

TABLE I
THE CD DATA AND ABSOLUTE CONFIGURATIONS

| Complex | Isomer | Circular dichroism | | Config ^a (C ₂) |
|----------------------------------|--------------|--|------------------------------------|--|
| | | λ_{\max} , cm ⁻¹ | $(\epsilon_1 - \epsilon_2)_{\max}$ | |
| [Co(gly) ₂ (L-val)] | $\beta(+)$ D | 18,500 | +1.30 | Δ |
| | | 20,900 | -0.20 | |
| | $\beta(-)$ D | 18,800 | -2.00 | Δ |
| [Co(L-val) ₂ (gly)] | $\beta(+)$ D | 18,860 | +2.60 | Δ |
| | | 22,200 | -0.01 | |
| [Co(L-val) ₂ (L-ala)] | $\beta(+)$ D | 18,510 | +1.08 | Δ |
| | | 20,900 | -0.03 | |
| [Co(L-val) ₂ (D-ala)] | $\beta(-)$ D | 18,500 | +0.92 | Δ |
| [Co(L-val) ₂ (L-ala)] | $\beta(+)$ D | 20,900 | -0.02 | |
| [Co(L-val) ₂ (D-ala)] | $\beta(-)$ D | 18,860 | -2.00 | Δ |
| [Co(gly) ₂ (L-ala)] | $\beta(+)$ D | 18,510 | +1.36 | Δ |
| | | 20,900 | -0.02 | |
| [Co(L-ala) ₂ (D-ala)] | $\beta(+)$ D | 18,500 | +1.33 | Δ |
| | | 20,900 | -0.03 | |

^a The symbols Δ and Λ are based upon the convention proposed by T. S. Piper, *J. Am. Chem. Soc.*, **83**, 3908 (1961).

hand, the observed values are +1.30 and +1.08, respectively. The magnitude of the vicinal effect of L-valine was also calculated from the data for $\beta(+)$ D-[Co(L-val)₂(L-ala)] and $\beta(-)$ D-[Co(L-val)₂(D-ala)], but the value was a little higher than that obtained from the data for the tris(valinato) complexes. From these, we conclude that Douglas' additive rule is essentially true, but not exactly in the case of our complexes containing optically active valine.

The absolute configuration for β isomers of the tris(aminoacidato) complex has been related to that of the

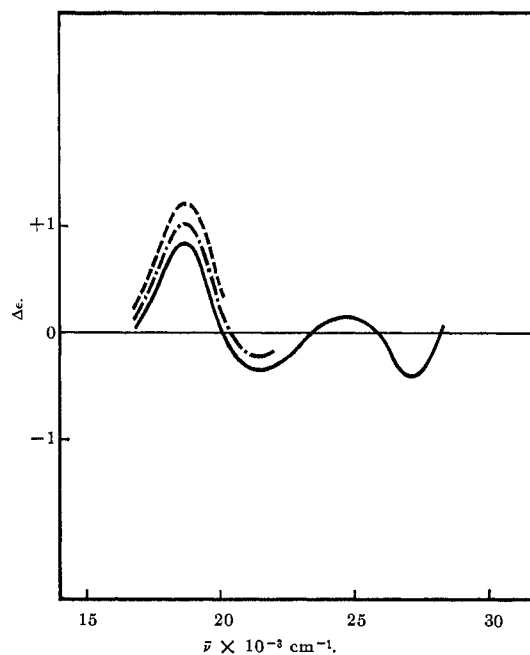


Figure 7.—Calculated CD curves for $\beta(+)$ D-[Co(gly)₂(L-val)] (---) and $\beta(+)$ D-[Co(L-val)₂(L-ala)] (- · -) and the observed CD curve for $\beta(+)$ D-[Co(L-val)₃] (—) (in 50% H₂SO₄).

tris(ethylenediamine)cobalt cation, while the absolute configuration for α isomers has been determined directly by an X-ray study.¹² By relating our CD spectra to the known data, we can assign the absolute configuration for the present isomers as is seen in Table I.

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An Electron Spin Resonance Study of a Low-Spin, Five-Coordinated Complex of Cobalt

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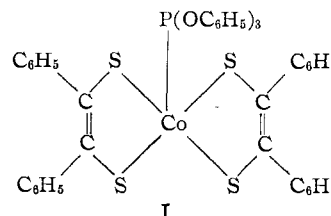
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The electron spin resonance study of a five-coordinated cobalt complex with $S = 1/2$ has been shown to be consistent with the geometry of a rectangular-based pyramid. The ligand hyperfine structure permitted a principal symmetry axis in the complex to be identified and thus helped to establish the configuration of the unpaired electron in the complex. An interpretation of the magnitude of the measured esr parameters is given which suggests that a significant amount of 3d-4p hybridization of the cobalt orbitals occurs in addition to the effects of covalency.

Introduction

Extensive studies of the square-planar bis-dithiodiketone complexes of transition metals have been reported.¹⁻⁴ Recently, the preparation of some five-coordinated derivatives of the bis compounds of iron and cobalt has been reported.⁵ In this report the

results of esr studies of the uncharged complex (I) of cobalt are given:



(1) G. N. Schrauzer and V. P. Mayweg, *J. Am. Chem. Soc.*, **84**, 3221 (1962).

(2) H. B. Gray, R. Williams, I. Bernal, and E. Billig, *ibid.*, **84**, 3596 (1962).

(3) A. H. Maki, N. Edelstein, A. Davison, and R. H. Holm, *ibid.*, **86**, 4580 (1964).

(4) G. N. Schrauzer and V. P. Mayweg, *ibid.*, **87**, 1483 (1965).

(5) G. N. Schrauzer, V. P. Mayweg, H. W. Finck, and W. Heinrich, *ibid.*, **88**, 4606 (1965).

A number of other compounds similar to I have also been studied in this laboratory and will be the subject of a future report. However, it appears that all of those studied thus far are quite similar to I and the purpose here is to provide a rationale for the whole class by explaining the relatively complete results obtained for I.

Experimental Section

The preparation of the complexes is discussed elsewhere.⁵ The esr experiments were performed on a Varian X-band spectrometer. The microwave frequencies were measured to wave-meter accuracy and the magnetic field measurements were made using a proton magnetometer along with a frequency counter. The glass studies at 77°K were made on chloroform-toluene mixtures and the host used for the dilute solid solutions was the isomorphous, diamagnetic iron complex.

Results

The solution spectrum of I consists of 16 lines. In addition to the cobalt (Co^{59} , $I = 7/2$) hyperfine structure of 8 lines, there is a small doublet splitting of each of these by the phosphorus (P^{31} , $I = 1/2$) nucleus. The solution Hamiltonian is

$$\mathcal{H} = g\beta H_0 S_z + AI_z S_z + aI_z' S_z \quad (1)$$

where the letters A and a refer to the cobalt and phosphorus nuclei, respectively. The measured parameters are: $g = 2.010 \pm 0.003$, $A = 23.7 \pm 0.6$ gauss, and $a = 7.9 \pm 0.6$ gauss.

Experiments on the rigid glasses and on a 1% solution of I in the Fe host gave similar results for the principal values of the g tensor and the cobalt hyperfine tensor. A comparison of the results of these two experiments is given below.

| | g_1 | A_1 , gauss |
|-------------------------------------|-------------------|----------------|
| Dilute glass at 77°K | 2.018 ± 0.004 | 52.6 ± 1.5 |
| 1% solution of Co in Fe at 300°K | 2.010 ± 0.004 | 54.0 ± 1.5 |

The spectrum exhibited nearly axial symmetry in both cases, but the principal values in the directions other than that designated 1 were not resolved. This designation is, of course, arbitrary and will be related to an axis system fixed in the complex. In another experiment, a 0.2% solid solution of Co in Fe was studied with the result that the lower-than-axial symmetry was resolved, as shown in Figure 1 along with the value of a_1 , *i.e.*, the phosphorus (P^{31}) hyperfine splitting along the principal axis designated 1. From these measurements the experimental parameters are computed as follows: $g_1 = 2.019$, $g_2 = 1.980$, $g_3 = 2.006$, $A_1 = 56.4$, $A_2 = 7.7$, $A_3 = \sim 0$, $a_{1\parallel} \cong a_{1\perp} = 10.4$, and $a_2 \cong a_3 \cong a_{\perp} = 6.6$. (Computed from the measured isotropic and parallel values of the tensor a . The symbolic subscripts $_{\parallel}$ and $_{\perp}$ anticipate the detailed arguments which follow.) The accuracy of these results is greatest along the direction 1, and the over-all accuracy may be appreciated by a comparison of the average values of g and A from the dilute solid and liquid solutions

| | g | A , gauss |
|------------------------|-------------------|----------------|
| Dilute solid solution | 2.002 ± 0.004 | 21.4 ± 1.0 |
| Dilute liquid solution | 2.010 ± 0.003 | 23.7 ± 0.6 |

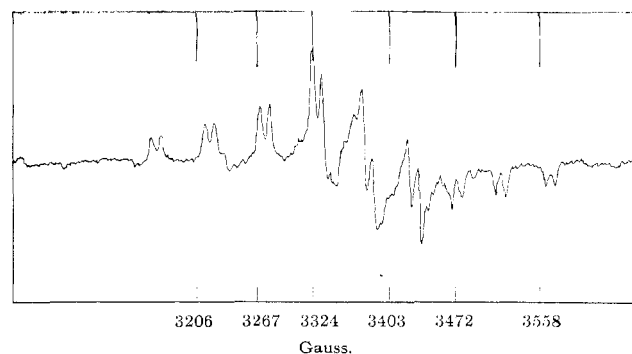


Figure 1.—Esr spectrum of the cobalt complex in dilute solid solution.

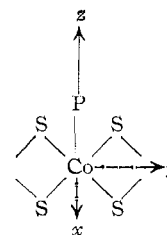
The specific effects of the solvent could account for the slight discrepancies observed.

Discussion

The objective here is to determine the particular 3d metal orbital which comprises that part of the molecular orbital containing the odd electron.⁶⁻⁹ The assignment is based primarily on the symmetry properties of the complex as deduced from the esr spectrum. Comparisons of the magnitude of the measured esr parameters with those based on the appropriate free ion (or atom) are also used in this regard.

It should be pointed out that it is not entirely clear just what the total occupancy of the d orbitals is—that is, whether the complex is properly viewed as a Co(II) $3d^7$ derivative with two monovalent bidentate ligands $\text{R}_2\text{S}_2\text{C}_2^-$, or as a Co(IV) derivative with two divalent ligands $\text{R}_2\text{C}_2\text{S}_2^{2-}$. (There is in addition, of course, the fifth ligand—an uncharged phosphite.) It is not possible to draw any definite conclusions on this point in the present investigation, but the results are perhaps intuitively more compatible with the first of these two views as discussed below.

The first step is to assume a principal axis system in the complex. The following choice of axes is convenient



where the z axis is perpendicular to the page, which contains the xy plane.

The additional assumption is made that the principal axes for the Co^{59} and P^{31} hyperfine tensors are collinear with the z axis in the complex. This assumption is justified by the following considerations. Subtracting the isotropic part of the phosphorus splitting we have $a_{z^*} = a_{\parallel} - a = 2.5$ gauss and $a_{\perp}^* =$

(6) J. H. Van Vleck, *J. Chem. Phys.*, **3**, 807 (1935).

(7) K. W. H. Stevens, *Proc. Roy. Soc. (London)*, **A219**, 542 (1953).

(8) J. Owen, *ibid.*, **A227**, 183 (1955).

(9) M. Tinkham, *ibid.*, **A236**, 549 (1956).

TABLE I
MATRIX ELEMENTS OF \mathcal{H}_{Co} (EQ 2) IN PURE d ORBITALS

| 3d orbital | A_z | A_y | A_x | P, cm^{-1} | κ | $A_{ }$ | A_{\perp} |
|----------------|--------------------|--------------------|--------------------|---------------------|----------|----------|-------------|
| $d_{x^2-y^2}$ | $P(-\kappa + 2/7)$ | $P(-\kappa + 2/7)$ | $P(-\kappa - 4/7)$ | 0.0058 | +0.35 | - | - |
| | | | | 0.0066 | +0.23 | - | + |
| d_{xz} | $P(-\kappa + 2/7)$ | $P(-\kappa - 4/7)$ | $P(-\kappa + 2/7)$ | | | | |
| d_{yz} | $P(-\kappa - 4/7)$ | $P(-\kappa + 2/7)$ | $P(-\kappa + 2/7)$ | | | | |
| $d_{3z^2-r^2}$ | $P(-\kappa - 2/7)$ | $P(-\kappa - 2/7)$ | $P(-\kappa + 4/7)$ | 0.0058 | -0.35 | + | + |
| | | | | 0.0066 | -0.23 | + | - |
| d_{xy} | $P(-\kappa + 2/7)$ | $P(-\kappa + 2/7)$ | $P(-\kappa - 4/7)$ | 0.0058 | +0.35 | - | - |
| | | | | 0.0066 | +0.23 | - | + |

$a_{\perp} - a_{||} = -1.3$ gauss. If the dominant mechanism for the anisotropic part of the splitting is a direct dipole-dipole interaction, then their ratio should be

$$\frac{a_{||}^*}{a_{\perp}^*} = \frac{(3 \cos^2 \theta - 1)_{\theta=0}}{(3 \cos^2 \theta - 1)_{\theta=\pi/2}} = -2$$

This is in good agreement with the experimental ratio of -1.9 . A further check involves the value of the "bond distance," R , computed from the experimental results, assuming no delocalization. This is intended merely to serve as an order of magnitude check on the absolute values obtained. The appropriate expression is

$$a_z^* = \frac{4\gamma\beta\beta_n}{\langle R^3 \rangle}$$

where $\gamma\beta_n$ is the P^{31} nuclear magnetic moment and β is the Bohr magneton. From $a_z^* = 2.5$ gauss, one computes a value of $R = 2.09$ Å which is comparable with the Co-P distances (*ca.* 2.2 Å) observed in various cobalt-phosphine complexes.¹⁰ This distance is perhaps a bit shorter than one might expect in view of the rather substantial delocalization discussed below. However it is not too surprising in view of the sizable experimental uncertainty in a_z^* and also due to the inherent limitations implied in the use of this simple model.

The conclusion of the foregoing arguments is that the z axis along the Co-P bond and the principal axis labeled 1 are identical.

As a further check of the data several small, dilute (5% Co in Fe), single crystals of the complex were grown. The spectra of the four different crystals studied exhibited similar orientation dependencies and revealed the presence of only one kind of magnetic complex per unit cell. (Preliminary X-ray studies of an isomorphous complex revealed a triclinic unit cell with two molecules per unit cell.¹¹) Since the faces of these small crystals were not well developed, the crystals were mounted in several arbitrary planes until something close to the maximum (56.6 gauss) and minimum (estimated ~ 4 gauss) Co hfs splittings were observed. These results are quite consistent with all of the other measurements in glasses and solid solutions corresponding to z and the $x \sim y$ principal axes, respectively.

The next step in the discussion is to consider the individual 3d orbitals in terms of a simplified model. It is to be expected that the d_{xy} orbital is used in strong σ bonding and that its antibonding counterpart is considerably raised in energy. One might also anticipate that the $d_{3z^2-r^2}$ orbital will be utilized in σ bonding between the metal and the phosphite ligand, but the possibility of occupancy of either of these orbitals is not excluded here.

The procedure is to compare the relative values of the measured esr parameters with those calculated from theory for each of the five orbitals $d_{x^2-y^2}$, d_{zz} , d_{yz} , d_{xy} , and $d_{3z^2-r^2}$. The one which gives the best agreement with experiment is then taken to be the most probable configuration.^{3,12}

Before proceeding further, the experimental fact of the small anisotropy in the g tensor of the complex should be noted.

One can therefore ignore the spin-orbit coupling as a first approximation and take the pure 3d states as proper eigenfunctions. The pertinent spin Hamiltonian for computation of the first-order perturbation energy of the cobalt hyperfine interaction along the three principal directions is^{12,13}

$$\mathcal{H}_{\text{Co}} = 2\gamma\beta\beta_n \left[\frac{3(\mathbf{r} \cdot \mathbf{s})(\mathbf{r} \cdot \mathbf{I})}{r^5} - \frac{\mathbf{S} \cdot \mathbf{I}}{r^3} + \frac{8\pi}{3} \mathbf{S} \cdot \mathbf{I} \delta(\mathbf{r}) \right] \quad (2)$$

For example, the expression for A_z in the $3d_{xz}$ orbital is

$$A_z = \frac{2\gamma\beta\beta_n}{\langle r^3 \rangle} \left\langle 3d_{xz} \left| \frac{z^2}{r^2} - 1 - \kappa \right| 3d_{xz} \right\rangle \quad (3)$$

The symbol κ denotes the contact interaction. Explicit account of covalent bonding is not taken here, but rather the quantity $P = 2\gamma\beta\beta_n / \langle r^3 \rangle$ is regarded as a parameter whose departure from the free-ion value may be attributed chiefly to the effects of covalency.

The results obtained, along with the values of $P = 2\gamma\beta\beta_n / \langle r^3 \rangle$ and κ which are fitted to the experimental results, are shown in Table I along with the sign choices in the last two columns for $A_{||}$ and A_{\perp} which lead to a positive value of P as required for cobalt. In view of the approximations of complete quenching of orbital angular momentum and of the consequent suppression of spin-orbit coupling, the following relationships

(12) J. S. Griffith, "The Theory of Transition Metal Ions," Cambridge University Press, London, 1961.

(13) A. Abragam and M. H. L. Pryce, *Proc. Roy. Soc. (London)*, **A205**, 135 (1951).

(10) J. A. Bertrand and D. L. Plymale, *Inorg. Chem.*, **5**, 879 (1966).

(11) A. E. Smith, Shell Development Co., private communication.

have been employed to simplify the computations of P and κ

$$A_z = A_{||}; \quad A_x \sim A_y \approx A_{\perp} = \frac{A_x + A_y}{2}$$

The orbitals d_{xz} and d_{yz} are rejected at this point since they do not fit the experimental results which show $A_z > A_x \sim A_y$.

It is helpful to consider the values of P for the remaining orbitals. Using Freeman and Watson's calculated values¹⁴ of $\langle r^{-3} \rangle$ for the Co^{2+} , Co^{3+} , and Co^{4+} ions, the respective values of P are 0.0257, 0.0286, and 0.0317 cm^{-1} . They are larger than the derived values in the range of 0.006 cm^{-1} for these orbital choices by a factor of 4 or 5. It would thus appear that the unpaired electron is in an orbital which has a significant covalent character. On this basis one might intuitively reject the $d_{x^2-y^2}$ orbital as a proper assignment since it is nominally nonbonding in the σ system and can π bond with only in-plane sulfur atoms—an effect that is not expected to be very important. For the $3d_{3z^2-r^2}$ orbital both choices of sign give nearly the same value of P and negative values of κ . The approximate value of κ derived from experimental data on ions of the 3d transition group is $\kappa \cong 0.3$.¹⁵ This would seem at first to eliminate the $d_{3z^2-r^2}$ orbital as a possibility. However, the 4s orbital of the metal belongs to the same symmetry representation (designation A_1) as the $d_{3z^2-r^2}$ orbital under the symmetry group of an assumed tetragonal pyramid, C_{2v} , and d-s hybridization may occur. The contribution from the 4s orbital to κ is opposite in sign to that from the 3d "core polarization," and, if the former dominates, the sign of κ could change. An example where this is important is discussed by Griffith for a square-planar Co(II) complex.¹⁶ The amount of hybridization required to give the observed result (following Griffith) based on an orbital of the type

$$\chi \approx (3d_{3z^2-r^2}) \cos \beta + (4s) \sin \beta$$

corresponds to $\sin^2 \beta = 0.14$. This is a substantial but physically plausible admixture and does not permit the exclusion of the $d_{3z^2-r^2}$ orbital as a possibility.

However, the isotropic P^{31} hfs does allow a decision to be reached on this point. To do this, an estimate is required of the magnitude of the constant, a , based on the assumption that the unpaired electron is in the $d_{3z^2-r^2}$ orbital. In this case, the odd electron resides in the antibonding σ MO and has a component on the phosphorus which we take to be an sp^3 hybrid orbital of the form (ignoring overlap)

$$\phi \approx \alpha(3d_{3z^2-r^2}) - (1 - \alpha^2)^{1/2} \sigma_L$$

where

$$\sigma_L \approx 1/2[(3s) + (3p_x) + (3p_y) + (3p_z)]$$

The 3s portion of the ligand contribution σ_L places an unpaired electron spin density at the P^{31} nucleus and thus provides the mechanism for a finite a .

A value of the orbital coefficient, α , must be derived from the experimental results to see if it is a plausible number.^{8,9} To do this, one must first evaluate the quantity $|\psi_{3s}(0)|^2$ for the phosphorus atom. From the Hartree-Fock wave function given by Clementi,¹⁷ this quantity has the value of $3.798 \times 10^{25} \text{ cm}^{-3}$. Taking account of the factor of $1/4$ due to sp^3 hybridization, we get the theoretical value

$$a = (4/3)\pi\beta\gamma\beta_n|\Psi_{3s}(0)|^2 = 0.0858 \text{ cm}^{-1}$$

In magnetic field units $a = 919$ gauss. An experimental value of 1350 gauss was obtained by Morton¹⁸ for the P^{31} hfs in the radical $\cdot\text{PF}_4$ produced by irradiation of polycrystalline NH_4PF_6 . That this radical is tetrahedral is shown by the equivalence of the fluorine atoms as manifested in the F^{19} hfs, as well as the fact that the alternative square-planar configuration would exhibit a much smaller hfs since the odd electron would be expected to occupy the lone p orbital not used in the dsp^2 planar hybrid bond and would thus possess no s character in the first approximation.

The squared coefficient of σ_L in the antibonding orbital Φ is

$$1 - \alpha^2 \approx \frac{a_{\text{exptl}}}{a_{\text{theoret}}} = \frac{7.9}{919} = 0.008$$

This is far too small to be very realistic and in addition is incompatible with the large reduction in the orbital parameter P , mentioned earlier. This conclusion is even more emphatic if the experimental value for $\cdot\text{PF}_4$ is used. On the basis of this very large discrepancy in the isotropic P^{31} hfs, the $3d_{3z^2-r^2}$ orbital is eliminated. This process of elimination leads to the conclusion that the $3d_{xy}$ orbital is the dominant metal component of the molecular orbital occupied by the unpaired electron. This result is in disagreement with a recent assignment⁵ based in part on optical spectra, in which the odd electron is placed in a ligand-based orbital with a $3d_{yz}$ metal component. It might be well to observe that the results of the present investigation are not inconsistent with the view of the complex as a Co(II) $3d^7$ derivative bound to the two ligands $(\text{C}_6\text{H}_5)_2\text{C}_2\text{S}_2^-$ and the triphenyl phosphite ligand. In this view, the nominal configuration in terms of holes is $3d^2_{3z^2-r^2}$, $3d^1_{xy}$. There are still some difficulties, however, which must be resolved. The first of these is the choice of signs which give different values for the parameters for $3d_{xy}$ as shown in Table I. The experimental value of the isotropic hfs obtained from solution (*viz.* 23.7 gauss), requires that the hyperfine tensor components have the same sign. The resulting values of the parameter from Table I are $\kappa = 0.35$ and $P = 0.0058 \text{ cm}^{-1}$. The point which must now be considered is that the magnitude of the parameter P is significantly smaller than the

(14) A. J. Freeman and R. E. Watson, "Magnetism," Vol. IIA, G. T. Rado and H. Suhl, Ed., Academic Press Inc., New York, N. Y., 1965.

(15) A. Abragam, J. Horowitz, and M. H. L. Pryce, *Proc. Roy. Soc. (London)*, **A230**, 169 (1955).

(16) J. S. Griffith, *Discussions Faraday Soc.*, **26**, 81 (1958).

(17) E. Clementi, unpublished supplementary tables to the article: *IBM J. Res. Develop.*, **9**, 2 (1965).

(18) J. R. Morton, *Can. J. Phys.*, **41**, 706 (1963).

calculated values given earlier and in fact amounts to only 20–30% of the “free-ion” value. This would apparently correspond to a predominantly ligand-based orbital with considerable ionic character of the type M^+L^- and would thus contradict the plausible expectation that the electron is in an antibonding σ orbital with its main component on the metal ion. A possible explanation for this apparent discrepancy could be as follows. Since the complex does not possess inversion symmetry, mixing of orbitals of opposite parity (*e.g.*, d and p orbitals) may occur through the agency of the crystal field. If, in addition, the appropriate molecular symmetry group is C_2 (or lower), then all of the 3d orbitals may form 3d–4p hybrids. For example, d_{xz} and d_{yz} belong to the same representation (B) as do p_x and p_y and thus may form hybrids with one another. The orbitals d_{xy} , $d_{3z^2-r^2}$, and $d_{x^2-y^2}$ belong to the same symmetry representation (A) as does p_z with which they may form hybrids. Suppose, for instance, that all of the 3d orbitals form hybrids of the type

$$\varphi_h \sim \rho 3d + (1 - \rho^2)^{1/2} 4p$$

Then all of the matrix elements of the orbital angular momentum and the spin–orbit coupling between the modified orbitals have a reduced 3d contribution to the esr parameters. Thus P' (*i.e.*, the free-ion parameter) becomes approximately $\rho^2 P'$. Of course, the 4p orbitals will contribute also, but their contributions are smaller and may even tend to cancel those from the 3d orbitals in certain cases.¹⁹ The free-ion parameter is further reduced owing to the effects of covalent bonding by the factor α^2 where α is the admixture coefficient of the 3d_{xy} orbital in the antibonding σ molecular

orbital. The combined result of these two effects has the approximate form $P_{\text{exptl}} \sim \alpha^2 \rho^2 P'$.

If one takes the somewhat arbitrary but plausible values of $\rho \sim 0.9$ and $\alpha \sim 0.7$, one gets $P_{\text{exptl}} \sim 0.4P'$, which is approaching the experimental result. This qualitative result is probably all that can be done at this time since the crystal structure is not yet complete and the actual geometry of the complex is not known. Even greater difficulties arise from the fact that there are so many bonding possibilities and therefore so many bonding parameters to be accounted for, detailed calculations are not warranted.

One further fact needs to be explained, namely, the existence of an isotropic hfs from the phosphorus nucleus. This could readily be accounted for by a small admixture of the 4s, the 4p_z, or the 3d_{3z²-r²} orbital with the 3d_{xy} orbital. These admixtures are possible under the assumed symmetry (C_2) and would give rise to a finite density of unpaired electron at the phosphorus nucleus *via* the σ (anti)bonding of the cobalt with the phosphite ligand.

In summary, the symmetry properties of the cobalt and phosphorus hyperfine tensors have been used along with the isotropic phosphorus hfs to infer the configuration of the unpaired electron. To explain the magnitudes of the cobalt hfs parameters, a significant amount of 3d–4p hybridization was invoked along with some appreciable covalent character in the designated orbital.

Acknowledgment.—The author is indebted to Dr. V. P. Mayweg, who prepared the cobalt and iron compounds used in this study. Stimulating discussions with Dr. G. N. Schrauzer, pertaining to the chemistry of complexes of the type described here, are gratefully acknowledged.

(19) C. A. Bates, W. S. Moore, K. J. Standley, and K. W. H. Stevens, *Proc. Phys. Soc. (London)*, **79**, 73 (1962).