direct copper(II)-sulfur(IV) reaction confirms that it is a minor pathway under the conditions employed in our studies. The direct reaction becomes significant at higher [Cu(II)]/[Fe(III)] ratios, however. In 1.0 M H^+, 0.01 M Cu(II), 0.01 M Fe(III), and 0.0 M Fe(II), for example, $-d[S(IV)]/dt$ from eq 6 and 7 is 0.054 times as great as $-d[S(IV)]/dt$ from eq 4 and 5.

The retardation of net reaction 2 by copper(I) indicates that reaction 12b is reversible (assuming that eq 12a and 12b do indeed represent the mechanism). The decreased retardation at the highest Cu(I) used in our experiments is not explained by eq 12; an additional pathway is required, and our data are not sufficiently extensive to warrant speculation.

Copper(I)-Sulfur(IV) Complexation. The linearity of the plots of ϵ_{app} *vs.* [S(IV)] indicates that Q_3 is small; if eq 3 does represent the complexation reaction and if only one complex is formed, then the slope of each line is equal to $\epsilon Q_3[H^+]/(Q_a + [H^+])$, where ϵ is the molar absorbancy coefficient for the complex. Use of this relationship gives an average value $\epsilon Q_3 = 260\ M^{-2}\ cm^{-1}$. Evidence that SO_2 is indeed the complexed species, as written in eq 3, is provided by the constancy of the slopes of the ϵ_{app} *vs.* [S(IV)] plots at 0.10 and 1.0 M H^+. Over this range of $[H^+]$, $[SO_2]/[S(IV)]$, $[HSO_3^-]/[S(IV)]$, and $[SO_3^{2-}]/[S(IV)]$ vary by factors about 1.4, 7.3, and 73, respectively. The composition of the copper(I) complex is at first surprising since most previous studies of metal ion-sulfur(IV) complexes have shown compositions of the form MSO_3^n, and, indeed, stable $Cu(SO_3)_n^{(n-1)-}$ and $Cu(SO_3)_3Cl^{6-}$ complexes have been reported.[21] However, literature precedents can be found for metal-sulfur dioxide complexes containing metal-sulfur bonds and also for metal-halide-sulfur dioxide complexes containing halide-sulfur bonds in crystals.[22] In addition to halide-sulfur dioxide linkages in metal complexes, free XSO_2^- complexes containing halide-sulfur dioxide linkages have been characterized in a variety of solvents, including water.[23]

Since copper(I) is extensively complexed by chloride in aqueous chloride media,[14] a Cu(I)-Cl-SO linkage is certainly possible. We think this formulation is as probable as the alternate Cu(I)-SO_2 formulation, but our evidence does not distinguish between the two linkages. We do not plan to pursue the study, but we think this first-row metal-sulfur dioxide complex, stable enough to be detectable in water solution, may be useful in understanding the general set of metal-sulfur dioxide complexes.

Registry No. S(IV), 20681-10-1; Fe(III), 20074-52-6; Fe(II), 15438-31-0; Cu(II), 15158-11-9; Cu(I), 17493-86-6.

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Base Adducts of β-Ketoenolates. VII.[1,2] Electron Paramagnetic Resonance Studies of Some Fluxional 1,1,1,5,5,5-Hexafluoro-2,4-pentanedionatocopper(II) Complexes

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Electron paramagnetic resonance parameters for tetragonal six-coordinate complexes of the type CuO_4N_2 and CuO_n for n = 4-6 have been evaluated. Increasing $g_\parallel$ and decreasing $A_\parallel$ hyperfine parameters are found for a series of similar complexes as the axial ligand field is strengthened. The trend observed correlates well with the shift to lower energies found for the d-d transitions. For both the CuO_4N_2 and CuO_6 complexes, fluxional molecules describable by a dynamic Jahn-Teller formalism have been observed. A correlation between the in-plane σ-bonding coefficients (α) and both the dipolar factor P (which takes into account the radial distribution of the unpaired electron) and the factor κ (which measures the amount of s-electron admixture) has been observed and is presented here for complexes of the type CuO_4N_2.

Introduction

Solution spectra of copper β-diketonates are solvent dependent. Spectral changes arise from coordination of the solvent to the copper atom of the complex. Funck and Ortolano[3] analyzed the effects of single and double coordination of pyridine and water upon the electronic spectrum of $Cu(F_6acac)_2$. Wayland and Garito[4] extended the molecular orbital calculations of Cotton and coworkers[5] to a model for a five-coordinate adduct having coordinates in accord with the known structural changes that occur[6] in $Cu(acac)_2$ upon axial ligation with quinoline. The principal results of this model are that all d-d transitions are shifted to lower energy, while the d energy level ordering is unchanged. Dudley and Hathaway[7] reported the polarized single-crystal

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[1] Abstracted from the Ph.D. thesis of J. Pradilla-Sorzano.

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electronic and epr spectra of the 2,2′-bipyridine adduct to $Cu(F_6acac)_2$. Dipolar selection rules with D_2 effective symmetry were used to assign the d–d transitions. These authors suggested a d-orbital ordering $d_{xy} >> d_{z^2} > d_{yz} > d_{xz} > d_{x^2-y^2}$. However, the experimental technique used has received some criticism.[8]

The formation of base adducts has a marked influence on the epr parameters of copper(II) β-diketonates. Parallel components of the g tensors for the adducts are greater than the corresponding components in the four-coordinate molecules. Hyperfine tensor components, A, decrease upon axial coordination.[9-13] These experimental observations are in accord with a theoretical treatment[14] which considers the perturbations to arise from two axial dipoles acting on the planar molecule. It has also been suggested that decreasing hyperfine constants upon coordination by a base may be due to a reduction in the d-orbital spin density and/or mixing of 4s character into the antibonding molecular orbital[10,12] singly occupied in the $3d^9$ system.

Kivelson and Neiman[15] in their analysis of the epr spectra of Cu(II) complexes by means of molecular orbital theory assumed that the electron spin density[16] in the nucleus is proportional, $\kappa = \alpha^2\kappa_0$, to the s-electron admixture where α is the molecular orbital coefficient for the d-orbital ground state. The subscript zero stands for the free-ion value of these parameters. A similar calculation has been used by most investigators to evaluate molecular orbital coefficients from spin-Hamiltonian parameters. However, Kuska and coworkers[10] have reported some epr measurements for substituted acetylacetonates which appear to contradict these assumptions. McGarvey[17] has calculated the electron spin density, χ, at the nucleus for the first transition series of metal ions by using a perturbation approach which permits an examination of the reasons for the changes that occur in χ with variations in the metal–ligand bonding.

The electron spin density at the copper(II) nucleus is given by

$$\chi = \alpha^2\chi_0 \quad \text{or} \quad \kappa P = \alpha^2\kappa_0 P_0 \tag{1}$$

where P is the dipolar term which is proportional to $\langle r^{-3}\rangle$. The subscript zero is associated with the free-ion values of these parameters. In (1) both the isotropic factor κ and P are assumed to be unknown parameters for the complex using the method of Swalen and coworkers[18] for calculating bonding parameters from epr data. These methods were applied to a series of similar Cu complexes to gain a better understanding of the chemical significance of epr data in studying tetragonal copper(II) complexes.

Experimental Section

Materials. Bis(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)copper(II) Hydrate, $Cu(F_6acac)_2 \cdot H_2O$. The method of preparation followed was similar to that reported by Bertrand and Kaplan.[19] A small excess of the β-diketone was added to a warm water solution of copper acetate or nitrate. The yellow-green precipitate which resulted turned grass green after drying in air. This compound was purified by sublimation.

Bis(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)copper(II), $Cu(F_6acac)_2$. Following the procedure of Walker and Li[20] the anhydrous complex was obtained by placing the monohydrate under vacuum over P_2O_5. The resulting purple powder reverted back to the green complex when exposed to air.

Copper-Doped Bis(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)zinc(II) Complexes. A similar method to that reported by Walker and coworkers[21] was followed to prepare $Cu\text{-}Zn(F_6acac)_2(H_2O)_2$. To a solution of copper and zinc acetates (Cu:Zn, 1:50) in warm water, a small excess of hexafluoroacetylacetonate was added. The pale yellow precipitate was filtered off and washed with water. The product was recrystallized from ethanol solution. Single crystals were obtained by slow evaporation of the above solution.

The monohydrate was obtained from the above complex by drying over Drierite ($CaSO_4$). Under these conditions a second molecule of water is lost from the complex very slowly. The anhydrous complex was readily obtained by drying the aquo adducts over P_2O_5. The changing compositions of these complexes were followed by weighing the samples. In order to get reliable information from the loss of weight obtained by drying, the process was carried out at atmospheric pressure to avoid sublimation. The hydrates could be obtained reversibly by exposing the anhydrous complexes to air.

Cu(II)-Doped Tris(hexafluoroacetylacetonato)zinc(II). The salt of monoprotonated 1,8-bis(dimethylamino)naphthalene, $[C_{14}H_{19}N_2][(C_5F_6O_2H)_3Cu^{II}\text{-}Zn^{II}]$, was obtained by the method reported by Truter and coworkers.[22] A stoichiometric mixture (1:1:1) in benzene of the amine, the diketone, and $Cu\text{-}Zn(F_6acac)_2$ reacted to give a pale yellow solution from which crystals were obtained by slow evaporation of the solvent.

The dipyridine adducts **$Cu\text{-}Zn(F_6acac)_2(py)_2$**, α and β forms, were obtained as reported.[2]

Solvents. Spectrograde solvents from freshly opened bottles were used without further purification.

Measurements. Epr spectra were measured with a Varian Model E-3 X-band spectrometer. Temperature control was provided by a suitable Varian (E4 540) variable-temperature unit. The field sweep was calibrated by employing standards with precisely known magnetic parameters.[2]

Calculation of Molecular Orbital Coefficients

Calculations of bonding parameters were accomplished on a UNIVAC 1108 computer, using two programs. One called MOPAR is based on the standard procedure of Kivelson and Neiman[15] and has been reported by Weeks and Fackler;[23] the second is based on the method of Swalen and coworkers,[18] who wrote the ground-state Kramers doublet wave functions as

$$\psi = a\phi_1\alpha + b\phi_3\alpha + ic\phi_2\alpha - id\phi_4\beta - e\phi_5\beta \tag{2}$$

$$\psi^* = i(a\phi_1\beta + b\phi_3\beta - ic\phi_2\beta - id\phi_4\alpha + e\phi_5\alpha) \tag{3}$$

where $\phi_1 \cong Z_{20} \equiv d_{3z^2-r^2}(A)$, $\phi_2 \cong Z_{22} \equiv d_{xy}(B_1)$, $\phi_3 \cong Z_{22} \equiv d_{x^2-y^2}(A)$, $\phi_4 \cong Z_{21} \equiv d_{yz}(B_2)$, and $\phi_5 \cong Z_{21} \equiv d_{xz}(B_2)$. The expressions for the g values

$$g_z = 2 - 4d^2 - 4e^2 + 8bc + 4de \tag{4}$$

$$g_x = 2 - 4c^2 - 4e^2 + 4\sqrt{3}ad - 4ce + 4bd \tag{5}$$

$$g_y = 2 - 4c^2 - 4d^2 + 4\sqrt{3}ac - 4be + 4cd \tag{6}$$

were calculated as matrix elements of the type $\psi | l_i + 2S_i | \psi$ for $i = x, y, z$.

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Equations 4-6 along with the normalization condition were solved for the four unknowns *a, b, c,* and *d,* for $e = xd$; where x is an empirical parameter which has a value near 1 when the ground state is mainly d_{z^2} or a value close to -1 for the more common case with a $d_{x^2-y^2}$ ground state.

The two unknowns P and κ were evaluated with a least-squares fit to the Cu(II) hyperfine parameters

$$A_z = P\{8bc + 4de + (6\zeta - \kappa)(1 - 2d^2 - 2e^2) - 3\zeta[4c^2 + 4b^2 - d^2 - e^2 + \sqrt{3}a(d + e) + 3(d - e)(c - b)]\} \tag{7}$$

$$A_x = P\{4\sqrt{3}ad - 4ec + 4bd + (6\zeta - \kappa)(1 - 2c^2 - 2e^2) - 3\zeta[\sqrt{3}a + b)^2 - c^2 + 4d^2 - e^2 - \sqrt{3}a(e + 2c) + 3dc - 3be + 3de]\} \tag{8}$$

$$A_y = P\{4\sqrt{3}ae + 4dc - 4be + (6\zeta - \kappa)(1 - 2c^2 - 2d^2) - 3\zeta[(\sqrt{3}a - b)^2 - c^2 - d^2 + 4c^2 - \sqrt{3}(d - 2c)a - 3ce + 3db + 3dc]\} \tag{9}$$

by using the sets of coefficients *a, b, c, d,* and *x* obtained from the *g* values. The constant ζ is related to the electronic configuration of the ion[24] [$^2/_{21}$ for Cu(II)].

All possible combinations for the signs of the A values compatible with positive P and κ factors were considered. The coefficients determined for Cu-Zn(F_6acac)$_2$(py)$_2$ correspond to the best fit obtained in the calculations. For all the other complexes reported, two pairs of P and κ factors are possible. Negative values for A_z and positive A_x and A_y have been chosen, in D_{4h} symmetry, as is usually assumed for most tetragonal Cu(II) complexes with a $d_{x^2-y^2}$ ground state. For Cu-Zn(F_6acac)$_2$(H_2O), a positive sign for A_z and negative signs for A_x and A_y were chosen; these signs for the hyperfine values correspond to the highest P and lowest κ factors calculated. The observed and calculated copper hyperfine parameters and g values for Cu-Zn(F_6acac)$_2$(py)$_2$ are given in Table I. A FORTRAN program[1] was used for the calculations.

The covalency of the in-plane σ bonding has been obtained by using the molecular orbital approach of Kivelson and Neiman.[15] The magnetic parameters obtained with the assumption of D_{4h} symmetry are

$$g_{\parallel} = 2.0023 - (8\lambda/\Delta E_{xy})[\alpha^2\beta^2 - f(\beta)] \tag{10}$$

$$g_{\perp} = 2.0023 - (2\lambda/\Delta E_{xz})[\alpha^2\beta^2 - g(\gamma)] \tag{11}$$

$$A_{\parallel} = P[-(4/7)\alpha^2 - \kappa - 2\lambda\alpha^2(4\beta^2/\Delta E_{xy} + 3\gamma^2/7\Delta E_{xz})] \tag{12}$$

$$A_{\perp} = P[(2/7)\alpha^2 - \kappa - (11/7)\alpha^2\gamma^2/\Delta E_{xz}] \tag{13}$$

where the ΔE terms refer to the electronic transitions between the B_{1g} ground state ($d_{x^2-y^2}$) and the orbitals indicated. The parameters α, β, γ, and δ are the coefficients corresponding to the antibonding wave functions

$$B_{1g} = \alpha d_{x^2-y^2} - \alpha(-\sigma_x^{(1)} + \sigma_y^{(2)} + \sigma_x^{(3)} - \sigma_y^{(4)})/2 \tag{14}$$

$$B_{2g} = \beta d_{xy} - (1 - \beta^2)^{1/2}(P_y^{(1)} + P_x^{(2)} - P_y^{(3)} - P_x^{(4)})/2 \tag{15}$$

$$E_g = \begin{cases} \gamma d_{xz} - (1 - \gamma^2)^{1/2}(P_z^{(1)} - P_z^{(3)})/\sqrt{2} \\ \gamma d_{yz} - (1 - \gamma^2)^{1/2}(P_z^{(2)} - P_z^{(4)})/\sqrt{2} \end{cases} \tag{16}$$

$$A_{1g} = \delta d_{z^2} - \frac{1}{2}(1 - \delta^2)^{1/2}[\sigma_x^{(1)} + \sigma_y^{(2)} - \sigma_x^{(3)} - \sigma_y^{(4)}] \tag{17}$$

Table I. Observed[2] and Calculated Copper Hyperfine Parameters and g Values for the α Form of Cu-Zn(F_6acac)$_2$(py)$_2$

Component	Obsd	Calcd	Component	Obsd	Calcd
g_z	2.344	2.344	A_z, 10^4 cm^{-1}	$\lvert 151 \rvert$	-151
g_y	2.070	2.069	A_y, 10^4 cm^{-1}	$\lvert 4 \rvert$	4.4
g_x	2.089	2.090	A_x, 10^4 cm^{-1}	$\lvert 3 \rvert$	-3.5

The B_{1g} and A_{1g} states represent the σ bonding to the copper atom, while the B_{2g} and E_g states refer to in-plane and out-of-plane π bonding, respectively. The functions f(β) and g(γ) are

$$f(\beta) = \alpha\alpha'\beta^2 S + \alpha\alpha'\beta(1 - \beta^2)^{1/2}T(n)/2 \tag{18}$$

$$g(\gamma) = \alpha\alpha'\gamma^2 S + \alpha\alpha'\gamma(1 - \gamma^2)^{1/2}T(n)/\sqrt{2} \tag{19}$$

In the above equations, λ is the spin-orbit coupling constant for the free ion; κ and P were previously defined in (1). P takes into account the radial distribution function of the unpaired electron. The constant $T(n)$ is an integral over ligand functions that has been evaluated by Maki and McGarvey.[25] S is the overlap integral for the in-plane σ bonding.

The program MOPAR first calculates an initial α from the approximate expression

$$A_{\parallel} = P[-{}^4/_7\alpha^2 - \kappa + (g_{\parallel} - 2.002) + {}^3/_7(g_{\perp} - 2.002) + 0.04]$$

The value of κ is given by the expression[23] (ignoring small terms) $\kappa = -A_s/P + g_s - 2.0023$, with $A_s = {}^1/_3(A_{\parallel} + 2A_{\perp})$ and $g_s = {}^1/_3(g_{\parallel} + 2g_{\perp})$.

The initial α is used in eq 10 and 11 to obtain β and γ, which are in turn used to calculate α employing eq 12. This cyclic process is continued until all values of α, α', β, and γ converge. The values of *s, T(n), P,* and γ used were taken from ref 15.

Results

The magnetic parameters extracted from the epr spectra of single crystals, dilute powder samples, and frozen solutions of the complexes are listed in Tables II and III, together with the electronic d-d transition energies. The coefficients and parameters obtained by the method of Swalen, *et al.*,[18] are listed in Table IV for some of the base adducts of Cu(F_6acac)$_2$. Molecular orbital coefficients calculated by the method of Kivelson and Neiman[15] are listed in Table V.

Discussion

The effect of increasing axial bonding on the epr parameters will be considered in complexes of the type CuO_4N_2 (Table II) and in the molecular system CuO_n for n = 4-6 (Table III).

The CuO_4N_2 System. In the solid state two different crystallographic forms (α and β) of the copper-doped dipyridine adduct of Zn(F_6acac)$_2$ have been observed.[2] A cis configuration has been found for the complexes α-Cu-Zn-(F_6acac)$_2$(py)$_2$ and Cu(F_6acac)$_2$(py)$_2$ by X-ray crystal structure determination.[26] Although there is no crystallographic evidence for a similar structure for β-Cu-Zn(F_6acac)$_2$(py)$_2$, unit cell volume and density measurements suggest that differences between the α and β crystal forms may be due to the presence or absence of solvent molecules in the crystal. The similarity of the nitrogen hyperfine structure for both the α and β forms suggests a cis configuration for β-Cu-Zn-(F_6acac)$_2$(py)$_2$.

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Table II. Magnetic Parameters and Electronic Transitions for the $\mathrm{CuO_4N_2}$ Molecular System[f]

No.	Compd	$g_\parallel$	$A_\parallel$	$g_\perp$	$A_\perp$	$A_{\mathrm{N}\parallel}$	$A_{\mathrm{N}\perp}$	$d_{xy} \rightarrow d_{x^2-y^2}$	$d_{xy} \rightarrow d_{xz}, d_{yz}$
I[a]	$\mathrm{Cu(F_6acac)_2bipy}$	2.292		2.075				14.6	14.4, 13.0
II[b]	$\mathrm{Cu\text{-}Zn(F_6acac)_2bipy}$	2.299 (4)	162 (2)	2.056 (4)	25.5 (1.0)	9.5 (1.0)	13.3 (1.0)		
III[c]	$\mathrm{Cu(F_6acac)_2(py)_2}$	2.302 (4)	147 (2)	2.077 (4)	11 (2)		14 (1)	14.0	12.1, 15.4
IV[d]	β-$\mathrm{Cu\text{-}Zn(F_6acac)_2(py)_2}$	2.325 (2)	153 (2)	2.059 (4)	12 (2)	9 (1)	13 (1)	14.7	14.7
V[d]	α-$\mathrm{Cu\text{-}Zn(F_6acac)_2(py)_2}$	2.344 (1)	151 (2)	2.079 (3)[e]	3.5 (2.0)		13.3 (5)	13.8	13.8

[a] Single-crystal measurements from ref 7. The tensor directions are referenced with respect to the axial symmetry of the *cis*-$\mathrm{CuO_4N_2}$ system. [b] Power data from ref 24. [c] Epr data were obtained from $\mathrm{CHCl_3}$-toluene glass at 133°K. Electronic transitions from $\mathrm{CCl_4}$ solutions were taken from ref 3. [d] Epr data and electronic transitions were taken from part VI.[2] [e] Average of g_x and g_y. [f] Copper hyperfine values are given in 10^4 cm^{-1}, nitrogen hyperfine values in gauss, and electronic transitions in kilokaisers (kK). Standard deviations given in parentheses.

Table III. Magnetic Parameters and Electronic Transitions for the CuO_n Molecular System

Species	n	$g_\parallel$	$A_\parallel$, 10^4 cm^{-1}	$g_\perp$	$A_\perp$, 10^4 cm^{-1}	Δ_{xy}, kK	Δ_{xz}, kK
$\mathrm{[Cu\text{-}Zn(F_6acac)_3]^-}$	6	2.387 (1)	122 (1)	2.07[c]	30[c]		
$\mathrm{Cu\text{-}Zn(F_6acac)_2(H_2O)_2}$	6	2.386 (1)	123 (1)		30[c]	12.5[a]	12.5
$\mathrm{Cu\text{-}Zn(F_6acac)_2}$	6	2.359 (1)	136 (1)		30[c]	14[a]	18
$\mathrm{Cu(F_6acac)_2}$ (toluene–$\mathrm{CHCl_3}$ soln)	4	2.282 (1)	177 (1)	2.064 (3)	22 (3)	14.1[b]	18.1
$\mathrm{Cu\text{-}Zn(F_6acac)_2(H_2O)}$	5	2.052 (1)	38 (1)	2.257 (1)	63 (1)	12.5[a]	14.5

[a] Electronic transitions refer to D_{4h} symmetry, for the complexes in the solid state. [b] These transitions refer to $\mathrm{CCl_4}$ solutions. All electronic spectra have been reported in ref 3. [c] The perpendicular band for these compounds has not been satisfactorily interpreted.

Table IV. Ground-State Coefficients and Parameters for the $\mathrm{CuO_4N_2}$ Molecular System and Some CuO_n Complexes

No.	Compd	a	b	c	d	x	P, 10^4 cm^{-1}	$P\kappa$, 10^4 cm^{-1}
II	$\mathrm{Cu\text{-}Zn(F_6acac)_2bipy}$	0.000	0.999	0.0377	0.0151	−1.00	323	82.7
III	$\mathrm{Cu(F_6acac)_2(py)_2}$	0.000	0.9988	0.0384	0.0203	−1.00	271	84.5
IV	β-$\mathrm{Cu\text{-}Zn(F_6acac)_2(py)_2}$	0.000	0.9989	0.0411	0.0163	−1.00	297	88.2
V[a]	α-$\mathrm{Cu\text{-}Zn(F_6acac)_2(py)_2}$	0.0267	0.9982	0.0437	0.0229	−0.86	279	98.7
	$\mathrm{Cu\text{-}Zn(F_6acac)_2(H_2O)}$	0.9907	0.0861	0.0861	0.0428	1.0	187	70.4
	$\mathrm{[Cu\text{-}Zn(F_6acac)_3]^-}$	0.000	0.9984	0.0490	0.0201	−1.0	296	78.7

[a] For this complex, the epr data at 4.2°K for signal 1 have been used; the labels g_x and g_y used in ref 3 were exchanged for this calculation.

Table V. Molecular Orbital Coefficients for the $\mathrm{CuO_4N_2}$ Molecular System

No.	Compd	α[a]	α^2	β	γ	Δ_{xy}	Δ_{xz}
II	$\mathrm{Cu\text{-}Zn(F_6acac)_2bipy}$	0.904	0.817	0.913	0.798	14.0	14.0
II	$\mathrm{Cu\text{-}Zn(F_6acac)_2bipy}$	0.904	0.817	0.931	0.790	14.6	13.7
III	$\mathrm{Cu(F_6acac)_2(py)_2}$	0.901	0.812	0.920	0.925	14.0	14.0
IV	β-$\mathrm{Cu\text{-}Zn(F_6acac)_2\text{-}(py)_2}$	0.923	0.852	0.947	0.814	14.7	14.7
V	α-$\mathrm{Cu\text{-}Zn(F_6acac)_2\text{-}(py)_2}$	0.943	0.889	0.909	0.884	13.8	13.8

[a] The constants used in the calculation were those reported by Kivelson and Neiman:[15] $s = 0.084$, $T(n) = 0.270$, $P = 0.036$ cm^{-1}, $\lambda = 828$ cm^{-1}.

We have seen[2] that the dynamic behavior of $\mathrm{Cu(F_6acac)_2(py)_2}$ doped into the α-crystallographic lattice of $\mathrm{Zn(F_6acac)_2(py)_2}$ can best be understood in terms of the effect of axial compression on the copper ion, apparently produced by crystal packing forces. We also indicated that energy of the d-d transitions and $g_\parallel$ values are different in the α and the β forms. There appears to be some decreased axial bonding to the copper in the β form of the complex.

The similarity of the structural properties found for $\mathrm{Cu(F_6acac)_2(py)_2}$ and $\mathrm{Cu(F_6acac)_2(bipy)}$[27] suggests that the ligand field influence on the Cu(II) ion is nearly the same in both complexes. The spectroscopic properties of $\mathrm{Cu(F_6acac)_2(py)_2}$ in solution are as close as can be expected to those of $\mathrm{Cu(F_6acac)_2(bipy)}$ on the basis of the structural features.[28] However, the solid-state electronic and epr spectra are significantly different for $\mathrm{Cu\text{-}Zn(F_6acac)_2(py)_2}$ (both the α and β forms). This is another indication that the molecule which is relatively unperturbed when dissolved in solution is subjected to structure-influencing solid-state forces when doped into a zinc complex.

An evaluation of the above perturbation can be obtained by correlating the spectroscopic properties found in the $\mathrm{CuO_4N_2}$ molecular system. Increasing $g_\parallel$ and decreasing $A_\parallel$ hyperfine parameters are found for the series $\mathrm{Cu(F_6acac)_2(bipy)}$, I, $\mathrm{Cu\text{-}Zn(F_6acac)_2(bipy)}$, II, $\mathrm{Cu\text{-}Zn(F_6acac)_2(py)_2}$, β form, IV, and $\mathrm{Cu\text{-}Zn(F_6acac)_2(py)_2}$, α form, V. These trends in the epr parameters mean that the ligand field of these tetragonal complexes is strengthened on the axis normal to the equatorial plane in going from molecule I to V. This result is consistent with the shift to lower energies found for the electronic transitions in the same series. Assuming a correlation exists for the variation in $g_\parallel$ and $A_\parallel$ with $1/\Delta$ (Tables II and VI), a value of ~8.1 kK may be estimated for the center of the broad band in the near-infrared spectrum for complex V.

The complex $\mathrm{Cu(F_6acac)_2(py)_2}$, III, is anomalous in the $\mathrm{CuO_4N_4}$ series. Its $g_\parallel$ tensor as observed in a $\mathrm{CHCl_3}$-toluene glass is small relative to the value of $A_\parallel$ and the observed low-energy electronic transition (in $\mathrm{CCl_4}$). Either no real correlation exists in the series I-V above (an unlikely possibility), or the complex III in solution is not well behaved. (An equilibrium can exist between cis and trans species and a five-coordinate $\mathrm{Cu(F_6acac)_2(py)}$ in the $\mathrm{CHCl_3}$-toluene solution studied here which was undetected in the glass.)

Hathaway and coworkers[29] have discussed the concept of tetragonality, T, which is defined to equal R_s/R_l, where R_s and R_l are the short and the long copper-ligand distances, respec-

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(27) M. V. Veidis, G. H. Schreiber, T. E. Gough, and G. J. Palenik, *J. Amer. Chem. Soc.*, 91, 1859 (1969).

(28) Dudley and Hathaway[7] have predicted the cis structure we have found[26] for $\mathrm{Cu(F_6acac)_2(py)_2}$ on the basis of the similarity of the electronic spectra of these adducts.

(29) B. J. Hathaway and D. E. Billing, *Coord. Chem. Rev.*, 5, 143 (1970).

Table VI. Tetragonality, *T*, and the Low-Energy Band

Complex[a]	*T*	In-plane bond length, Å	d_{xy}, $d_{x^2-y^2} \rightarrow d_{z^2}$, kK	Ref
$Cu(OMPA)_3ClO_4$	1.0	2.07	8.0	28
$K_3PbCu(NO_2)_6$	1.0	2.11	7.0	28
$CuH_2(EDTA)H_2O$	0.85	2.07	8.2	29
$Cu(F_6acac)_2bipy$, I	0.86	1.967	9.4	7
$Cu(F_6acac)_2(py)_2$, III	0.87	1.998	8.1[b]	This work
β-Cu-$Zn(F_6acac)_2(py)_2$, IV			8.5	This work
α-Cu-$Zn(F_6acac)_2(py)_2$, V			8.0	This work

[a] Abbreviations used: OMPA, octamethylphosphoramide; EDTA, ethylenediaminetetraacetate. [b] Ortolano and Funck[3] estimated the position from gaussian curve analysis. See also ref 31.

tively, and have related it to the energy of the lowest electronic transition.[30,31] Some relevant examples of octahedral complexes ($T = 1$) and tetragonal-octahedral complexes ($T < 1.0$) with nitrogen and oxygen ligands are listed in Table VI. The calculated energy for the α form suggests that for the copper ion a tetragonality value near 1.0 exists. We might expect this on the basis of the dynamic behavior found for this molecule.

The anisotropy of the in-plane *g* tensor for both $Cu(F_6acac)_2(py)_2$ and $Cu(F_6acac)_2(bipy)$ suggests that these complexes are best described to have a d_{xy} ground state. However, we have assumed an approximate D_{4h} symmetry, *i.e.*, $g_x = g_y$, $A_x = A_y$, in order to evaluate the variations in the bonding parameters for the entire series of complexes I-V. (To obtain a more rigorous analysis of the system, precise measurements of the in-plane tensors would be needed with single crystals of compounds II and IV.) The correlation between the in-plane σ-bonding coefficients (α) and the bonding parameters, P and κP, obtained as described, is presented in Figure 1. These results indicate that when P values decrease, α^2 and κP values increase for the compounds II-V excluding III as indicated above. This trend suggests (quite reasonably) that an increasing axial ligand field causes a decreasing strength of the in-plane σ bonding. Donation of electrons along the *z* axis to the metal presumably reduces electron donation from the ligand atoms in the *xy* plane.

The factor P takes into account the mean radial distribution function of the unpaired electron. Its value is reduced from the free-atom value (360×10^{-4} cm^{-1}) by electron delocalization into the ligands and by electronic expansion. Axial compression appears to decrease its value while increasing α^2, Figure 1. Conceivably P can be factored linearly into distribution terms, P_s and P_l, related to the ground-state electron-nuclear spin-spin dipolar interactions and the interactions with orbital moments of excited states, respectively. Since P_s is expected to increase with α^2 (decreasing covalency), the experimental result of a decreasing P with increasing α^2 requires that P_l must decrease more rapidly than P_s increases. This interpretation suggests that the dominant electronic effect of the increased axial strength of the coordination to these planar copper(II) complexes is an orbital expansion of the out-of-plane orbitals (d_{z^2}, d_{xz}, d_{yz}) on the metal.

Equation 1 implies that s orbitals remain as atomic orbitals upon coordination of ligands to the metal ion. An assumption that the 4s metal orbital is involved in bonding introduces, along with the inner-shell s orbitals, another filled orbital having some s character. Polarization of spin in this bonding orbital has been suggested to account for the variation of χ with covalency.[17] Thus positive deviations are expected for the Fermi contact term (κP) from increased 4s bonding. A contribution of opposite sign also is possible in instances where the 4s orbital is directly mixed into the σ-antibonding (largely d-orbital) ground state. In such a case low absolute values of χ (and κP) would be expected.

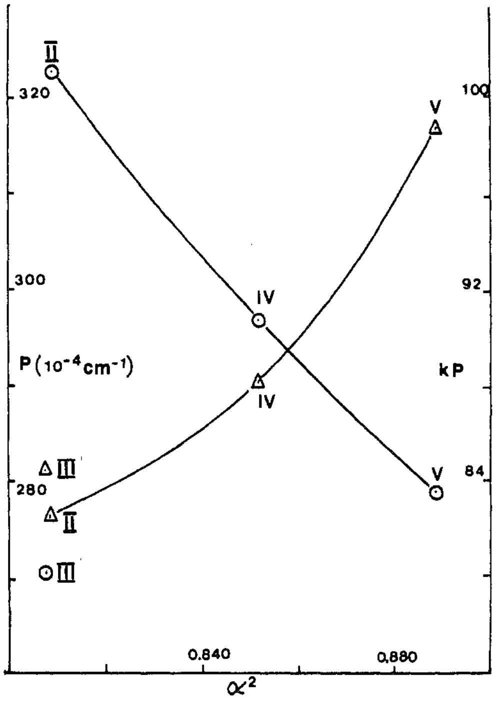

Figure 1. Correlation between molecular orbital in-plane σ-bonding coefficient (α^2) and bonding parameters P and κP (10^{-4} cm^{-1}) for complexes of the type CuO_4N_2. Data points are marked with ○ and △ for P and κP values, respectively. II is Cu-$Zn(F_6acac)_2bipy$, III is $Cu(F_6acac)_2(py)_2$ in $CHCl_3$-toluene glass, IV is β-Cu-$Zn(F_6acac)_2(py)_2$, and V is α-Cu-$Zn(F_6acac)_2(py)_2$.

As seen in Figure 1, the Fermi contact term κP increases with α^2 over the series of complexes II, IV, and V. Although the number of data points is too limited to test the theory adequately, the proportionality expressed by eq 1 appears to hold approximately. (The curve has been drawn with a slight positive deviation.) It suggests that the 4s contribution to the metal-ligand bonding is nearly unchanged, at a value different from the free-ion value, in the series of CuO_4N_2 complexes studied.

Smith[32] has discussed the relative importance of the various terms involved in the calculation of the *g* values. He correctly pointed out the importance of often neglected matrix elements such as those involving charge-transfer states. He has concluded that meaningful molecular orbital coefficients can only be obtained if these terms are considered together with hyperfine parameters. However, it is apparent from our analysis of the CuO_4N_2 molecular system that semiempirical molecular orbital coefficients are useful and thus meaningful when a series of similar compounds is studied. The simplifications involved in the molecular orbital calculations thus appear valid when considering variations in the bonding of obviously closely related species.

The CuO_n System. For both the diaquo adduct and the anhydrous chelates, the epr spectra indicate a $d_{x^2-y^2}$ (or d_{xy}) ground state. The monohydrate, however, exhibits an

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(30) B. J. Hathaway, M. J. Bew, D. E. Billing, R. J. Dudley, and P. Nicholls, *J. Chem. Soc. A*, 2312 (1969).

(31) P. E. Rakita, S. J. Kopperl, and J. P. Fackler, Jr., *J. Inorg. Nucl. Chem.*, 30, 2139 (1968).

(32) D. W. Smith, *J. Chem. Soc. A*, 3108 (1970).

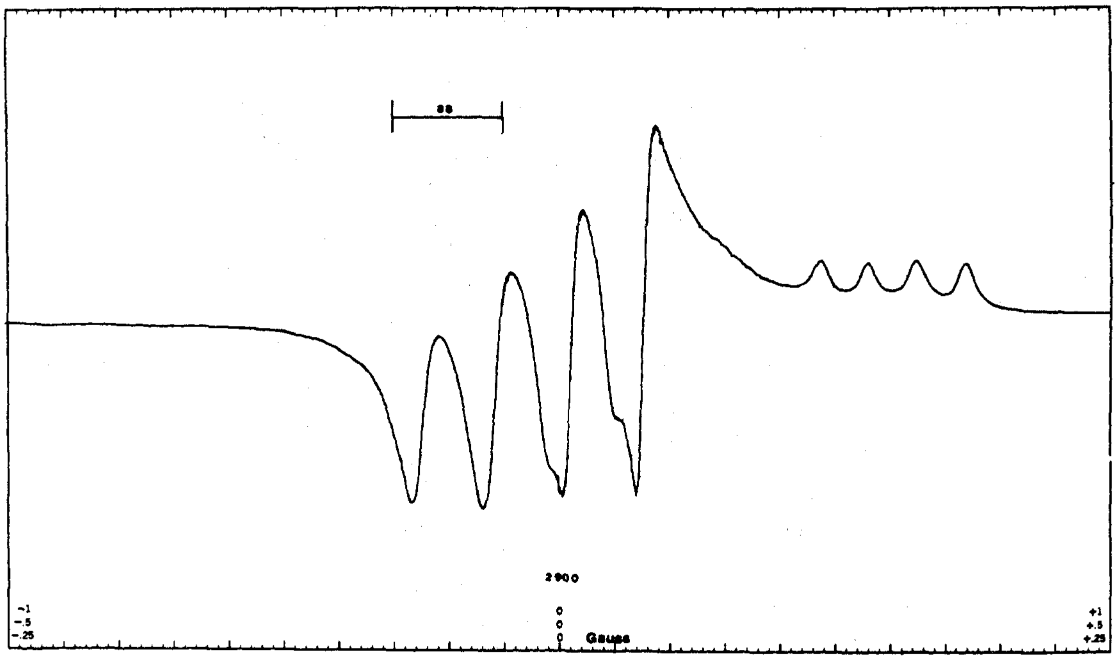

Figure 2. Epr powder spectrum for Cu-Zn(F_6acac)$_2$(H_2O) (1:50 Cu:Zn) at 77°K; microwave frequency 9.14 GHz.

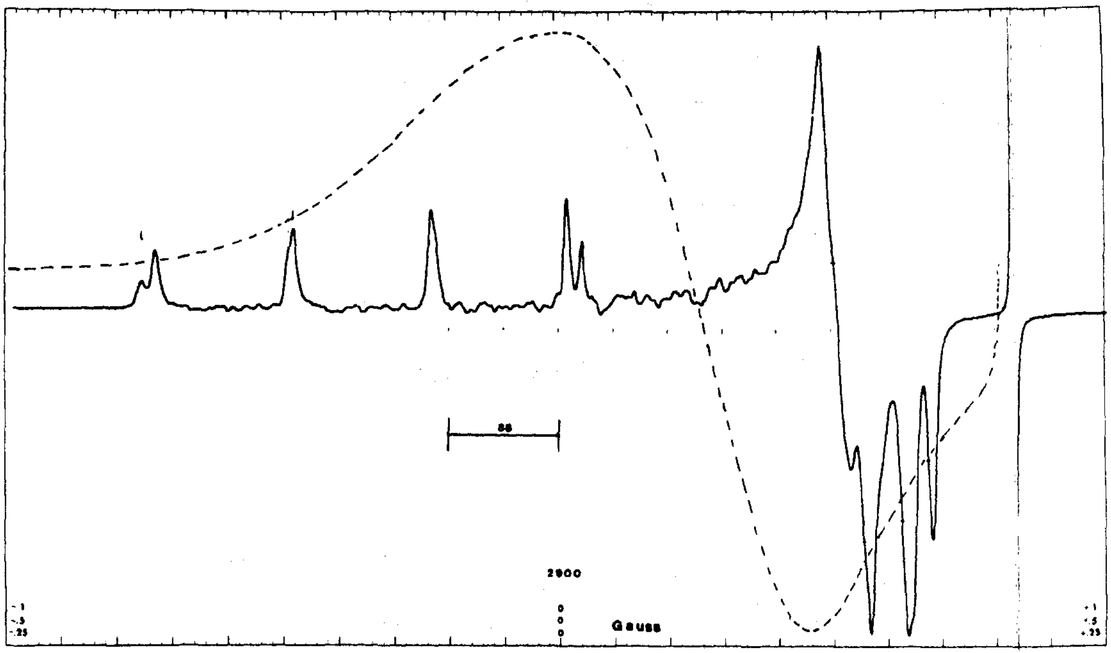

Figure 3. Epr powder spectra for [Cu-Zn(F_6acac)$_3^-$] (1:50 Cu:Zn) at 115°K (full line) and 350°K (dashed line); microwave frequency 9.067 GHz.

unusual epr spectrum (Figure 2) for which the parallel component, $g_{\parallel}$, is smaller than the $g_{\perp}$ value. This is indicative of d_{z^2} ground state and suggests a trigonal-bipyramidal structure or a tetragonal structure[33] with axial compression. The bonding coefficients shown in Table IV for Cu(F_6acac)$_2$(H_2O) indicate a d_{z^2} ground state with some admixture of $d_{x^2-y^2}$. Since mixing between these two orbitals cannot be achieved directly by L-S coupling, one must conclude that they are mixed by symmetry; *i.e.*, they belong to the same representation in the point group of the molecule. A distorted trigonal-bipyramidal configuration with C_2 or C_{2v} approximate symmetry can produce the observed magnetic parameters.

Variation of the epr parameters, $g_{\parallel}$ and $A_{\parallel}$, in the CuO_n complexes, with increasing axial coordination, follows the same pattern observed for the CuO_4N_2 system. Increasing $g_{\parallel}$ and decreasing $A_{\parallel}$ values were found for the series: Cu(F_6acac)$_2$ (in solution), Cu-Zn(F_6acac)$_2$, Cu-Zn(F_6acac)$_2$(H_2O)$_2$, and [Cu-Zn(F_6acac)$_3$]$^-$. Since Cu(F_6acac)$_2$ is a strong Lewis acid, its epr spectrum is very sensitive to the solvent used as well as to small quantities of impurities, such as H_2O or C_2H_5OH. Unfortunately a suitable noninteracting glass-forming solvent system was not found. Without better data, then, the epr parameters $g_{\parallel} = 2.270$ and $A_{\parallel} = 175$ G reported in ref 12 for Cu(F_6acac)$_2$ in a Nujol mull are considered the "true values" for the four-coordinate complex (Table III). Relatively high $g_{\parallel}$ and low $A_{\parallel}$ values have been observed for Cu-Zn(F_6acac)$_2$. This result strongly suggests

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(33) R. C. Slade, A. A. G. Tomlinson, B. J. Hathaway, and D. E. Billing, *J. Chem. Soc. A*, 61 (1968).

that in the solid state, the axial coordination sites about the metal ion are partly occupied by atoms of neighboring molecules.

For [Cu-Zn(F_6acac)$_3^-$] a dynamic Jahn-Teller behavior is observed. At 115°K a spectrum, Figure 3, typical of a tetragonally elongated octahedron is observed. A continuous variation from the low-temperature spectrum to a nearly isotropic spectrum with $g = 2.177 = {}^1/_3(g_\parallel + 2g_\perp)$ at about 350°K is seen.

The temperature dependence of the epr spectrum for [Cu-Zn(F_6acac)$_3^-$] suggests that the complex oscillates or pseudorotates between three tetragonally distorted configurations. An isotropic g value is observed at about the same temperature for copper(II)-doped tris(phenanthroline)zinc(II) nitrate dihydrate.[34] Thus it is reasonable to assume that similar energy barriers separate the three possible configurations in both of these tris chelates. In contrast, Cu-Zn(F_6acac)$_2$(py)$_2$ shows an anisotropic spectrum to 370°K and appears far from reaching isotropic behavior (a result of a relatively high energy barrier). The crystallographic data indicate a smaller tetragonality value for the pyridine adduct than for the CuO_6 complex.[35] However, the *cis*-CuO_4N_2 species cannot, by symmetry, become isotropic (as is possible for CuO_6 or CuN_6 complexes).

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Registry No. Zn(F_6acac)$_2$(py)$_2$, 38402-93-6; Cu(F_6acac)$_2$bipy, 29868-71-1; Zn(F_6acac)$_2$bipy, 42087-49-0; Cu(F_6acac)$_2$(py)$_2$, 38496-50-3; Zn(F_6acac)$_3^-$, 42087-51-4; Zn(F_6acac)$_2$(H_2O)$_2$, 42087-52-5; Zn(F_6acac)$_2$, 14949-70-3; Cu(F_6acac)$_2$, 14781-45-4; Zn(F_6acac)$_2$-(H_2O), 42087-53-6; Cu, 7440-50-8.

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(34) G. F. Kokoszka, C. W. Reinmann, H. C. Allen, and G. Gordon, *Inorg. Chem.*, 6, 165 (1967).

(35) P. T. Miller, P. G. Lenhert, and M. D. Joestin, *Inorg. Chem.*, **12**, 218 (1973), recently stated that "most literature reports on distortions in six-coordinate Cu(II) complexes are incorrect in attributing these distortions to the Jahn–Teller effect." This comment, although fundamentally correct, is misleading. The Jahn–Teller theorem, loosely stated, requires that the lowest energy electronic configuration in a nonlinear molecule be nondegenerate. However, the energy difference between the hypothetically undistorted molecule with orbital degeneracy and the distorted species in its equilibrium geometry is the point of interest. This energy difference will depend on several factors, some of which are only poorly understood at present. Clearly metal–ligand bonding parameters are involved and must be taken into account (see T. S. Davis, J. P. Fackler, and M. J. Weeks, *Inorg. Chem.*, 7, 1994 (1968)). These appear to be fairly constant for similar ligands. In the solid state, various intermolecular forces also play an important role in stabilizing the equilibrium geometry. This is shown in our work[2] on Zn-Cu(F_6acac)$_2$(py)$_2$ where, strictly speaking, the Jahn–Teller theorem is not applicable. It is also apparent from the structural and epr studies on Cu(F_6acac)$_3^-$, a $Cu^{II}O_6$ species with significantly different Cu–O bond lengths.[22] The important consideration is that a large Jahn–Teller distortion force (A. D. Liehr, *Progr. Inorg. Chem.*, 3, 281 (1962)), which produces a significant electronic splitting of the E ground state, requires that the minimum in the potential surface occurs at a fairly large value of the vibration coordinate q (of the order of 0.16 Å) for normal (2×10^5 dyn/cm) metal–ligand force constants. The crystallographic detectability of this distortion, however, will depend on whether the crystal forces present are large enough in a given system to prevent pseudorotation. It is the barrier to pseudorotation which appears to be small in most ML_6 complexes—not the Jahn–Teller distorting force.

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Paramagnetic Resonance Investigation of Au[1,2-$S_2C_2(CN)_2$]$_2^{2-}$, a Formal Gold(II) Complex

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Electron paramagnetic resonance spectra of the square-planar complex Au[$S_4C_4(CN)_4$]$^{2-}$ have been obtained over a range of temperature in magnetically dilute single crystals of Ni[$S_4C_4(CN)_4$][(n-Bu)$_4$N]$_2$·2CH_3CN and M[$S_4C_4(CN)_4$][(n-Bu)$_4$N] (M = Ni, Pd, Pt). In the former host the principal axes of **g** and **P** are coincident with the molecular axes while in the latter hosts only the axes of **P** are coincident with the molecular axes, the **g** axes being rotated ~8.5° at a temperature of 22°. The parameters are found to be temperature dependent including the angle of noncoincidence; g_{zz} increases markedly with increasing temperature. The results are shown to be consistent with a ground-state hole configuration $(B_{1g})^2(A_g)^1$ where A_g is primarily a ligand-based orbital with ~15% 6s and smaller 5d admixtures and B_{1g} is the normally half-filled antibonding orbital in square-planar d^9 complexes. The rotation of **g** is explained in terms of a reduction of the site symmetry. The temperature dependences are ascribed to the vibronic mixing of the excited configuration $(A_g)^2(B_{1g})^1$. Asymmetries in the spectra allowed the determination of the relative signs of A_{iso} and P_{zz} (opposite) and the absolute sign of the nuclear g value (positive).

Introduction

Although complexes in which gold is present in a 2+ formal oxidation state are of great interest because of their possible electronic similarity with Cu(II) complexes, very few have been reported in the literature. Bis(diethyldithiocarbamato)gold(II) was synthesized by Vanngard and Akerstrom,[1] who did not isolate the complex but did observe its solution epr spectrum which showed a characteristic four-line hyperfine pattern expected for ^{197}Au ($I = {}^3/_2$). van Willigen and van Rens[2] were able to incorporate the Au(II) complex into a single crystal of the diamagnetic Ni(II) complex and obtain epr spectra of an oriented magnetically dilute sample. The spectra showed the anomalous feature of having weak satellites outside of the main four-line pattern which was unequally spaced. In contrast to this is the normal situation in which the satellites lie within an approxi-

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(1) T. Vanngard and S. Akerstrom, *Nature (London)*, 184, 183 (1959).

(2) H. van Willigen and J. G. M. van Rens, *Chem. Phys. Lett.*, 2, 283 (1968).