Magnetic and Structural Properties of *trans*-bis (D,L-Isoleucine) Copper(II)

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A magnetic and structural characterization of single crystals of the copper derivative of the amino acid D,L-isoleucine, $Cu[NH_2(CH)_2CH_2(CH_3)_2CO_2]_2$, was performed by EPR and X-ray diffraction techniques. The complex crystallizes in the orthorhombic space group $Aba2$, with $a = 11.165(3)$ Å, $b = 11.111(3)$ Å, $c = 25.985(6)$ Å, and $Z = 8$. The copper ions occupy sites of point symmetry C_2. The position and peak-to-peak linewidth of the single EPR line observed were measured at 9.7 GHz and 293 K in three perpendicular planes of the sample. The gyromagnetic tensor $\overleftrightarrow{g}$ has near axial symmetry around $\hat{c}$, with a small anisotropy in the perpendicular plane, in agreement with the orthorhombic symmetry indicated by the crystallographic results. The principal values of $\overleftrightarrow{g}$ are $g_1 = 2.0607(5)$, $g_2 = 2.0616(5)$, and $g_3 = 2.2619(3)$, with principal directions parallel to the crystal axes. The observed angular variation of the linewidth suggests a layered arrangement of the copper ions. © 1991 Academic Press, Inc.

Introduction

Complexes of transition-metal ions with amino acids constitute adequate model systems which reproduce the electronic behavior of metal ions in some metalloproteins. On the other hand, and because of their relative simplicity, these complexes are amenable to thorough studies by solid state physics techniques (*1–4*).

We report hereby crystal data and the electronic and magnetic properties of the copper derivative of the amino acid D,L-isoleucine, $Cu[NH_2(CH)_2CH_2(CH_3)_2CO_2]_2$. Though the complete molecular structure of the complex could not be determined, the obtained crystallographic data provide useful information to analyze the EPR results. Our results are compared to those reported for $Cu(L\text{-Ile})_2 \cdot H_2O$ (*1, 3, 5*).

Experimental Methods

Single crystals of $Cu(D,L\text{-Ile})_2$ were grown from a water solution of the compound by slow evaporation (12–13 days) at room temperature (*6*). They are thin, deep blue-col-

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ored, square plates parallel to (001) de-
limited by well-defined [110] and [1̄10]
directions.

A complete X-ray diffraction data set was
obtained at room temperature, with a Huber
four-circles diffractometer used with graph-
ite-monochromated Mo$K\alpha$ radiation.

EPR measurements were performed at X-
band (9.7 GHz) and room temperature (293
K), with an ER-200 Bruker spectrometer
and a rotating 12 in. electromagnet. A single
crystal of $0.76 \times 0.72 \times 0.1$ mm^3 was glued
to an L-shaped sample holder defining an
orthogonal set of axes xyz, with the sides of
the square plate along the $\hat{x}$ and $\hat{y}$ axes. The
sample holder was positioned in a pedestal
having a horizontal plane inside the micro-
wave cavity. By rotating the magnet in this
plane, we measured the angular variation of
the position and the peak-to-peak linewidth
of the single resonance observed, for the
magnetic field vector on the xy, xz, or yz
plane of the sample.

Results and Discussion

Crystallographic Data

The complex Cu(D,L-Ile)$_2$ crystallizes in
the orthorhombic space group $Aba2$ (No.
41), with $a = 11.165(3)$ Å, $b = 11.111(3)$
Å, $c = 25.985(6)$ Å and $z = 8$. A partial
molecular model of the complex was ob-
tained by the heavy-atom technique.

As usual, each copper ion is coordinated
by a pair of amino acid molecules through
their corresponding amine nitrogen and two
of the carboxylate oxygens in a Cu(N$_2$O$_2$)
configuration. The eight complexes per unit
cell can be grouped into two inequivalent
sets, each having four symmetry-related
molecules with their Cu(II) ions on two-fold
axes along $\hat{c}$. The preliminary crystallo-
graphic data suggest that the corresponding
Cu(N$_2$O$_2$) groups in these inequivalent sets
are rotated about 90° from each other, a
result consistent with the observed quasite-
tragonality exhibited by the X-ray diffrac-

tion pattern and the EPR data (see below)
(7). Within each set, different complexes are
related by either the A-centering transla-
tion, or a glide-mirror operation. Therefore,
the two amino acid molecules bonded to a
given Cu(II)· ion must be of the same iso-
meric type, L or D , and hence the crystal is
constituted by *trans*-coordinated Cu(L-Ile)$_2$
and Cu(D-Ile)$_2$ molecules. The above
mentioned pseudotetragonal symmetry of
the X-ray diffraction pattern and the possi-
ble presence of positional disorder of the
amino acid residual groups prevented a
complete molecular structure determination
and refinement of the complex. However,
our current crystallographic information af-
ford the conclusion that Cu(D,L-Ile)$_2$ is
structurally different from Cu(L-Ile)$_2$ (5),
where the Cu(II) ions are in *cis*-coordination
and occupy general positions in the lattice.
Hence, Cu(D,L-Ile)$_2$ and Cu(L-Ile)$_2$ are com-
pounds where the restrictions imposed by
the crystal packing determines different co-
ordination schemes (*cis* or *trans*) to essen-
tially the same molecule.

Infrared spectroscopic studies (6, 8) and
diffuse reflectance data (6, 9) have been re-
ported for Cu(D,L-Ile)$_2$. In these studies the
stretching vibrations of compounds having
known and unknown crystal structures are
compared in order to draw conclusions on
the coordination geometry around the cop-
per ion in the latter group of compounds.
Herlinger *et al.* (8) and Yasui *et al.* (9) re-
ported *cis*-coordination of Cu(II) in Cu(D,L-
Ile)$_2$ while Szabó-Plánka (6) reported *trans*-
coordination. This contradiction could be
explained if those authors (8, 9) chose differ-
ent crystallization conditions and obtained
Cu(L-Ile)$_2$ or Cu(D-Ile)$_2$ complexes from the
solution, instead of the racemic mixture.

Electron Paramagnetic Resonance Data

The effective spin hamiltonian (2),

$$\mathcal{H} = \mu_B \cdot \overrightarrow{S} \cdot \overleftrightarrow{g} \cdot \overrightarrow{H}, \qquad (1)$$

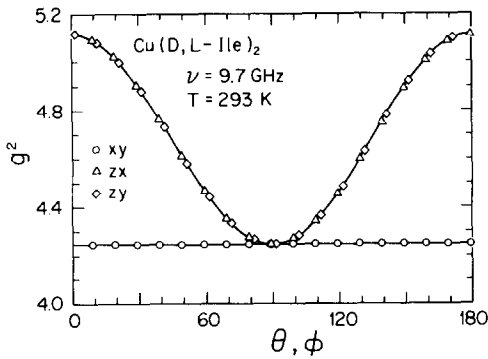was used to interpret the EPR data. In Eq.

FIG. 1. Angular variation of the squared gyromagnetic factor measured at 9.7 GHz and 293 K, in three orthogonal planes of a Cu(D,L-Ile)$_2$ single crystal. The solid lines were obtained from a least-squares fit of the data employing the symmetric $\overleftrightarrow{g^2}$ tensor, whose components are in Table I. The angles θ and ϕ are defined in the *xyz* system of axes of the sample holder (see text).

(1) $\overrightarrow{S}$ is the effective spin ($S = \frac{1}{2}$), μ_B the Bohr magneton, and $\overrightarrow{H}$ the applied magnetic field. The values measured for the squared gyromagnetic factor of Cu(D,L-Ile)$_2$ are displayed in Fig. 1 as a function of the polar θ and azimuthal ϕ angles of $\overrightarrow{H}$ in the *xyz* system of axes of the sample holder. Defining $g^2(\theta, \phi) = \hat{h} \cdot \overleftrightarrow{g} \cdot \overleftrightarrow{g} \cdot \hat{h}$ with $\hat{h} = \overrightarrow{H}/|\overrightarrow{H}| = (\sin\theta\cos\phi, \sin\theta\sin\phi, \cos\theta)$, we calculated the components of the tensor $\overleftrightarrow{g^2}$ using a least-squares procedure. These values are given in Table I, and the solid lines in Fig.

TABLE I

VALUES OF THE COMPONENTS OF $\overleftrightarrow{g^2}$, EIGENVALUES AND EIGENVECTORS OF $\overleftrightarrow{g}$ TENSOR IN THE *xyz* SYSTEM OF AXES OF THE SAMPLE HOLDER. THE VALUES OF THE PARAMETERS A_i OBTAINED BY A LEAST-SQUARES FIT OF THE ANGULAR VARIATION OF THE LINEWIDTH TO EQ. (4), ARE ALSO INCLUDED.

$(g^2)_{xx} = 4.2484(4)$	$(g^2)_{yy} = 4.2485(4)$	$(g^2)_{zz} = 5.1163(3)$
$(g^2)_{xy} = -0.0018(4)$	$(g^2)_{xz} = (g^2)_{yz} = 0$	
$g_1 = 2.0607(5)$	$\hat{a}_1 = (0.72(5), 0.69(5), 0)$	
$g_2 = 2.0616(5)$	$\hat{a}_2 = (0.69(5), -0.72(5), 0)$	
$g_3 = 2.2619(3)$	$\hat{a}_3 = \hat{c} = (0, 0, 1)$	
$A_1 = 41.1(3)$ G	$A_2 = 6.6(2)$ G	$A_3 = 11.9(2)$ G

1 were calculated with them. Table I also includes the principal directions of $\overleftrightarrow{g^2}$, which are respectively parallel to the crystal $\hat{a}$, $\hat{b}$, and $\hat{c}$ axes.

The single EPR line observed for Cu(D,L-Ile)$_2$ is interpreted as a collective resonance, produced by the collapse of the resonances due to the individual copper sites in the lattice, caused by the exchange interaction (*10, 11*). The observed Lorentzian lineshape also indicates that the spin system is coupled by exchange interactions. The position of the resonance corresponding to a set of four symmetry-related copper sites is determined by the g^2-tensor $\overleftrightarrow{g_s^2} = \frac{1}{4}\sum_{i=1}^{4}\overleftrightarrow{g_i^2}$, where the $\overleftrightarrow{g_i^2}$ are the gyromagnetic tensors of individual copper ions (*2*). If one considers the symmetry operations relating the copper sites within a set in the *Aba2* space group, it is seen that $\overleftrightarrow{g_s^2}$ results diagonal in the crystal *abc* axes. Besides, if there are two symmetry unrelated sets of four copper ions in the lattice ($s = A, B$), we should measure

$$\overleftrightarrow{g^2} = (\overleftrightarrow{g_A^2} + \overleftrightarrow{g_B^2})/2, \qquad (2)$$

which is still diagonal in the coordinate system defined by the crystal axes, as observed.

It can be appreciated in Fig. 1 that the symmetry exhibited by $\overleftrightarrow{g^2}$ is very close to axial, with $g_\parallel = 2.2619(3)$ along the $\hat{z} \equiv \hat{c}$ crystal axis and $g_\perp = 2.0612(4)$ in the *xy* plane. A strictly axial gyromagnetic tensor would indicate either a tetragonal point symmetry C_4 for the copper site, or four copper sites related by C_4 operations, and therefore a crystal with tetragonal structure. This last hypothesis was apparently supported by the external morphology of the samples and the gross features of the X-ray diffraction pattern. However, the residual $\Delta g(\phi) = g(\phi) - g_\perp$ angular variation of the gyromagnetic factor measured in the *xy* plane (see Fig. 2) evidences a
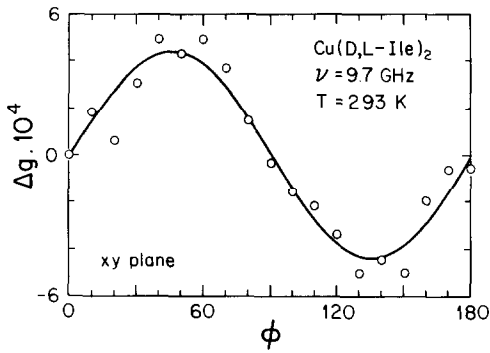
FIG. 2. Angular variation of the difference $\Delta g = g - g_\perp$ in the $xy \equiv ab$ plane of Cu(D,L-Ile)$_2$, where $g_\perp = 2.0612(4)$ is the average of the principal values of $\overleftrightarrow{g}$ in this plane.

small, though statistically significant, orthorhombic anisotropy $\Delta g \simeq 10^{-3}$ around the crystal axis $\hat{c}$. The $\Delta g(\phi)$ data can be described assuming

$$g^2(\phi) = (g_1)^2 \sin^2(\alpha\text{-}\phi) + (g_2)^2 \cos^2(\alpha\text{-}\phi), \quad (3)$$

with $\alpha = 45°$ and the best least-squares principal gyromagnetic values $g_1 = 2.0607(5)$ and $g_2 = 2.0616(5)$. This corresponds to the full curve in Fig. 2, whose extreme values at the principal directions $\phi = 45°$ and $135°$ are reached when $\overrightarrow{H}$ is along either the $\hat{a}$ or the $\hat{b}$ axis.

The value obtained for $g_\parallel$ and $g_\perp$ are typical for cupric ions in a N$_2$O$_2$ square coordination (1–4), and indicate a $d_{x^2-y^2}$ ground orbital state for the unpaired electron.

The observed angular variation of the EPR linewidth is displayed in Fig. 3. These data can be described by the axially symmetric function:

$$\Delta H\,(\theta) = A_1 + A_2\,(3\cos^2\theta - 1)^2 + A_3\cos(2\theta), \quad (4)$$

whose best least-squares parameters are included in Table I. The corresponding $\Delta H(\theta)$ curves are compared in Fig. 3 with the experimental data.

The long-time behavior of the spin dynamics of a paramagnet is governed by spin diffusion effects. It was proved (12) that, for a two-dimensional system, the exchange-narrowed dipole–dipole interaction gives rise to an anisotropic contribution to the EPR linewidth proportional to $(3\cos^2\theta - 1)^2$, where θ is the angle between the magnetic field and the normal to the layers. Therefore, the sizable presence of this contributing term in Eq. (4) suggests a two-dimensional magnetic behavior of Cu(D,L-Ile)$_2$ with layers perpendicular to the $\hat{c}$ axis.

Studies of the temperature dependence of the magnetic susceptibility, the specific heat, or the measurement of the positions and widths of the EPR lines at very low temperature would be useful to verify the low-dimensional magnetic behavior. These experiments, however, have not been performed yet in Cu(D,L-Ile)$_2$.

The third term of Eq. (4) takes into account contributions to $\Delta H(\theta)$ describable by second-order angular functions, like the ones arising from exchange-modulated hyperfine and anisotropic and antisymmetric exchange interaction (4).
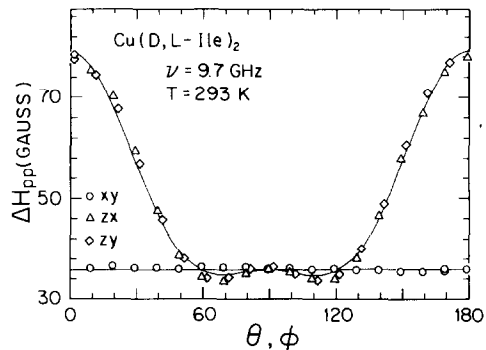

FIG. 3. Angular variation of the peak-to-peak EPR linewidth measured at 9.7 GHz and 293 K in three orthogonal planes of a Cu(D,L-Ile)$_2$ single crystal. The curves were calculated with Eq. (4). The angles θ and ϕ are defined in the xyz system of axes of the sample holder (see text).

Acknowledgments

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