

conformations. Since there is, in fact, a significant percentage (13%) of the former present, it is evident that while it is less stable, it is not a great deal less stable. The percentage here is near the center of the range previously known (Table I) of 6-23%.

The conformations of the six-membered rings can also be designated as  $\delta$  or  $\lambda$ , just as in the case of five-membered chelate rings<sup>8</sup> if the center of the Mo-Mo bond is supposed to occupy the position of the single metal atom in the mononuclear chelate complex. It will be seen that all rings in Figure 3 have the  $\lambda$  conformation.

When we compare Figure 4 with Figure 5, one more remarkable and important fact becomes clear. The two molecules partially occupying a given site have *opposite chiralities*. In the case chosen, the principal molecule has a clockwise or right-hand helicity ( $\Delta$ ), while the minor molecule has a

counterclockwise or left-hand helicity ( $\Lambda$ ). Thus, the two molecules shown in Figures 4 and 5 could be designated as  $\lambda\Delta\lambda$  and  $\lambda\Lambda\lambda$ , respectively. Those related to them by inversion would be  $\delta\Lambda\delta$  and  $\delta\Delta\delta$ . Besides these four, two other possibilities can be envisioned,  $\delta\Delta\lambda$  and  $\delta\Lambda\lambda$ , but we know of no evidence for their existence.

It is interesting that, in the minor molecule shown in Figure 5, the P-Mo-Mo-Cl type torsion angles, though opposite in sign to those of the principal molecule, are very similar in magnitude, viz., 27.5, 27.0, 31.7, and 24.6°, for a mean value of 27.7° as compared to 30.5° for the principal molecule.

**Acknowledgment.** We thank the National Science Foundation for the support of this work.

**Registry No.**  $\beta$ -Mo<sub>2</sub>Cl<sub>4</sub>(dppe)<sub>2</sub>, 64508-32-3;  $\alpha$ -Mo<sub>2</sub>Cl<sub>4</sub>(dppe)<sub>2</sub>, 64490-77-3; Mo<sub>2</sub>(O<sub>2</sub>CCF<sub>3</sub>)<sub>4</sub>, 36608-07-8; Mo, 7439-98-7.

**Supplementary Material Available:** Tables of anisotropic thermal vibration parameters, bond distances, bond angles, torsion angles, and observed and calculated structure factors (22 pages). Ordering information is given on any current masthead page.

(8) See, for example: Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 4th ed.; Wiley: New York, 1980; p 78.

Contribution from the Laboratoire de Chimie des Métaux de Transition, ERA 608, and Laboratoire de Chimie du Solide, LA 302, Université Pierre et Marie Curie, 75230 Paris, France

## X-ray, ESR, and Optical Absorption Studies of Tetrakis(cyclohexylamine)copper(II) Nitrate: An Example of a Flattened-Tetrahedral Copper(II) Complex

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The preparation, spectroscopic and redox properties, and crystal structure of [Cu(C<sub>6</sub>H<sub>11</sub>NH<sub>2</sub>)<sub>4</sub>](NO<sub>3</sub>)<sub>2</sub> are described. Crystals are orthorhombic, space group *P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>, with *a* = 13.68 (4) Å, *b* = 16.21 (2) Å, *c* = 13.55 (1) Å, and *Z* = 4. The structure has been solved and refined to *R* = 0.066. The copper environment is a flattened tetrahedron, with the four amine nitrogens ligated to copper. Symmetry elements are not far from those of the *D*<sub>2d</sub> symmetry group. Optical and ESR results suggest that the properties of Cu(II) are closer to those of a pseudoplanar geometry, since the  $\omega$  distortion angle is 40° and since LCAO-MO calculations place the change from *T*<sub>2</sub> to *D*<sub>4h</sub> at 65°. Potential measurements in the solid state and in acetonitrile solution show a shift of potential toward more positive values.

### Introduction

Blue copper proteins (BCP) exhibit unusual properties with respect to other copper complexes, i.e. a large extinction coefficient for the absorption near 17 000 cm<sup>-1</sup>, an unusually small copper hyperfine coupling constant, and a markedly positive redox potential. Many authors have investigated the relation between these properties and the coordination geometry of copper(II);<sup>1</sup> among several suggestions, one assumes that a pseudotetrahedral geometry of copper environment allows an easier change from copper(II) to copper(I). Low-molecular-weight copper(II) complexes, such as CuS<sub>4</sub>, Cu-S<sub>2</sub>N<sub>2</sub>, CuSN<sub>3</sub>, CuN<sub>4</sub>, can be useful models for these investigations.

The title compound is an example of a flattened-pseudotetrahedral environment and can be then proposed as a model for BCP. Several such examples have been already described and discussed; however, this one has the rare feature of having four monodentate ligands. The purpose of the present paper is to contribute to the above discussion, with careful study of the structural and spectral properties of this pseudotetrahedral CuN<sub>4</sub> complex.

### Experimental Section

**Synthesis.** Eleven milliliters of a 5.2 mol L<sup>-1</sup> ethanolic solution of cyclohexylamine was poured into 25 mL of a 1.3 × 10<sup>-3</sup> mol L<sup>-1</sup>

ethanolic solution of Cu(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O. Slow evaporation under a nitrogen flow led to slightly air-unstable blue crystals suitable for X-ray analysis. Anal. Calcd for Cu(C<sub>6</sub>H<sub>11</sub>NH<sub>2</sub>)<sub>4</sub>(NO<sub>3</sub>)<sub>2</sub>: Cu, 10.88; H, 8.9; C, 49.36; N, 14.40; O, 16.45. Found: Cu, 10.57; H, 9.0; C, 49.0; N, 14.97; O, 16.6.

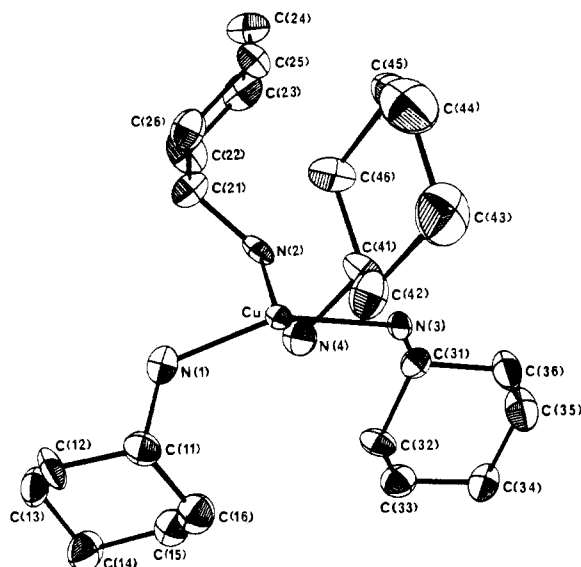
**Electronic Spectra** were recorded at room temperature on a Beckman 5240 UV-visible spectrophotometer, between 25 000 and 5000 cm<sup>-1</sup>. For the solid compound, its concentration in KBr pellets was 0.013 mg/mg of KBr. Solutions of the compound in nitromethane and propylene carbonate were 0.55 and 0.64 mg mL<sup>-1</sup>, respectively.

**ESR Spectra** were recorded on a Varian CST 104 spectrometer, working at 9.3 GHz (X band) with a 100-kHz field modulation and supplied with a variable-temperature accessory in the range 293-77 K. The components of the *g* tensor have been measured with respect to a DPPH sample (*g* = 2.0037). The magnetic field was checked with a NMR proton probe.

**Redox Potential Measurements.** Cyclic voltammetry was carried out in the solid state and in solution, with a Tacussel potentiostat. Potentials were referred to a saturated calomel electrode. For the solid compound, the electrode was made of carbon powder<sup>2</sup>, with 1.45

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**Figure 1.** ORTEP drawing of the complex cation  $[\text{Cu}(\text{C}_6\text{H}_{11}\text{NH}_2)_4]^{2+}$  with 50% probability ellipsoids.

mg of complex/51 mg of carbon. It was immersed in dried acetonitrile containing tetrabutylammonium tetrafluoroborate as supporting electrolyte and deoxygenated by bubbling nitrogen; the temperature was  $25 \pm 0.5^\circ\text{C}$ .

For the complex dissolved in dried acetonitrile, a concentration of about  $5 \times 10^{-4} \text{ mol L}^{-1}$  was obtained by leaving the solvent in contact with the solid complex for 2 days. Cyclic voltammetry was then performed at room temperature, with a solid carbon electrode and tetrabutylammonium tetrafluoroborate as supporting electrolyte.

**Crystal Structure and Refinement.** The crystal selected for X-ray analysis was octahedrally shaped, with a basal square plane edge of 0.3 mm. It was screened with varnish and set up on the goniometric head along its tetragonal axis.

Preliminary Laue and precession photographs led to an orthorhombic unit cell: space group  $P2_12_12_1$ ; lattice constants  $a = 13.68(4) \text{ \AA}$ ,  $b = 16.21(2) \text{ \AA}$ ,  $c = 13.55(1) \text{ \AA}$ ,  $V = 3004.75 \text{ \AA}^3$ ;  $Z = 4.02$  for  $\rho = 1.3 \times 10^3 \text{ kg m}^{-3}$  (measured by flotation in a trichloromethane-chlorobenzene mixture).

Intensity data were collected on a homemade automatic diffractometer: radiation,  $\text{Mo K}\alpha$ ; takeoff angle,  $1^\circ$ ; crystal-focus distance, 230 mm; crystal-counter distance, 230 mm; scan type,  $\theta$ - $2\theta$  scan technique ( $1.5^\circ \text{ min}^{-1}$ ); scan length,  $1.1^\circ$  symmetrical scan at zero Bragg angle, corrected for  $\text{K}\alpha_1$ - $\text{K}\alpha_2$  dispersion; background measurements, 10 s in fixed positions before and after every scan. The scintillation counter was connected to a pulse height analyzer set on  $\text{Mo K}\alpha$  energy so that 90% of the intensity was counted. The graphite monochromator was set in front of the counter window. Two standard reflections, 044 and 211, were measured every 100 reflections; a correction has been made for taking into account the observed intensity decrease. A total of 2373 independent reflections have been collected at room temperature to  $\theta_{\text{Bragg}} = 23^\circ$ , and the 1387 reflections with intensity higher than  $3\sigma$  have been kept for refinement. Intensities were corrected for Lorentz and polarization factors.

The absorption coefficient is equal to  $7.78 \text{ cm}^{-1}$ ; this low value and the nearly regular pseudooctahedral geometry led us not to make any absorption corrections.

For every observed structure factor  $F_o$ , a standard deviation  $\sigma$  was computed:  $\sigma = F_o(\Delta c)/c$ , where  $c$  is the integrated intensity and  $\Delta c$  the error.

Atomic form factors were taken from Cromer and Waber<sup>3</sup> for all atoms except hydrogen atoms, for which values of Stewart, Davidson, and Simpson<sup>4</sup> were applied. Copper, nitrogen, oxygen, and carbon atoms were corrected for the real and imaginary parts of anomalous dispersion.

**Table I.** Atomic Parameters

atom	$x/a$	$y/b$	$z/c$	$B_{\text{iso}}, \text{ \AA}^2$
Cu	0.2233 (2)	0.1248 (1)	0.0122 (2)	3.46 (5)
N(1)	0.084 (1)	0.0800 (9)	0.024 (1)	5.4 (5)
N(2)	0.213 (2)	0.1466 (9)	-0.131 (1)	5.6 (5)
N(3)	0.3716 (8)	0.1082 (9)	0.005 (2)	5.4 (5)
N(4)	0.227 (1)	0.162 (1)	0.156 (1)	5.7 (5)
C(1)	0.056 (2)	0.023 (2)	0.108 (2)	6.7 (8)
C(12)	-0.051 (2)	0.001 (1)	0.104 (2)	7.6 (8)
C(13)	-0.077 (1)	-0.061 (1)	0.025 (2)	8.2 (8)
C(14)	-0.015 (2)	-0.141 (2)	0.033 (2)	9.4 (10)
C(15)	0.096 (2)	-0.113 (2)	0.033 (2)	8.0 (8)
C(16)	0.120 (2)	-0.054 (2)	0.112 (2)	7.6 (9)
C(21)	0.127 (2)	0.203 (2)	-0.172 (2)	7.6 (9)
C(22)	0.131 (2)	0.212 (2)	-0.285 (2)	9.7 (10)
C(23)	0.208 (2)	0.269 (2)	-0.321 (2)	8.5 (9)
C(24)	0.206 (2)	0.352 (1)	-0.269 (2)	8.7 (9)
C(25)	0.202 (2)	0.343 (1)	-0.157 (2)	5.7 (7)
C(26)	0.122 (2)	0.282 (2)	-0.126 (2)	7.3 (8)
C(31)	0.410 (1)	0.040 (1)	-0.051 (2)	5.7 (6)
C(32)	0.363 (1)	-0.0415 (9)	-0.020 (2)	5.8 (6)
C(33)	0.407 (2)	-0.117 (2)	-0.069 (2)	7.9 (7)
C(34)	0.518 (2)	-0.118 (1)	-0.059 (2)	7.5 (7)
C(35)	0.565 (2)	-0.039 (2)	-0.088 (2)	9.1 (10)
C(36)	0.522 (1)	0.034 (1)	-0.038 (2)	7.4 (9)
C(41)	0.287 (2)	0.236 (1)	0.180 (1)	5.5 (6)
C(42)	0.272 (2)	0.256 (2)	0.290 (2)	7.6 (7)
C(43)	0.329 (2)	0.334 (2)	0.317 (2)	10.0 (11)
C(44)	0.302 (2)	0.405 (2)	0.257 (3)	10.9 (12)
C(45)	0.311 (2)	0.385 (2)	0.145 (2)	8.0 (9)
C(46)	0.258 (2)	0.306 (1)	0.118 (2)	7.7 (8)
N(5)	0.469 (2)	0.254 (1)	-0.161 (2)	6.2 (6)
O(51)	0.466 (1)	0.267 (1)	-0.069 (1)	7.5 (5)
O(52)	0.421 (1)	0.196 (1)	-0.193 (1)	7.9 (6)
O(53)	0.024 (1)	0.206 (1)	0.211 (1)	8.4 (6)
N(6)	0.407 (2)	0.029 (1)	0.263 (1)	5.5 (6)
O(61)	0.313 (1)	0.0204 (9)	0.265 (1)	7.3 (5)
O(62)	0.441 (1)	0.084 (1)	0.215 (1)	9.1 (6)
O(63)	0.454 (1)	-0.018 (1)	0.315 (1)	7.6 (5)

**Table II.** Main Interatomic Distances and Bond Angles<sup>a</sup>

Distances (Å)			
Cu-N <sub>1</sub>	2.04 (1)	N <sub>1</sub> -C <sub>11</sub>	1.51 (2)
Cu-N <sub>2</sub>	1.97 (1)	N <sub>2</sub> -C <sub>21</sub>	1.58 (2)
Cu-N <sub>3</sub>	2.05 (1)	N <sub>3</sub> -C <sub>31</sub>	1.44 (2)
Cu-N <sub>4</sub>	2.04 (1)	N <sub>4</sub> -C <sub>41</sub>	1.49 (2)
Angles (deg)			
N <sub>1</sub> -Cu-N <sub>2</sub>	93.3 (5)	N <sub>2</sub> -Cu-N <sub>4</sub>	152.7 (3)
N <sub>2</sub> -Cu-N <sub>3</sub>	92.7 (7)	Cu-N <sub>1</sub> -C <sub>11</sub>	121 (1)
N <sub>3</sub> -Cu-N <sub>4</sub>	93.1 (6)	Cu-N <sub>2</sub> -C <sub>21</sub>	120 (1)
N <sub>4</sub> -Cu-N <sub>1</sub>	93.2 (5)	Cu-N <sub>3</sub> -C <sub>31</sub>	119 (1)
N <sub>1</sub> -Cu-N <sub>3</sub>	151.4 (4)	Cu-N <sub>4</sub> -C <sub>41</sub>	118 (1)

<sup>a</sup> Standard deviations on the last significant figures are given in parentheses.

Refinements were made by full-matrix least squares, minimizing the  $R_w$  factor,  $R_w = [\sum_i (w_i |F_o - kF_c|)^2 / \sum_i w_i F_o^2]^{1/2}$ , where  $w_i$  is  $1/\sigma$  and  $k$  is the scale factor. (Calculations were made at the Atelier d'Informatique de Paris VI-Paris VII with an IRIS 80 computer.)

A three-dimensional Patterson map showed copper and one nitrogen atom. Refinement of their coordinates led to  $R = 0.336$ . Successive Fourier syntheses and refinements dropped  $R$  to 0.10 with isotropic temperature factors and to  $R = 0.083$  with anisotropic temperature factors for the 37 atoms different from hydrogen. The 52 hydrogen positions were calculated and introduced in the refinement without variation;  $R$  dropped to 0.066. No secondary extinction was observed for the low Bragg angle reflections.

Final reliability factors were as follows: nonweighted  $R$ , excluding zeros, 0.076; weighted  $R$ , excluding zeros, 0.066;  $F(000) = 1065$ .

The atomic parameters are shown in Table I. The main interatomic distances and angles are shown in Table II. Three ORTEP<sup>5</sup> drawings were computed with 50% probability thermal ellipsoids (Figures 1 and 2).

(2) M. Lamache and D. Bauer, *Anal. Chem.*, **51** (8), 1320 (1979).

(3) D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965).

(4) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

(5) C. K. Johnson, personal communication, 1965.

Table III. ESR Parameters Measured and Obtained from Computer Simulation for the Solid Title Compound and Solutions<sup>a</sup>

	$g_x$	$g_y$	$g_z$	$A_x$	$A_y$	$A_z$	$\Delta H_x$	$\Delta H_y$	$\Delta H_z$	$A_{iso}$	$g_{iso}$
powder	2.040	2.000	2.232	40	40	163	120	120	70		
nitromethane soln	2.050	2.060	2.240	20	30	177	35	40	45	70.5	2.12
propylene carbonate soln	2.045	2.050	2.240	30	29	180	40	45	35	69.5	2.128

<sup>a</sup> Accuracy: 0.005 on  $g_x$  and  $g_y$  components, 0.002 on  $g_z$ , 5 G on  $A_x$  and  $A_y$ , and 2.5 G on  $A_z$  components. Line width and hyperfine parameters are expressed in gauss.

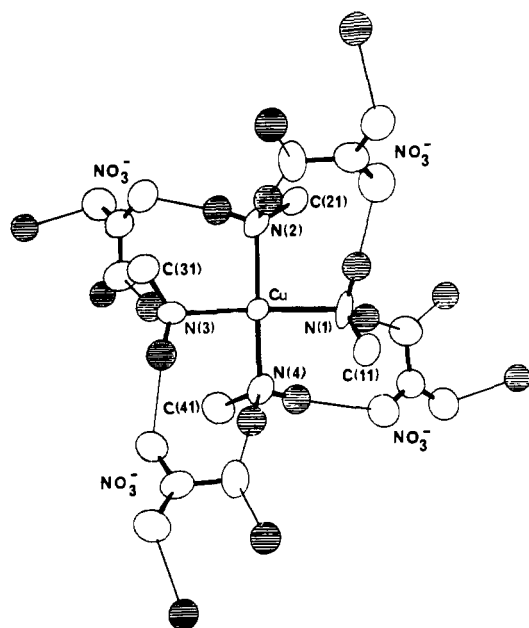


Figure 2. Set of hydrogen bonds.

## Results

**Crystal Structure.** Figure 1 represents the complex cation  $[\text{Cu}(\text{C}_6\text{H}_{11}\text{NH}_2)_4]^{2+}$ . The four cyclohexylamine ligands are coordinated to the copper atom through the amine nitrogen atom. Table II gives the main interatomic distances and bond angles. It can be seen that the copper environment is a flattened tetrahedron. The nitrate ions are not coordinated to the copper atom. This feature must be pointed out; indeed, many  $[\text{Cu}^{\text{II}}(\text{ligand})_4(\text{anion})_2]$  compounds have been studied, having monodentate ligands with N as a donor atom. In these compounds, anions often are weakly bound to the metal atom. The observed geometry is then a distorted octahedron; distortion depends on the coordination strength of axial ligands. With *N*-ethylimidazole and *N*-propylimidazole, J. Reedijk<sup>6</sup> has studied ESR spectra and ligand fields in the cases of  $\text{BF}_4^-$ ,  $\text{ClO}_4^-$ ,  $\text{NO}_3^-$ ,  $\text{Br}^-$ , and  $\text{Cl}^-$  anions. He has concluded that the geometry of these complexes is tetragonal for weakly coordinated ligands and that axial bonding strength increases from  $\text{BF}_4^-$  and  $\text{ClO}_4^-$  to  $\text{NO}_3^-$ ,  $\text{Br}^-$ , and  $\text{Cl}^-$ . In contrast, Massaccesi and al.<sup>7</sup> have suggested a semicoordination for  $\text{NO}_3^-$  and no coordination for the others. The situation is thus quite controversial. In that context, it is interesting to note that the title compound, the formula of which is  $\text{Cu}^{\text{II}}(\text{ligand})_4(\text{NO}_3)_2$ , exhibits a distorted-square-planar environment, with noncoordinated nitrate ions; this is inconsistent with Massaccesi's conclusion.

Moreover, the complex structure shows a set of hydrogen bonds between nitrogen atoms of ligand molecules and oxygen atoms of nitrate ions. (Figure 2). One of the three oxygen atoms of each nitrate group contracts two hydrogen bonds and

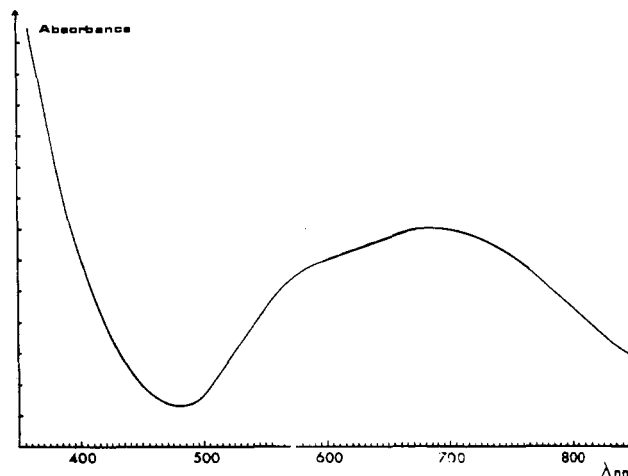


Figure 3. Transmission UV spectrum of the solid title compound.

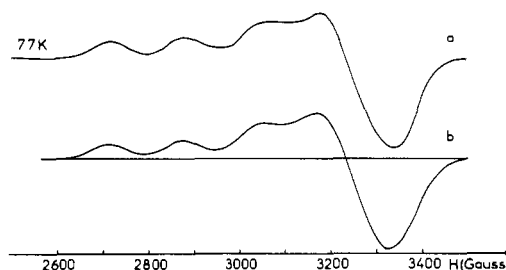


Figure 4. (a) ESR spectrum of the solid title compound at 77 K. (b) Simulation using a Gaussian line shape.

the two other oxygen atoms contract only one hydrogen bond. All hydrogen atoms of amine groups participate in this set of hydrogen bonds.

**Visible Absorption Spectra.** For the solid compound, one absorption maximum appears between 10 000 and 20 000  $\text{cm}^{-1}$  ( $\epsilon \approx 100$ ), with a shoulder on the high-energy side, as previously reported<sup>1f,8</sup> (Figure 3). The absorption envelope can be resolved into at least two Gaussian components, as done by Addison<sup>1f</sup> for pseudotetrahedral copper(II) complexes. The Gaussian peaks correspond to 14 500 and 17 500  $\text{cm}^{-1}$ .

For complex solutions in nitromethane or propylene carbonate, the color turns from blue to green and then to yellow after a while. This corresponds to a noticeable modification of the visible spectrum; the yellow solution exhibits only one band at 15 400  $\text{cm}^{-1}$  ( $\epsilon = 65$ ).

**ESR Spectra.** The ESR spectrum of the solid complex was recorded at 77 K (Figure 4a). It is typical of a  $\text{Cu}^{\text{II}}$  ion in an at least axially distorted ligand field. The corresponding ESR parameters are reported in Table III. They were obtained from computer simulation (Figure 4b) using a Gaussian line shape.

The isotope effect due to the occurrence of  $^{63}\text{Cu}$  and  $^{65}\text{Cu}$  cannot be resolved and is included in the line width.

In order to take into account anisotropic dipolar interactions in the solid matrix, an anisotropic line width has been used.<sup>9</sup>

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(8) U. Sakaguchi, and A. W. Addison, *J. Chem. Soc., Dalton Trans.*, 600 (1979).

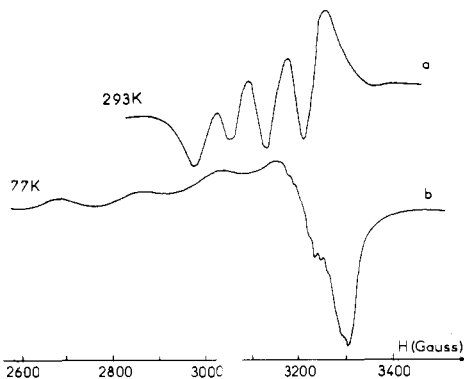


Figure 5. ESR spectrum of (a) a solution of the title compound at room temperature and (b) a frozen solution at 77 K.

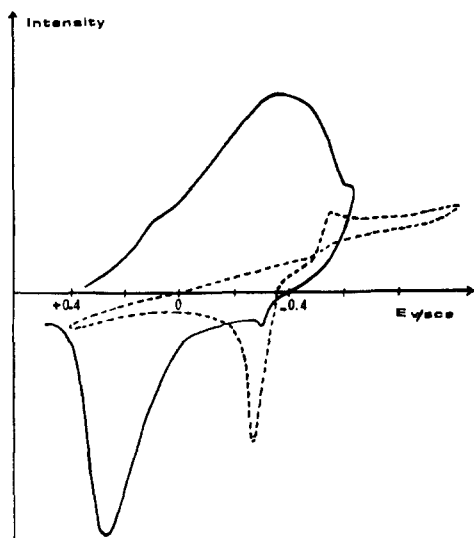


Figure 6. Cyclic voltammograms of the title compound as (—) a solid complex (speed  $10^{-3}$  V s $^{-1}$ ) and (---) a complex solution (speed  $5 \times 10^{-3}$  V s $^{-1}$ ).

$\Delta H = 1/g(\Delta H_x^2 g_x^2 \sin^2 \theta \cos^2 \phi + \Delta H_y^2 g_y^2 \sin^2 \theta \sin^2 \phi + \Delta H_z^2 g_z^2 \cos^2 \theta)^{1/2}$ , where  $\theta$  and  $\phi$  are polar angles,  $\Delta H_x$ ,  $\Delta H_y$ , and  $\Delta H_z$  are peak to peak line widths, and  $g$  is given by  $g^2 = g_x^2 \sin^2 \theta \cos^2 \phi + g_y^2 \sin^2 \theta \sin^2 \phi + g_z^2 \cos^2 \theta$ .

The room-temperature ESR spectrum of the complex in nitromethane (or propylene carbonate) solution is shown in Figure 5a. It exhibits the four hyperfine lines resulting from the coupling of the unpaired electron of copper(II) with the nuclear spin ( $I = 3/2$ ) of both  $^{63}\text{Cu}$  (69%) and  $^{65}\text{Cu}$  (31%).

Measured magnetic parameters are reported in Table III. The dilute sample exhibits a superhyperfine structure (10 G) due to interaction with the  $^{14}\text{N}$  nuclear spin ( $\text{N}^{14} \Rightarrow I = 1$ , 99.4%) of cyclohexylamine nitrogen atoms.

The frozen-solution spectrum recorded at 77 K is given in Figure 5b. It is typical of a copper(II) ion in a rhombic ligand field. The corresponding ESR parameters determined by computer simulation are reported in Table III. The nitrogen hyperfine interaction is about 12 G in the perpendicular spectrum ( $g_x$ ,  $g_y$ ).

**Redox Measurements.** Figure 6 shows the curves obtained in both cases described in the Experimental Section. It can be seen that the redox potential is about  $-0.05$  V vs. SCE for the solid complex (solid line). Concerning the species in solution (dotted line), the redox potential is markedly shifted to negative values.

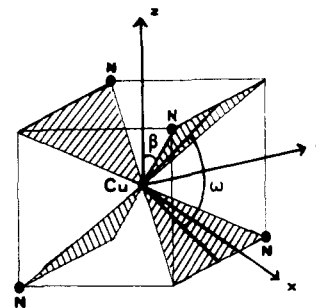


Figure 7.  $\omega$ ,  $\beta$ , and axis definitions.

Table IV. Magnetic Parameters for the Solid Title Compound and Solutions

$\text{CuN}_4$	$\alpha^2$ <sup>a</sup>	$K_0$	$\beta^2$ <sup>b</sup>	$\delta^2$ <sup>b</sup>	$f_S$ , %
solid powder	0.68	0.46	0.87	0.48	...
nitromethane soln	0.78	0.42	0.71	...	2
propylene carbonate soln	0.78	0.42	0.71	...	2

<sup>a</sup>  $A_{\parallel}$  and  $A_{\perp}$  are taken with the same sign from the  $A_{\text{iso}}$  value.  
<sup>b</sup> Values of  $\Delta_1$  and  $\Delta_2$  are 14 500 and 16 000  $\text{cm}^{-1}$ , respectively. They are discussed in the text.

It seems difficult to give the actual value for the potential, since the symmetrical shape of the oxidation peak suggests adsorption;<sup>10</sup> thus, the found potential may not be very accurate. Nevertheless, the observed shift is quite significant in indicating a definitely more positive value for the solid complex.

## Discussion

From these experimental results, it was interesting to look for a more comprehensive view. Crystallographic data leads to a pseudotetrahedral environment for copper in the solid state. Symmetry elements are not far from those of  $D_{2d}$  symmetry group; this led us to consider this group as a good starting point for calculations.

**ESR Spectra.** Two angles, denoted as  $\omega$  and  $\beta$ , are generally used to estimate the deviation from pure tetrahedral or square-planar geometry in copper(II) complexes.<sup>14,11-14</sup>  $\omega$  is the dihedral angle between the two  $\text{N}_2\text{Cu}$  planes (Figure 7). It is equal to  $39.5^\circ$  in the title compound and varies from  $0^\circ$  in square-planar to  $90^\circ$  in tetrahedral geometry.  $\beta$  varies from  $54.73^\circ$  for the tetrahedron to  $90^\circ$  for the square plane.

If  $\alpha$  is the  $\text{NCuN}$  bond angle, i.e.  $93.5^\circ$  in our compound, the relation<sup>11</sup>  $\cos \beta = \sin(\omega/2) \sin(\alpha/2)$  leads to a  $\beta$  value of about  $75.7-76^\circ$ . Reference axes are shown in Figure 7. In such a system, the  $T_2$  set corresponds to  $\{(xz), (yz), (x^2 - y^2)\}$  orbitals for a tetrahedral geometry. It is then easier to correlate tetrahedral and square-planar coordinations: the ground state always is the  $^2B_1$  state, which is the usual result for the copper(II) ion.<sup>15</sup>

The ESR spectrum is easily observed at room temperature; this means that the unpaired electron is located in an orbitally nondegenerated ground state. Therefore, the relation  $g_z > g_x g_y$  indicates a  $b_1(d_{x^2-y^2})$  orbital.<sup>16</sup>

Analysis of ESR parameters of copper complexes is based on the perturbation method described by Abragam and

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Table V

compd	R, cm	$\omega$ , deg	ref
CuN <sub>4</sub> powder	131	39.5	this work
CuN <sub>4</sub> soln	119		this work
Cu(AcG <sub>2</sub> H) <sup>a</sup>	107	0	20
Cu <sup>II</sup> (dipyrrromethene)	165	63	21
	210	68	21
	221	73	21
Cu <sup>II</sup> (pea) <sup>2+b</sup>	128	40	13
(Me <sub>2</sub> Ga(dmpz) <sub>2</sub> ) <sub>2</sub> Cu <sup>c</sup>	244	72	32
CuClCS <sub>2</sub>	954	74	33

<sup>a</sup> AcG<sub>2</sub>H is acetylglucylglycyl-L-histidine. <sup>b</sup> pea is (2-pyridylethyl)bis(2-(ethylthio)ethyl)amine. <sup>c</sup> Bis(dimethylbis(3,5-dimethyl-1-pyrazolyl)gallato)copper(II).

Pryce.<sup>17</sup> With a <sup>2</sup>B<sub>1</sub> ground state, ESR parameters can be expressed as

$$A_{\parallel} = P(-\alpha^2/7 + K_0) + (g_{\parallel} - 2.0023) + \frac{3}{7}(g_{\perp} - 2.0023)$$

$$A_{\perp} = P(\alpha^2/7 - K_0) + \frac{11}{14}(g_{\perp} - 2.0023)$$

$$g_{\parallel} = 2.0023 + 8 \frac{\lambda^0 \alpha^2 \beta^2}{\Delta_1}$$

$$g_{\perp} = 2.0023 + 2 \frac{\lambda^0 \alpha^2 \delta^2}{\Delta_2}$$

$\lambda^0$  is the spin-orbit coupling constant for free Cu(II)<sup>18</sup> and is about 828 cm<sup>-1</sup>.  $K_0$  is the Fermi contact term for the free ion.  $\Delta_1$  and  $\Delta_2$  are ligand field transitions ( $E_{xy} \rightarrow E_{x^2-y^2}$  and  $E_{xz,yz} \rightarrow E_{x^2-y^2}$ ).  $P$  depends on the effective charge carried by the copper atom, and its usual value is 0.0360 cm<sup>-1</sup> for Cu(II) complexes. The calculated values are reported in Table IV.

LCAO-MO analysis leads to results consistent with several other data obtained for similar complexes;<sup>16,11</sup> as a matter of fact, when the geometry changes from square planar to tetrahedral, the  $\alpha^2$  coefficient decreases. This clearly shows an increase of the participation of nitrogen p orbitals in the ground state (<sup>2</sup>B<sub>1</sub>). Our observed low values ( $\alpha^2 \approx 0.7$ ,  $K_0 \approx 0.4$ ) are in good agreement with structural results. In contrast, when the complex is dissolved,  $\alpha^2$  increases while  $K_0$  does not change very much, from which the structure is expected to be very close to square planar. Addison and co-workers,<sup>1f,12</sup> studying CuN<sub>4</sub> complexes, have shown that distortion from the tetrahedron decreases  $A_{\parallel}$  and increases  $g_{\parallel}$ , with a more important relative variation for  $A_{\parallel}$ <sup>14</sup> than for  $g_{\parallel}$ .

It must be noted that the change of our complex from solid state to solution leads to a 15-G increase for  $A_{\parallel}$ , pointing out the occurrence of a copper square-planar environment in solution.

Recently, Bencini and Gatteschi<sup>19</sup> have proposed a somewhat higher value for  $P$ :  $438.69 \times 10^{-4}$ . This would lead roughly to an increase of  $\alpha^2$  by 10% and no change of  $K_0$  (0.61 for powder, 0.68 for both solutions). However, this new  $P$  value does not change the preceding conclusion since  $\alpha^2$  and  $K_0$  vary the same way from the powder to the solution.

In some homologous series, it has been shown that the  $R$  value ( $R$  (cm) =  $g_{\parallel}/A_{\parallel}$ ) is a good indication of the distortion magnitude. Figure 8 shows the results obtained for different copper environments. The  $\omega$  value of about 65° divides the curve in two parts, a square plane and tetrahedron, respectively. From this, our solid complex (distorted tetrahedron,  $\omega = 40^\circ$ ) is located in the square-plane range.

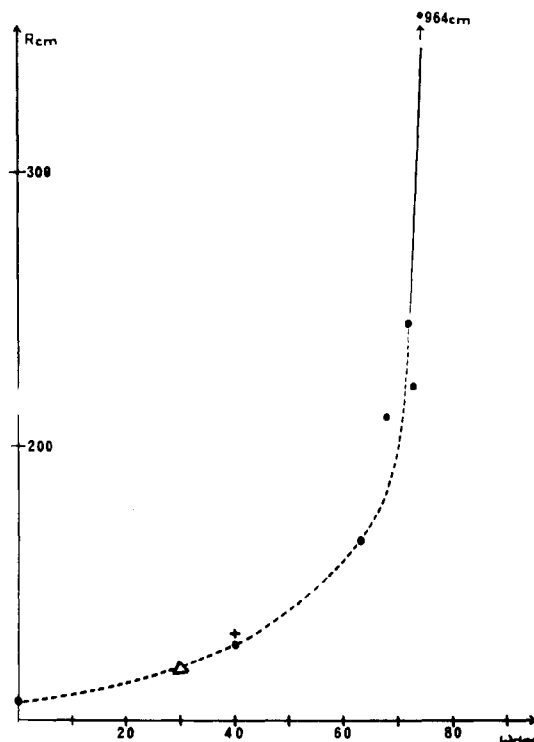


Figure 8. Variation curve of  $R = g_{\parallel}/A_{\parallel}$  with respect to  $\omega$  values (see Table V): (●) literature values; (+) data for the title compound in the solid state; (▲) data for the title compound in solution in nitromethane.

Concerning the complex solution, the  $\omega$  value is shifted to 30° with regard to that for the solid state; this points out the modification of the copper environment in solution, probably due to a weak coordination of the solvent molecules or of the nitrate ion (see discussion above).

**Superhyperfine Coupling Constant.** The coupling constant for superhyperfine interaction with the nitrogen donor has been calculated from the solution spectrum. The observed values (10–12 G) are in agreement with previous work.<sup>20,21</sup> The resonance spectrum is not resolved enough to determine the  $A_{\parallel}^N$  component; only  $A_{\perp}^N$  was obtained, equal to  $12 \pm 1$  G. The isotropic nitrogen hyperfine splitting,  $A_{\text{iso}}^N$ , was measured at room temperature; its value is  $10 \pm 2$  G. Within the experimental accuracy,  $A_{\perp}$  and  $A_{\text{iso}}$  appear to be almost identical, suggesting that the superhyperfine coupling is mostly isotropic. A rough calculation of the dipolar term leads to  $A_D = 0.3$  G, with Cu–N = 2.04 Å.

As a first approximation, the main contribution to the measured  $A^N$  value is isotropic. It arises from the effective fraction  $f_S$  of copper d electrons transferred into a nitrogen 2s orbital:

$$A^N = \frac{16}{3} \pi \gamma_N \beta_c \beta_N f_S |\rho| |\rho|^{-2}$$

where  $|\rho| |\rho|^{-2}$  is equal to  $33.4 \times 10^{-24}$  cm<sup>-3</sup> from Maki and McGarvey's<sup>22</sup> estimate.

From  $A^N \approx 12 \times 10^{-4}$  cm<sup>-1</sup> and the above relation,  $f_S$  is found equal to 2%. This value, reported in Table IV, is in agreement with Murakami's results for copper(II) dipyrromethene complexes.<sup>23</sup>

**d-d Transition Bands.** The assignment of d-d transition bands is a difficult problem in the case of pseudotetrahedral

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copper(II) complexes.<sup>1d,f,11,15,18,24</sup> They generally appear in the 10 000–20 000-cm<sup>-1</sup> range, with  $\epsilon$  between 100 and 1000. When the compound does not lead to crystals suitable for polarization measurements, a quantitative study of observed transitions can be made through an intermediate model.

The simplest model determination was carried out by crystal field method, with a  $D_{2d}$  symmetry.<sup>17</sup> With use of the electron hole formalism, the energy levels can be expressed as<sup>14,15,18,25</sup>

$$|a_1\rangle = -12(3 \cos^2 \beta - 1)D_S - 3\delta D_t$$

$$|b_1\rangle = 12(3 \cos^2 \beta - 1)D_S + \frac{1}{2}(35 \sin^4 \beta - \delta)D_t$$

$$|e\rangle = -6(3 \cos^2 \beta - 1)D_S + 2\delta D_t$$

$$|b_2\rangle = 12(3 \cos^2 \beta - 1)D_S - \frac{1}{2}(35 \sin^4 \beta + \delta)D_t$$

where  $\delta = 35 \cos^4 \beta - 30 \cos^2 \beta + 3$  and  $\beta$  is the distortion angle described above (Figure 7).  $D_t$  and  $D_S$  are the crystal field parameters corresponding to tetragonal and tetrahedral distortions; they depend on the actual charge present at each nitrogen atom, on copper–nitrogen distances, and on integrals related to spherical harmonics.

From the  $\beta$  value, equal to 75.7° for the title compound, and from Solomon's calculation method,<sup>18</sup> the following sequence is expected:

$$\left. \begin{array}{l} E_1 [xy \rightarrow x^2 - y^2] \\ E_2 [xz, yz \rightarrow x^2 - y^2] \end{array} \right\} 14500 \text{ cm}^{-1}$$

$$E_3 [z^2 \rightarrow x^2 - y^2] \quad 17400 \text{ cm}^{-1}$$

Our experimental values and the above equations lead to the calculated values  $D_S$  and  $D_t$ :

$$D_S = 595 \text{ cm}^{-1} \quad D_t = 470 \text{ cm}^{-1}$$

These parameters are related to tetrahedral ( $\Delta_t$ ) and tetragonal ( $\Delta_S$ ) crystal fields:

$$\Delta_S = 6D_S = 3570 \text{ cm}^{-1} \quad \Delta_t = \frac{10}{9}D_t = 7310 \text{ cm}^{-1}$$

For a pure tetrahedral environment and for copper–nitrogen distances of 2 Å,  $\Delta_t$  must be lower than  $\Delta_S$ .<sup>14</sup> This involves a quite flattened pseudotetrahedral environment for the title compound and confirms the ESR results, since the compound seems to be in the range of pseudo-square-planar compounds.

We have then calculated again the variation of energy levels in terms of the  $\beta$  angle (Figure 9). It can be seen that the tetrahedral range corresponds to  $\beta$  lower than 70–68°. This corresponds to a  $\omega$  angle of about 60–65°, which is in good agreement with the observed correlations between ESR parameters and angular distortion (cf. Figure 8).

Another method can be used for these calculations, especially when the compound exhibits  $\pi$  overlaps.<sup>15</sup> In the case of the title compound, the crystal field model gives the sequence  $d_{x^2-y^2} > d_{xy} > d_{z^2} > d_{xz}d_{yz}$ , as proposed by Solomon and Smith.<sup>18,25</sup> However, it has been seen that the compound has a pseudotetrahedral geometry; from the studies of Ferguson<sup>26</sup> and Addison<sup>12</sup> on tetrahedral  $(\text{CuCl}_4)^{2-}$  complexes, this implies the following sequence:  $d_{x^2-y^2} > d_{xz}d_{yz} > d_{xy} > d_{z^2}$ .

It could then be interesting to choose the right sequence corresponding to our own compound. A more comprehensive LCAO–MO calculation has been carried out by the extended Hückel method.<sup>27,28</sup> The copper–nitrogen distances were 2.04

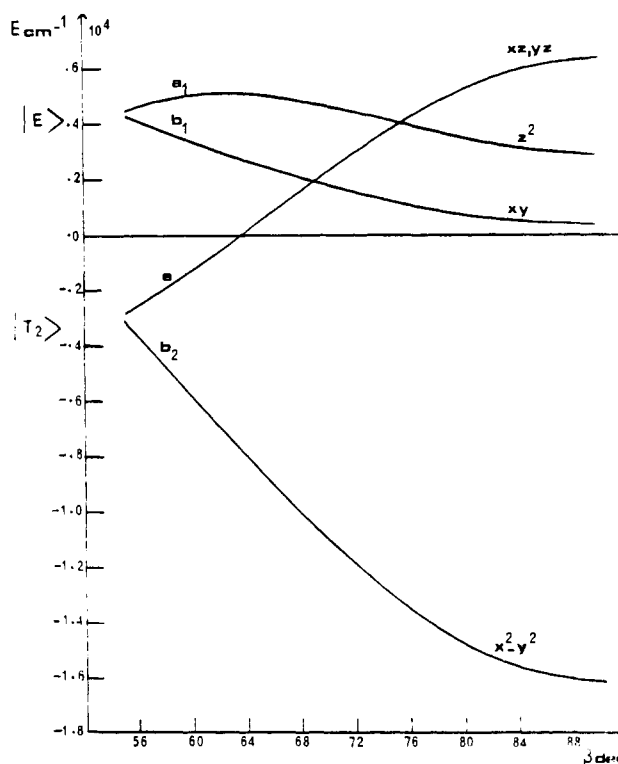


Figure 9. Angular dependence of the  $b_2(d_{x^2-y^2})$ ,  $e(d_{xz}d_{yz})$ ,  $b_1(d_{xy})$ , and  $a_1(d_{z^2})$  hole energies as a function of  $\beta$  for the Cu(II) ion ( $D_S = 595 \text{ cm}^{-1}$ ,  $D_t = 470 \text{ cm}^{-1}$ ).

Å, and the  $\omega$  angle was 39.5°. The energy levels of atomic orbitals were those usually used for copper and nitrogen.<sup>29,30</sup> The exponents of s and p orbitals were calculated from Burns' rules<sup>30,31</sup> for nitrogen; they were taken from Ballhausen and Gray's tables<sup>30</sup> for copper(II).

These calculations lead to the sequence  $d_{x^2-y^2} > d_{xz}d_{yz} > d_{xy} > d_{z^2}$ , in agreement with Addison and Ferguson's attribution.

A refinement of simulation with observed transitions gives the best values

transition	$E_n(\text{calcd}), \text{cm}^{-1}$	$E_n(\text{exptl}), \text{cm}^{-1}$
$E \rightarrow B_1$	14 450	14 500
$B_2 \rightarrow B_1$	15 550	~16 000 (bulk soln)
$A_1 \rightarrow B_1$	17 150	17 400

The energy levels are shown in Figure 10. The ground state is  $d_{x^2-y^2}$ , with a coefficient equal to 0.828. This is in perfect agreement with ESR results:  $\alpha^2 = 0.68$  and  $\alpha = 0.824$ . It is possible to calculate the spin density in 2s nitrogen orbitals from atomic orbital coefficients:  $f_s$  is found equal to 2.5% instead of 2% from hyperfine ESR parameters (see above). Charge repartition indicates a positive charge of 1.2+ on copper, i.e. a copper–nitrogen bond.

Moreover, it is possible to correlate energy levels to angle, keeping constant copper–nitrogen distances and parameters derived from the best simulation. The results are reported in Figure 11.  $\omega$  is equal to 0° and 90° for a pure square plane and tetrahedron, respectively.

Splitting due to a tetrahedral ligand field is about 5000 cm<sup>-1</sup>, instead of 7000 cm<sup>-1</sup> obtained by the crystal field method. The curve plotted in Figure 8 has such a shape that it is not easy

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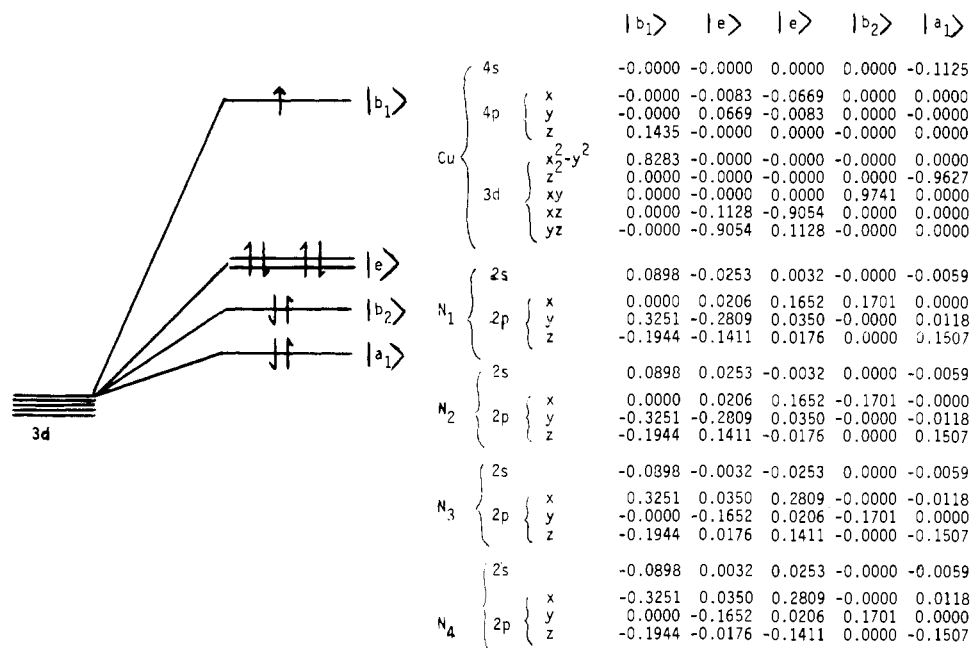


Figure 10. Computed energy levels for the copper atom as a function of  $\beta$  defined in Figure 7.

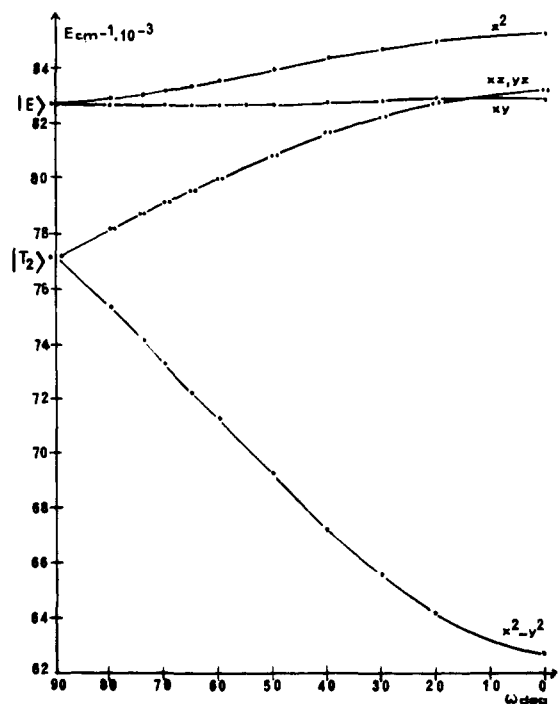


Figure 11. Energy of the d level with respect to  $\omega$  values.

to define the  $\omega$  angle for which the complex can be clearly treated as tetrahedral. Nevertheless, a rough extrapolation of the vertical part suggests a value close to  $65^\circ$ ; for this value, the splitting of the  $T_2$  level is close to  $8000\text{ cm}^{-1}$  from Figure 11.

## Conclusion

X-ray diffraction analysis shows that the title compound exhibits a flattened tetrahedral coordination around the copper atom, with a distortion angle  $\omega$  of  $40^\circ$ . In the solid state, redox measurements lead to a potential value more positive than that expected for a tetragonal symmetry, but more negative than in copper proteins. Optical and ESR spectra suggest that the properties of copper(II) are closer to those corresponding to a pseudo-square-planar geometry. Crystal field and LCAO-MO calculations show that the energy level distribution turns from  $T_d$  to  $D_{4h}$  symmetry for an angle  $\omega$  of about  $65^\circ$ . Moreover, our results clearly show that some structural relaxation may occur when the complex is dissolved, the  $\omega$  angle shifting from  $40$  to  $30^\circ$ . Thus, some care must be taken when one compares X-ray diffraction experiments performed on solids and redox measurements performed only in solution.

The title compound therefore does not appear to be a realistic model for blue copper proteins, as far as redox potential is concerned. A better model should exhibit a  $\omega$  angle larger than  $65^\circ$  and a more positive redox potential. This could be achieved either by using larger ligands or by including the copper(II) ion in a tetrahedral matrix. However, the title compound is a rare example of a tetrakis(monodentate) system with a geometry intermediate between a tetrahedron and a square plane.

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**Registry No.**  $[\text{Cu}(\text{C}_6\text{H}_{11}\text{NH}_2)_4](\text{NO}_3)_2$ , 35637-91-3.

**Supplementary Material Available:** Tables of structure factors and complete interatomic distances and bond angles (12 pages). Ordering information is given on any current masthead page.