = \lambda/\lambda_0$, where P_0 and λ_0 are the values appropriate to the free Co^{2+} ion. These have been given as $P_0 = 254 \times 10^{-4}$ cm^{-1},[32] and $\lambda_0 = 533$ cm^{-1}.[29] Using the value of P determined from the experimental values of the spin Hamiltonian parameters (69×10^{-4} cm^{-1}) we obtain a value of $\lambda = 145$ cm^{-1}. Using this value of λ, the energies of the excited state configurations are 375 cm^{-1} ($\Delta_{x^2-y^2\rightarrow xz}$), 905 cm^{-1} ($\Delta_{x^2-y^2\rightarrow yz}$), and 32 200 cm^{-1} ($\Delta_{x^2-y^2\rightarrow xy}$) above the ground state. Whilst we do not wish to place too much reliance on the numerical values obtained, we feel that the description of the orbital ordering of the cobalt ion is correct, and that the excitation energies have at least a semi-quantitative meaning. We would also point out that the separation of the d_{xz} and d_{yz} levels is very small (*ca.* 500 cm^{-1}), indicating that the symmetry of the central cobalt ion is indeed close to D_{4h}, as proposed earlier, and that the problem may be treated within the approximations used.

The value of $P = 69 \times 10^{-4}$ cm^{-1} obtained for the present complex is quite similar to that obtained by Lin *et. al.* (88×10^{-4} cm^{-1}) for cobalt(II) ions in X-irradiated single crystals of $K_3Co(CN)_6$,[33] and indicates that there is significant delocalisation of the unpaired electron onto the ligand moiety. The value of $K = -1{\cdot}04$ is unusually large and negative. It may be compared with $K = +0{\cdot}32$ for hydrated cobalt(II) salts,[34] $-0{\cdot}333$ for cobalt(II) ions in the $K_3Co(CN)_6$ lattice,[33] and a value of about $-0{\cdot}4$ for cobalt(II) phthalocyanin.[35] The value of K in the present complex may be explained by mixing of the 4s metal orbital into the $d_{x^2-y^2}$ ground state which has the same symmetry (A_g) in D_{2h}.[27,29,32,35]

(ii) *Cobalt*(II) *1,19-diethoxycarbonyltetradehydrocorrin perchlorate.* The e.s.r. spectrum of the cobalt(II) 1,19-diethoxycarbonyltetradehydrocorrin complex observed in THF at both room temperature and 77 K are shown in Figure 6, whilst those observed in methanol and pyridine are shown in Figure 7. In frozen solution each shows hyperfine coupling to the central cobalt(II) ion, but the coupling was not resolved at room temperature. In THF, the spectrum at 77 K shows a set of eight cobalt hyperfine lines on the parallel component of the g-tensor, with a g-value close to spin free. At lower fields a complex series of lines is observed, as in the case of the cobalt(II) corrole anion. Complete analysis of these low-field lines is extremely difficult. As with the cobalt(II) corrole anion, more than one species appears to contribute to the system of lines; however, it is also likely that the g-tensor is not truly axial, which adds to the complexity of the low-field part of the spectrum. It seems

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* We thank one of the referees for pointing out an error in sign in the expression for g_{yy} given in ref. 26.

[31] B. R. McGarvey in 'Transition Metal Chemistry,' vol. 3, ed. R. L. Carlin, Dekker, New York, 1966.

[32] B. R. McGarvey, *J. Phys. Chem.*, 1967, **71**, 51.

[33] W. C. Lin, C. A. McDowell, and D. J. Ward, *J. Chem. Phys.*, 1968, **49**, 2883.

[34] A. Abragam and M. H. L. Pryce, *Proc. Roy. Soc.*, 1951, **206**, 173.

[35] J. F. Gibson, D. J. E. Ingram, and D. Schonland, *Discuss. Faraday Soc.*, 1958, **26**, 72.

that any such rhombic distortion is small, however, and to a reasonably good approximation the complex may be assumed to have an axially symmetric g-tensor. This is in contrast to the cobalt(II) corrole anion, where a much larger rhombic distortion of the g-tensor is observed.

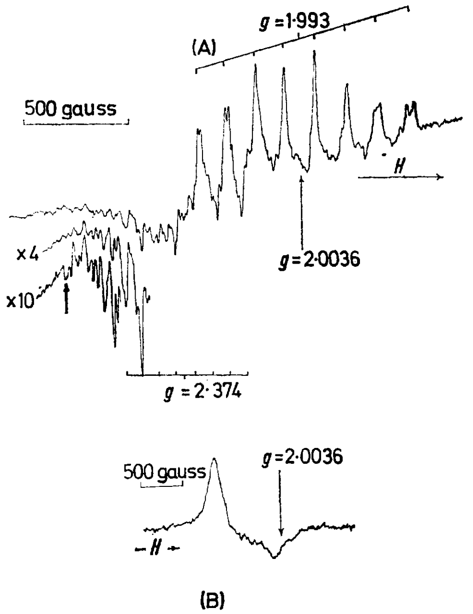

FIGURE 6 E.s.r. spectrum of the cobalt(II) 1,19-diethoxycarbonyltetradehydrocorrin perchlorate in THF (10^{-3}M). A at 77 K and B at room temperature (The $g_\perp$ hyperfine splittings indicated are for only one of species observed.)

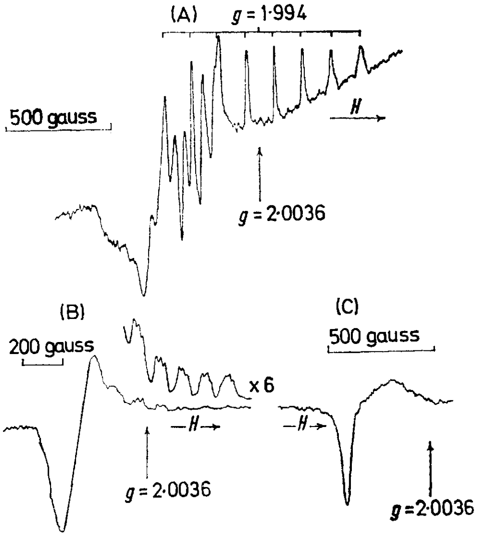

FIGURE 7 E.s.r. spectrum of the cobalt(II) 1,19-diethoxycarbonyltetradehydrocorrin perchlorate in methanol and pure pyridine (10^{-3}M). A In methanol at 77 K; B in pyridine at 77 K; C in pyridine at room temperature

This is most likely due to the fact that the 1—19, 1—20, and 19—23 bonds of the tetradehydrocorrin complex should be rather longer than in the corrole anion since they are single bonds, whereas in the corrole anion they have considerable double bond character.[36] The increase in these bond lengths would allow the bipyrrole side of the molecule to open out slightly, so that the complex can assume a configuration in which the local symmetry of the cobalt ion is more nearly D_{4h}.

The spectra of the complex in methanol and pyridine at 77 K also show effectively axial symmetry, so that the spectra have all been analysed in terms of the spin Hamiltonian (20) in the manner previously described for the cobalt(II) corrole anion. The parameters of the spin Hamiltonian in equation (20) evaluated from the experimental spectra are given in Table 2. The value of $g_\perp$ given for the complex in THF corresponds to the most intense set of hyperfine lines observed, as does the parameter $A_\perp$. In methanol and pyridine, the $g_\perp$ component is much less well resolved. For the complex in methanol it is still possible to evaluate $g_\perp$ and $A_\perp$ with reasonable accuracy. In pyridine, however, the value of $A_\perp$ was estimated from the linewidth of the $g_\perp$ component, and the value of $g_\perp$ taken as the point at which the derivative curve crosses the baseline. This should be regarded as a lower limit for $g_\perp$.[9] The e.s.r. spectra at room temperature do not show any resolved cobalt hyperfine coupling, presumably owing to linewidth variation of the hyperfine lines. It is difficult, therefore, to obtain accurate

$$\mathscr{H}_s = g_\parallel\beta_e H_z S_z + g_\perp\beta_e(H_x S_x + H_y S_y) + A_\parallel S_z I_z + A_\perp(S_x I_x + S_y I_y) + P[I_z^2 - \tfrac{1}{3}I(I+1)] - g_n\beta_n H \cdot I \quad (20)$$

TABLE 2

Spin Hamiltonian parameters for cobalt(II) 1,19-diethoxycarbonyltetradehydrocorrin perchlorate

(a) In THF

at 77 K:
$g_\parallel = 1{\cdot}991 \pm 0{\cdot}002$
$g_\perp = 2{\cdot}374 \pm 0{\cdot}003\,\dagger$
$A_\parallel = 146 \pm 2$ gauss $= 136 \pm 2 \times 10^{-4}$ cm^{-1}
$A_\perp = 80 \pm 2$ gauss $= 89 \pm 2 \times 10^{-4}$ cm^{-1} *

At room temperature: *
$g_{\text{iso}} = 2{\cdot}268 \pm 0{\cdot}010$
$A_{\text{iso}} = 97 \pm 6$ gauss

(b) In methanol

At 77 K:
$g_\parallel = 1{\cdot}994 \pm 0{\cdot}002$
$g_\perp = 2{\cdot}236 \pm 0{\cdot}002$
$A_\parallel = 133 \pm 4$ gauss $= 123 \pm 4 \times 10^{-4}$ cm^{-1}
$A_\perp = 51 \pm 5$ gauss $= 53 \pm 5 \times 10^{-4}$ cm^{-1}

(c) In pyridine

At 77 K:
$g_\parallel = 1{\cdot}998 \pm 0{\cdot}002$
$g_\perp = 2{\cdot}180 \pm 0{\cdot}002\,\ddagger$
$A_\parallel = 106 \pm 2$ gauss $= 99 \pm 2 \times 10^{-4}$ cm^{-1}
$A_\perp = 33 \pm 9$ gauss $= 34 \pm 9 \times 10^{-4}$ cm^{-1} ‡
$A^{\text{N}} = 19 \pm 1$ gauss $= 18 \pm 1 \times 10^{-4}$ cm^{-1}

At room temperature: *
$g_{\text{iso}} = 2{\cdot}169 \pm 0{\cdot}010$
$A_{\text{iso}} = 32 \pm 3$ gauss

* g_{iso} Assumed to be midway between maxima of resonance. A_{iso} Calculated using maxima as limits of linewidth. The reasons for the difference between g_{iso} and $\frac{1}{3}(g_\parallel + 2g_\perp)$ and A_{iso} and $\frac{1}{3}(A_\parallel + 2A_\perp)$ in (a) and (c) are given in the text. † Taken for strongest series of hyperfine lines observed. ‡ $g_\perp$ Taken as point where derivative curve crosses baseline. $A_\perp$ Estimated from linewidth.

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[36] N. S. Hush, J. M. Dyke, M. L. Williams, and I. S. Woolsey, *Mol. Phys.*, 1969, **17**, 559.

values of the isotropic g-values and hyperfine coupling constants, g_{iso} and A_{iso}, without computer simulation of the spectra. Accordingly, g_{iso} was taken as the mid-point between the maxima of the resonance, and A_{iso} was estimated using the maxima as limits of the linewidth. The latter should be regarded as lower limits for the isotropic hyperfine couplings. The differences between $\frac{1}{3}(A_{\parallel} + 2A_{\perp})$ and the isotropic values undoubtedly arise mainly from the difficulties in estimating the isotropic values, and also $g_{\perp}$ and $A_{\perp}$ in the case of the complex in pyridine.

Consideration of the theoretical expressions for the parameters of the spin Hamiltonian as in the case of the cobalt(II) corrole anion shows that only two possibilities for the location of the unpaired electron need be considered. These are the configurations with the unpaired electron in the $d_{x^2-y^2}$ and d_{z^2} orbitals, the principal axes again being defined as for the cobalt(II) corrole anion. With axial symmetry, however, the d_{xz} and d_{yz} orbitals are degenerate and the expressions for the parameters of the spin Hamiltonian simplify to:

(i) for the unpaired electron in the $d_{x^2-y^2}$ orbital

$$g_{\perp} = 2 - 2a_1 \tag{21}$$

$$g_{\parallel} = 2 + 8a_3 \tag{22}$$

$$A_{\parallel} = P[8a_3 - K - \tfrac{4}{7} - \tfrac{6}{7}\, a_1] \tag{23}$$

$$A_{\perp} = P[-\tfrac{11}{7}\, a_1 - K + \tfrac{2}{7}] \tag{24}$$

(ii) for the unpaired electron in the d_{z^2} orbital

$$g_{\perp} = 2 - 6b_1 \tag{25}$$

$$g_{\parallel} = 2 \tag{26}$$

$$A_{\parallel} = P[-K + \tfrac{4}{7} + \tfrac{6}{7}\, b_1] \tag{27}$$

$$A_{\perp} = P[-\tfrac{45}{7}\, b_1 - K - \tfrac{2}{7}] \tag{28}$$

where

$$a_1 = \frac{\lambda}{\Delta_{x^2-y^2\rightarrow xz,yz}}, \quad a_3 = \frac{\lambda}{\Delta_{x^2-y^2\rightarrow xy}}, \quad b_1 = \frac{\lambda}{\Delta_{z^2\rightarrow xz,yz}}$$

and the other symbols are as given previously. For the cobalt(II) 1,19-diethoxycarbonyltetradehydrocorrin complex it is not possible to solve the equations for the g- and hyperfine tensor components uniquely as in the case of the cobalt(II) corrole anion, since the values deduced for P and K cannot be used to evaluate a third hyperfine coupling which may be compared with experiment. It is necessary in this case therefore to consider whether the values of P and K obtained by solving the equations for the g- and hyperfine tensor components are reasonable for the type of complex under investigation. However, we may note that the values of the isotropic hyperfine couplings in the various solvents indicate that $A_{\parallel}$ and $A_{\perp}$ must have the same sign. This immediately reduces the number of possibilities we need consider when solving equations (21) to (28).

(*a*) In THF. For the unpaired electron in the $d_{x^2-y^2}$ orbital, the experimentally determined spin Hamiltonian parameters give $a_1 = -0{\cdot}186$ and $a_3 = -0{\cdot}0016$. Thus the hyperfine coupling constants are given by $A_{\parallel} = P[-0{\cdot}403 - K]$ and $A_1 = P[0{\cdot}578 - K]$. The experimental values of $A_{\parallel}$ and $A_{\perp}$ are only compatible with the unpaired electron being in the $d_{x^2-y^2}$ orbital if $P = 48 \times 10^{-4}$ cm^{-1} and $K = +2{\cdot}43$, in which case they are negative. The very large positive value of K is highly improbable, since it is not expected to be greater than about $+0{\cdot}3$,[32,37] and the value of P is unusually low. We may therefore conclude that the unpaired electron is unlikely to be in the $d_{x^2-y^2}$ orbital of the complex in THF. If the unpaired electron is in the d_{z^2} orbital, then $b_1 = -0{\cdot}062$, in which case $A_{\parallel} = P[0{\cdot}519 - K]$ and $A_{\perp} = [0{\cdot}113 - K]$. The experimental values of $A_{\parallel}$ and $A_{\perp}$ then give $P = 116 \times 10^{-4}$ cm^{-1} and $K = -0{\cdot}65$, in which case they are both positive. Since the $3d_{z^2}$ and $4s$ orbital have the same symmetry in D_{4h}, it is again possible to explain the rather negative value of K by mixing a small contribution from the $4s$ orbital into the $3d_{z^2}$ ground state.[27,32] The value of P is consistent with there being marked delocalisation of the unpaired electron onto the ligand. It may be concluded therefore that the unpaired electron is, in fact, in the d_{z^2} orbital of the cobalt ion for the complex in THF.

(*b*) In methanol. If the unpaired electron is in the $d_{x^2-y^2}$ orbital $a_1 = -0{\cdot}117$ and $a_3 = -0{\cdot}001$. These give $A_{\parallel} = P[0{\cdot}480 - K]$ and $A_{\perp} = P[0{\cdot}470 - K]$. It is clear by inspection of these expressions that no values of P and K are consistent with the experimental values of $A_{\parallel}$ and $A_{\perp}$, since any values of P and K imply that they should be almost equal, whereas in fact $A_{\parallel} \sim 2A_{\perp}$. Clearly therefore the unpaired electron cannot be located in the $d_{x^2-y^2}$ orbital.

If the unpaired electron is in the d_{z^2} orbital, $b_1 = -0{\cdot}039$, giving $A_{\parallel} = P[0{\cdot}539 - K]$ and $A_{\perp} = P[-0{\cdot}035 - K]$. Values of $P = 122 \times 10^{-4}$ cm^{-1} and $K = -0{\cdot}47$ are consistent with the experimental values of $A_{\parallel}$ and $A_{\perp}$ if they are both positive. We may again conclude therefore that the unpaired electron is in the d_{z^2} orbital for the complex in methanol.

(*c*) In pyridine. Since a triplet nitrogen superfine coupling due to axial co-ordination of a solvent pyridine molecule is observed on the parallel cobalt hyperfine lines for the complex in pyridine, it may be concluded that the unpaired electron of the cobalt ion is again in the d_{z^2} orbital.[10,11] This is also confirmed by analysis of the parameters of the spin Hamiltonian from which values of $b_1 = -0{\cdot}0297$, $P = 101 \times 10^{-4}$ cm^{-1}, and $K = -0{\cdot}43$ are obtained, $A_{\parallel}$ and $A_{\perp}$ again being positive.

The hyperfine coupling of the axially co-ordinated pyridine nitrogen (18×10^{-4} cm^{-1}) is quite large, indicating quite marked interaction between the unpaired electron in the d_{z^2} orbital and the pyridine nitrogen. It is larger than that observed for the cobalt(II) porphyrins [9] and phthalocyanins,[10] but similar to that observed for the vitamin B_{12r} and its derivatives with pyridine-type ligands.[11] The triplet splitting indicates that only one pyridine co-ordinates to the central cobalt(II) ion, even

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[37] A. Abragam, J. Horowitz, and M. H. L. Pryce, *Proc. Roy. Soc.*, 1955, *A*230, 169.

in pure pyridine. Whilst this does not exclude the possibility of weak association with solvent molecules in the sixth co-ordination site, it indicates that the complex is effectively five-co-ordinate in pyridine, having a square pyramidal structure.

A similar situation is observed for vitamin B_{12r},[12] and presumably results from the cobalt ion being displaced slightly out of the mean plane of the four pyrrole nitrogens towards the co-ordinating pyridine, thus preventing effective co-ordination at the other axial position. Monopyridine adducts of metalloporphyrins are also thought to adopt this conformation in solution.[38]

Having established that the unpaired electron of the cobalt(II) 1,19-diethoxycarbonyltetradehydrocorrin complex is in the d_{z^2} orbital in all these solvents, it is interesting to follow the variation of the excitation energy $\Delta_{z^2 \rightarrow xz,xy}$ Following the procedure used in the case of the cobalt(II) corrole anion, these are found to be 3 930, 6 560, and 7 140 cm^{-1} in THF, methanol, and pyridine respectively. Again, whilst not wishing to place too much significance on the numerical values of these energies, it may be noted that they indicate that the d_{z^2} orbital rises in energy with the increasing donor power of the axial ligand as might be expected, since the dominant effect of the axial ligands is a σ-donation of electrons.

CONCLUSIONS

The foregoing discussion has shown that these two complexes, although very similar in structure, exhibit different electronic ground states for the central cobalt(II) ion. The two situations are represented diagramatically in Figure 8. Unfortunately it is not possible to place all the cobalt 3*d* orbitals energetically in either case. It is certain, however, that the d_{xy} orbital of the cobalt(II) 1,19-diethoxycarbonyltetradehydrocorrin cation is highest in energy as for the cobalt(II) corrole anion, since this orbital is directed towards the four ligating pyrrole nitrogens. The position of the d_{z^2} orbital of the cobalt corrole anion, and $d_{x^2-y^2}$ orbital of the cobalt 1,19-diethoxycarbonyltetradehydrocorrin cation are uncertain, and have been placed lowest for clarity.

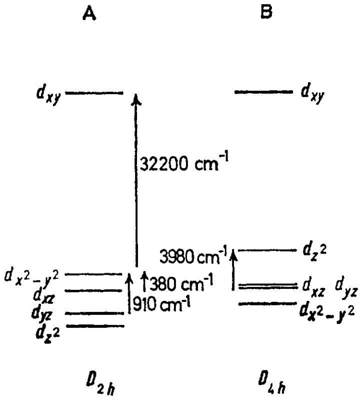

FIGURE 8 Orbital-energy diagram for the cobalt(II) ion of the cobalt(II) corrole anion (A) and cobalt(II) 1,19-diethoxycarbonyltetradehydrocorrin cation (B).

The situation represented by the cobalt tetradehydrocorrin cation complex is that usually observed for cobalt(II) porphyrins [10,18] cobalt(II) phthalocyanin,[11,19,23] and vitamin B_{12r} and its derivatives.[11] However, the situation represented by the cobalt corrole anion does not appear to have been observed previously in tetrapyrrole cobalt(II) complexes. There appear to be two possible explanations for the differences in the electronic structure of the cobalt ion in the complexes studied. The first is that the in-plane π-interaction between the pyrrole nitrogens and the cobalt $d_{x^2-y^2}$ orbital is likely to be somewhat greater in the case of the cobalt(II) corrole anion. This should result from the 1—20, 1—19, and 19—23 bonds being shorter, due to their double-bond character, thus forcing the pyrrole nitrogens into closer contact with the central cobalt ion. This would have the effect of raising the energy of the $d_{x^2-y^2}$ orbital relative to the d_{z^2} orbital, and in the present case raising it sufficiently to make it the highest occupied cobalt 3*d* orbital. It is worth pointing out in this context that the average diameter of the central cavity of the corrole ring in which the cobalt(II) ion sits is likely to be rather smaller than that in corresponding porphyrin and phthalocyanin complexes.* One would therefore expect greater interaction between the central metal ion and the ligand and hence greater electron delocalisation for the corrole complexes. This is reflected in the low values of *P* found for the corrole complexes.

An alternate explanation for the different ground states observed for the two complexes is based on the difference in charge of the two species. In the case of the anion, approach of donor-type molecules along the *z*-axis should be less favourable than in the case of the cation, owing to the negative charge of the species, as a whole, and probably an associated reduction of the positive charge of the central cobalt ion. Since the energy of the d_{z^2} orbital is largely determined by its interaction with axial ligands, in the absence of σ-donor ligands in these positions, the d_{z^2} orbital should be relatively low in energy. This is clearly illustrated by the increase in energy of the d_{z^2} orbital of the cobalt(II) 1,19-diethoxycarbonyltetradehydrocorrin cation complex with the increasing donor strength of the solvent. In the case of the cobalt(II) corrole anion in THF however, the axial interaction is evidently so weak that the d_{z^2} orbital is no no longer the highest occupied cobalt 3*d* orbital. Unfortunately, the e.s.r. spectrum of the cobalt corrole anion was not observed in pyridine, thus the electronic ground state of the cobalt(II) ion in this solvent is not known. However, since the electronic spectrum was unchanged from that in THF indicating very little interaction between the central cobalt(II) ion and the

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* As yet, no crystallographic studies have been made on cobalt corrole complexes. However, crystallographic studies of free-base corrole[39] indicate that the average diameter of the central cavity of the fully conjugated corrole ring is *ca.* 0·3 Å less than that of the porphyrin ring.

[38] C. B. Storm, *J. Amer. Chem. Soc.*, 1970, **92**, 1424.

[39] H. R. Harrison, O. J. R. Hodder, and D. C. Hodgkin, *J. Chem. Soc.* (*B*), 1971, 640.

solvent [*cf.* the cobalt(II) 1,19-diethoxycarbonyltetradehydrocorrin cation and the cobalt(III) corrole], it seems unlikely that the ground state of the cobalt ion has changed in pyridine. We would conclude therefore that the negative charge on the species tends to prevent further axial co-ordination, which in turn gives rise to a $d_{x^2-y^2}$ rather than d_{z^2} ground state for the cobalt(II) ion.

It seems likely that both the change in in-plane π-bonding and the charge effect contribute to the change in electronic ground state for the cobalt(II) ion in these two complexes.

Since this work was completed, two reports have appeared in which it was shown that the central cobalt(II) ion in cobalt salen and cobalt amben complexes may in certain solvents have the unpaired electron in the $d_{x^2-y^2}$ orbital rather than the d_{z^2} orbital.[40,41] In poor donor solvents, the complexes existed with the $(d_{yz})^2(d_{xz})^2(d_{z^2})^2d_{x^2-y^2}$ ground state, whilst in the presence of strong donor molecules they adopt the $(d_{yz})^2(d_{xz})^2(d_{x^2-y^2})^2d_{z^2}$ configuration. This effect was traced to the rise in energy of the d_{z^2} orbital with increasingly strong axial donation as described earlier, and nicely compliments and supports the present work.

Most notable was the discovery by Ochiai[40] that the $d_{x^2-y^2}$ state prevented oxygenation of the complex, and indeed, we found no evidence for the formation of oxygenated products of the cobalt(II) corrole anion. Exposure of the species to air simply resulting in its oxidation to the neutral cobalt(III) corrole.

It is quite conceivable that the effects previously described may operate in other cobalt(II) complexes, notably vitamin B_{12r} and its derivatives. Cockle *et. al.*[42] have recently reported the e.p.r. spectra of cobalt(II) corrins in both 'base-on' and 'base-off' forms in various aqueous solvent mixtures. These are remarkably similar to the spectra observed for the cobalt(II) 1,19-diethoxycarbonyltetradehydrocorrin cation in pyridine and methanol respectively, indicating that the d_{z^2} ground state is retained under these experimental conditions. However, the corrin ligand system is thought to be rather flexible,[43] and so may be capable of changing the electronic ground state of the cobalt(II) ion in non-co-ordinating solvents.

The results presented here and elsewhere[40,41] are not in agreement with the ligand-field calculations of Engelhardt and Green,[44] who conclude that the unpaired electron lies in the d_{z^2} orbital in all forms of cobalt(II) phthalocyanin, as well as vitamin B_{12r} and its model compounds. However, their results do show that variation of the ligand-field parameters can produce the $d_{x^2-y^2}$ ground state rather than the more normal d_{z^2} one.

Finally, we note that the complexity of the low-field e.p.r. signals of these and other cobalt(II) tetrapyrrole complexes may be explained in terms of very small changes in the energy separations between the ground and excited states due to changes of conformation and solvent environment. Since the energy separations are themselves rather small, even very small changes will produce quite marked changes in the e.p.r. spectrum. Also, for the cobalt(II) corrole anion in pyridine, it is possible that the lack of e.p.r. signal may be due to the ground and excited states being so close in energy that they provide a means of rapid spin relaxation.

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[40] E. Ochiai, *J.C.S. Chem. Comm.*, 1972, 489.

[41] L. M. Engelhardt, J. D. Duncan, and M. Green, *Inorg. Nuclear Chem. Letters*, 1972, **8**, 725.

[42] S. Cockle, H. A. O. Hill, S. Ridsdale, and R. J. P. Williams, *J.C.S. Dalton*, 1972, 297.

[43] R. A. Firth, H. A. O. Hill, J. M. Pratt, R. J. P. Williams, and W. R. Jackson, *Biochemistry*, 1967, **6**, 2178.

[44] L. M. Engelhardt and M. Green, *J.C.S. Dalton*, 1972, 724.