Crystal Structures † of *N*-Benzenesulphonyl-DL-alanine and Aqua-[*N*-benzenesulphonyl-DL-alaninato(2—)]copper(II) Monohydrate: A Model for Metal Ion–Sulphonamide Binding

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The crystal structures of the title complex (1) and the ligand (2) have been determined and refined by full-matrix least squares to residuals of 0.050 (1 965 observed reflections) and 0.041 (1 585 observed reflections), respectively. Complex (1) crystallises in the space group $P2_1/c$ with a = 13.533(1), b = 7.908(1), c = 12.066(1) Å, β = 111.04(1)°, and Z = 4, while the ligand crystallises in the space group $P2_1/n$ with a = 5.251(1), b = 16.638(15), c = 12.628(1) Å, β = 99.19(3)°, and Z = 4. In complex (1), which is in a polymeric form, copper has an irregular stereochemistry. The alanine moiety forms a five-membered chelate ring in the equatorial square plane by co-ordinating through one of the carboxy-oxygens and the deprotonated nitrogen, the third and fourth corners of the square being occupied by a water oxygen and the 'free' carboxy-oxygen of a screw-related complex; one of the sulphonyl oxygens of a glide-related complex co-ordinates axially, while the oxygen from the chelate ring of the above screw-related complex co-ordinates in an off-axial direction. The co-ordinated water molecule is involved in an interligand hydrogen bond with the unco-ordinated sulphonyl oxygen, forming a six-membered water-bridged chelate ring. In packing, the complex (1) segregates into hydrophobic and hydrophilic regions with the water molecules forming a network of hydrogen bonds. The ligand (2) forms typical carboxylic acid hydrogen-bonded dimers which are linked by N–H · · · O bonds. The major conformational change in the ligand, upon metal co-ordination, is a reorientation of the molecule about the C(carboxy)–C_α and C_α–N bonds to accommodate the metal ion.

Benzenesulphonamide has been shown to be the most potent amongst the sulphonamides in the selective inhibition of animal and bacterial carbonic anhydrases.[1] That this inhibitory action is at least partially due to the ionisation of the sulphonamide molecule by deprotonation at the amido-nitrogen, upon co-ordination to the metallo-enzyme, has been shown from several crystallographic [2] and spectroscopic [3] studies. The ligand *N*-benzenesulphonyl-DL-alanine, which can be viewed either as a N-substituted sulphonamide or as a N-substituted amino acid, was expected to undergo deprotonation at the acidic sulphonamide nitrogen [4] in co-ordinating to a metal ion, effectively resulting in a deprotonated amino-nitrogen in the alanine moiety. This would then be reminiscent of a deprotonated peptide nitrogen in a metal–peptide complex.[5a]

The present crystal structure analyses were undertaken with the objective of studying the complex aqua[*N*-benzenesulphonyl-DL-alaninato(2−)]copper(II) (1) as a model sulphonamide–metal ion complex and observing the structural changes in the ligand resulting from co-ordination to the metal. Both the free ligand (2) and the complex (1) occurred as racemates, the chirality being referred to the alanine α-carbon.

Experimental

Crystal Growth.—The copper complex (1) was obtained in the form of a crystalline powder (prepared by the method of ref. 5*b* and donated by Professor N. N. Ghosh), a solution of which in hot water produced, on cooling, small blue prisms elongated along the c axis. The crystals, apparently single under a polarising microscope, were found to be twinned in upper-layer Weissenberg photographs. An interesting feature of the twinning was that each prism consisted of a pair of crystals of almost equal size but with their c axes antiparallel. This was inferred from the appearance of a false mirror in oscillation photographs taken about the c axis. Although the tendency to form twins persisted throughout, repeated crystallisation yielded a specimen which proved to be single and this was used for all subsequent work.

Crystals of the ligand (2) in the form of transparent needles elongated along the a axis were grown from an aqueous solution.[5b]

Crystal Data.—The space groups of the crystals were determined from oscillation and Weissenberg photographs. Two sets of intensity data were collected for complex (1), the first being obtained from multiple-film equi-inclination Weissenberg photographs taken with Cu-K_α radiation and used for determining the positions of the non-hydrogen atoms. The second set was collected on an Enraf–Nonius CAD4 diffractometer, after refinement of the cell parameters by least-squares fit of 25 accurately centred reflections, and used for determining the hydrogen positions and complete refinement of the structure. The unit-cell parameters and intensity data for the ligand (2) were similarly obtained on the same diffractometer. Crystal data for both compounds are given in Table 1.

Crystal Structure Solution and Refinement.—Both structures were solved by Patterson and heavy-atom methods and refined by full-matrix least squares, minimising the function $\Sigma w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2(|F_o|)$. The non-hydrogen atoms were assigned anisotropic thermal parameters. In both structures, all the hydrogen atoms were located from electron-density difference maps and their co-ordinates and isotropic thermal parameters were refined. The final residuals are given in Table 1. The scattering factors for the non-hydrogen atoms

† *Supplementary data available* (No. SUP 23853, 47 pp.): thermal parameters, H-atom parameters, least-squares planes, torsion angles, structure factors. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

were taken from ref. 6 and those for the hydrogen atoms from ref. 7. The former values were corrected for anomalous dispersion.[8] The final non-hydrogen atomic parameters are given in Table 2.

Patterson and Fourier syntheses were computed on an IBM 1130 computer using the general Fourier summation program SIFOR written by the author. Least-squares refinements were carried out on a Burroughs B6700 computing system using the program ORFLS of Busing, Martin, and Levy.

Table 1. Crystal data

	Complex (1)	Ligand (2)
Empirical formula	$C_9H_{13}CuNO_6S$	$C_9H_{11}NO_4S$
Formula weight	326.8	229.3
Space group	$P2_1/c$	$P2_1/n$
a/Å	13.533(1)	5.251(1)
b/Å	7.908(1)	16.638(15)
c/Å	12.066(1)	12.628(1)
β/°	111.04(1)	99.19(3)
U/Å^3	1 205.2(4)	1 089.1(24)
D_m/g cm^{-3} (by flotation)	1.79	1.41
D_c/g cm^{-3}	1.80	1.40
Radiation (λ/Å) (graphite monochromated)	Cu-K_α (1.5418)	Mo-K_α (0.7107)
μ/cm^{-1}	43.7	2.9
Crystal size (mm^3)	0.12 × 0.12 × 0.14	0.18 × 0.30 × 0.25
Precision required by final scan	$\sigma(I)/I \leqslant 0.02$	$\sigma(I)/I \leqslant 0.05$
Maximum scan time allowed (s)	80	60
Scan width (°)	(0.7 + 0.14tanθ)	(0.6 + 0.35tanθ)
Range of 2θ(°)	4—140	4—54
No. of unique reflections	2 291	2 374
No. of ' observed ' reflections with $I \geqslant 3\sigma(I)$	1 965	1 585
$R = \Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|$ (' observed ' reflections)	0.050	0.041
R (all reflections)	0.059	0.073
$R' = [\Sigma w(\|F_o\| - \|F_c\|)^2/ w\|F_o\|^2]^{\frac{1}{2}}$	0.073	0.052

Parameters common to both structures: crystal class, monoclinic; $Z = 4$; scan mode, ω–2θ.

Results

Perspective views of the two structures, along with the atom-labelling schemes, are shown in Figure 1. The intramolecular bond distances and angles are listed in Table 3. In complex (1), O(17) is the oxygen of the water molecule directly co-ordinated to the copper ion while O(18) is that of the water of crystallisation.

Changes in the O(2)–C(3)–C(5)–N(7) and C(3)–C(5)–N(7)–S(8) torsion angles, from −145.9(15) and 79.8(16)° in the free ligand (2) to −20.1(24) and −140.7(14)° in the complex (1), comprise the most significant conformational differences between the two structures. The reorientation of the ligand about the C(carboxy)–C_α and C_α–N bonds has permitted the deprotonated nitrogen to bind to the copper ion and thus be shared by a five-membered chelate ring and an adjacent six-membered water-bridged chelate ring (Figure 1). The expected deprotonation of the acidic sulphonamide nitrogen,[4] evident from its trigonal surroundings (Table 3), is similar to that occurring in metal–peptide complexes.[5a]

Co-ordination about Cu, N, *and* S.—The copper(II) ion in complex (1) has an irregular stereochemistry. The N-substituted amino acid forms a five-membered chelate ring by binding to a copper ion in the equatorial square plane *via* the amino nitrogen, N(7), and one of the carboxy-oxygens, O(2). The third corner of the square, *trans* to O(2), contains a water oxygen, while the fourth is occupied by the second ' free ' carboxy-oxygen, O(4^i), of a screw-related complex. One of the sulphonyl oxygens, O(10^{ii}), of a glide-related complex binds axially, while a sixth off-axial co-ordination by the carboxy-oxygen, O(2^i), from the chelate ring of the above screw-related complex, results in a 4 + 1 + 1* co-ordination for the copper ion.[9] The Cu(1)–O(2) and Cu(1)–N(7) bond lengths in the five-membered chelate ring are different from corresponding distances in copper(II)–peptide complexes with two adjacent chelate rings,[10] but agree with those found in the copper(II) complex of glycyl-L-leucyl-L-tyrosine which forms only one chelate ring with the metal ion.[11] The O(2)–Cu(1)–N(7) and O(2)–Cu(1)–O(4^i) angles are in agreement with those found in other copper(II)–peptide complexes.[10,11] The angles involving the Cu(1)–O(2^i) bond indicate that this off-axis bond is forced by the geometry of the carboxy-group to deviate from the normal to the basal plane.[10]

As in many peptides,[12] the configurations about the trigonal

Table 2. Fractional co-ordinates, with estimated standard deviations in parentheses

	Complex (1)			Ligand (2)		
Atom	x	y	z	x	y	z
Cu(1)	0.1012(1)	0.1899(1)	−0.2366(1)			
O(2)	0.0363(2)	0.4106(4)	−0.2414(2)	0.2475(4)	0.4261(1)	−0.0188(2)
C(3)	0.0678(3)	0.4880(5)	−0.1436(3)	0.4244(5)	0.3978(2)	0.0546(2)
O(4)	0.0210(2)	0.6168(4)	−0.1252(2)	0.6261(3)	0.4317(1)	0.0866(2)
C(5)	0.1683(3)	0.4304(5)	−0.0472(3)	0.3631(4)	0.3154(1)	0.0946(2)
C(6)	0.2575(4)	0.5480(6)	−0.0477(6)	0.4797(6)	0.2526(2)	0.0301(2)
N(7)	0.1887(2)	0.2563(4)	−0.0737(3)	0.4607(3)	0.3036(1)	0.2080(2)
S(8)	0.2324(1)	0.1334(1)	0.0364(1)	0.3101(1)	0.3390(1)	0.3004(1)
O(9)	0.2357(2)	−0.0355(4)	−0.0089(3)	0.4382(4)	0.3056(1)	0.3983(1)
O(10)	0.1778(2)	0.1479(4)	0.1198(2)	0.0429(3)	0.3240(1)	0.2662(1)
C(11)	0.3665(3)	0.1880(5)	0.1159(3)	0.3570(4)	0.4438(2)	0.3063(2)
C(12)	0.4006(3)	0.2320(8)	0.2345(4)	0.1836(6)	0.4945(2)	0.2461(3)
C(13)	0.5072(4)	0.2686(9)	0.2935(5)	0.2339(7)	0.5762(2)	0.2460(3)
C(14)	0.5776(4)	0.2530(8)	0.2386(5)	0.4509(7)	0.6056(2)	0.3054(3)
C(15)	0.5439(4)	0.2086(8)	0.1208(5)	0.6222(7)	0.5558(2)	0.3658(3)
C(16)	0.4376(4)	0.1761(8)	0.0593(4)	0.5777(6)	0.4740(2)	0.3665(3)
O(17)	0.1846(2)	−0.0121(4)	−0.2432(3)			
O(18)	−0.0883(3)	0.2282(5)	−0.1083(3)			

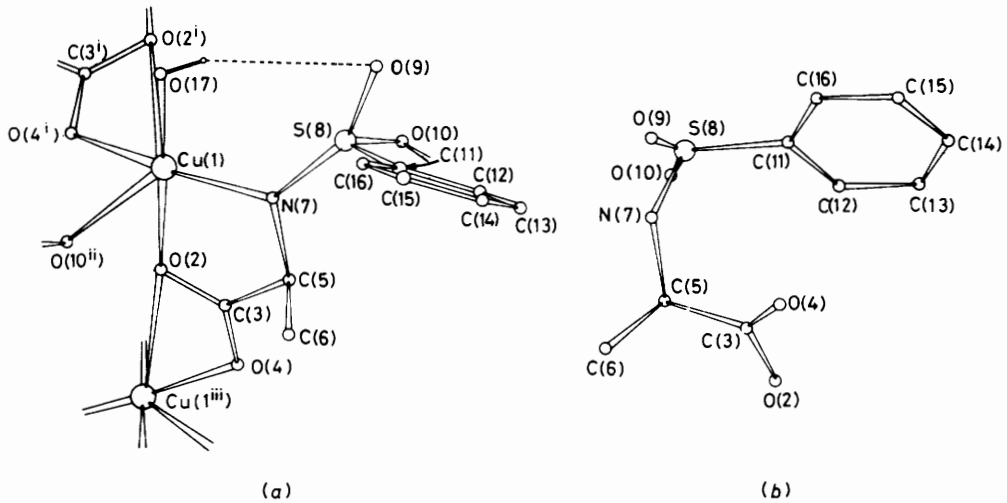

Figure 1. (*a*) Complex (1) viewed down the *a* axis; O(18), the oxygen atom of the water of crystallisation, is not shown. The interligand hydrogen bond between the co-ordinated water oxygen, O(17), and the sulphonyl oxygen, O(9), is shown by a broken line. The superscripts refer to the symmetry operations: i $-x, -\frac{1}{2}+y, -\frac{1}{2}-z$; ii $x, \frac{1}{2}-y, -\frac{1}{2}+z$; and iii $-x, \frac{1}{2}+y, -\frac{1}{2}-z$. (*b*) Ligand (2) viewed down the *a* axis

Table 3. Bond distances (Å) and angles (°), with estimated standard deviations in parentheses (see Figure 1 for symmetry codes)

(*a*) In the $CuNO_5$ chromophore of complex (1)

Cu(1)–O(2)	1.945(2)	Cu(1)–N(7)	1.968(2)	Cu(1)–O(17)	1.974(2)
Cu(1)–O(4^{i})	1.966(2)	Cu(1)–O(10^{ii})	2.648(2)	Cu(1)–O(2^{i})	2.838(2)

O(2)–Cu(1)–N(7)	83.89(8)	O(2)–Cu(1)–O(17)	169.57(8)	O(2)–Cu(1)–O(4^{i})	90.32(8)
O(2)–Cu(1)–O(2^{i})	114.95(8)	O(2)–Cu(1)–O(10^{ii})	79.89(7)	N(7)–Cu(1)–O(17)	96.20(10)
N(7)–Cu(1)–O(4^{i})	161.25(9)	N(7)–Cu(1)–O(2^{i})	116.13(8)	N(7)–Cu(1)–O(10^{ii})	106.70(8)
O(17)–Cu(1)–O(4^{i})	92.69(9)	O(17)–Cu(1)–O(2^{i})	74.42(7)	O(17)–Cu(1)–O(10^{ii})	90.13(8)
O(4^{i})–Cu(1)–O(2^{i})	50.87(7)	O(4^{i})–Cu(1)–O(10^{ii})	89.72(7)	O(2^{i})–Cu(1)–O(10^{ii})	135.52(6)

(*b*) In the *N*-benzenesulphonyl-DL-alanine moieties of complex (1) and ligand (2)

	Complex (1)	Ligand (2)		Complex (1)	Ligand (2)
O(2)–C(3)	1.260(3)	1.292(2)	C(3)–O(4)	1.261(3)	1.211(2)
C(3)–C(5)	1.509(4)	1.513(3)	C(5)–C(6)	1.525(5)	1.513(3)
C(5)–N(7)	1.461(3)	1.455(3)	N(7)–S(8)	1.580(2)	1.622(2)
S(8)–O(9)	1.450(2)	1.422(2)	S(8)–O(10)	1.451(2)	1.423(1)
S(8)–C(11)	1.775(3)	1.760(2)	C(11)–C(12)	1.380(4)	1.378(3)
C(11)–C(16)	1.368(4)	1.375(3)	C(12)–C(13)	1.391(5)	1.385(4)
C(13)–C(14)	1.348(6)	1.352(5)	C(14)–C(15)	1.374(5)	1.363(5)
C(15)–C(16)	1.386(6)	1.382(4)			

	Complex (1)	Ligand (2)		Complex (1)	Ligand (2)
O(2)–C(3)–O(4)	122.3(2)	124.0(2)	O(2)–C(3)–C(5)	118.9(2)	113.8(2)
O(4)–C(3)–C(5)	118.6(2)	122.1(2)	C(3)–C(5)–C(6)	107.9(3)	108.7(2)
C(3)–C(5)–N(7)	107.7(2)	112.9(2)	C(6)–C(5)–N(7)	111.2(2)	109.1(2)
C(5)–N(7)–S(8)	116.0(2)	121.6(1)	N(7)–S(8)–O(9)	107.6(1)	105.4(1)
N(7)–S(8)–O(10)	113.9(1)	106.7(1)	N(7)–S(8)–C(11)	107.8(1)	108.0(1)
O(9)–S(8)–O(10)	115.3(1)	120.1(1)	O(9)–S(8)–C(11)	105.3(1)	107.9(1)
O(10)–S(8)–C(11)	106.4(1)	108.2(1)	S(8)–C(11)–C(12)	121.2(2)	120.5(2)
S(8)–C(11)–C(16)	118.6(2)	119.0(2)	C(12)–C(11)–C(16)	120.1(3)	120.4(2)
C(11)–C(12)–C(13)	118.9(3)	119.5(3)	C(12)–C(13)–C(14)	121.0(3)	119.9(3)
C(13)–C(14)–C(15)	120.1(3)	120.9(3)	C(14)–C(15)–C(16)	119.7(3)	120.3(3)
C(11)–C(16)–C(15)	120.1(3)	119.0(3)			

(*c*) Other angles in complex (1)

Cu(1)–O(2)–C(3)	114.3(2)	Cu(1)–N(7)–C(5)	112.2(2)	Cu(1)–N(7)–S(8)	125.8(1)
Cu(1)–O(2)–Cu(1^{iii})	167.1(1)	C(3)–O(2)–Cu(1^{iii})	72.5(2)	C(3)–O(4)–Cu(1^{iii})	114.2(2)

nitrogens, as indicated by the angle sums around them, somewhat deviate from planarity. In complex (1) the angles at N(7) are quite dissymmetric; such dissymmetry has also been observed in other compounds where interligand hydrogen bonding or chelation occurs.[13] The trend in the distribution of angles around this atom is similar to that observed in (glycyl-L-leucyl-L-tyrosinato)copper(II);[11] the narrowing of the Cu(1)–N(7)–S(8) angle by about 10° from the expected

value of 136° can be attributed to the formation of the water-bridged chelate ring.* In both compounds (1) and (2), the S–N distances are shorter than the corresponding single-bond distance of 1.764 Å in sulphamic acid,[14] indicating considerable double-bond character. The shortening is more pronounced in complex (1) owing to enhanced d_{π}–p_{π} interaction following deprotonation of the nitrogen atom.[4]

The sulphur atoms in both structures have the usual distorted-tetrahedral configuration with bond lengths and angles involving them lying within the ranges quoted in the literature.[15] The near equality of the two S–O bond distances in either structure indicates that the participation of the sulphonyl oxygens in hydrogen-bond formation [O(9) in (1) and O(10) in (2)] or in metal co-ordination [O(10) in (1)] does not significantly affect the S–O bond length. The decrease in the double-bond character of the S–O bonds in complex (1), compared to that in the free ligand (2), may be attributed to the enhanced double-bond character of the S–N bond in the former.

The Alanine Moiety.—The C(carboxy)–O bond lengths and the C_{α}–C(carboxy)–O bond angles indicate that the carboxy-group is un-ionised in the ligand (2), while in the complex (1) there is a complete delocalisation of the π electron as in other metal–peptide complexes.[10] While the C(carboxy)–C_{α} bond lengths in both (1) and (2) are somewhat shorter than the average values quoted in the literature, the C_{α}–N bond lengths are in good agreement with the corresponding average values.[10,16]

Conformation.—In complex (1) there are considerable deviations [−0.298(3) to 0.218(3) Å] from planarity of the equatorial atoms in the copper co-ordination square plane; pairs of diagonally opposite atoms lie on either side of the least-squares plane with the copper almost in the plane. The endocyclic torsion angles [Cu(1)–O(2)–C(3)–C(5) 16.5(23), O(2)–C(3)–C(5)–N(7) −20.1(24), C(3)–C(5)–N(7)–Cu(1) 13.6(19), C(5)–N(7)–Cu(1)–O(2) −5.4(13), and N(7)–Cu(1)–O(2)–C(3) −6.0(15)°] indicate a somewhat flattened half-chair conformation for the five-membered chelate ring.[17] In complex (1), one of the sulphonyl oxygens, O(10), is nearly coplanar with the benzene ring, while in the free ligand (2) both these oxygens are out of the benzene plane.

Molecular Packing.—Figure 2(*a*) shows the crystal structure of complex (1) projected down the *b* axis. The monomers of the complex are linked into infinite polymeric chains around two-fold screw axes. Adjacent monomers are linked through bridges of the type –Cu–O–C–O–Cu– with the oxygen atoms co-ordinating in the basal planes. In addition, the O(2) atoms are simultaneously co-ordinated off-axially to form –Cu–O–Cu– bridges. The Cu · · · Cu distance of 4.754(1) Å and the Cu–O–Cu angle of 167.1(1)° are in agreement with the corresponding values, computed from the published co-ordinates, of 4.754 Å and 168.1° in (L-valyl-L-tyrosinato)-copper(II) tetrahydrate where the copper ions are similarly bridged.[18]

In complex (1) there are two centres of chirality, the copper ion, Cu(1), and the α-carbon, C(5). Since the screw-related monomers are linked together to form polymeric chains, the chains themselves have chirality. With the compound being a racemate, chains of both chiralities are present in the crystal structure. The links between chains of opposite chiralities are provided by the axial co-ordination of the sulphonyl oxygens, O(10), from glide-related complexes.

The crystal structure of complex (1) is characterised by the presence of alternate layers of hydrophobic and hydrophilic regions extending along the *y* and *z* directions. The metal ions, together with the co-ordinating groups, lie in the hydrophilic regions, while the benzene rings lie in the hydrophobic regions. The molecules of water of crystallisation lie deeply buried in the hydrophilic regions, being held in crystalline space by hydrogen bonds. The co-ordinated water oxygen, O(17), in addition to forming an interligand hydrogen bond,

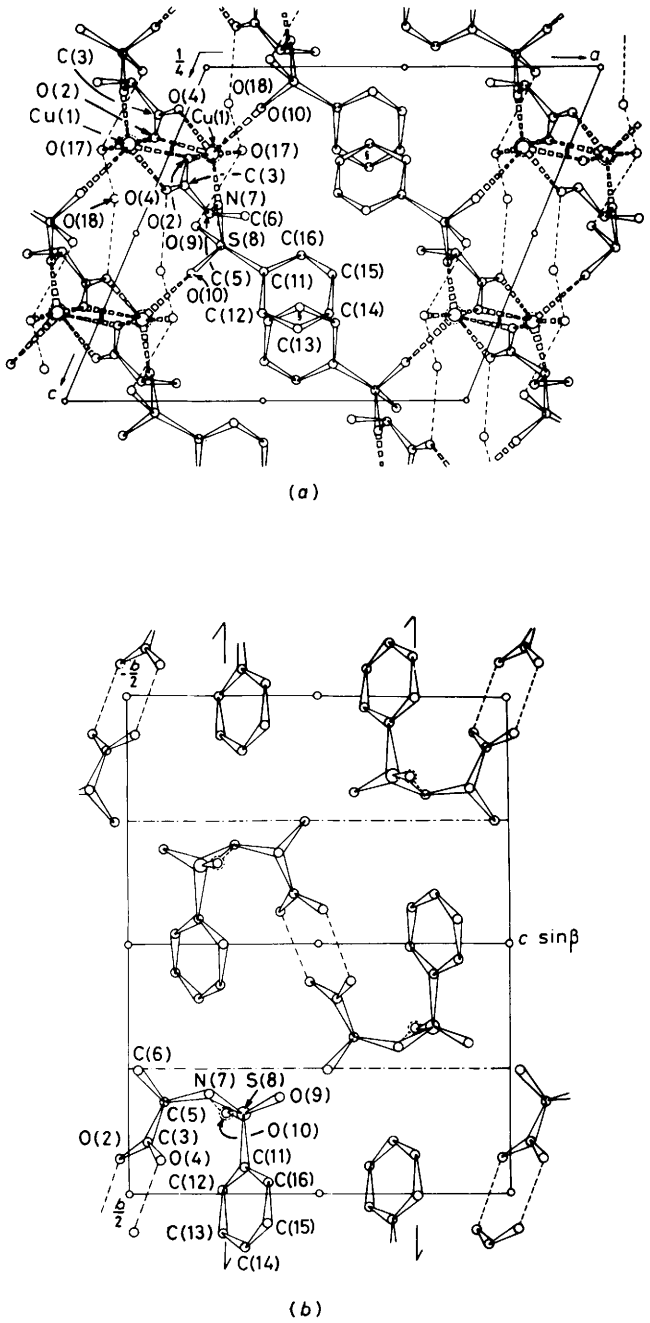

Figure 2. (*a*) The *b* axis projection of the crystal structure of complex (1). (*b*) The *a* axis projection of the crystal structure of ligand (2)

* For a peptide forming only one chelate ring with a metal ion, Franks and van der Helm [11] have suggested that the angles Cu–N–C_{α}, Cu–N–C(carboxy), and C(carboxy)–N–C_{α} should be 109, 136, and 115° rather than 116, 120, and 123° as found in complexes with two chelate rings.

Table 4. Hydrogen bonds [a] D–H · · · A

	Bond/Å			Angle/[c]
	D · · · A	D–H	H · · · A	D–H · · · A
Complex (1)				
O(17)–H(O17)1 · · · O(9)	2.664(3)	0.78(5)	1.92(5)	157(5)
O(17)–H(O17)2 · · · O(18^{i})	2.730(3)	1.08(5)	1.72(5)	154(4)
O(18)–H(O18)1 · · · O(4^{iv})	2.903(3)	0.77(5)	2.17(5)	157(5)
O(18)–H(O18)2 · · · O(2) [b]	3.073(3)	1.09(5)	2.49(5)	112(3)
Ligand (2)				
N(7)–H(N7) · · · O(10^{v})	3.047(2)	0.78(2)	2.27(2)	176(2)
O(2)–H(O2) · · · O(4^{vi})	2.638(2)	0.96(4)	1.69(4)	169(3)

[a] Symmetry codes: i $-x, -\frac{1}{2}+y, -\frac{1}{2}-z$; iv $-x, 1-y, -z$; v $1+x, y, z$; vi $1-x, 1-y, -z$. [b] Short non-bonded contact.

acts as the donor in a hydrogen bond with the oxygen, O(18), of the water of crystallisation. Of the two possible hydrogen bonds in which O(18) could be the donor, the contact O(18) · · · O(2) does not conform to a hydrogen bond (Table 4) but could, however, be described as a short non-bonded contact.[19]

Figure 2(*b*) shows the molecular packing of the free ligand (2) projected down the *a* axis. As is typical of carboxylic acids,[20] the ligand molecules form dimers, being linked together by pairs of O–H · · · O hydrogen bonds across centres of symmetry. The dimers are linked into infinite chains by hydrogen bonds of the type N–H · · · O.

Discussion

Effect of Intermolecular Links.—An interesting feature of the crystal structure of complex (1) is the bridging of copper ions *via* the equatorial and out-of-plane co-ordination of the carboxy-oxygens to form intermolecular links of the type –Cu–O–C–O–Cu–, somewhat similar to that found in the crystal structure of (L-valyl-L-tyrosinato)copper(II) tetrahydrate.[18] Such bridges are capable of providing pathways for electron transfers to and from copper(II) ions and for magnetic superexchange between them.[19] This has been verified experimentally in an e.s.r. study of the crystalline complex (1) which showed only a very weak spectrum, unlike normal copper(II) ion.[21]

The poor solubility of the complex in water can be attributed to its polymerisation in the crystalline state. However, once solution is achieved it appears that the equatorially co-ordinated carboxy-oxygen, O(4), is replaced by a water oxygen and the (weakly co-ordinating) out-of-plane ligands, O(2) and O(10), are removed, giving a formula unit similar to that proposed in the literature.[5b] This explains the e.s.r. spectrum, with the usual hyperfine structure, observed for an aqueous solution of this complex.[21]

Effect of C · · · O *Contacts.*—The short intramolecular contact [3.044(4) Å] between the carboxy-oxygen, O(4), and the side chain β-carbon, C(6), is a feature common to many copper–dipeptide complexes with non-functional side chains and deprotonated peptide nitrogens.[19] This contact is, however, not strained; although the sum of the van der Waals radii of methyl carbon and oxygen is 3.2 Å, the lower limit for the C · · · O contact in the calculation of peptide conformations is taken as 3.0 Å.[22] The effect of this contact is to restrict the amino acid side chain to a quasi-axial orientation with respect to the chelate ring.[19] It has also been shown that such short intramolecular contacts do not have any significant role in influencing the conformations of chelate rings.[19]

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