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.

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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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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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