ligand X is sufficiently small by comparison to the tertiary phosphine to permit expansion of the P–Cu–P angle. This effect is especially well illustrated by compound **8** which contains the very crowded tricyclohexylphosphine ligand; here the P–Cu–P angle opens to 140° (compare compound **7**). In compound **11** there are three phosphine ligands bonded to copper, which results in a reduction of the average P–Cu–P angle to ~115°.

One of the more noteworthy features of the results summarized in Table I is the variation in P–Cu–P angle in $((C_6H_5)_3P)_2CuX$ compounds (1–5, **7**, **9**, **10**) with choice of anion. This trend can also be explained purely on steric grounds, and, while alternative explanations exist,[3,4] they involve complicating assumptions and will not be considered further. In particular, the largest angles occur in compounds where the X group is (to a first approximation) planar (NO_3^-, $Cl_2CuP(C_6H_5)_3^-$), and the smallest angles occur in compounds where the shortest Cu–X bonds are and where X is decidedly more bulky ($B_3H_8^-$, BH_4^-, and possibly the puckered azide dimer, **10**). Since the phenyl ring protons of the $(C_6H_5)_3P$ ligands extend well across the P–Cu–X angles,[1–4] the P–Cu–P angle can open only until there is a balance between nonbonded repulsions of $(C_6H_5)_3P$–$(C_6H_5)_3P$ and $(C_6H_5)_3P$–X types. Wherever possible there will be relief of intramolecular, interligand crowding, as illustrated by the rotation of the thienyl group in **2** so that the sulfur atom points away from the rest of the molecule and by the preference in the two $(C_6H_5)_2$-CH_3P complexes **6** and **11** for the rotational conformer which directs the methyl groups toward the anion. Comparison of the geometries for compounds **5** and **6** is especially revealing, where substitution of $(C_6H_5)_2$-CH_3P for $(C_6H_5)_3P$ reduces the steric interactions between phosphine and hydroborate groups with a resultant increase of 8° in the P–Cu–P angle.

As shown in Figure 1, there is a very approximate correlation among the P–Cu–P angles and Cu–P distances for the various $((C_6H_5)_3P)_2CuX$ compounds. The trend may be somewhat better than it appears from the figure, since no attempt has been made to correct for the widely variant electronic properties and chelate ring sizes of the anions, but there is clearly a need for more data. The increase in the per cent s character in the copper–phosphorus bonds with increasing angle results in shorter Cu–P distances, as would be expected from steric as well as theoretical considerations.[12] In the extreme case of $((C_6H_5)_3P)Cu(\pi$-$C_5H_5)$, the distance of 2.135 (1) Å is the shortest yet observed for a Cu–P bond, a result which has been attributed at least in part to steric factors.[13]

It is interesting to focus on the three β-diketonate complexes, **1–3**, where intramolecular steric interactions are nearly constant. The most electron donating of these ligands is trifluoroacetylacetonate, and compound **1** is observed to have the shortest Cu–O bond lengths. Correspondingly, the Cu–O bond lengths in the hexafluoroacetylacetonate complex, **3**, are longer. A parallel, but inverse, trend occurs in the Cu–P bond distances for these three compounds indicating that, as the donor strength of the anion varies, an adjustment occurs in the copper–phosphorus σ bonding in order to main-

tain a balance of total charge density contributed by the ligands to the copper atom.[14–16] It may be noted (Table I) that the P–Cu–P angles follow nearly the same trend, with the greater steric relief of the TTA ligand (the thienyl group is planar and almost coplanar with the β-diketonate backbone) allowing the P–Cu–P angle to open a little more. It is also of interest that, since the donor strengths of the β-diketonate ligands correlate with the Cu–P bond lengths, copper–phosphorus back (π)-bonding appears to be minimal. If π bonding were operative, the Cu–P distances would be expected to decrease as negative charge accumulated on the copper atom.

Although the foregoing discussion has been specifically limited to copper(I) complexes with tertiary phosphine ligands, the conclusions are considered to be more generally applicable, especially to four-coordinate d^{10} systems where substantial metal–ligand π bonding is absent. For example, it would appear that structural results for certain Zn(II) complexes containing nitrogen and chloride donor ligands[17] could be explained in an analogous manner, although extensive data are not available.[18,19] The appearance of new structural results which should be "predictable" by inductive reasoning from the five generalizations will be of interest.

(14) The inductive effect of the β-diketonate anion alters the net positive formal charge on the copper atom resulting in weaker (longer) or stronger (shorter) Cu–P bonds. The concept of ligand inductive effects has been introduced by previous investigators, for example, in the interpretation of electronic[15] or infrared[16] spectral results.

(15) D. A. Rowley and R. S. Drago, *Inorg. Chem.*, **7**, 795 (1968).

(16) W. A. G. Graham, *ibid.*, **7**, 315 (1968), and references cited therein.

(17) H. S. Preston and C. H. L. Kennard, *J. Chem. Soc. A*, 1956 (1969).

(18) In at least one instance,[19] the existence of interligand nonbonded interactions has actually been cited in partial support of the formulation of a species, the $Ir(NO)_2(P(C_6H_5)_3)_2^+$ cation, as a tetrahedral d^{10} rather than a planar d^8 complex, since planar d^8 compounds generally show only small distortions due to intramolecular steric factors.

(19) D. M. P. Mingos and J. A. Ibers, *Inorg. Chem.*, **9**, 1105 (1970).

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Reevaluation of the Dipolar Contribution to the Contact Shifts of the Square-Planar Complex Bis(dithioacetylacetonato)cobalt(II)

Sir:

Recently,[1] we have interpreted the nmr contact shift data for the square-planar complex $Co(SacSac)_2$

(12) H. A. Bent, *Chem. Rev.*, **61**, 275 (1961).

(13) F. A. Cotton and J. Takats, *J. Amer. Chem. Soc.*, **92**, 2353 (1970).

(1) R. J. Fitzgerald and G. R. Brubaker, *Inorg. Chem.*, **8**, 2265 (1969).

(SacSac = dithioacetylacetonato) in terms of an "axial field" model, where the z axis was the principal axis. However, we cautioned at that time, "...in the event that the anisotropy lies in the xy plane, as in the cobalt–maleonitriledithiolato complex,[2] our conclusions (would) be altered." Subsequent to our investigation, an esr and bulk magnetic anisotropy study[3] has shown that there is a large in-plane anisotropy for this complex. In addition, recent articles[4–6] have suggested that second-order Zeeman effects may contribute substantially to the dipolar shifts in transition metal complexes.

We present here a reinterpretation of our data consistent with the anistropy measurements and an evaluation of the importance of second-order Zeeman terms to the dipolar shifts in this complex.

Before discussing the implications for bonding, as deduced from the contact shift data, we must evaluate the dipolar contribution to the observed isotropic shifts. Since the crystal structure,[7] g-tensor anistropy,[3] and bulk susceptibility anisotropy[3] are known, we can calculate both the dipolar shifts and the second-order Zeeman contribution to the *dipolar* shifts. We define our coordinate axes according to the convention of Gregson, *et al.*, as shown in Figure 1. The x axis is now
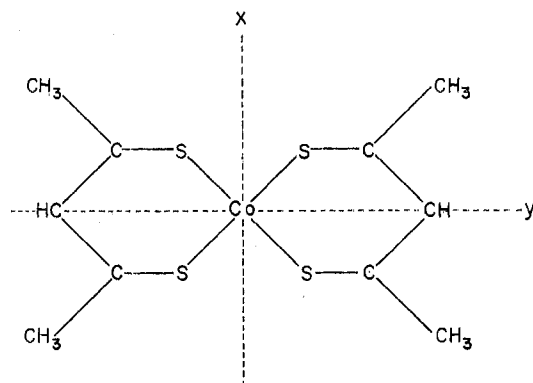

Figure 1.—The coordinate-axis system for Co(SacSac)₂. The z axis is perpendicular to the plane of the paper.

the principal axis and the factors necessary for the calculation of the dipolar shift in Co(SacSac)₂ are given in Table I. These symbols have been defined by us previously.[1]

TABLE I
DIPOLAR FACTORS FOR Co(SacSac)₂

Group	$((3\cos^2\theta - 1)/r^3 \times 10^{-21})$	$g_{\|}{}^a$	$g_{\perp}{}^a$	$10^6\chi_{\|}{}^a$	$10^6\chi_{\perp}{}^b$
CH	8.85	3.28	1.90	3567	1397
CH₃	0.132	3.28	1.90	3567	1397

a Data taken from ref 3. *b* Data taken from ref 3: $\chi_{\perp} = \chi_y + \chi_z/2$.

The value of the geometric factor for the methyl group, which is free to rotate about its C_3 axis, repre-

(2) A. H. Maki, N. Edelstein, A. Davison, and R. H. Holm, *J. Amer. Chem. Soc.*, **86**, 4580 (1964).
(3) A. K. Gregson, R. L. Martin, and S. Mitra, *Chem. Phys. Lett.*, **5**, 310 (1970).
(4) W. D. Horrocks, Jr., *Inorg. Chem.*, **9**, 690 (1970).
(5) J. R. Kurland and B. R. McGarvey, *J. Magn. Res.*, **2**, 286 (1970).
(6) B. R. McGarvey, *J. Chem. Phys.*, **53**, 86 (1970).
(7) R. Beckett and B. F. Hoskins, *Chem. Commun.*, 909 (1967).

sents the average of the geometric factors calculated by program MEGOM for every 15° increment. Although magnetic measurements show the complex to be slightly rhombic,[3] we have treated it as possessing axial symmetry.

We can then calculate the dipolar contribution, using Jesson's equation[8]

$$\frac{\Delta\nu}{\nu_0} = -\frac{\beta_e^2 S(S+1)(3\cos^2\theta_i - 1)(3g_{\|} + 4g_{\perp})(g_{\|} - g_{\perp})}{45kTr^3} \tag{1}$$

We can also calculate the dipolar contribution, including second-order Zeeman effects, using an equivalent equation due to Horrocks[4]

$$\frac{\Delta\nu}{\nu} = -\frac{\left[\chi_{\|}/5 + \frac{(\chi_{\|}\chi_{\perp})^{1/2}}{15} - \frac{4\chi_{\perp}}{15}\right](3\cos^2\theta_i - 1)}{Nr_i^3} \tag{2}$$

The results of these calculations are given in Table II.

TABLE II
DIPOLAR SHIFT DATA (Hz) FOR Co(SacSac)₂

Group	$\Delta\nu_i{}^a$	$\Delta\nu_i{}^b$	Second-order Zeeman contribution
CH	+445	+432	−13
CH₃	+8	+6	−2

a Calculated according to eq 1. *b* Calculated according to eq 2.

The separation of our data into observed isotropic shifts, dipolar contributions, and Fermi contact shifts is given in Table III.

TABLE III
CONTACT SHIFT DATA (Hz) FOR Co(SacSac)₂

Group	ν_{obsd}	ν_D	ν_F
CH	+218	+432	−214
CH₃	+64	+6	+57

Originally, we concluded that the unpaired electron in this complex resided in the d_{z^2} orbital on the basis of the *small magnitude* of the Fermi contact shift. This would produce a ^2A_g ground state. Our conclusion is unaltered and has been substantiated on the basis of later work.[3]

However, we must alter the mechanism by which the unpaired electron spin density reaches the ligand protons. This may now be understood as an admixture of the 4s and 3d$_{z^2}$ orbitals which both transform as a_g under D_{2h} symmetry. This mechanism is similar to that postulated by Ingram, *et al.*, for the β-cobalt(II)–pthalocyanine complex.[9]

Thus, the second-order Zeeman contributions to the dipolar shift in this complex are extremely small. We also note that these results differ substantially from those presented elsewhere.[10]

(8) J. P. Jesson, *J. Chem. Phys.*, **47**, 579 (1967).
(9) J. F. Gibson, D. J. E. Ingram, and D. Schonland, *Trans. Faraday Soc.*, **26**, 72 (1958).
(10) W. D. Horrocks, Jr., Joint Conference, American Chemical Society–Chemical Institute of Canada, Toronto, Canada, May 1970.

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