

Crystal and Molecular Structure of Bis(β -Alanine) Zinc Nitrate Tetrahydrate. Electron Spin Resonance and Optical Studies of Copper(II) Diluted in This Compound.

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The structure of the title compound has been established by three-dimensional X-ray crystal structure analysis from diffractometer data. Crystals are monoclinic, space group $P2_1/n$, with $a = 23.891$, $b = 6.576$, $c = 5.519$ Å, $\beta = 95.67^\circ$, $Z = 2$. The structure was solved by direct methods (MULTAN) and refined by least-squares calculations to $R = 0.042$ for 886 independent reflexions. The zinc atom coordination in the centrosymmetric cation is octahedral with Zn–O(ala) 2.072 and Zn–O(water) 2.082 and 2.165 Å.

ESR and optical studies reveal that copper(II) substitutes the Zinc ions in the host matrix, the local symmetry around Cu being at most C_{2h} . The experimental g and hyperfine values ($g_1 = 2.400$, $g_2 = 2.097$, $g_3 = 2.084$; $A_1 = 0.0135$, $A_2 = 0.0022$, $A_3 = 0.0024$ cm^{-1}) could be reproduced within a crystal field model incorporating orbital reduction factors ($k_z = 0.875$, $k_x = 0.860$, $k_y = 0.860$). M.O. coefficients are roughly estimated.

Introduction

Several studies of Copper(II)–amino acid complexes by physical methods (ESR, Optical Spectro-

scopy, X-ray diffraction) have been published recently [1–6], showing the interest actually brought to this kind of compounds. In particular, bis(β -alaninato) Copper(II) has already been studied in the powder form, in glasses and solutions [4, 5] and in the pure monocrystalline form [6].

For the purpose of comparison with the results obtained in [6] on the hexahydrate (Fig. 1a), attempts were made to dilute the Copper(II) ion in the corresponding diamagnetic Zinc complex. The try remained unsuccessful but led to the production of an other compound, the bis(β -Alanine) Zinc(II) Nitrate Tetrahydrate. Here, the two β -Alanine molecules, lying in *trans*-position, act as unidentate ligands and coordinate the metal ion by a carboxylic oxygen. The octahedral environment is completed by the four water molecules of hydration (Fig. 1b).

We now report the X-ray crystallographic determination of the structure of the bis(β -Alanine) Zinc(II) Nitrate Tetrahydrate together with the single crystal E.S.R. and optical studies of the Copper(II) incorporated in this compound.

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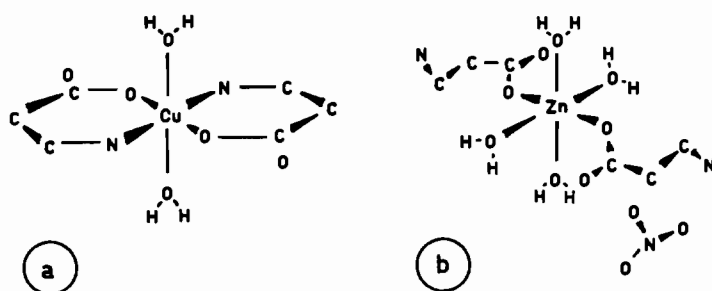


Figure 1. a) Copper(II) environment in the bis(β -Alaninato) Copper(II) Hexahydrate. b) Zinc(II) environment in the bis(β -Alanine) Zinc(II) Nitrate Tetrahydrate.

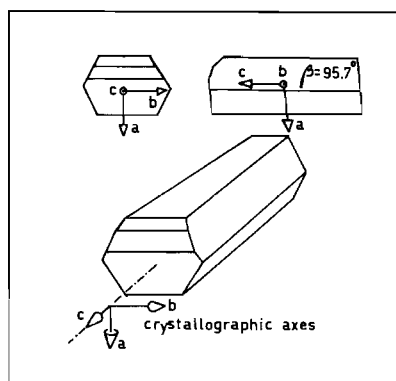


Figure 2. Bis(β -Alanine) Zinc(II) Nitrate Tetrahydrate. Crystal morphology and crystallographic axes.

Experimental

Preparation

Single crystals of bis(β -Alanine) Zinc(II) Nitrate Tetrahydrate are obtained by the following procedure. 8.909 g (0.1 mol) of β -Alanine and 13.071 g (0.05 mol) of $\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ are separately dissolved in the minimum of water. The solutions are mixed and slow evaporation yields, after about ten days, small colourless crystals suitable for X-ray analysis.

Doped crystals of greater size (5 - 6 mm length), prepared in the same way but substituting 0.005 mol of the Zinc Nitrate by the corresponding quantity of Copper Nitrate, are used for ESR and optical spectroscopy.

The doped crystals show a light blue-green coloration. The presence of more intense blue spots indicates, however, an irregular doping.

The crystals are obtained as prisms elongated along the c -axis (Figure 2).

Crystallographic Measurements

Crystal data

$\text{C}_6\text{H}_{22}\text{ZnN}_4\text{O}_{14}$, $M = 439.6$. Monoclinic, $a = 23.891(8)$, $b = 6.576(2)$, $c = 5.519(2)$ Å, $\beta = 95.67(3)^\circ$, $U = 862.8$ Å³, $D_m = 1.69$ (by flotation), $Z = 2$, $D_c = 1.692$, $F(000) = 456$. Space group $P2_1/n$ (C_2^5). Radiation: Mo-K α , $\lambda = 0.7107$ Å.

Intensity measurements

The intensities of 1118 independent reflexions were measured on a Syntex P2₁ automatic four-circle diffractometer up to $2\theta_{\text{max}} = 45^\circ$ using graphite-monochromated Mo-K α radiation. All reflexions were recorded by use of the ω scanning technique with a constant scan width of 3° . Background measurements were taken on each side of the scan range for a time equal to half the scan period. A standard reflexion measured every 50 reflexions throughout the course of data collection showed no significant intensity variation. 886 reflexions with $I \geq 2.5\sigma(I)$ were used in the structure analysis. Corrections for the Lorentz and polarization effects, but not for absorption, were applied.

Structure analysis

With $Z = 2$ the asymmetric crystal unit consists of one half the formula-unit and the zinc atoms are constrained to be at crystallographic centers of symmetry. Positions for the other non-hydrogen atoms were obtained by direct methods, applying the MULTAN 76 programmes [7]. The structure was refined by block-diagonal least-squares using the X-RAY 72 system [8] to a final R value of 0.042 for the 886 observed reflexions. A difference Fourier synthesis did not show clearly the hydrogen atoms.

Final positional and thermal parameters are given in Table I. A table of the measured and calcu-

TABLE I. Fractional Atomic Coordinates ($\times 10^4$) and Anisotropic Temperature Parameters^a with Estimated Standard Deviations in Parentheses.

	x	y	z	B ₁₁	B ₂₂	B ₃₃	B ₂₃	B ₁₃	B ₁₂
O(1)	9766(2)	8002(6)	7648(7)	13	150	209	50	16	0
O(2)	9431(2)	8423(6)	2339(7)	11	132	179	-25	12	-5
O(3)	9355(2)	11916(7)	5809(7)	11	143	233	34	15	3
O(4)	9404(2)	14465(7)	3148(8)	15	168	248	41	14	6
C(5)	9195(2)	13599(9)	4891(11)	7	116	233	-25	-1	-3
C(6)	8700(3)	14673(11)	5887(15)	12	171	485	-40	36	2
C(7)	8493(3)	13653(12)	8102(13)	13	289	292	-91	23	-8
N(8)	8212(3)	11663(10)	7364(11)	19	175	360	3	26	-7
N(9)	7081(2)	3670(8)	2741(9)	10	180	254	-32	0	-2
O(10)	6653(2)	4739(9)	2201(11)	10	287	511	107	3	10
O(11)	7385(2)	3150(10)	1222(11)	23	347	431	-62	45	12
O(12)	7187(2)	3205(9)	4939(9)	25	301	293	18	-3	15
Zn ⁺⁺	10000(0)	10000(0)	5000(0)	8	107	160	19	11	2

^a $\times 10^4$; in the form $B \sin^2 \theta / \lambda^2 = B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl$.

TABLE II. Eigenvalues and Eigenvectors of the \bar{g} and Hyperfine $\bar{A}(\text{Cu})$ Tensors.

Eigenvalues ^a		Eigenvectors of \bar{g} with respect to the a^* , b , c axes ^b		
$g_1 = 2.400$	$A_1 = 135 \text{ (cm}^{-1} \times 10^4)$	\hat{z} 0.610	\hat{z} 0.481	\hat{z} 0.625
$g_2 = 2.097$	$A_2 = 22$	\hat{y} 0.390	\hat{y} 0.500	\hat{z} 0.770
$g_3 = 2.084$	$A_3 = 24$	\hat{x} 0.683	\hat{z} 0.717	\hat{z} 0.120

^aThe estimated error is 0.005 on the g -values, $2 \text{ (cm}^{-1} \times 10^4)$ on A_1 and 6 on A_2 and A_3 . ^bThe signs in parentheses correspond to the second paramagnetic centre.

lated structure factors may be obtained from the authors.

Optical Spectroscopy

Absorption spectra of pure and doped single crystals were recorded at room temperature in the UV-visible and near Infra-red regions ($30000\text{--}5000 \text{ cm}^{-1}$), on Beckman Acta V and Acta M-IV spectrophotometers. Polarized spectra were also taken in the (b , c) plane by means of polaroids or nicol prisms but did not show any polarization effect. The spectrum of the doped single crystals consists of a broad band approximately located between 16 kK and 9.0 kK with a maximum at 12.3 kK.

E.S.R. Spectroscopy

The E.S.R. spectra were measured at normal temperature with a X-band Bruker spectrometer as previously described [9]. The doped single crystal was rotated in three orthogonal planes (c , b), (c , a^*) and (b , a^*), it was always cemented on the same face (parallel to the (b , c) plane). The line width is about 25 gauss.

Two magnetically non equivalent species are observed. Their spectra (consisting of four hyperfine lines) coincide along the axes in the (a^* , b) and (b , c) planes and at all angles in the (a^* , c) plane. By means of the procedure detailed in [10], the complete rotational data (spectra centres, hyperfine distances) yield the eigenvalues and vectors of the \bar{g} and hyperfine $\bar{A}(\text{Cu})$ tensors (Table II). The data of Table II are the mean values of the results obtained for the 2 centres.

The principal axes of the \bar{g} and \bar{A} tensors are the same within experimental error. The ambiguity in the signs of the off-diagonal elements of the tensors [10] leads to two different sets of principal values. One of these could be eliminated using a measurement on the powdered crystal.

Discussion

Crystal and Molecular Structure of Bis(β -Alanine) Zinc Nitrate Tetrahydrate

The coordination geometry in the complex cation and the atom numbering are shown in Figure 3. A

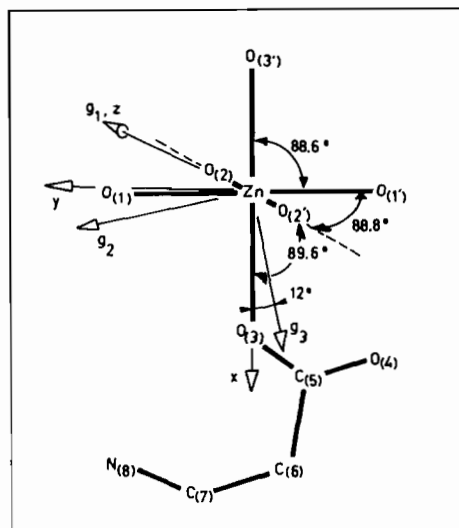


Figure 3. Atom numbering in the centrosymmetrical cation. N(9), O(10), O(11) and O(12) refer to the atoms of the NO_3^- anion. Position of the principal g -axes and of the x , y , z molecular frame.

stereoscopic view of the crystal structure seen along [010] is illustrated in Figure 4. The crystals contain centrosymmetric $[\text{Zn}(\beta\text{-ala})_2(\text{H}_2\text{O})_4]^{2+}$ cations and pairs of nitrate anions related by an inversion center. This Zinc(II) structure is unusual in having a clearly rhombic $\text{ZnO}_2\text{O}'_2\text{O}''_2$ chromophore (Fig. 3). Interatomic distances and valency angles in the ions are listed in Table III. Some torsion angles of interest are given in Table IV.

Bond lengths and angles in the organic part of the cation are consistent with those observed in β -alanine crystals [11]. The nearly equal distances between carbon and oxygen in the carboxylic group show the alanine ligand to be in the zwitterion form $^-\text{NH}_3\text{--CH}_2\text{--CH}_2\text{--COO}^-$. The $\text{O}(6)\text{O}(5)\text{O}(3)\text{O}(4)$ alanine fragment lies in the approximate octahedral symmetry plane $\text{O}(1)\text{ZnO}(3)$: all relevant torsion angles do not differ from 0 or π by more than 2° (Table IV). The $\text{O}(4)\cdots\text{O}(1')$ distance (2.631 Å) probably indicates an intracationic hydrogen bond, O(4) acting as acceptor. The distances and angles reported in Table V suggest other hydrogen bonds:

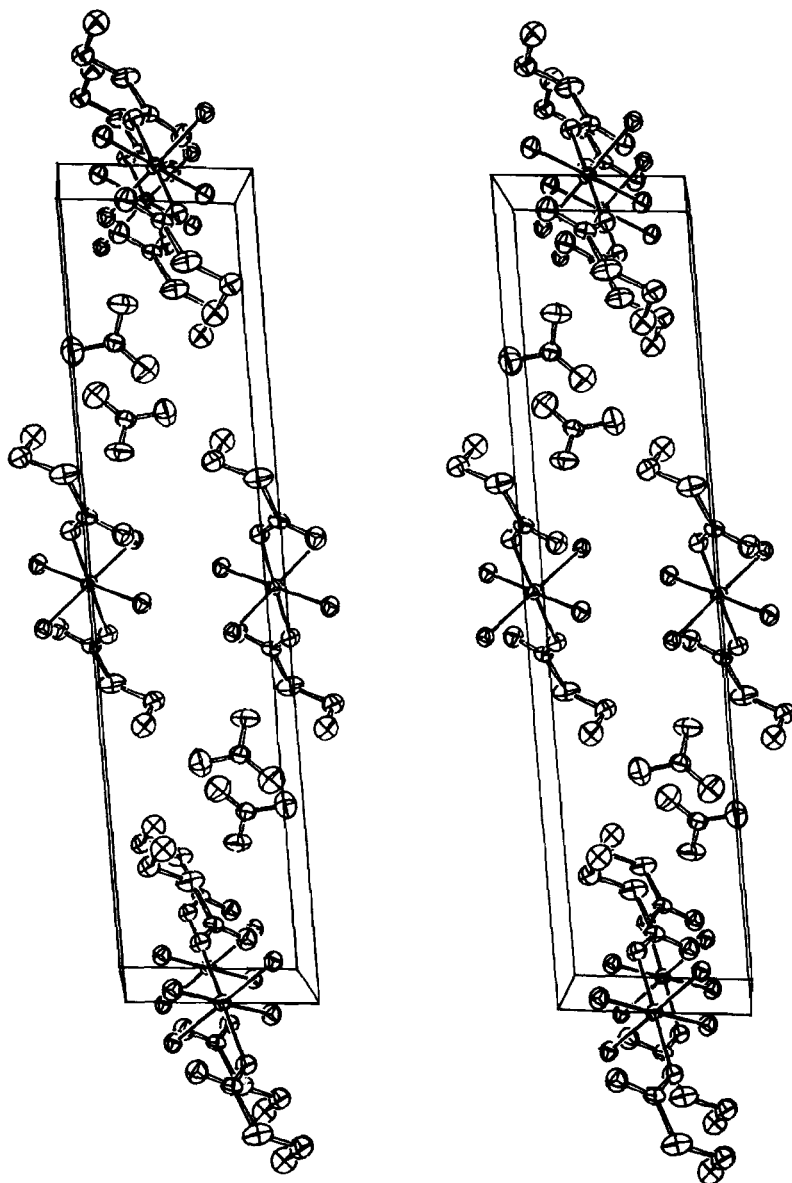


Figure 4. ORTEP drawing of the unit-cell content.

TABLE III. Intraionic Interatomic Distances (Å) and Valency Angles ($^{\circ}$) with Standard Deviations.

O(1)—Zn ⁺⁺	2.082(4)	N(9)—O(10)	1.253(7)
O(2)—Zn ⁺⁺	2.165(4)	N(9)—O(11)	1.211(8)
O(3)—O(4)	2.239(6)	N(9)—O(12)	1.253(7)
O(3)—C(5)	1.261(7)	O(10)—O(11)	2.152(8)
O(3)—C(6)	2.398(8)	O(10)—O(12)	2.132(8)
O(3)—Zn ⁺⁺	2.072(4)	O(11)—O(12)	2.151(8)
O(4)—C(5)	1.263(7)		
O(4)—C(6)	2.374(9)	O(4)—O(3)—C(5)	27.5(3)
C(5)—C(6)	1.525(9)	O(4)—O(3)—C(6)	61.5(2)
C(6)—C(7)	1.519(11)	O(4)—O(3)—Zn ⁺⁺	103.0(2)
C(6)—N(8)	2.476(10)	C(5)—O(3)—C(6)	34.0(3)
C(7)—N(8)	1.508(10)	C(5)—O(3)—Zn ⁺⁺	130.5(4)

TABLE III (continued)

C(6)-O(3)-Zn ⁺⁺	164.5(3)
O(3)-O(4)-C(5)	27.4(3)
O(3)-O(4)-C(6)	62.6(2)
C(5)-O(4)-C(6)	35.1(4)
O(3)-C(5)-O(4)	125.1(6)
O(3)-C(5)-C(6)	118.5(5)
O(4)-C(5)-C(6)	116.4(5)
O(3)-C(6)-O(4)	56.0(2)
O(3)-C(6)-C(5)	27.5(3)
O(3)-C(6)-C(7)	86.9(4)
O(3)-C(6)-N(8)	74.4(3)
O(4)-C(6)-C(5)	28.5(3)
O(4)-C(6)-C(7)	142.6(5)
O(4)-C(6)-N(8)	123.4(4)
C(5)-C(6)-C(7)	114.3(6)
C(5)-C(6)-N(8)	98.9(4)
C(7)-C(6)-N(8)	35.0(4)
C(6)-C(7)-N(8)	109.7(6)
C(6)-N(8)-C(7)	35.3(4)
O(10)-N(9)-O(11)	121.7(6)
O(10)-N(9)-O(12)	116.7(5)
O(11)-N(9)-O(12)	121.6(6)
N(9)-O(10)-O(11)	28.6(3)
N(9)-O(10)-O(12)	31.7(3)
O(11)-O(10)-O(12)	60.3(3)
N(9)-O(11)-O(10)	29.7(3)
N(9)-O(11)-O(12)	29.7(3)
O(10)-O(11)-O(12)	59.4(3)
N(9)-O(12)-O(10)	31.7(3)
N(9)-O(12)-O(11)	28.6(3)
O(10)-O(12)-O(11)	60.3(3)
O(1)-Zn ⁺⁺ -O(2)	88.8(2)
O(1)-Zn ⁺⁺ -O(3)	88.6(2)
O(2)-Zn ⁺⁺ -O(3)	90.4(2)

TABLE IV. Torsion Angles (°).

Zn-O(3)-C(5)-O(4)	2
Zn-O(3)-C(5)-C(6)	-180
C(5)-O(3)-Zn-O(1)	-179
C(5)-O(3)-Zn-O(2)	-90
O(3)-C(5)-C(6)-C(7)	6
O(4)-C(5)-C(6)-C(7)	-176
C(5)-C(6)-C(7)-N(8)	-70

(i) Between cations; chains O(1)···O(2)-Zn-O(2')···O(1')-Zn-O(1)··· parallel to [001] and O(2)···O(4)CO-Zn-OCO(4')···O(2')-Zn-O(2) parallel to [010] assure the formation of cationic sheets parallel to (100);

(ii) Between cation and anion; the nitrate oxygen atom O(10) seems to be an acceptor for two bonds from O(2)H and N(8)H; moreover N(8) makes two other bonds with O(12) and O(12').

The shortest N-O bond in NO₃⁻ appears between N(9) and O(11) the only nitrate oxygen not involved in an hydrogen bond. The difference in the O-N-O

TABLE V. Interionic Hydrogen Bonds.

Bond Lengths (Å)	
O(1)···O(2a)	2.799
O(2)···O(4b)	2.643
O(2)···O(10c)	2.765
N(8)···O(10c)	2.866
N(8)···O(12d)	2.859
N(8)···O(12'c)	2.928
Bond Angles (°)	
O(2a)···O(1)···O(4b)	120
Zn-O(1)···O(2a)	135
Zn-O(1)···O(4b)	91
O(4b)···O(2)···O(10c)	104
Zn-O(2)···O(4b)	112
Zn-O(2)···O(10c)	109
O(10c)···N(8)···O(12d)	85
O(10c)···N(8)···O(12'c)	100
O(12d)···N(8)···O(12'c)	102
C(7)-N(8)···O(12d)	99
C(7)-N(8)···O(10c)	122
C(7)-N(8)···O(12'c)	134

The letters a, b, c, d refer to the following transformation of the coordinates of Table I:

a $x, y, z + 1$
b $x, y - 1, z$
c $3/2 - x, y + 1/2, 1/2 - z$
d $x, y + 1, z$

valency angles is probably significant and could be explained by simple electronic repulsion: the smallest angle is between the longest bonds.

Information about the Cu(II) Ion Diluted in Bis(β -Alanine) Zinc Nitrate Tetrahydrate

The direction cosines, relative to a*, b, c axes, of the directions of the metal-ligand bonds in bis(β -Alanine) Zinc(II) Nitrate Tetrahydrate as obtained from crystallographic data are given in Table VI.

A comparison with the eigenvectors of the \bar{g} tensors shows that the Copper(II) ion observed by ESR has truly substituted for the Zinc(II) ion in the host matrix. Indeed, the g_1 -eigenvector lies at $\sim 2^\circ$ only from the normal to the equatorial plane and such a value being of the order of magnitude of the experimental error, one may consider that the g_1 -eigenvector and this normal do coincide. On the other hand, the g_1 principal directions are seen to lie at $\sim 12^\circ$ from the in-plane bond directions.

The presence of less intense supplementary lines, visible mainly in the powder spectrum, shows that Copper must also be present in other positions, probably interstitial.

TABLE VI. Direction Cosines, Relative to a*, b, c Axes, of the Directions of the Metal-Ligand Bonds in Bis(β -Alanine) Zinc(II) Nitrate Tetrahydrate.

	a*	b	c
Zn-O ₁	(-) 0.26684	0.63116	(+) -0.72831
Zn-O ₂	(-) 0.62503	0.47899	(-) 0.61636
Zn-O ₃	(-) 0.73948	-0.60801	(+) -0.28895
Normal to the Equatorial Plane (Zn, O ₁ , O ₃ , O _{1'} , O _{3'})	(-) 0.62537	0.46160	(-) 0.62916

The precise geometry of the doping site is obviously not known but in the following it will be assumed that the guest cations accept the structure of the host. This view is supported by the E.S.R. data. Indeed, when compared with the results obtained in other Copper complexes [13], g_1 (2.400) is a high value and A_1 (0.0136 cm^{-1}) a rather low one. Such a trend is expected when the axial perturbation of the Copper environment becomes important (decrease in tetragonal character), which is precisely the case if Copper substitutes Zinc without modifying its environment: $\text{Zn-O}_{\text{axial}} = 2.165$, $\text{Zn-O}_{\text{equat.}} \cong 2.07$ Å. In the bis(β -Alaninato) Cu(II) Hexahydrate for example [6], where the axial perturbation is much less strong ($\text{Cu-O}_{\text{axial}} = 2.53$ Å, $\text{Cu-O}_{\text{equat.}} \cong 2.02$ Å) we found $g_1 = 2.288$, $g_2 = 2.070$, $g_3 = 2.051$.

The real symmetry of the host molecule is C_i (Fig. 3) but it approximates closely to C_{2h} and even D_{2h} . Strictly, however, this latter point group should be rejected because of the non coincidence of the in-plane \bar{g} -eigenvectors with the bond directions [12].

The absence of polarization effects in the optical spectrum is easily understandable. The existence of 2 molecules in the unit cell, with their Z-axes wide apart (*ca.* 57°), is not favourable to the observation of dichroism. Moreover, in the C_{2h} symmetry with a $|X^2 - Y^2\rangle$ ground state (according to the axes frame of Fig. 3) all the d-d transitions appear to be vibronically allowed along the three molecular axes directions.

Although the Crystal Field Model is a rather crude approximation to the reality, it offers the advantage of allowing the calculation of spectral and magnetic quantities with the use of a small number of parameters [14]. This model will be used here to give a first and overall approach of the compound. Referring to Companion and Komarynski's work [15], each ligand around the Copper ion is characterized by its polar and azimuthal angles θ and ϕ , known from the crystallographic data, and by two empirical parameters α_2 and α_4 (or α_2/α_4). A computer program has been used which calculates the perturbation crystal field, spin-orbit coupling and Zeeman interaction matrix elements and diagonalizes completely the corresponding matrices. Covalency effects are taken into account by introducing an orbital reduction

factor k as described in [6]. The program was extended to include the hyperfine interaction. The A values were calculated by applying the operator [16]:

$$P(\hat{I}_i + (4/7 - \kappa)\hat{S}_i - 1/7(\hat{I} \cdot \hat{S})\hat{I}_i - 1/7\hat{I}_i(\hat{I} \cdot \hat{S}))$$

where $i = x, y, z$, to the 2 lowest Zeeman eigenfunctions and by diagonalizing the three 2×2 matrices. In the operator, $P = g_e g_N \beta_e \beta_N \cdot r^{-3}$ and κ is the isotropic part of the hyperfine interaction; ζ , the spin-orbit coupling constant, is taken as -828 cm^{-1} . A set of parameters which leads to a satisfactory agreement with experiment is listed in Table VII.

The values of α_4 and α_2/α_4 for the six ligands have been scaled according to the actual metal-ligand separation [17]. The equatorial value of α_2/α_4 has been chosen as 0.9 [18] but it appeared through our calculations to be not a critical parameter. An α_4 value of $\sim 7200 \text{ cm}^{-1}$ for oxygen in the equatorial plane corresponds to $10 Dq = 12000 \text{ cm}^{-1}$ which is a typical value for a Cu(II) complex.

The calculated optical transitions, after spin-orbit coupling has been taken into account, are 1.4, 11.3 and 12.5, 12.4 kK for the $|Z^2\rangle$, $|XZ, YZ\rangle$ and $|XY\rangle \rightarrow |X^2 - Y^2\rangle$ transitions respectively. The first transition ($|Z^2\rangle \rightarrow |X^2 - Y^2\rangle$) could not be observed experimentally. The calculated value of 1400 cm^{-1} seems to be very low because the presence of a so close excited state should normally cause a drastic broadening of the ESR signal at room temperature which was not observed. On the other hand one might expect for the copper ion a ligand environment with a greater tetragonal distortion than that shown by the Zinc complex: this should enhance the splitting between the $|X^2 - Y^2\rangle$ and $|Z^2\rangle$ states while it has very little effect on the g values.

In order to produce the in-plane g -anisotropy, a slight difference has to be introduced between the α_4 equatorial values: $\alpha_4(\text{COO}) = 7200$, $\alpha_4(\text{H}_2\text{O}) = 7160 \text{ cm}^{-1}$. The highest α_4 value is associated with the nearest oxygen (O_3 of COO). The orbital reduction factors reduce the theoretical g -values to the experimental ones within 0.001.

The principal values of the \bar{A} tensor could be reasonably reproduced with $\kappa = 0.314$ and $P = 0.0365 \text{ cm}^{-1}$. Such values for the parameters κ and P are

TABLE VII. Experimental and Theoretical Results.

Angular Coordinates of Ligands			Radial Parameters			
Atom	θ	ϕ	α_4 (cm ⁻¹)		α_2/α_4	
O ₂	1.25°	109°	-5893		0.97	
O' ₂	181.25°	289°	-5893		0.97	
O ₃	90°	0°	-7200		0.90	
O ₁	90°	89°	-7160		0.90	
O' ₃	90°	180°	-7200		0.90	
O' ₁	90°	269°	-7160		0.90	
Observed Optical Transition			~12.3 kK			
Calculated Transitions (spin-orbit included)			12.5	12.4	11.3	1.4
Orbital Reduction Factor k			k _z = 0.875		k _x = 0.860	k _y = 0.860
Calculated g-Values			g ₁ = 2.401 (g _z)		g ₂ = 2.096 (g _y)	g ₃ = 2.083 (g _x)
κ			0.314			
P (cm ⁻¹ × 10 ⁴)			365			
Calculated A-Values (cm ⁻¹ × 10 ⁴)			A _z = 136		A _y = 21	A _x = 28

quite usual [16]. After application of the crystal field perturbation, the ground state is as follows:

$$-0.0191|Z^2\rangle - 0.0171|XY\rangle + 0.9997|X^2 - Y^2\rangle$$

The contribution of $|Z^2\rangle$ to the ground state, which is due to the rhombic perturbation along the bonds in the equatorial plane, is largely responsible for the g_{\perp} anisotropy. The tilt of the Zn-O₂ bond on the equatorial plane also leads to the mixing of $|Z^2\rangle$ but to a minor extent. The slight departure from orthogonality between the Zn-O₁ and Zn-O₃ bonds (which corresponds to a difference in energy of the $|XZ\rangle$ and $|YZ\rangle$ crystal field orbitals) gives a contribution of $|XY\rangle$ to the ground state and is accountable of the non coincidence of the g_{\perp} principal axes with the equatorial bond directions (rotation of g_3 -direction towards bond bisectors [12]).

The $|XY\rangle$ contribution to the ground state has a small effect of about 0.001 on the g_{\perp} anisotropy. From the preceding it follows that the main low symmetry effects are almost completely described by the mixing of $|Z^2\rangle$ alone. This is in agreement with Hitchman's statement that when the g_{\perp} axes are close to the metal-ligand bond directions within ca. 15°, the complex can be considered as belonging to class IIa(D_{2h}) [19].

It is a difficult task to evaluate correctly M.O. coefficients from orbital reduction factors or directly from the E.S.R. parameters.

Many workers have used the expressions of Kivelson and Neiman [20] (D_{4h}) or similar ones in spite of the fact that they imply numerous approximations as discussed in [21].

We have used the corresponding expressions for D_{2h} symmetry cited in [22], to get an idea of α , β , γ , δ , the M.O. coefficients of the $d_{x^2-y^2}$, d_{xy} , d_{xz} , d_{yz} orbitals.

Taking the same (negative) sign for the hyperfine values yields:

$$\alpha^2 \cong 0.67, \beta^2 \cong 1, \gamma^2 \cong 1, \delta^2 \cong 1$$

The choice of a different sign for A_z (<0) and A_x, A_y, gives:

$$\alpha^2 \cong 0.97, \beta^2 \cong 0.80, \gamma^2 \cong 0.65, \delta^2 \cong 0.71$$

The first set shows a very strong σ -bond covalency while in-plane and out-of-plane π bonding is ionic. The second set exhibits a practically opposite situation. Both cases thus appear to be unrealistic since covalency of the metal-ligand bond is expected in the kind of compounds in question here. Beyond the numerous approximations mentioned above, the lack of reliability of the M.O. coefficients may also be due to the use, for their calculation, of the metal rather than the ligand hyperfine data [22].

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