Electron Spin Resonance and Electronic Spectra and Crystal and Molecular Structures of Copper(II) Amino Acid Complexes[‡]

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The crystal and molecular structures of the *trans* complexes [Cu(DL-alaO)$_2$(H$_2$O)], [Cu(L-alaO)$_2$], [Cu(DL-proO)$_2$(H$_2$O)$_2$], and [Cu(acpc)$_2$] [alaO = alaninate(1−), proO = prolinate(1−), and acpc = 1-aminocyclopentane-1-carboxylate] are reported, these being redeterminations except in the case of [Cu(DL-alaO)$_2$(H$_2$O)]. The single-crystal *d–d* and e.s.r. spectra of the complexes were recorded and interpreted in terms of a progressive increase in the axial ligand co-ordination, accompanied by a decrease in the in-plane Cu–O(carboxylate) bond length. In agreement with simple theoretical predictions, the principal axes of the *g* tensors tend to lie close to the metal–ligand bond axes and the sign and magnitude of the in-plane *g* anisotropy of each complex are consistent with the expected difference in σ-bonding power of the amine nitrogen and carboxylate oxygen atoms and the observed bond lengths. The single-crystal e.s.r. spectrum of *cis*-[Cu(glyO)$_2$(H$_2$O)] [glyO = glycinate(1−)] was also measured, and the small in-plane anisotropy of the molecular *g* tensor confirmed the interpretation of the *g* values of the *trans* amino acid complexes. Angular overlap calculations of the *d–d* transition energies and molecular *g* values of the complexes suggest metal–ligand bonding parameters consistent with their molecular structures. However, in agreement with similar findings on analogous compounds the $d_{z^2} \rightarrow d_{x^2-y^2}$ transitions were found to lie at anomalously high energy, this discrepancy being most marked when the axial bonds are very long.

Perhaps because of their biochemical importance[1] the complexes formed by copper(II) with various amino acid ligands have been the subject of numerous spectroscopic investigations.[2] However, these studies have almost invariably involved measurements of the e.s.r. and optical spectra of powders or frozen solutions.[3–11] Recent investigations of the metal–ligand bonding parameters in low-symmetry complexes, and the way in which these are correlated with the ligand co-ordination geometry, have proved highly successful,[12–14] but they depend upon a detailed knowledge of the molecular orientation of the magnetic axes which can only be obtained from the study of single crystals. In this context, it is interesting to note that reports of the e.s.r. spectra of trace amounts of Cu^{2+} doped into single crystals of various amino acids have appeared.[15–17] These have yielded valuable information on the magnetic parameters and covalency of copper(II) amino acid complexes, but are unable to provide direct information on the way in which the metal–ligand interactions are related to stereochemical factors such as bond length, as the nature, geometry, and orientation of the copper(II) guest complexes are not known with certainty. Similar arguments apply to the various studies which have been reported of the e.s.r. spectra of powders of Zn^{II} amino acid complexes containing trace amounts of Cu^{2+}.[8,18]

In order more fully to investigate the molecular *g* values and electronic spectra of copper(II) bis(amino acid) complexes the present study reports the single-crystal e.s.r. and optical spectra of the *trans* complexes with L-alanine, DL-alanine, DL-proline, and 1-aminocyclopentane-1-carboxylic acid and the single-crystal e.s.r. spectrum of the *cis* complex formed by glycine.

The spectral parameters have been interpreted in terms of angular overlap metal–ligand bonding parameters, and in order that these may be correlated with the molecular structures of the complexes the *X*-ray structures of the *trans* complexes have been determined (in every case except that of the DL-alanine complex: this involved the redetermination of a structure solved previously by film techniques).

Experimental

Preparation of the Complexes.—The complex *cis*-[Cu(glyO)$_2$(H$_2$O)] [glyO = glycinate(1−)] was prepared as fine pale blue needles by the method of Low *et al.*[19] and recrystallized from water (Found: C, 20.7; H, 4.3; N, 11.9. $C_4H_{10}CuN_2O_5$ requires C, 20.9; H, 4.4; N, 12.2%). The method of Graddon and Munday[20] was used to prepare [Cu(L-alaO)$_2$] [alaO = alaninate(1−)] (Found: C, 30.2; H, 5.0; N, 11.2. $C_6H_{12}CuN_2O_4$ requires C, 30.1; H, 5.1; N, 11.7%). The compound [Cu(DL-proO)$_2$(H$_2$O)$_2$] [proO = prolinate(1−)] was made by the method of Mathieson and Welsh[21] (Found: C, 36.6; H, 6.3; N, 8.5. $C_{10}H_{20}CuN_2O_6$ requires C, 36.6; H, 6.2; N, 8.4%). The complex [Cu(acpc)$_2$] [acpc = 1-aminocyclopentane-1-carboxylate(1−)] was also prepared by the method of Mathieson and Walsh[21] (Found: C, 45.2; H, 6.1; N, 8.9. $C_{12}H_{20}CuN_2O_4$ requires C, 45.1; H, 6.3; N, 8.8%). The compound [Cu(DL-alaO)$_2$(H$_2$O)] was made by the method of Graddon and Munday[20] and was recrystallized from a methanol–water mixture (Found: C, 27.7; H, 5.3; N, 11.0. $C_6H_{14}CuN_2O_5$ requires C, 28.0; H, 5.5; N, 10.9%).

X-*Ray Crystal-structure Analyses.*—The general procedure used in each analysis has been described elsewhere[22] and crystallographic details for the compounds studied are listed in Table 1.

E.S.R. and Optical Measurements.—The e.s.r. spectra of single crystals of the complexes were measured at room temperature

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[‡] *Supplementary data available* (No. SUP 56649, 7 pp.): observed crystal *g* values. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

Table 1. Crystallographic data

Complex	[Cu(L-alaO)$_2$]	[Cu(DL-alaO)$_2$(H$_2$O)]	[Cu(DL-proO)$_2$(H$_2$O)$_2$]	[Cu(acpc)$_2$]
Formula	$C_6H_{12}CuN_2O_4$	$C_6H_{14}CuN_2O_5$	$C_{10}H_{20}CuN_2O_6$	$C_{12}H_{20}CuN_2O_4$
M	239.7	257.8	327.8	319.9
Crystal class	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1$ (no. 4)	$C2/c$ (no. 15)	$P2_1/n$ (no. 14)	$P2_1/a$ (no. 14)
a/Å	9.166(5)	12.087(6)	5.579(1)	10.838(4)
b/Å	5.045(3)	9.592(4)	17.903(5)	5.504(2)
c/Å	9.521(6)	8.988(4)	7.003(2)	10.839(4)
β/°	94.60(4)	110.98(4)	104.53(3)	94.38(3)
U/Å^3	438.9(5)	973.0(8)	677.2(3)	644.7(4)
D_c/g cm^{-3}	1.81	1.76	1.61	1.65
Z	2	4	2	2
F(000)	246	532	342	330
μ(Mo-K_α)/cm^{-1}	25.7	23.3	17.0	17.7
Specimen/mm	0.04 × 0.4 × 0.15	0.11 × 0.07 × 0.30	0.30 × 0.05 × 0.25	0.4 × 0.16 × 0.06
$2\theta_{max.}$/°	60	50	60	60
N	1 330	854	1 992	1 889
$N_o[I > 3\sigma(I)]$	1 207	651	1 334	1 469
R	0.032 *	0.046	0.036	0.046
R'	0.038 *	0.057	0.048	0.052

* Preferred chirality.

Table 2. Atomic co-ordinates for [Cu(L-alaO)$_2$][a]

Atom	x	y	z
Cu	0.486 79(4)	$\frac{3}{4}$[b]	0.748 51(4)
Ligand a			
O(1)	0.541 8(3)	0.951 6(7)	0.585 8(2)
C(1)	0.655 9(4)	0.867 0(10)	0.531 3(4)
O(2)	0.696 8(3)	0.938 1(8)	0.417 4(3)
C(2)	0.747 2(4)	0.666 4(9)	0.625 4(4)
H(2)	0.802(5)	0.783(11)	0.691(5)
N(1)	0.641 4(4)	0.503 9(8)	0.696 5(3)
H(1a)	0.596(5)	0.429(13)	0.652(5)
H(1b)	0.677(5)	0.397(13)	0.763(5)
C(3)	0.854 5(5)	0.503 4(11)	0.549 3(5)
H(3a)	0.924(5)	0.631(14)	0.504(6)
H(3b)	0.914(6)	0.391(16)	0.602(6)
H(3c)	0.814(6)	0.367(15)	0.487(6)
Ligand b			
O(3)	0.434 6(3)	0.547 3(7)	0.911 1(2)
C(4)	0.334 0(4)	0.649 4(9)	0.980 4(4)
O(4)	0.297 4(3)	0.557 4(8)	1.093 4(3)
C(5)	0.254 0(4)	0.892 0(10)	0.916 0(4)
H(5)	0.236(5)	1.024(11)	0.988(5)
N(2)	0.344 0(4)	1.011 2(8)	0.810 2(3)
H(2a)	0.389(5)	1.154(12)	0.838(5)
H(2b)	0.297(5)	1.084(12)	0.738(5)
C(6)	0.107 0(5)	0.804 1(16)	0.854 9(6)
H(6a)	0.114(7)	0.713(19)	0.764(6)
H(6b)	0.053(7)	0.732(20)	0.906(7)
H(6c)	0.059(8)	0.979(17)	0.823(7)

[a] Non-hydrogen atom numbering of the complex follows that of the original report of the structure determination,[24] as does the co-ordinate setting, *except in respect of the original chirality which appears to be wrong*. Residuals quoted are for the preferred chirality which is in agreement with the known structure of the base. [b] Defines origin.

Table 3. Atomic co-ordinates for [Cu(DL-alaO)$_2$(H$_2$O)] *

Atom	x	y	z
Cu	0	0	$\frac{1}{2}$
N(1)	−0.147 3(4)	0.086 9(5)	0.504 9(6)
H(1a)	−0.136(5)	0.116(6)	0.604(6)
H(1b)	−0.166(5)	0.159(6)	0.426(7)
C(2)	−0.240 1(5)	−0.021 4(6)	0.464 0(8)
H(2)	−0.237(6)	−0.057(7)	0.564(8)
C(3)	−0.363 3(6)	0.031 1(7)	0.409 9(11)
H(3a)	−0.373(−)	0.091(−)	0.487(−)
H(3b)	−0.375(−)	0.088(−)	0.313(−)
H(3c)	−0.424(−)	−0.036(−)	0.379(−)
C(1)	−0.215 2(5)	−0.128 0(5)	0.352 8(6)
O(1)	−0.110 1(3)	−0.129 9(4)	0.351 1(4)
O(2)	−0.294 5(3)	−0.207 8(4)	0.272 5(5)
Water			
O(3)	0	−0.152 7(6)	$\frac{3}{4}$
H(3)	0.046(6)	−0.209(6)	0.745(9)

* Non-hydrogen atom numbering of the complex follows that of the structure determination of the anhydrous species (B. K. Vainshtein, I. A. D'yakon, and A. V. Ablov, *Dokl. Acad. Nauk SSSR Krist.*, 1970, **193**, 330). Parameters for H(3*n*) are estimates.

using a JEOL FE3X spectrometer operating at *X*-band (~9.2 GHz) frequency. The crystals were rotated using the standard JEOL accessory, and it is estimated that the orientation was determined to better than ~2°. The mounting of the crystals, measurement of the *g* values, and treatment of the data to obtain molecular *g* values followed a procedure described in detail previously.[12,13] Crystal morphologies were deduced using a stereoscopic polarizing microscope. For each compound, complete sets of data were obtained on two different crystals and the uncertainties in the molecular *g* tensors were obtained by comparing the results. Three orthogonal rotations of each crystal were made, and the observed crystal *g* values for each position of the magnetic field are listed in SUP 56649. Electronic spectra were recorded using a Cary 17 spectrophotometer by a technique described elsewhere,[23] the samples being cooled using a closed-cycle Cryodyne model 22 cryostat.

Results and Discussion

Crystal and Molecular Structures of the Complexes.—The atomic co-ordinates of the four compounds studied by *X*-ray diffraction, [Cu(L-alaO)$_2$], [Cu(DL-alaO)$_2$(H$_2$O)], [Cu(DL-

Table 4. Atomic co-ordinates for [Cu(DL-proO)$_2$(H$_2$O)$_2$]*

Atom	x	y	z
Cu	0	0	0
C(1)	−0.173 8(5)	0.054 9(2)	0.306 2(4)
O(1)	−0.211 4(4)	0.000 6(1)	0.185 7(3)
O(2)	−0.314 8(4)	0.071 9(2)	0.409 5(3)
C(2)	0.061 5(6)	0.100 3(2)	0.323 9(5)
H(2)	0.172(−)	0.085(−)	0.447(−)
C(3)	0.020 5(9)	0.185 2(2)	0.316 2(10)
H(3a)	−0.146(−)	0.197(−)	0.265(−)
H(3b)	0.066(−)	0.205(−)	0.455(−)
C(4)	0.192 0(9)	0.214 9(2)	0.202 6(8)
H(4a)	0.135(−)	0.262(−)	0.138(−)
H(4b)	0.360(−)	0.223(−)	0.280(−)
C(5)	0.188 7(8)	0.155 8(2)	0.055 0(6)
H(5a)	0.049(−)	0.161(−)	−0.057(−)
H(5b)	0.336(−)	0.158(−)	0.003(−)
N(1)	0.175 8(4)	0.083 9(1)	0.159 1(4)
H(1)	0.312(6)	0.071(2)	0.207(5)
Water			
O(3)	−0.348 9(5)	0.085 5(1)	−0.200 9(4)
H$_O$(3a)	−0.325(8)	0.083(2)	−0.309(7)
H$_O$(3b)	−0.465(8)	0.057(2)	−0.198(6)

* Non-hydrogen atom numbering of the complex follows that of the original report of the structure determination,[26] as does the co-ordinate setting. Parameters of hydrogen atoms attached to parent carbon atoms are estimates.

Table 5. Atomic co-ordinates for [Cu(acpc)$_2$]*

Atom	x	y	z
Cu	½	½	0
N	0.381 4(3)	0.338 4(6)	0.102 2(3)
H(a)	0.337(−)	0.458(−)	0.145(−)
H(b)	0.323(−)	0.246(−)	0.051(−)
C(1)	0.449 7(3)	0.175 1(7)	0.192 8(3)
C(2)	0.368 8(4)	−0.030 7(8)	0.237 0(4)
H(2a)	0.294(−)	−0.044(−)	0.184(−)
H(2b)	0.412(−)	−0.183(−)	0.234(−)
C(3)	0.340 9(5)	0.031 2(14)	0.367 7(5)
H(3a)	0.255(−)	0.010(−)	0.379(−)
H(3b)	0.386(−)	−0.074(−)	0.426(−)
C(4)	0.379 8(5)	0.291 2(12)	0.389 6(4)
H(4a)	0.315(−)	0.402(−)	0.363(−)
H(4b)	0.403(−)	0.324(−)	0.475(−)
C(5)	0.489 5(4)	0.316 4(8)	0.311 6(4)
H(5a)	0.506(−)	0.484(−)	0.293(−)
H(5b)	0.563(−)	0.248(−)	0.353(−)
C(0)	0.566 9(3)	0.089 5(8)	0.132 9(4)
O(1)	0.605 2(2)	0.228 4(6)	0.049 0(3)
O(2)	0.621 7(3)	−0.094 8(6)	0.169 3(3)

* Non-hydrogen atom numbering of the complex follows that of the original report of the structure determination,[25] as does the co-ordinate setting. Hydrogen atom parameters are estimates.

proO)$_2$(H$_2$O)$_2$], and [Cu(acpc)$_2$], are listed in Tables 2—5 respectively. The Cu–O bond lengths are given in Table 6. The structures of the compounds [Cu(L-alaO)$_2$],[24] [Cu(acpc)$_2$],[25] and [Cu(DL-proO)$_2$(H$_2$O)$_2$][26] had each been determined previously by film techniques; in the case of the L-alanine complex the refinement had been carried out by two-dimensional methods. The bond lengths in the copper(II) co-ordination sphere from the present, more accurate structure determinations of the complexes [Cu(L-alaO)$_2$] and [Cu(acpc)$_2$] are broadly similar to those in the previous determinations. The Cu–N bonds are approximately equal [1.977(4) and 1.979(4), and 1.972(3) Å], while the bonds to the carboxylate oxygen atoms are 1.953(3) and 1.947(3) Å in the former complex and 1.930(3) Å in the latter. The co-ordination sphere of the copper(II) ion in both compounds is completed by the formation of long bonds to an oxygen atom of a carboxylate group of a neighbouring molecule. However, this is significantly shorter in [Cu(L-alaO)$_2$] than in [Cu(acpc)$_2$] (2.85 *vs.* 3.12 Å). Possibly the abnormally short in-plane Cu–O bonds in the latter complex occur to compensate for the weak axial co-ordination; an inverse correlation between the in-plane and axial bonds of six-co-ordinate copper(II) complexes seems well established.[27,28] The structure of [Cu(DL-proO)$_2$(H$_2$O)$_2$] was determined by Mathieson and Welsh[21] on the basis of a two-dimensional refinement, and redetermined by Shamala and Venkatesan[26] using a three-dimensional refinement. While the present redetermination confirms the general features of the earlier studies, the Cu–O(carboxylate) bond length was found to be significantly shorter than that determined in the earlier work [1.963(2) Å, compared with 2.028[26] and 2.03 Å[21]]. In contrast to the previous studies, the present determination thus suggests that, as is also the case for each of the other amino acid complexes, the Cu–O(carboxylate) bonds are slightly shorter than the Cu–N bonds [1.978(2) Å in the present study, 1.959[26] and 1.99 Å[21] in the previous ones]. The axial co-ordination in [Cu(DL-proO)$_2$(H$_2$O)$_2$] is to two water molecules at 2.595(3) Å, this bond length being similar to those found previously (2.538[26] and 2.52 Å[21]). As the crystal packing in the above three compounds has been adequately described in the previous reports of their structures, this aspect will not be covered further.

The ligand co-ordination geometry about the Cu^{II} ion in the centrosymmetric complex [Cu(DL-alaO)$_2$(H$_2$O)] (Figure 1) is quite similar to that in [Cu(L-alaO)$_2$], the bonds to the carboxylate oxygen atoms [1.959(3) Å] being marginally shorter than those to the amine nitrogen atoms [1.981(5) Å]. Although the length of the axial bonds (2.682 Å) is similar to that in [Cu(L-alaO)$_2$] and [Cu(DL-proO)$_2$(H$_2$O)$_2$], the nature of the co-ordination is novel, as it involves bridging water molecules [see Figure 1(*a*)]. These link the copper(II) ions in zig-zag chains running parallel to the *c* crystal axis, the CuOCu angle being 113.8(2)°.

The metal–ligand bond lengths in the four complexes are listed in Table 6 and it is interesting to note that the Cu–N bond lengths are essentially equal (1.997 ± 0.005 Å), the changes in the copper(II) co-ordination sphere being taken up almost entirely by the variation in the Cu–O bond lengths. The in-plane bond is invariably to a carboxylate oxygen atom, this ranging progressively from 1.930(3) to 1.963(2) Å as the axial co-ordination decreases from 3.12 to 2.595 Å. This inter-relationship between the axial and in-plane bond lengths, which appears to be a general feature of the chemistry of copper(II),[27,28] extends to the two independent complexes, (**A**) and (**B**), present in the unit cell of the compound Cu(β-alaO)$_2$·4H$_2$O.[29] Both of these are reported to have structures similar to those in the present study, being centrosymmetric, with short bonds to the *trans* chelating amino acid ligands and long bonds to water molecules [complex (**B**)] or the 'non-bonded' carboxylate oxygen of a neighbouring molecule [complex (**A**)]. While complex (**B**) has bond lengths quite similar [Cu–N 1.987, Cu–O(carboxylate) 1.960, Cu–O(ax) 2.596 Å] to those in [Cu(DL-alaO)$_2$(H$_2$O)], complex (**A**) has abnormally long in-plane Cu–O bonds (2.015 Å) which may be correlated with the rather short Cu–O(ax) bond lengths of 2.460 Å; the Cu–N distance in (**A**) is also rather short, being 1.967 Å.[29]

Electronic Spectra of the Complexes.—The electronic spectra of the most prominent crystal face of each of the four *trans* amino acid complexes were measured at room temperature and

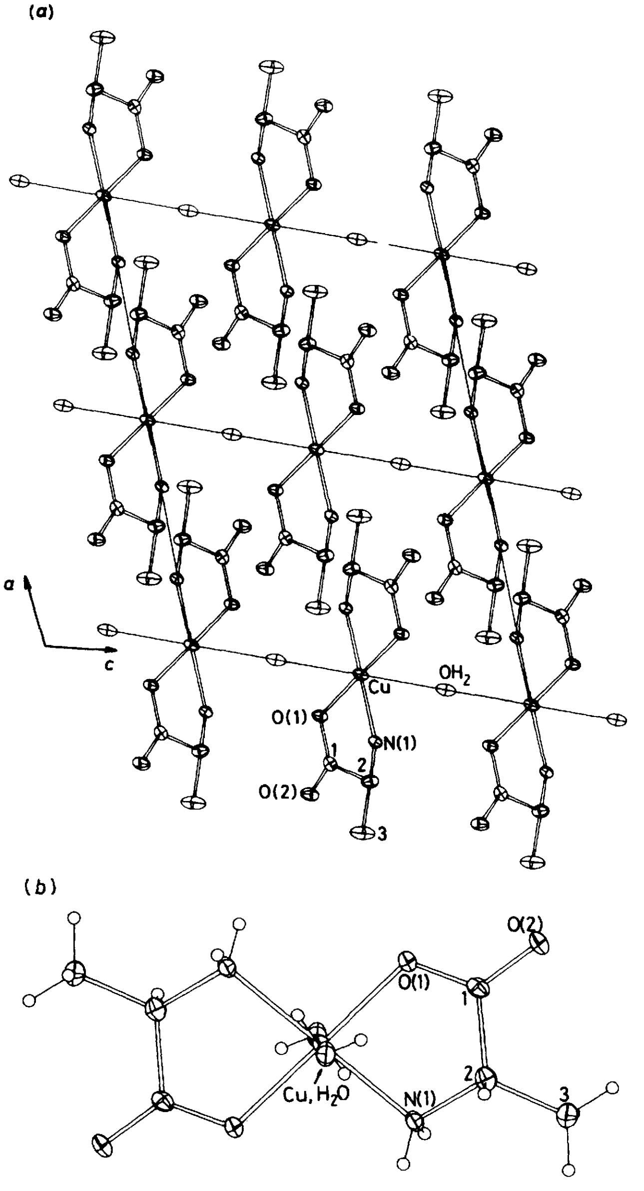

Figure 1. (*a*) Projection of the structure of [Cu(DL-alaO)$_2$(H$_2$O)] viewed down the *b* axis. (*b*) A single molecule of [Cu(DL-alaO)$_2$(H$_2$O)]

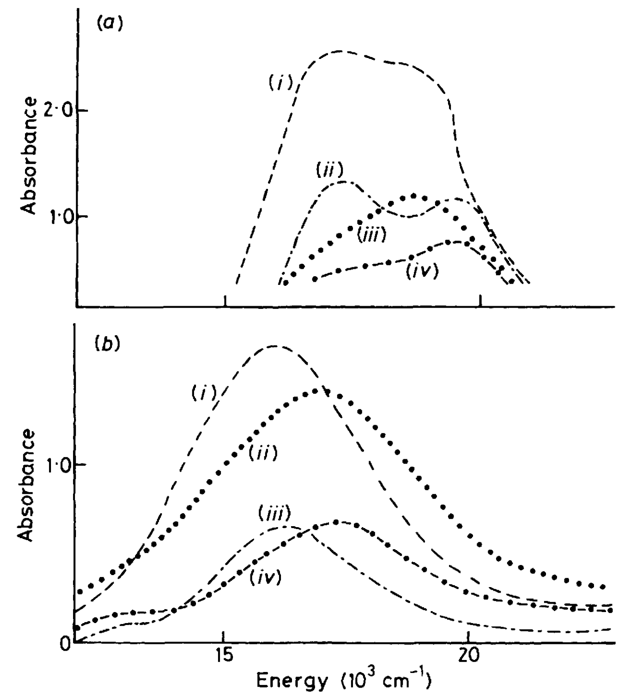

Figure 2. (*a*) Electronic spectrum of the (001) crystal face of [Cu(acpc)$_2$] with the electric vector parallel to the *a* axis at 290 K (*i*) and ~10 K (*ii*) and the *b* axis at 290 K (*iii*) and ~10 K (*iv*). (*b*) Electronic spectrum of (010) crystal face of [Cu(DL-proO)$_2$(H$_2$O)$_2$] with the electric vector making an angle of 60° to the *a* axis at 290 K (*i*) and ~10 K (*ii*), and −30° to the *a* axis at 290 K (*iii*) and ~10 K (*iv*)

~10 K using polarized light directed along the two extinction directions. Typical spectra are shown in Figures 2 and 3. For [Cu(acpc)$_2$] at 10 K well resolved peaks were observed at 21 300 and 17 900 cm^{-1} when the electric vector was parallel to *a*. With the electric vector parallel to *b* the spectrum was considerably weaker, consisting of a peak at 21 300 cm^{-1} and a pair of poorly resolved bands centred at ~19 200 and ~17 400 cm^{-1} [Figure 2(*a*)]. For [Cu(DL-proO)$_2$(H$_2$O)$_2$] [Figure 2(*b*)] the spectrum with the electric vector at 60° to the *a* axis showed a band centred at 16 200 cm^{-1}, with a weak peak at ~13 200 cm^{-1}; when the electric vector was at −30° to the *a* axis, the most intense band occurred at 17 400 cm^{-1}, with a shoulder at ~15 500 cm^{-1} and a weak peak at ~13 200 cm^{-1}. The complex [Cu(L-alaO)$_2$] showed a band centred at 16 400 cm^{-1} and a

Table 6. Bond lengths, band maxima, and molecular *g* values of the complexes

Complex	Bond lengths (Å)			Band maxima (cm^{-1}) and tentative assignment				Molecular *g* values				
	Cu–O in-plane	Cu–N	Cu–O axial	d_{z^2}	d_{xy}	d_{xz}	d_{yz}	g_x	g_y	g_z	α/°[a]	Δg_{av}[b]
[Cu(acpc)$_2$]	1.930(3)	1.972(3)	3.116	21 300[c] ~17 400[d]	17 900[c] ~19 200[d]	~19 200[c] 21 300[d]	~17 400[c] 17 900[d]	2.071(7)	2.038(2)	2.210(3)	9(2)	0.104
[Cu(L-alaO)$_2$]	1.953(3) 1.947(3)	1.977(4) 1.979(4)	2.716 2.848	*e*	*e*	18 300	16 400	2.037(6)	2.057(5)	2.253(2)	−3(3)	0.113
[Cu(DL-alaO)$_2$(H$_2$O)]	1.959(3)	1.981(5)	2.682	~14 000	*e*	~18 000	16 800	2.041(3)	2.068(3)	2.255(2)	−15(2)	0.119
[Cu(DL-proO)$_2$(H$_2$O)$_2$]	1.963(2)	1.978(2)	2.595	~13 200	16 200	17 400	~15 500	2.046(11)	2.081(11)	2.263(1)	29(5)	0.128
[Cu(glyO)$_2$(H$_2$O)][f]	1.95[g]	1.98[g]	2.4, 2.7	~10 500	~16 000	~16 000	~16 000[h]	2.068(1)	2.061(1)	2.277(1)	*i*	0.133

[a] Angle specifying in-plane orientation of *g* axes, see Figure 4(*a*). [b] Average *g* shift. [c] Assignment 1, assuming d_{z^2} orbital lowest in energy. [d] Assignment 2, assuming d_{xz} orbital lowest in energy. [e] Band unresolved. [f] Bond length data from ref. 40, electronic spectra from ref. 44. [g] Average value. [h] All three *d–d* transitions probably contribute to this band. [i] Principal in-plane *g* axes required by symmetry to lie along molecular axes, see Figure 4(*b*).

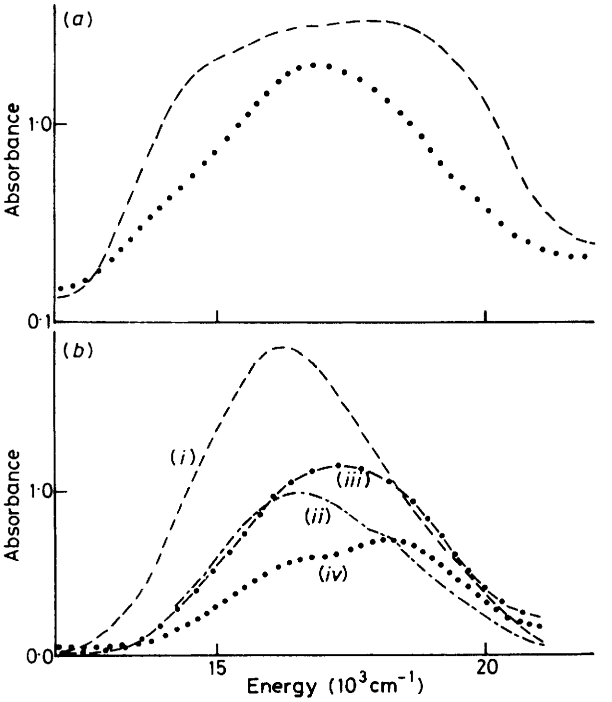

Figure 3. (*a*) Electronic spectrum at ~10 K of an arbitrary crystal face of [Cu(DL-alaO)$_2$(H$_2$O)] with the electric vector along each of the two extinction directions. (*b*) Electronic spectrum of the (100) crystal face of [Cu(L-alaO)$_2$] with the electric vector parallel to the *c* axis at 290 K (*i*) and ~10 K (*ii*), and parallel to the *b* axis at 290 K (*iii*), and ~10 K (*iv*)

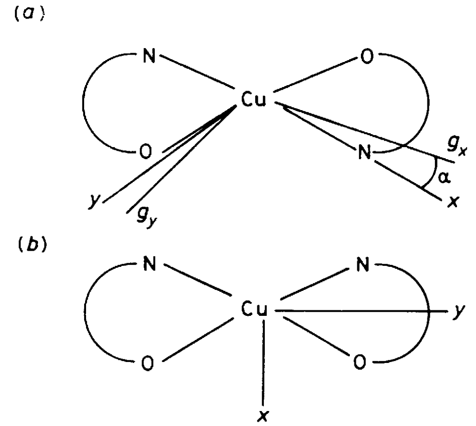

Figure 4. (*a*) Schematic diagram of the ligand co-ordination geometry, molecular co-ordinate system and orientation of the molecular *g* axes of a *trans* Cu$^{\text{II}}$ amino acid complex viewed down the *z* axis. (*b*) Schematic digram of the ligand co-ordination geometry and *x* and *y* molecular axes of a *cis* Cu$^{\text{II}}$ amino acid complex

shoulder at ~18 000 cm^{-1} with the electric vector parallel to the *c* axis, and peaks at 18 300 and ~16 400 cm^{-1} with the electric vector parallel to *b* [Figure 3(*b*)]. In one polarization of an arbitrary face of [Cu(DL-alaO)$_2$(H$_2$O)] the spectrum consists of a peak centred at 16 800 cm^{-1}, with a shoulder at ~14 000 cm^{-1}. The other polarization shows a broad band with maxima at ~18 000 and ~14 400 cm^{-1} [Figure 3(*a*)]. The band maxima observed for the complexes are summarized in Table 6.

Assignment of the Spectra and Correlation with the Molecular Structures.—The stylized stereochemistry of the *trans* complexes is illustrated schematically in Figure 4(*a*) from which it may be seen that they belong to the centrosymmetric point group C_{2h}. The *d–d* transitions thus gain their intensity by coupling with *ungerade* vibrations and in agreement with this the band intensities decrease significantly on cooling from 290 K to ~10 K (Figures 2 and 3). Unfortunately, in the point group C_{2h} at least one vibration exists which may induce intensity in each *d–d* transition so that vibronic selection rules cannot be used to assist in the assignment of the spectra. It has sometimes been assumed that the electronic spectral bands are polarized along directions which coincide with the principal *g* axes, which in the present complexes lie approximately parallel to the Cu–O and Cu–N bonds (see following section), and the optical spectrum of the *trans* complex [Cu(β-alaO)$_2$(H$_2$O)$_2$]·4H$_2$O has previously been interpreted in this fashion.[30] However, as has been pointed out elsewhere[12,31] this assumption is unwarranted, as the orientations of the *g* and optical absorption tensors are derived from totally different sources. This difference is well illustrated by the behaviour of bis(*N*-methylsalicylideneiminato)copper(II) which has a co-ordination geometry of *trans* nitrogen and oxygen ligand atoms similar to those in the present amino acid complexes. For this complex, the principal in-plane *g* axes lie close to the metal–ligand bond directions,[32] while the *d–d* electronic transitions are polarized more nearly along the bisectors of the chelate rings.[33] For the present compounds the assignment of the electronic spectra must therefore be based simply upon 'chemical' arguments, the likely effects of the metal–ligand interactions in the complexes, and is hence quite tentative.

The ligand field of these six-co-ordinate complexes may be considered to deviate from regular octahedral symmetry by the addition of three low-symmetry components: a pronounced tetragonal component due to the fact that two metal–ligand bonds are much longer than the other four, and two minor rhombic perturbations, an along-the-bonds component caused by the difference in bonding between the carboxylic oxygen and amine nitrogen atoms, and a between-the-bonds component due to the presence of the chelate rings. It has been suggested[12,34] that, regarding the *d* orbitals, for copper(II) complexes of the type considered here the along-the-bonds rhombic perturbation is likely to be considerably more important than the between-the-bonds perturbation, and in discussing the *d*-orbital energies it is thus convenient to use a co-ordinate system in which the *x* and *y* axes lie close to the Cu–N and shorter Cu–O bonds, respectively, with *z* being approximately parallel to the long Cu–O bonds [Figure 4(*a*)].

In assigning the electronic spectra the strong tetragonal elongation of the ligand field means that the d_{z^2} orbital is quite similar in energy to the $d_{xz,yz,xy}$ set of orbitals, with all four *d–d* transitions to the higher energy $d_{x^2-y^2}$ orbital contributing to the bands observed in the visible region. The likely ordering of the $d_{xz,yz,xy}$ set may be deduced from the π-bonding capabilities of the amine nitrogen and carboxylate oxygen ligand atoms. The out-of-plane π interaction of the carboxylate oxygen should be greater than the in-plane interaction,[35] while the π-bonding capacity of the amine groups should be small, leading to the energy sequence $d_{yz} > d_{xy} > d_{xz}$. The energy of the d_{z^2} orbital is likely to be quite sensitive to the type of axial co-ordination. For the DL-proline and DL-alanine complexes, which have quite short axial bonds (~2.6 Å), the d_{z^2} orbital should be high in energy, leading to the sequence $d_{x^2-y^2} \gg d_{z^2} > d_{yz,xy} > d_{xz}$. In [Cu(acpc)$_2$], on the other hand, the weak axial interaction (3.12 Å) will have both a direct and an indirect effect on the energy of the d_{z^2} orbital. It is well established that in planar four-co-ordinate copper(II) complexes this orbital is depressed by ~6 000 cm^{-1}, becoming effectively non-bonding.[36] Some workers have explained this in terms of configuration interaction between the $a_{1g}(3d_{z^2})$ and $a_{1g}(4s)$ metal orbitals[23,36,37] while others have introduced the concept of ligand voids.[38] Whatever the cause, it seems clear that this depression depends on the difference in metal–ligand interaction along the *xy* and *z* directions, so that the effect should be considerably greater for [Cu(acpc)$_2$] than for the other complexes. It seems likely that the d_{z^2} orbital will therefore be effectively non-bonding in this complex, thus being comparable in energy to the d_{xz} orbital. These arguments lead to the band assignments shown in Table 6, the only ambiguity being for [Cu(acpc)$_2$], where it is unclear whether the d_{z^2} orbital lies above or below d_{xz} in energy. In making these assignments, which it must be stressed are only tentative, it has been assumed that when not all the *d–d* transitions have been resolved, those observed are the ones involving the $d_{xz,yz}$ orbitals since these generally give rise to the strongest absorptions in tetragonal copper(II) complexes.[23,39] The most obvious trend in the band maxima is a significant shift to higher energy as the axial bonds become longer. This is due first to a large shift in the $d_{z^2} \rightarrow d_{x^2-y^2}$ transition, and secondly to smaller shifts in the other transitions which accompany the increase in energy of the $d_{x^2-y^2}$ orbital caused by the slight contraction in the in-plane Cu–O bonds (Table 6).

Interpretation of the Molecular g *Tensors*.—For each complex the unit cell contains two molecules having different orientations (note that molecules related by an inversion centre have identical orientations as far as their magnetic properties are concerned). However, in every case, only a single e.s.r. signal was observed for all orientations of the magnetic field, showing that the unpaired electrons exchange between the copper(II) ions more rapidly than the e.s.r. time-scale [for the DL-proline complex quite broad lines were observed when the magnetic field was between the *b* crystal axis and the (010) plane, making it hard to measure the *g* value accurately; this probably caused the relatively large uncertainties in the molecular *g* parameters of this compound]. As has been discussed in detail elsewhere,[12] the fact that exchange-narrowed e.s.r. signals were observed, combined with the monoclinic crystal symmetry, means that it is impossible completely to determine the principal values and directions of the *g* tensor of each complex. However, assuming an effective C_{2h} point group means that the direction of g_z is defined by symmetry. The experimentally observed crystal *g* values were therefore used to determine the molecular tensor elements $g_{zz}^2, g_{xx}^2, g_{yy}^2, g_{xy}^2$ by a least-squares procedure described previously.[12] These were then diagonalized to give the principal molecular *g* values and the angle α defining the orientation of the in-plane *g* axes [Figure 4(*a*)] in the molecular co-ordinate system, and these are listed in Table 6. Here, the uncertainty in each parameter was obtained by comparing the results of two independent sets of measurements.

In order to investigate the effects of the disposition of the amino acid ligand donor atoms on the *g* values, the e.s.r. spectrum of a crystal of the *cis* complex [Cu(glyO)$_2$(H$_2$O)] was studied. A schematic diagram of the ligand co-ordination geometry of this complex is shown in Figure 4(*b*). This also showed an exchange-narrowed signal, though this was very broad in two rotations [the (001) and (100) planes]. However, the complex crystallizes in an orthorhombic space group,[40] so that the crystal *g* tensor axes must be coincident with the unit-cell axes.[12] As the *g* value when the magnetic field is parallel to *b* could be measured accurately, these data were therefore used in conjunction with those from rotations in the (010) plane to determine the molecular *g* values of [Cu(glyO)$_2$(H$_2$O)]. In an orthorhombic space group only three elements of the molecular *g* tensor may be deduced.[12] However, if the difference between the two long axial bonds is ignored, the ligand co-ordination geometry has approximate $C_{2v}(x)$ symmetry [Figure 4(*b*)]. In this point group the orientation of the *g* tensor is defined by symmetry, so the observed crystal *g* values could be used to deduce the principal molecular *g* values directly, these being also listed in Table 6.

Orientation of the g *Tensors in the* trans *Complexes*.—The directions of the in-plane *g* axes in complexes of the present kind have been the subject of a detailed theoretical study.[34] As noted already, the ligand field may be considered to be composed of two rhombic perturbations, an along-the-bonds component and a between-the-bonds component, superimposed upon a basic tetragonal ligand field. For copper(II) complexes it has been suggested[12,34] that the along-the-bonds perturbation should generally dominate the in-plane *g* anisotropy, causing the principal *g* axes to lie close to the metal–ligand bond directions.

This expectation has generally been borne out by experiment,[12,32,34] and this is also the case in the present study (Table 6). The principal g_x axes were found to make angles of between ~3 and 29° with the Cu–N bond direction, the largest value (that of the DL-proline complex) being relatively poorly defined. The direction of rotation shows no obvious pattern, being into the chelate ring for [Cu(acpc)$_2$] and [Cu(DL-proO)$_2$(H$_2$O)$_2$], and out of the chelate ring for the other two compounds. For each complex the 'bite' of the chelate ring is ~84°.

Interpretation of the Molecular g *Values*.—For a complex of C_{2h} symmetry the perturbation expressions relating the *g* values to the excited-state energies are extremely complicated,[34] so that the only practical way of estimating the *g* tensor assuming the true point-group symmetry is by means of a full calculation such as that presented in the following section. However, when the along-the-bonds contribution dominates the rhombic perturbation to the ligand field, the expressions[41] (1a)—(1c) appropriate to a complex of D_{2h} symmetry may be

$$g_x = 2.0023 - \frac{2\lambda k_x^2}{E_{yz}}(a - \sqrt{3}b)^2 \qquad (1a)$$

$$g_y = 2.0023 - \frac{2\lambda k_y^2}{E_{xz}}(a + \sqrt{3}b)^2 \qquad (1b)$$

$$g_z = 2.0023 - \frac{8\lambda k_z^2 a^2}{E_{xy}} \qquad (1c)$$

used to interpret the *g* values;[12] $k_{x,y,z}$ are the so-called orbital reduction factors, λ is the spin-orbit coupling constant (−829 cm^{-1} for Cu^{2+}), and $E_{xz,yz,xy}$ are the excited-state energies in which an electronic transition has occurred from the *d* orbital indicated by the subscript. The coefficients *a* and *b* represent the contributions of the $d_{x^2-y^2}$ and d_{z^2} orbitals in the metal part of the ground-state wavefunction.[41] In the absence of spin-orbit coupling this has the form $\psi = a\,(d_{x^2-y^2}) - b\,(d_{z^2})$, where $a^2 + b^2 = 1$. Here, *b* represents the minor contribution of the d_{z^2} orbital to the ground state caused by the difference in σ-antibonding interaction of the ligands along the *x* and *y* axes. The admixture of the d_{z^2} orbital is generally expected to dominate the in-plane *g* anisotropy, so it has been proposed[12,34,41] that, for complexes with *g* axes close to the bond directions, this should provide a useful guide to the difference in σ-bonding strength of the ligands, with the stronger interaction being associated with the smaller *g* value. The present complexes provide a useful test of these ideas, as while the Cu–N bonds are approximately constant in length, the in-plane Cu–O(carboxylate) bonds differ significantly. A plot of δg_{xy} (= $g_y - g_x$) against the difference between the Cu–N and Cu–O bond lengths is shown in Figure 5. The value previously reported[30] for the complex *trans*-[Cu(β-alaO)$_2$(H$_2$O)$_2$]·4H$_2$O is included in the plot. In each case the Cu–O bond is shorter

Table 7. Metal–ligand bonding parameters and 'best-fit' transition energies and molecular g values of the complexes

	Perturbation equations			CAMMAG Calculation parameters															
				Bonding parameters (10^3 cm^{-1})								Calculated transition energies (10^3 cm^{-1})					Calculated g values		
Complex	k_z[a]	$k_\perp$[a]	b[b]	e_σ(N)	e_π(N)	e_σ(O)	$e_{\pi s}$	$e_{\pi c}$	e_σ(ax)	e_π(ax)	k[c]	d_{xz}	d_{yz}	d_{xy}	d_{z^2}	δ_{z^2}[d]	g_x	g_y	g_z
$[Cu(acpc)_2]$	0.75[e]	0.75	0.09	5.90	0.0	6.90	0.8	0.4	0.4	0.03	0.7	19.2	18.3	17.2	11.8	9.5	2.069	2.037	2.214
	0.77[f]	0.78	−0.09	6.60	0.0	7.60	1.6	0.8	0.4	0.03	0.80	21.2	19.6	17.8	13.1	4.3	2.071	2.038	2.215
$[Cu(L\text{-}alaO)_2]$		0.68	0.07	6.05	0.0	5.75	0.8	0.4	0.75	0.13	0.74	18.3	17.3	16.5	11.7		2.040	2.059	2.213
$[Cu(DL\text{-}alaO)_2(H_2O)]$		0.74	0.07	6.50	0.0	5.60	0.5	0.25	0.8	0.15	0.78	18.0	17.5	16.5	10.2		2.043	2.070	2.230
$[Cu(DL\text{-}proO)_2(H_2O)_2]$	0.80	0.77	0.08	6.30	0.0	5.30	0.8	0.4	0.9	0.15	0.80	17.4	16.7	15.3	9.8	3.4	2.047	2.082	2.262
				6.73	0.5	5.63	1.3	0.9	0.9	0.15	0.82	17.5	16.1	15.3	10.5	2.7	2.046	2.081	2.276

[a] Orbital reduction parameters obtained using equation (1). [b] Coefficient of d_{z^2} orbital obtained using equation (1). [c] Orbital reduction parameter. [d] Observed energy − calculated energy of $d_{z^2}\rightarrow d_{x^2-y^2}$ transition (values in 10^3 cm^{-1}). [e] Values obtained using assignment 1 of electronic spectrum. [f] Values obtained using assignment 2 of electronic spectrum.

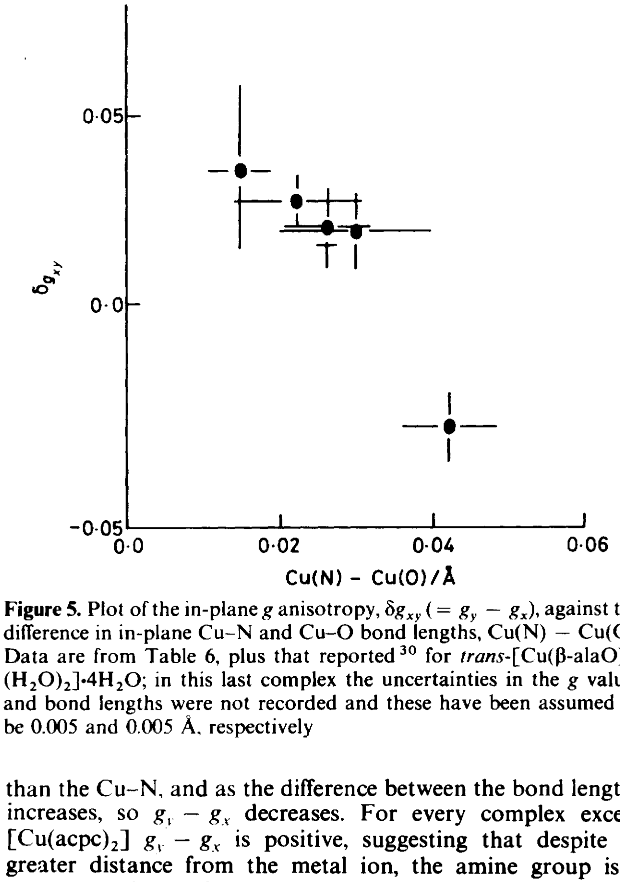

Figure 5. Plot of the in-plane g anisotropy, δg_{xy} ($= g_y - g_x$), against the difference in in-plane Cu–N and Cu–O bond lengths, Cu(N) − Cu(O). Data are from Table 6, plus that reported[30] for *trans*-$[Cu(\beta\text{-alaO})_2(H_2O)_2]\cdot 4H_2O$; in this last complex the uncertainties in the g values and bond lengths were not recorded and these have been assumed to be 0.005 and 0.005 Å, respectively

than the Cu–N, and as the difference between the bond lengths increases, so $g_y - g_x$ decreases. For every complex except $[Cu(acpc)_2]$ $g_y - g_x$ is positive, suggesting that despite its greater distance from the metal ion, the amine group is a stronger σ donor than the carboxylate oxygen atom. This is consistent with the fact that amines are higher than carboxylate ligands in the spectrochemical series[42] (though π-antibonding effects will also contribute to this difference). It is noteworthy that the covalent radius of N is ~0.04 Å greater than that of oxygen,[43] though this will be offset somewhat by the partial negative charge of the carboxylate group. In $[Cu(acpc)_2]$ the fact that g_x is greater than g_y suggests that here the carboxylate oxygen produces a stronger ligand perturbation than the amine, and it is tempting to ascribe this to the very short Cu–O bond in the complex. Possibly, the fact that the amine in the acpc ligand is a member of a ring system and is secondary, rather than primary, may affect its ligating power though the calculations presented in the following section imply that this is not the case.

Assuming axially-symmetric orbital reduction parameters ($k_\perp^2 = k_x^2 = k_y^2$), equations (1a)—(1c) yield the values of b listed in Table 7 and these confirm the above conclusions. The positive values of b for the L- and DL-alanine and DL-proline complexes imply an expansion of the ground-state lobes pointing towards the ligand nitrogen atoms, and a contraction of those directed towards the oxygen atoms, this being most pronounced for the last complex. For $[Cu(acpc)_2]$, on the other hand, the relatively large negative value of b implies an expansion of the ground-state lobe directed towards the oxygen ligands.[41]

The complex *cis*-$[Cu(glyO)_2(H_2O)]$ is interesting because the along-the-bonds rhombic perturbation to the tetragonal ligand field is effectively zero [Figure 4(*b*)], so that the effect of the between-the-bonds perturbation on the g tensor may be investigated in isolation. Here, the single unpaired electron occupies the d_{xy} orbital which is not coupled to d_{z^2} by the rhombic component of the ligand field.[34] The in-plane g anisotropy is therefore expected to be quite small, as is indeed the case (Table 6), and the g values are given by the expressions (2a)—(2c). Assuming $k_\perp^2 = k_x^2 = k_y^2$, the in-plane g

$$g_x = 2.0023 - 2\lambda k_x^2/E_{xz} \qquad (2a)$$

$$g_y = 2.0023 - 2\lambda k_y^2/E_{yz} \qquad (2b)$$

$$g_z = 2.0023 - 8\lambda k_z^2/E_{x^2-y^2} \qquad (2c)$$

anisotropy is due solely to the difference between E_{xz} and E_{yz}. The electronic reflectance spectrum of $[Cu(glyO)_2(H_2O)]$ shows an intense peak centred at ~16 000 cm^{-1}, with a shoulder at ~10 500 cm^{-1}.[44] Presumably, the transitions $d_{xz}, d_{yz}, d_{x^2-y^2}\rightarrow d_{xy}$ each contribute to the former band, while $d_{z^2}\rightarrow d_{xy}$ causes the latter. If the energy separation between d_{xz} and d_{yz} is comparable to those observed for the *trans* complexes (~1 500 cm^{-1}), the in-plane g anisotropy is expected to be ~0.006, in good agreement with that measured experimentally (0.007 ± 0.001).

The orbital reduction parameters k_z and $k_\perp$ of the complexes (Table 7) are quite similar, both to each other, and to those of other analogous complexes.[12,13,39] The average g shift δg_{av} [$= (g_x + g_y + g_z)/3 - 2.0023$] increases progressively in conjunction with the strength of the axial ligand interaction (Table 6). It is likely that this is due largely to the red shift of the *d–d* transitions involving the d_{xz}, d_{yz}, and d_{xy} orbitals [Table 6 and equations (1) and (2)], which in turn is caused by the lengthening of the in-plane Cu–O bonds concomitant to the shortening of the axial bonds.

Parametrization of the Metal–Ligand Bonding in the Complexes.—The angular overlap model (a.o.m.) provides a convenient method of investigating the metal–ligand bonding in a complex,[45] and a powerful computer program CAMMAG written by Gerloch and co-workers[46] has recently become available which allows the *d–d* transition energies and molecular *g* values of molecules of low symmetry to be estimated using this approach. For a chelating ligand such as an amino acid, each metal–ligand interaction is defined using three parameters e_σ, $e_{\pi s}$, and $e_{\pi c}$. The first of these represents the σ interaction, and the second two the π interaction in and out of the plane of the ligand, respectively. For a *trans* complex of the generalized stereochemistry shown in Figure 4(*a*) if the minor deviations of the bond axes from orthogonality are ignored, the *d*-orbital energies are given by equations (3a)—(3e). Here,

$$E(x^2 - y^2) = 1.5[e_\sigma(\mathrm{N}) + e_\sigma(\mathrm{O})] \tag{3a}$$

$$E(z^2) = 0.5[e_\sigma(\mathrm{N}) + e_\sigma(\mathrm{O})] + 2e_\sigma(\mathrm{ax}) \tag{3b}$$

$$E(xy) = 2e_\pi(\mathrm{N}) + 2e_{\pi s}(\mathrm{O}) \tag{3c}$$

$$E(xz) = 2e_\pi(\mathrm{N}) + 2e_\pi(\mathrm{ax}) \tag{3d}$$

$$E(yz) = 2e_{\pi c}(\mathrm{O}) + 2e_\pi(\mathrm{ax}) \tag{3e}$$

e_σ(N), e_σ(O), e_σ(ax) *etc.* refer to the metal–ligand bonding parameters of the amine nitrogen, and in-plane and axial oxygen atoms respectively. The relatively weak π interactions of the axial ligands have been assumed to be isotropic about the bond axis. It should be stressed that CAMMAG uses an angular overlap matrix appropriate to the true geometry of each complex; however, equations (3a)—(3e) indicate the dominant metal–ligand interactions affecting each *d* orbital and hence were used to provide initial estimates of the parameters appropriate to each complex.

For a molecule as complicated as those considered here it is clearly impractical to allow complete flexibility in the choice of the a.o.m. parameters in optimizing agreement between the calculated transition energies and *g* values and those observed experimentally. As in other similar studies[14,47,48] it was therefore assumed initially that the π interactions due to the amine ligands are negligible [$e_\pi(\mathrm{N}) = 0$]. The effect of assigning a modest π-donor capability to the N atoms was explored in the case of [Cu(DL-proO)$_2$(H$_2$O)$_2$] (see following discussion). Approximate estimates of the effects of the axial ligands were obtained by assuming the relationship $e_\sigma \propto r^{-6}$, where *r* is the metal–ligand bond distance; the pressure dependence of the optical spectra of metal complexes suggests a relationship of this kind.[49] Rather smaller values of e_π(ax) than those suggested by this relationship were chosen, as it is likely that metal–ligand π interactions fall off rather steeply as the bond length increases.[50] It must be recognized that these estimates can give only a very approximate guide to the bonding effects of the axial ligands. However, they significantly influence only the calculated energy of the d_{z^2} orbital. Having made these approximations, the π-bonding parameters of the carboxylate oxygen atoms were obtained using CAMMAG by optimizing the agreement between the calculated and observed electronic transition energies involving the d_{yz} and d_{xy} orbitals (for the L- and DL-alanine complexes the latter transition was not resolved, and here the relationship $e_{\pi c} \approx 0.5 e_{\pi s}$ was assumed). The average values of the parameters e_σ(N) and e_σ(O) were obtained by fitting the transitions involving the d_{xz} orbital [equations (3a) and (3d)]. Individual values for e_σ(N) and e_σ(O) were then deduced by varying these parameters about their average value, and comparing the calculated estimates of g_x and g_y with those observed experimentally. The orbital reduction parameter was in each case estimated by optimizing the calculated average *g* value. The 'best-fit' bonding parameters, together with the calculated values of the transition energies and molecular *g* values are listed in Table 7.

Agreement between the calculated and observed *g* values and transition energies is good with the exception of the $d_{z^2} \rightarrow d_{x^2-y^2}$ transition which is consistently calculated to lie at lower energy than is observed experimentally. It is now well established that in planar, four-co-ordinate metal complexes the d_{z^2} orbital is depressed in energy compared with the predictions of simple theories such as the a.o.m. becoming, in effect, non-bonding.[36–38] This has been ascribed by some workers to configurational interaction between the d_{z^2} and metal 4*s* orbitals,[23,36,37] and others to what are in effect ligand voids.[38] In tetragonally elongated six-co-ordinate complexes, the anomalous depression of the d_{z^2} orbital will diminish as the axial ligand interaction increases.[36,37] Thus, a planar four-co-ordinate copper(II) amino acid complex should experience a depression of the d_{z^2} orbital of ~7 000 cm^{-1}, and this should progressively decrease with the approach of ligands along the *z* axis. The values of the discrepancy δ_{z^2} listed in Table 7 are broadly in agreement with these suggestions, falling from ~9 500 (assignment 1) or ~4 300 cm^{-1} (assignment 2) for [Cu(acpc)$_2$] with axial bonds of length 3.12 Å, to ~1 000 cm^{-1} obtained for a similar calculation on [Cu(glyO)$_2$(H$_2$O)] with axial bonds of lengths 2.40 and 2.72 Å. The estimates obtained using the two possible assignments of the electronic spectrum of [Cu(acpc)$_2$] effectively bracket the value expected assuming the axial ligands have little effect on the depression, making it hard to decide between the alternatives. It should be noted that if the amine ligands function as weak π donors, the estimated values of δ_{z^2} would be somewhat reduced; a value of $e_\pi(\mathrm{N}) = 500$ cm^{-1} would reduce δ_{z^2} from 3 400 to 2 700 cm^{-1} for [Cu(DL-proO)$_2$(H$_2$O)$_2$] (Table 7). The present deviations are consistent with those reported by Deeth and Gerloch[38] for a range of tetragonal copper(II) complexes, described in terms of a parameter e_v which ranges from ~ −3 000 to ~1 000 cm^{-1} on going from planar, four-co-ordinate complexes to tetragonal complexes with axial bonds of ~2.35 Å [the parameter e_v incorporates the effect of the ligand 'voids' along the *z* axis, and is related to those used in the present study by $e_\mathrm{v} = e_\sigma(\mathrm{ax}) - (\delta_{z^2}/2)$].

The σ-bonding parameters of the complexes, e_σ(N) and e_σ(O), are generally similar to those reported for analogous complexes,[14,47,48] and confirm the conclusions described in the preceding sections. Thus, e_σ(N) is approximately constant at ~6 300 cm^{-1}, while e_σ(O) increases progressively from 5 300 cm^{-1} in [Cu(DL-proO)$_2$(H$_2$O)$_2$] to 6 900 cm^{-1} (assignment 1) or 7 600 cm^{-1} (assignment 2) in [Cu(acpc)$_2$]. While an increase in e_σ(O) is certainly to be expected, as the Cu–O bond decreases from 1.963 to 1.930 Å, that observed is considerably greater than simple theoretical models would suggest.[49,51] Thus, a dependence of the form $e_\sigma \propto r^{-6}$, where *r* is the bond distance,[49] would only imply an increase in e_σ of ~600 cm^{-1}. The out-of-plane π-bonding parameters, while not unreasonable, are somewhat smaller than might be expected,[14,47,48] being ~0.15 e_σ(O). If the amine nitrogen atoms function as weak π donors, however, this would produce rather higher estimates for $e_{\pi s}$(O) and $e_{\pi c}$(O) (Table 7).

Conclusions

The variation in the spectral properties of the *trans* amino acid complexes [Cu(DL-proO)$_2$(H$_2$O)$_2$], [Cu(L-alaO)$_2$], [Cu(DL-alaO)$_2$(H$_2$O)], and [Cu(acpc)$_2$] may be explained in terms of the increasing elongation of the axial bonds, and concomitant decrease in in-plane Cu–O bonds, which occur along this series. These cause a significant blue shift of the *d–d* transition energies as well as a decrease in the average *g* shift. In agreement with simple theoretical predictions the principal directions of the g tensor tend to lie close to the bond axes, and the in-plane g anisotropy follows the trend expected from the above structural changes. For the first three complexes, the data imply that the amine ligands produce a stronger perturbation than the carboxylate oxygen atoms, but for [Cu(acpc)$_2$] this situation is reversed, probably because of the very short Cu–O bonds in this complex. In agreement with the supposition that in-plane g anisotropy observed for the above complexes is caused largely by the difference in ligand-field strength of the amine nitrogen and carboxylate oxygen atoms the molecular g tensor of *cis*-[Cu(glyO)$_2$(H$_2$O)] was found to show a very small in-plane anisotropy consistent with a minor rhombic perturbation caused by the presence of the chelate rings. Calculations of the spectral and e.s.r. parameters of the molecules using the angular overlap model suggest metal–ligand bonding parameters generally consistent with the structures of the compounds. As with other similar complexes, the $d_{z^2} \rightarrow d_{x^2-y^2}$ transition is higher in energy than is suggested by the predictions of the simple bonding model, and this discrepancy increases progressively as the axial metal–ligand bond lengths increase.

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References

1 'The Biochemistry of Copper,' eds. J. Peisach, P. Aisen, and W. E. Blumberg, Academic Press, New York, 1966; R. B. Martin, 'Metal Ions in Biological Systems,' ed. H. Sigel, Marcel Dekker, New York, 1974, vol. 1, ch. 4; K. Lerch, *ibid.*, 1981, vol. 13, ch. 9.
2 J. Peisach and W. E. Blumberg, 'Electron Spin Resonance of Metal Complexes,' ed. T. F. Yen, Plenum Press, New York, 1969, p. 71; T. Vanngard, 'Biological Applications of Electron Spin Resonance,' Wiley-Interscience, New York, 1972.
3 H. A. Kuska and M. T. Rogers, *J. Chem. Phys.*, 1965, **43**, 1744.
4 H. Yokoi and T. Isobe, *Bull. Chem. Soc. Jpn.*, 1969, **42**, 2085.
5 H. Yokoi, M. Sai, and T. Isobe, *Bull. Chem. Soc. Jpn.*, 1972, **45**, 3488.
6 H. Yokoi, M. Sai, T. Isobe, and S. Ohsawa, *Bull. Chem. Soc. Jpn.*, 1972, **45**, 2189.
7 H. Yokoi, *Bull. Chem. Soc. Jpn.*, 1974, **47**, 639.
8 H. C. Allen, jun., M. I. Mandrioli, and J. W. Becker, *J. Chem. Phys.*, 1972, **56**, 997.
9 M. Fujimoto and Y. Tomkiewicz, *J. Chem. Phys.*, 1972, **56**, 749.
10 B. N.. Misra and S. D. Sharma, *J. Chem. Phys.*, 1975, **63**, 5322.
11 B. N. Misra, S. D. Sharma, and S. K. Gupta, *J. Magn. Reson.*, 1974, **16**, 193.
12 K. Dawson, M. A. Hitchman, C. K. Prout, and F. J. C. Rossotti, *J. Chem. Soc., Dalton Trans.*, 1972, 1509.
13 M. A. Hitchman and T. D. Waite, *Inorg. Chem.*, 1976, **15**, 2150.
14 A. Bencini, C. Benelli, and D. Gatteschi, *Coord. Chem. Rev.*, 1984, **60**, 131 and refs. therein.
15 A. Lösche and W. Windsch, *Phys. Status Solidi*, 1965, 575.
16 K. Takeda, Y. Arata, and S. Fujiwara, *J. Chem. Phys.*, 1963, **35**, 854.
17 M. Fujimoto and J. Janeska, *J. Chem. Phys.*, 1971, **55**, 1152.
18 T. Szabó-Plánka and L. I. Horváth, *J. Chem. Phys.*, 1984, **13**, 163.
19 B. W. Low, F. L. Hirshfeld, and F. M. Richards, *J. Am. Chem. Soc.*, 1959, **18**, 4412.
20 D. P. Graddon and L. Munday, *J. Inorg. Nucl. Chem.*, 1960, **23**, 231.
21 A. McL. Mathieson and H. K. Welsh, *Acta Crystallogr.*, 1952, **5**, 599.
22 M. A. Hitchman, R. Thomas, B. W. Skelton, and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1983, 2273 and refs. therein.
23 M. A. Hitchman and P. J. Cassidy, *Inorg. Chem.*, 1979, **18**, 1745.
24 A. Dijkstra, *Acta Crystallogr.*, 1966, **20**, 588.
25 G. A. Barclay and F. S. Stephens, *J. Chem. Soc.*, 1963, 2027.
26 N. Shamala and K. Venkatesan, *Cryst. Struct. Commun.*, 1973, **2**, 5.
27 J. Gažo, I. B. Bersuker, J. Garaj, M. Kabesová, J. Kohout, H. Langfelderova, M. Melnik, M. Serátor, and F. Valach, *Coord. Chem. Rev.*, 1976, **19**, 253.
28 B. J. Hathaway and P. G. Hodgson, *J. Inorg. Nucl. Chem.*, 1973, **35**, 4071.
29 Y. Miteui, Yu. Iitaka, and H. Sakaguchi, *Acta Crystallogr., Sect. B*, 1976, **32**, 1634.
30 F. Dejehet and R. Debuyst, *J. Chem. Soc., Dalton Trans.*, 1978, 526.
31 M. A. Hitchman, *J. Chem. Soc., Faraday Trans. 2*, 1976, 54.
32 B. W. Moores and R. L. Belford, in 'Electron Spin Resonance of Metal Complexes,' ed. T. F. Yen, Plenum, New York, 1969, p. 17.
33 J. Ferguson, *J. Chem. Phys.*, 1961, **34**, 611; **35**, 1612.
34 M. A. Hitchman, C. D. Olson, and R. L. Belford, *J. Chem. Phys.*, 1969, **50**, 1195.
35 A. B. P. Lever, *Coord. Chem. Rev.*, 1982, **43**, 63 and refs. therein.
36 A. Ceulemans, D. Beyens, and L. G. Vanquickenbourne, *Inorg. Chim. Acta*, 1982, **61**, 199.
37 D. W. Smith, *Inorg. Chim. Acta*, 1977, **22**, 107.
38 R. J. Deeth and M. Gerloch, *Inorg. Chem.*, 1984, **23**, 3846.
39 B. J. Hathaway and D. E. Billing, *Coord. Chem. Rev.*, 1970, **5**, 143 and refs. therein.
40 H. C. Freeman, M. Snow, I. Nitta, and K. Tomita, *Acta Crystallogr.*, 1964, **17**, 1463.
41 M. A. Hitchman, *J. Chem. Soc. A*, 1970, 4.
42 A. B. P. Lever, 'Inorganic Electronic Spectroscopy,' 2nd edn., Elsevier, Amsterdam, 1984, p. 151.
43 F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry,' 3rd edn., Interscience, New York, p. 117.
44 T. Yasui and Y. Shimura, *Bull. Chem. Soc. Jpn.*, 1966, **39**, 604.
45 C. E. Schäffer, *Struct. Bonding (Berlin)*, 1968, **5**, 68; 1973, **14**, 69; D. W. Smith, *ibid.*, 1978, **35**, 87.
46 D. A. Cruse, J. E. Davies, M. Gerloch, J. H. Harding, D. J. Mackey, and R. F. McMeeking, 'CAMMAG, A Fortran Computing Package,' University Chemical Laboratory, Cambridge.
47 A. B. P. Lever, 'Inorganic Electronic Spectroscopy,' 2nd edn., Elsevier, Amsterdam, 1984, ch. 9 and refs. therein.
48 M. Gerloch, 'Magnetism and Ligand-Field Analysis,' Cambridge University Press, New York, 1983.
49 M. Bermejo, *J. Chem. Phys.*, 1983, **78**, 854; S. Minomura and H. G. Drickamer, *ibid.*, 1961, **35**, 903.
50 D. W. Smith, *Struct. Bonding (Berlin)*, 1972, **12**, 49.
51 M. A. Hitchman, *Inorg. Chem.*, 1982, **21**, 821 and refs. therein.

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