Table VI. Bond Distances (Å) for Selected Phosphine and Phosphite Derivatives of $Cr(CO)_6$

complex	Cr–P	Cr–CO(trans)	C–O(trans)	Cr–CO(cis)	C–O(cis)
fac-$Cr(CO)_3(PEt_3)_3$	2.429 [8]	1.829 [8]	1.162 [3]		
$Cr(CO)_5(PPh_3)^1$	2.422 (1)	1.845 (4)	1.154 (5)	1.880 [11]	1.150 [5]
cis-$Cr(CO)_4(PH_3)_2{}^{16}$	2.349 (2)	1.847 (4)	1.162 (6)	1.914 (7)	1.113 (33)
fac-$Cr(CO)_3(PH_3)_3{}^4$	2.346 (4)	1.84 (1)	1.16 (1)		
cis-$Cr(CO)_2(PH_3)_4{}^5$	2.338 $(4)^a$ 2.282 $(4)^b$	1.817 (7)			
$Cr(CO)_5[P(OPh)_3]^1$	2.309 (1)	1.861 (4)	1.136 (6)	1.896 [6]	1.131 [3]
trans-$Cr(CO)_4[P(OPh)_3]_2{}^{17}$	2.252 (1)			1.878 [4]	1.140 [6]

[a] Trans to CO. [b] Trans to another phosphine ligand.

[average = 2.429 [8] Å]—represent the longest chromium(0)–phosphorus bonds characterized to date (see Table VI). Of particular interest is a comparison with the closely related species *fac*-$Cr(CO)_3(PH_3)_3$,[4] in which the Cr–P distances average 2.346 (4) Å. The longer Cr–P distances in *fac*-$Cr(CO)_3(PEt_3)_3$ suggest a weakening of the Cr–P bonds caused by steric interactions between the adjacent PEt_3 ligands.

The short Cr–CO bond lengths [1.829 [8] Å (average)] and long C–O bond lengths [1.162 [3] Å (average)] in *fac*-$Cr(CO)_3(PEt_3)_3$ are consistent with strong d_π–π^*(CO) backdonation and suggest that PEt_3 behaves essentially as a σ-donor ligand, with little or no π-acceptor capability.

Acknowledgment. This work was supported by the National Science Foundation and by the donors of the Petroleum Research Fund, administered by the American Chemical Society.

Registry No. *fac*-$Cr(CO)_3(PEt_3)_3$, 73505-52-9; $Na^+[Mn(CO)_5^-]$, 13859-41-1.

Supplementary Material Available: Tables of structure factors and data processing formulas (10 pages). Ordering information is given on any current masthead page.

Correspondence

Effects of Planar and Tetrahedral Distortions on the ESR Parameters of Bis(salicylaldiminato)copper(II) Complexes

Sir:

Many papers have been dealing with pseudotetrahedral copper(II) complexes[1-4] and much is known on the ESR parameters of such compounds as well as of similar chromophores present in naturally occurring compounds like the blue proteins.[5,6] In order to avoid exchange narrowing effects which might wash out any hyperfine interaction, researchers often have diluted the paramagnetic complexes into diamagnetic host lattices. The host lattice, however, may induce some changes on the geometry of the guest complex with respect to the geometry of the pure paramagnetic complex.[7] This is well-known to happen for example for the complex bis(*N*-methylsalicylaldiminato)copper(II) which is planar when pure but is able to undertake the dimeric five-coordinate structure of the host zinc(II) complex.[8]

In order to better understand the effects of a pseudotetrahedral distortion upon a planar chromophore with respect to the ESR parameters, we studied a series of bis(*N*-alkylsalicylaldiminato)copper(II) complexes.

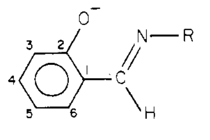

Table I. ESR Data of Some Bis(salicylaldiminato)copper(II) Complexes

compd	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}{}^a$	$A_{\perp}{}^a$	g_0	$A_0{}^a$
(Cu,Zn)-5-Me-Sal-*i*-Pr	2.27	2.03–2.11	113			
(Cu,Pd)-5-Me-Sal-*i*-Pr	2.22	2.04	186			
(Cu,Zn)-3-Me-Sal-*i*-Pr	2.27	2.03–2.11	120			
(Cu,Pd)-3-Me-Sal-*i*-Pr	2.22	2.05	186			
(Cu,Ni)Sal-Et	2.22	2.05	194			
(Cu,Pd)Sal-Et	2.22	2.05	194			
(Cu,Ni)Sal-*n*-Pr	2.22	2.05	190			
(Cu,Pd)Sal-*n*-Pr	2.21	2.05	190			
(Cu,Ni)Sal-NH[b]	2.20	2.05	185			
(Cu,Ni)Sal-NMe[c]	2.21	2.04–2.06	186	21		
CuSal-NMe[d]	2.22	2.05	195		2.109	76
(Cu,Zn)Sal-*i*-Pr[e]	2.28	2.095–2.014	117	≃30, ≃15		
(Cu,Zn)Sal-*t*-Bu[f]	2.29	2.08–2.03	117	≃20, ≃12		
CuSal-*t*-Bu[d]	2.27	2.07	145	≃8	2.135	43

[a] $cm^{-1} \times 10^{-4}$. [b] A. H. Maki and B. R. McGarvey, *J. Chem. Phys.*, **29**, 35 (1958). [c] M. A. Hitchman, C. D. Olson, and R. L. Belford, *ibid.*, **50**, 1195 (1968). [d] Glassy solutions in toluene, see ref 2. [e] H. P. Fritz, B. M. Golla, and H. J. Keller, *Z. Naturforsch., B*, **21**, 1015 (1966). [f] H. P. Fritz, B. M. Golla, and H. J. Keller, *ibid., B*, **23**, 876 (1968).

The geometry of the donor atoms around the copper(II) ion depends on the nature of the R group, the tetrahedral distortion increasing with the bulkiness of R.[9] The pure palladium complexes are planar whereas the pure zinc derivatives are pseudotetrahedral. Through slow evaporation of the chloroform–methanol solutions containing the bis(*N*-alkylsalicylaldiminato)zinc(II) or -palladium(II) complexes and 1% of the analogous copper(II) complex,[10] doped compounds have been obtained which show X-ray diffraction patterns equal to those of the host complexes. Through this procedure the compounds 5-CH_3-CuSal-*i*-Pr and 3-CH_3-CuSal-*i*-Pr have

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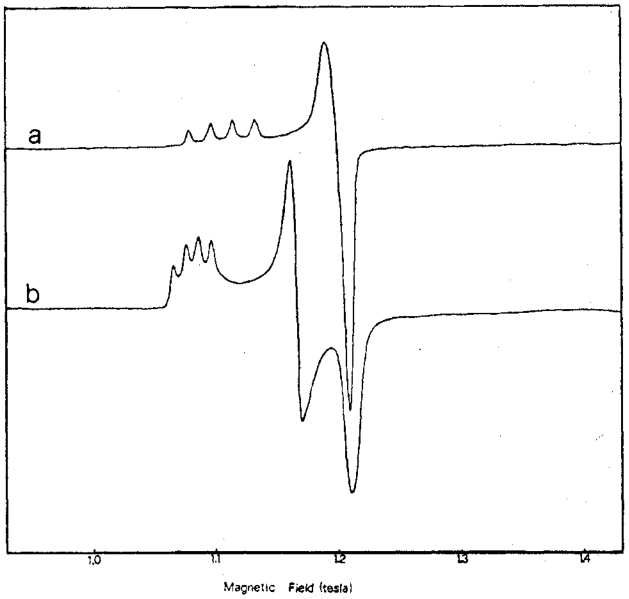

Figure 1. Polycrystalline powder ESR spectra of (a) (Cu,Pd)-5-CH_3Sal-*i*-Pr and (b) (Cu,Zn)-5-CH_3Sal-*i*-Pr.

Table II. Expression for the g and **A** Tensors in D_{2d} Symmetry[a]

$$|1\rangle = \gamma_1 |xy\rangle$$
$$|2\rangle = \gamma_2 |z^2\rangle$$
$$|3\rangle = \gamma_3 |xz\rangle = \gamma_3 |yz\rangle$$
$$|4\rangle = \gamma_4 |x^2 - y^2\rangle$$
$$\Delta g_\parallel = \frac{8\gamma_1{}^2\gamma_4{}^2\lambda}{\Delta_{x^2-y^2}} \qquad \Delta g_\perp = \frac{2\gamma_1{}^2\gamma_3{}^2\lambda}{\Delta_{xz}}$$
$$A_\parallel = P[-K\gamma_1{}^2 - {}^4/{}_7\gamma_1{}^2 + (\Delta g_\parallel) + {}^3/{}_7(\Delta g_\perp)]$$
$$A_\perp = P[-K\gamma_1{}^2 + {}^2/{}_7\gamma_1{}^2 + {}^{11}/{}_{14}(\Delta g_\perp)]$$

[a] The Δi's are the energy separation between the ground and the indicated orbital, $P = 2g_N\beta_N\beta_0\langle 1/r^3\rangle$ where β_0 is the Bohr magneton, g_N is the nuclear *g* factor, and *r* is the distance between the electron and the nucleus. *K* accounts for the contribution which brings the contact interaction into the value for the hyperfine splitting. The γ_i's are the molecular orbital coefficients.

been doped into both the palladium and the zinc analogues. The ESR spectra of copper(II) doped into the palladium complexes are characterized by a large value of the hyperfine splitting $A_\parallel$ (185×10^{-4} cm^{-1}), by a $g_\parallel$ value of 2.22, and by a very small anisotropy of the $g_\perp$ values. When doped into the zinc analogues the pattern of the ESR parameters is completely different in the sense that $g_\parallel$ increases up to 2.27 whereas $A_\parallel$ decreases down to 115×10^{-4} cm^{-1} and a noticeable anisotropy of the $g_\perp$ appears. In particular when recorded in Q band the spectra show three well-separated absorptions which allow one to determine the three *g* values reported in Table I. In the case of palladium-doped compounds, also in Q band, the signal in the $g_\perp$ region appears almost isotropic (see Figure 1). These two patterns of the ESR parameters are quite general; all the other compounds of Table I display either one pattern of the ESR parameters depending on whether they are doped into the planar palladium (or nickel) complexes or into the pseudotetrahedral zinc complexes. Table I includes for comparison purposes also some compounds of the same class already reported in the literature. These results indicate that the ESR parameters are quite sensitive to geometrical distortions between the planar and the tetrahedral limiting geometries, the variations in $A_\parallel$ being absolutely dramatic.

If the difficulties in doping a pseudotetrahedral complex into a planar host and vice versa are neglected, from the present data it appears that the *g* and *A* patterns as well as the resulting geometries depend on the host lattice rather than on the R group.

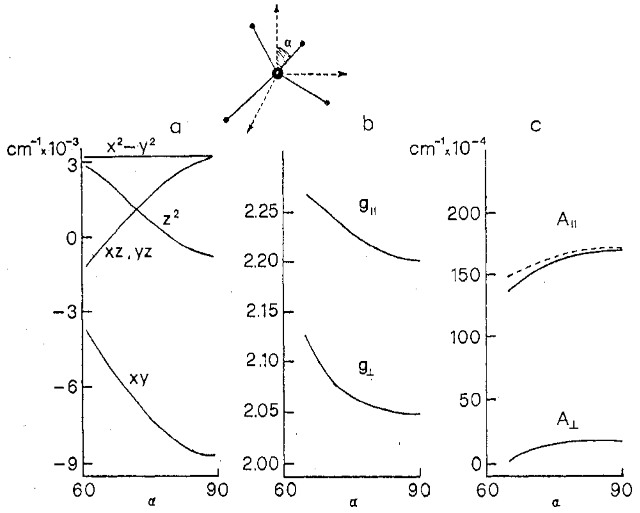

Figure 2. (a) Energy level diagrams (hole formalism) for a D_{2d} tetracoordinate complex as a function of the angle α, $e_\sigma = 4000$, $e_\pi = 0$. (b,c) Dependence of the *g* and *A* values on the angle α, $P = 0.023$ cm^{-1}, $K = 0.40$.

Investigation of the *A* values as they depend on the extent of deviation from planarity in homologous series of pseudotetrahedral complexes have been reported by using formulas of the type of those reported in Table II which have been obtained through a second-order perturbation treatment.[11-13] Such formulas indicate that the contributions to the overall *A* values are three. The first one, expressed as $-KP$ is the so-called contact term and arises from the presence of unpaired spin density at the nucleus. The second term arises from the electron spin-nuclear spin dipole-dipole interaction and is represented by the quantities $-{}^4/{}_7P$ and ${}^2/{}_7P$. This contribution averages to zero under fast rotation, e.g., in liquid solution.[12] The third contribution, which is expressed in terms of the *g* anisotropy, arises from the coupling of the orbital momentum with the nuclear spin and does not vanish under rapid rotation.

Although of qualitative help in the discussion of the variation of the various contributions along a continuous geometrical distortion, such formulas do not provide correct answers when the energy separation between the ground and the excited levels decreases as compared to the spin-orbit parameter. Indeed, when a tetrahedral geometry is approached, the levels are expected to become closer and closer in energy[14] (Figure 2). Therefore a diagonalization of the spin-orbit coupling perturbation matrix (all order perturbation) is necessary in order to calculate reliable values, instead of a second-order perturbative method.

The energy levels, *g* and *A* patterns in D_{2d} symmetry, are reported in Figure 2 as a function of the extent of deviation from planarity using a single angular overlap parameter $e_\sigma = 4000$ cm^{-1} which according to Smith corresponds to a copper-nitrogen distance of ca. 215 pm.[15-19] All the ligand field parameters (i.e., the orbital reduction factor *k*, the spin-orbit coupling constant λ, and the Fermi contact contribution to *A*) are kept constant during the angular variation. For planar

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complexes a value of 170×10^{-4} cm^{-1} is obtained by taking the Fermi contact contribution to A close to that (-92×10^{-4} cm^{-1}) which reproduces the pattern of the hyperfine coupling constants in C_{2v} five-coordinate bis(salicylaldiminato)copper(II) derivatives.[20] By introduction of a distortion toward a tetrahedron $A_{\parallel}$ decreases to about 138×10^{-4} cm^{-1} when the angle α approaches 65°. Small is the effect of geometrical distortion on $A_{\perp}$. This type of calculation is able to account for the observed A pattern as long as the planar and the pure CuSal-*t*-Bu complexes, the latter investigated as a frozen solution, are taken into consideration[21] (see Table I). For α equal to 69°, which is close to the angle of the idealized structure of CuSal-*t*-Bu,[21] a value of $A_{\parallel}$ of 150×10^{-4} cm^{-1} is calculated. Calculation of A through the second-order perturbation formula reported in Table II overestimates $A_{\parallel}$ particularly when the deviation from planarity is large and therefore the energy level separation becomes smaller (see broken line in Figure 2). This point appears to be particularly important for the blue copper proteins where very low energy d–d transitions have been shown to occur.[22,23]

Below the value of 65° for the angle α, the $g_{\perp}$ values become larger than ever observed in synthetic or naturally occurring compounds. Therefore, although the $A_{\parallel}$ values would still decrease toward the value of ca. 100×10^{-4} cm^{-1} observed for the zinc-doped complexes, the whole model is not reliable any more; the introduction of new parameters which allow the decrease of $A_{\parallel}$ but not the increase of $g_{\perp}$ is necessary. This may be a consequence of the change in bonding along the planar-tetrahedral interconversion[4] and hence of the parameters describing the chemical bond.[4] Attempts to reproduce the observed ESR parameters in pseudotetrahedral copper complexes have used anisotropic orbital reduction factors ($k_{\parallel}$, $k_{\perp}$) or have included 3d–4p orbital mixing.[11,24] Furthermore the Fermi contact contribution to A should be considered to decrease in absolute value when the complex deviates from planarity. The latter property has been experimentally demonstrated through solid and fluid solution measurements.[2,3]

The conclusion of the present research is that through a full-matrix spin–orbit perturbation the angular dependence of the ESR parameters in distorted planar complexes can be confidently fitted without relaxing the spin Hamiltonian and ligand field parameters for large deviations from planarity (ca. 65°). The relaxation of these parameters is necessary when the tetrahedral geometry is more closely approached. This is the case of copper(II) doped into zinc analogues: presumably the copper(II) ion experiences large geometrical distortion toward the tetrahedron with respect to the pure compounds.

Acknowledgment. Thanks are expressed to Dr. D. Gatteschi and Dr. A. Bencini for providing the computer program. The technical assistance of Mr. B. Valenti from the University of Parma in recording the Q-band ESR spectra is also gratefully acknowledged.

Registry No. Cu(5-Me-Sal-i-Pr)$_2$, 15379-85-8; Zn(5-Me-Sal-i-Pr)$_2$, 57335-10-1; Pd(5-Me-Sal-i-Pr)$_2$, 73466-72-5; Cu(3-Me-Sal-i-Pr)$_2$, 15412-65-4; Zn(3-Me-Sal-i-Pr)$_2$, 73466-73-6; Pd(3-Me-Sal-i-Pr)$_2$, 16970-08-4; Cu(Sal-Et)$_2$, 14096-19-6; Ni(Sal-Et)$_2$, 13987-25-2; Pd(Sal-Et)$_2$, 14444-53-2; Cu(Sal-n-Pr)$_2$, 14077-15-7; Ni(Sal-n-Pr)$_2$, 15379-66-5; Pd(Sal-n-Pr)$_2$, 73466-74-7.

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Received October 19, 1979

Additions and Corrections

1979, Volume 18

Leh-Yeh Hsu and Donald E. Williams*: Potential Energy Models for Nonbonding and Bonding Interactions in Solid Chlorine.

Pages 79–82. In the paper[1] described by the title we reported that the best potential energy model for the chlorine crystal structure included both an effective molecular dipole and a partial intermolecular bond. This effective dipole for the chlorine molecule required that the observed *Cmca* space group symmetry be relaxed to $Cmc2_1$.[2]

Further calculations by us[3] now show that the assumption of a molecular dipole and the lower symmetry space group are not necessary to describe the chlorine crystal structure. We find that a partial intermolecular bond is still required, however, plus a molecular quadrupole; i.e., the best fit is given by the B + Q + M model of the title paper. This model uses isotropic (exp-6-1) nonbonded potential functions.

It should be noted that Nyburg and Wong-Ng[4] have fitted the chlorine crystal structure by using anisotropic nonbonded potential functions. These authors found that it was unnecessary to use a partial intermolecular bonding function to fit the chlorine crystal structure if the anisotropic nonbonded potential functions were used.—Donald E. Williams

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