Single-crystal Electron Spin Resonance and Electronic Spectra of Bis-(β-alaninato)copper(II) Hexahydrate

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The single-crystal e.s.r. and polarized electronic spectra of the title complex are reported. The data are interpreted by use of a crystal-field model (approximate D_{2h} symmetry, $10Dq \simeq 13\,000$ cm^{-1}, $Cp \simeq 2\,300$ cm^{-1}) and are seen to be consistent with the relative one-electron orbital energies $d_{x^2-y^2} > d_{z^2} > d_{xy} > d_{xz} > d_{yz}$. Anisotropic orbital-reduction factors are also obtained and briefly discussed (k_z 0.775, $k_x = k_y$ = 0.81).

SEVERAL e.s.r. studies on copper(II)–amino-acid complexes have been carried out recently.[1-5] In some cases [1,3] the copper(II) ions are accommodated as impurities in amino-acid crystals. In another case [2] the zinc complex is doped with small amounts of Cu^{II}.

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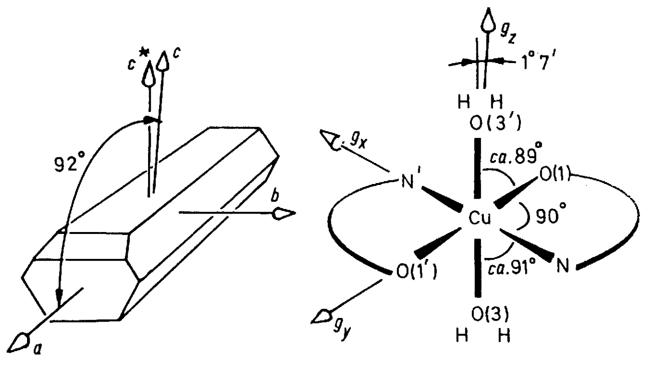
[4] B. N. Misra and S. D. Sharma, *J. Chem. Phys.*, 1975, **63**, 5322.

[5] B. N. Misra and S. D. Sharma, *J. Magnetic Resonance*, 1976, **24**, 1.

The copper complex itself was studied [4,5] in the powder form or in solution and glasses. In particular, bis(β-alaninato)copper(II) has been studied under these conditions,[4] and it seemed interesting to us to supply additional information about this complex from a single-crystal study by e.s.r. and optical spectroscopy. The e.s.r. study of a non-diluted ion allows the determination of the molecular g values by means of the procedure developed by Billing and Hathaway.[6] Notwithstanding the loss of the hyperfine structure, the interest in this method arises when magnetic dilution appears to be difficult.[7]

EXPERIMENTAL

Preparation.—Single crystals of bis(β-alaninato)copper(II) hexahydrate were prepared as reported previously.[8] Our attempts to obtain the tetrahydrate following the procedure described in ref. 9 were unsuccessful as indicated by X-ray analysis. The hexahydrate is unstable under normal conditions because of the loss of water molecules. This causes the crystals to become pale, and can be considerably reduced by keeping the crystals in a water-saturated atmosphere.



(*a*) (*b*)

FIGURE 1 Bis(β-alaninato)copper(II) hexahydrate: (*a*) crystal morphology; (*b*) structure of the chromophore and principal axes of the g tensor

Crystallographic Data.—The crystals of $[Cu(\beta\text{-AlaO})_2]\cdot 6H_2O$ are monoclinic (space group $P2_1/c$) with $a = 5.46$, $b = 7.71$, $c = 18.11$ Å, $\beta = 92°$, and $Z = 2$.[8] They were obtained as deep blue prisms elongated along the a axis, with the faces parallel to (a,b) often well developed [Figure 1(*a*)]. The complex has an elongated octahedral stereochemistry [Figure 1(*b*)] with two molecules of β-alaninate acting as bidentate ligands and approximately located in the equatorial plane. The two β-AlaO residues are *trans* to each other. Two water molecules lie on the tetragonal axis on both sides of the equatorial plane. The four remaining water molecules allow the formation of hydrogen bridges and ensure the connection between the complex molecules in the crystal lattice. The bonds to the two apical water oxygen atoms are much longer [Cu–O(3) 2.53 Å] than those to the co-ordinating atoms in the equatorial plane [Cu–O(1) 2.01, Cu–N 2.04 Å]. The bond directions are practically orthogonal [Figure 1(*b*)].

Physical Measurements.—The e.s.r. spectra were recorded at room temperature (25°C) with a X-band Bruker spectrometer as previously described.[10] Three different crystals were analysed in three orthogonal planes from which two [(a,b) and (a,c)] are crystallographic planes. The crystals were always cemented on the same face [parallel to the (a,b) plane]. The linewidth of the single line observed varies with orientation and ranges from 20 to 60 G.*

Polarized optical spectra were obtained using a Beckman ACTA V u.v.–visible spectrophotometer and polaroids or nicol prisms. Spectra in the near-i.r. region were recorded on a Beckman ACTA M-IV spectrophotometer. Some experiments were performed at *ca.* 120 K using the Beckman variable-temperature cell but the spectra were not improved. The crystals, cemented by means of a cyanoacrylate adhesive (Mach 10, Woodhill) on iron masks, with 1.5-mm aperture, were ground to a thickness of 0.2, sometimes 0.1, mm. In order to avoid the loss of water, the freshly prepared crystal plates were always coated with liquid paraffin and immediately analysed. Optical spectra could be taken with the $\vec{E}$ vector parallel to the a, b, and c^* crystallographic axis.

RESULTS AND DISCUSSION

E.S.R. Spectra.—As do most undiluted copper(II) compounds, single crystals of $[Cu(\beta\text{-AlaO})_2]\cdot 6H_2O$ exhibit only one e.s.r. line.[11] This is due to exchange coupling which averages the spectra of the two non-equivalent molecules in the unit cell. The complete rotational data yield three *crystal* g values: $g_1 = 2.069\,9$, $g_2 = 2.111\,8$, and $g_3 = 2.231\,2$. The procedure described in refs. 6 and 11 was used for obtaining the *molecular* g values from the crystal g values. This method requires an assumption regarding the direction of the z axis in the molecule: it is assumed to be perpendicular to the equatorial plane. That choice yields the value $\alpha = 29.854°$. The x and y axes of the molecule lie somewhere in the equatorial plane; they are generally found to be along the bonds or bisecting them.

An initial direction is chosen for the y axis defined by the angle β. If the y axes are chosen so as to be the Cu–O(1') directions, $\beta = 1.895°$. Allowing β to vary and solving a system of two linear and one quadratic equations [equation (25), ref. 11, p. 201] yields the molecular g values in Table 1. Actually, the resolution of the system gives two solutions, one of which (the less axial) can be rejected using another approach to the problem, as already described.[7] Table 1 shows that only a localization of the x and y axes in the vicinity of the equatorial bond directions gives acceptable molecular g values.

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* Throughout this paper: $1\ G = 10^{-4}\ T$.

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[7] F. Dejehet and R. Debuyst, *J. Phys. Chem. Solids*, 1977, **38**, 517.

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Thus, it seems reasonable to retain as the best g values the set which corresponds to g_{xx} and g_{yy} being along the molecular axes: $g_{xx} = 2.051$, $g_{yy} = 2.070$, and $g_{zz} = 2.288$. The in-plane anisotropy is 0.87%, reducing the symmetry from D_{4h} to D_{2h}. The magnitudes of the g values as well as the localization of the principal axes suggest a $d_{x^2-y^2}$ ground state.[11]

TABLE 1

Molecular g values as a function of β

β/°	g_{xx}^2	g_{yy}^2	g_{zz}^2
1.895 [direction Cu–O(1′)]	4.204 8	4.284 6	5.233 0
11.895	4.198 9	4.289 8	5.233 7
21.895	4.161 8	4.320 7	5.239 9
31.895 41.895 51.895 61.895		No solutions	
71.895	4.300 5	4.186 5	5.235 5
81.895	4.286 8	4.202 4	5.233 3
91.895	4.284 6	4.204 8	5.233 0

Electronic Spectra.—Figure 2 shows the optical spectra recorded with the electric vector $\vec{E}$ parallel to the a, b, and c^* crystallographic axes respectively. Two groups of bands are observed: an intense one which clearly contains two components (17 100 and 16 000 cm^{-1}) and a less intense one whose components are less easily discernible (13 300 and 12 800 cm^{-1}). An exploration of the near-i.r. region (between 12 500 and 5 000 cm^{-1}) does not reveal any supplementary band.

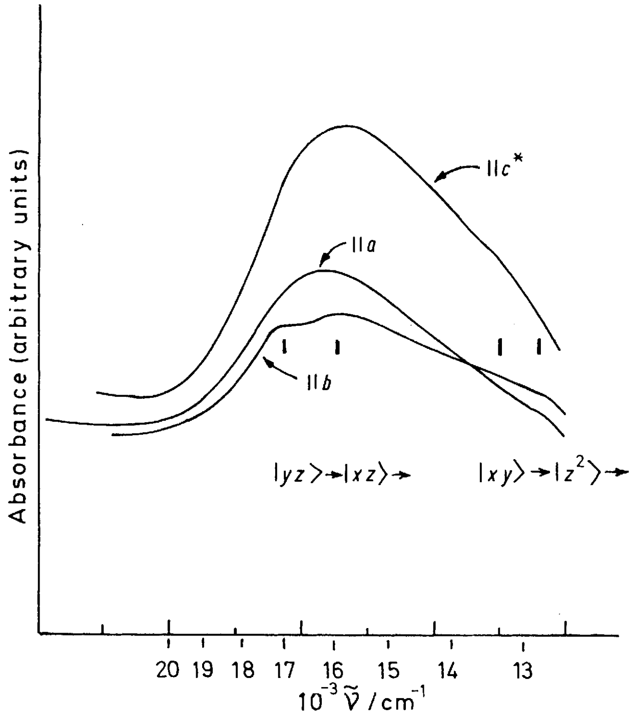

FIGURE 2 Electronic polarized spectra at ambient temperature. Spectra parallel to a and b axes were recorded for the same crystal

Because the two molecules in the unit cell are differently orientated and the d–d transitions are only vibronically allowed in this centrosymmetrical complex, an unambiguous assignment of the spectra is difficult. The vibronic selection rules in the D_{2h} symmetry and assuming a $d_{x^2-y^2}$ ground state are in Table 2. Table 3 collects the squares of the projections which the molecular electric-dipole vectors (x, y, and z as determined by e.s.r. spectroscopy) make on the a, b, and c^* axes. The spectrum polarized parallel to the b axis is mainly molecular z in origin, the a-axis and c^*-axis spectra being mainly x and y. This fact, together with the observation by several workers [12-14] of the particular efficiency of the B_{1u} vibrational mode in D_{2h}, leads us to attribute the two bands at higher wavenumbers, which are the more intense in a and c^* polarization, to yz, $xz \rightarrow x^2 - y^2$ transitions. In b polarization the yz, $xz \rightarrow x^2 - y^2$ transitions are mainly allowed by the B_{2u} and B_{3u} vibrational modes, while the efficiency of the B_{1u} mode of vibration is responsible for the emergence of the $z^2 \rightarrow x^2 - y^2$ transition (12 800 cm^{-1}). The order of the one-electron orbital energies should be: $d_{x^2-y^2} > d_{z^2} > d_{xy} > d_{xz} > d_{yz}$.

TABLE 2

Vibrational symmetries which permit possible d–d transitions in a D_{2h} octahedral complex

	Symmetry of the product of d states and polarization			Polarization allowed by vibration of given symmetry		
Transition	z	y	x	B_{1u}	B_{2u}	B_{3u}
$z^2 \rightarrow x^2 - y^2$	B_{1u}	B_{2u}	B_{3u}	z	y	x
$xy \rightarrow x^2 - y^2$	A_u	B_{3u}	B_{2u}		x	y
$xz \rightarrow x^2 - y^2$	B_{3u}	A_u	B_{1u}	x		z
$yz \rightarrow x^2 - y^2$	B_{2u}	B_{1u}	A_u	y	z	

TABLE 3

Squares of the projections of the molecular electric-dipole vectors x, y, and z on the a, b, and c^* axes

	z	y	x
a	0.161	0.320	0.501
b	0.755	0.000	0.247
c^*	0.085	0.680	0.252

The above tentative assignment is compatible with a crystal-field approach based on the Companion and Komarynsky treatment.[15] In this approach, each ligand around the copper ion is characterized by the polar and azimuthal angles, θ and ϕ, known from the crystallographic data, and by two empirical parameters α_2 and α_4, or α_4 and α_2/α_4. A computer program has been written which calculates the perturbation crystal-field

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[12] D. E. Billing and B. J. Hathaway, *J. Chem. Soc.* (*A*), 1968, 1516.

[13] B. J. Hathaway, D. E. Billing, P. Nicholls, and I. M. Procter, *J. Chem. Soc.* (*A*), 1969, 319.

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matrix elements as given in Tables 1 and 2 in ref. 15 and diagonalizes this 5 × 5 matrix. This program also includes the spin–orbit coupling and Zeeman interaction and diagonalizes completely the corresponding 10 × 10 matrices.[16] Figure 3 shows that the experimental band positions are satisfactorily fitted by considering only the four equatorial ligands each having the values $\alpha_4 = -8\,000$ cm^{-1} and $\alpha_2/\alpha_4 = 1$. For good agreement with experiment, the influence of the two axial water oxygen atoms needs to be neglected ($\alpha_4 \simeq 0$). Scaling the values of α_4 and α_2 for the six ligands according to the actual metal–ligand separation[17,18] did not yield a satisfactory result (fitting of experimental bands is only possible for negative values of α_2/α_4).

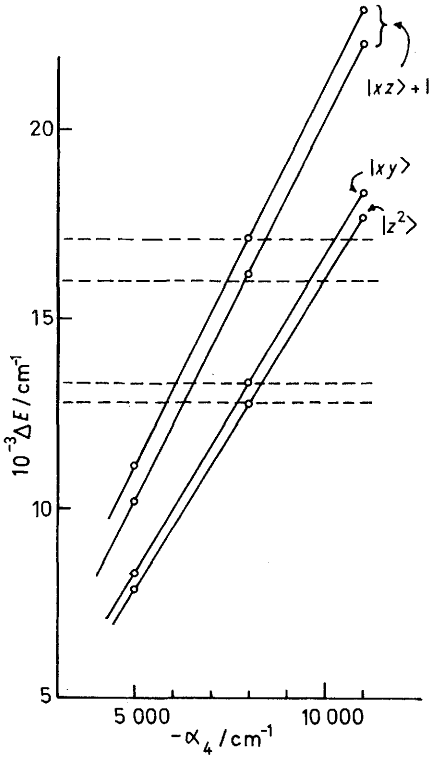

FIGURE 3 Variation of the transition energies for $\alpha_2/\alpha_4 = 1$ (spin–orbit coupling included). Broken lines represent experimental transition energies

A certain amount of anisotropy has to be introduced by assigning different α_4 values to the oxygen and nitrogen atoms, in order to restore the experimental in-plane g anisotropy ($g_y - g_x$ 0.019). It is possible to take into account covalency effects by introducing an orbital-reduction factor, k. This parameter has been introduced in the computer program as a coefficient of the $\vec{L}$ operator everywhere where this symbol appeared, *i.e.* in the spin–orbit coupling operator as $\xi(k_xL_xS_x + k_yL_yS_y + k_zL_zS_z)$ and in the Zeeman operator as $k_iL_i + 2.0023S_i$ with $i = x, y$, or z.[17,18] ξ is the single-electron spin–orbit coupling constant (for Cu$^{\text{II}}$, $\xi = -829$ cm^{-1}). Calculated g values corresponding to the experimental values within the limits of errors were obtained for $k_z = 0.775$ and $k_y = k_x = 0.810$. The final set of parameters is listed in Table 4.

TABLE 4

Summary of the experimental and theoretical results

	Angular co-ordinates (°) of ligands			Radial parameters		
Atom	θ	φ		α_4/cm^{-1}	α_2/α_4	
O_1	90	269.76		$-7\,700$	1.0	
O_1'	90	89.76				
N	90	180		$-8\,300$	1.0	
N′	90	0				
Observed optical transitions (10^3 cm^{-1})			17.1	16.0	*ca.* 13.3	12.8
Calculated transitions (10^3 cm^{-1}) (spin–orbit coupling included)			17.1	16.2	13.3	12.8
(orbital-reduction factor k included)			17.0	16.2	13.3	12.8
Experimental g values			g_{zz} 2.288	g_{yy} 2.070	g_{xx} 2.051	
Calculated g values (without orbital-reduction factor k)			2.475	2.100	2.077	
(with k)			2.288	2.067	2.052	
Orbital-reduction factor k			k_z 0.775	k_y 0.810	k_x 0.810	

The α_2 and α_4 parameters are related to the more familiar quantities Dq and Cp by $\alpha_4 = 6Dq$ and $\alpha_2 = \frac{7}{2}Cp$ so that $Dq(\text{O}) = -1\,283$ cm^{-1}, $Dq(\text{N}) = -1\,383$ cm^{-1}, $Cp(\text{O}) = -2\,200$ cm^{-1}, and $Cp(\text{N}) = -2\,371$ cm^{-1} (Cu–N 2.04, Cu–O 2.01 Å). These values of Dq ($10\,Dq \simeq 13\,000$ cm^{-1}) and of $\alpha_2/\alpha_4 = 1.0$ are frequently encountered in copper(II) complexes.[19,20] In D_{2h} symmetry the orbital-reduction factor k can be related to the coefficients of the d orbitals in the copper antibonding molecular orbitals. In particular, when the crystal field causes little mixing between the $d_{x^2-y^2}$ and d_{z^2} oritals (in our case: $0.999\,5\ |x^2 - y^2\rangle - 0.320\,4|z^2\rangle$) the relations are approximately: $k_z = \alpha\beta$, $k_x = \alpha\gamma_1$, and $k_y = \alpha\gamma_2$ where α (σ bonding), β (in-plane π bonding), γ_1, γ_2 (out-of-plane π bonding) are the coefficients of the $d_{x^2-y^2}$ d_{xy}, d_{yz}, and d_{xz} orbitals in the molecular orbitals.[17,18] The relative magnitudes of k_z, k_x, and k_y lead to $\beta < \gamma_1 = \gamma_2$. This sequence implies a more significant overlap of the d_{xy} than of the d_{xz} and d_{yz} metal orbitals with the p_π orbitals of the ligands.

Finally, we compare our results with those previously reported for copper(II)–alanine complexes.[2,4] Where the copper(II) ion is diluted in a bis(alaninato)zinc(II) complex the g values ($g_\parallel$ 2.257, $g_\perp$ 2.058) [2] are not very different from ours. These workers also calculated the

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molecular-orbital (m.o.) coefficients, $\alpha \simeq 0.87$, $\beta \simeq 0.93$, and $\gamma_1 = \gamma_2 \simeq 1$, although their optical information was rather poor (one band at 15 800 cm^{-1}). Nevertheless, applying the values $\gamma_1 = \gamma_2 \simeq 1$ to our case yields $\alpha = 0.81$ and $\beta = 0.96$, revealing for our complex a predominant covalent character of the σ bonding and a low covalent character of the in-plane π bonding. Recently, Misra and Sharma[4] studied the [Cu(β-AlaO)$_2$] in glycerine–water at −80 °C. They found higher g values ($g_{\parallel}$ 2.344, $g_{\perp}$ 2.115) and their m.o. coefficients (α 0.92, $\beta \simeq 1$, and $\gamma_1 = \gamma_2 \simeq 1$) are not in agreement with our conclusions ($\beta < \gamma_1 = \gamma_2$). It must be stressed, however, that the experimental conditions are so different that a straightforward comparison might not be pertinent. On the other hand, these workers seem to discuss their polycrystalline g values (g_3 2.220 3, g_2 2.101 5, g_1 2.063 7) as if they were molecular g values.

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