Molecular and Crystal Structure of *cis*-Bis(L-hydroxyprolinato)-copper(II) Tetrahydrate and *trans*-Bis(D-allohydroxyprolinato)-copper(II)–Water(2/5)†

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The structures of *cis*-bis(L-hydroxyprolinato)copper(II)tetrahydrate (**1**) and *trans*-bis(D-allohydroxyprolinato)copper(II)–water(2/5) (**2**) have been determined by *X*-ray analysis. These compounds provide an unusual example of epimeric amino acids supporting different geometrical arrangements in the copper(II) square plane. Crystals of complex (**1**) are monoclinic, space group $P2_1$, a = 10.209(6), b = 8.071(3), c = 9.698(3) Å, β = 100.33(4)°, and Z = 2. Crystals of complex (**2**) are orthorhombic, space group $P2_12_12_1$, a = 8.678(5), b = 17.737(4), c = 18.686(7) Å, and Z = 8, with two molecules per asymmetric unit. Both structures were solved by Patterson and difference electron-density syntheses. Final R values of 0.037 for 2 248 reflections and 0.045 for 2 207 reflections were obtained for complexes (**1**) and (**2**) respectively. In both structures each copper atom has an essentially square-planar environment with the hydroxyproline co-ordinating by the pyrrolidine nitrogen and carboxylate oxygen. A distorted six-fold co-ordination is completed by weak Cu $\cdots$ O interactions. The Cu–N, Cu–O bond lengths and Cu $\cdots$ O axial distances in the two structures are within the range observed in similar complexes. Extensive systems of hydrogen bonding are present in both structures.

There have been many studies of the geometrical and optical isomerism of bis(amino acidato)copper complexes.[1–4] A particularly interesting aspect of this chemistry concerns *cis/trans* isomerism in the solid state. Structurally confirmed examples are confined to the *cis* (*X*-ray)[5] and *trans* (electron diffraction)[6] glycinato and the *cis*-(D-alaninato)[7] and *trans*-(L-alaninato)[8] complexes (both *X*-ray). For the majority of other complexes geometric isomerism is unknown, although Laurie[9] has suggested that the *cis* and *trans* isomers of L-phenylalaninato copper(II) are formed.

Copper(II) amino acid complexes are among the simplest species available for the study of biologically relevant metal ion co-ordination and many molecular and crystal structures of such complexes are known.[10–13] It is hence surprising that relatively little is known of the factors which influence geometric isomerism and virtually nothing is known of the isomers present in solution. Although most solution studies on copper amino acid complexes assume *trans* geometry, recent e.s.r. work[14] has provided some evidence for the presence of both *cis* and *trans* isomers.

In the present paper we compare and contrast the structures of the copper(II) complexes of the epimeric forms of hydroxyproline. The most readily isolated complexes are *cis*-bis(L-hydroxyprolinato)copper(II) tetrahydrate (**1**) and *trans*-bis(D-allohydroxyprolinato)copper(II)–water(2/5) (**2**), isomers which provide a unique example of epimeric amino acids supporting different geometries on the copper(II) centre.

Experimental

Preparations.—Complex (**1**). To a solution of L-hydroxyproline (10 cm^3, 0.2667 g), copper(II) acetate (0.2084 g) was added. The final mixture was allowed to evaporate slowly at room temperature. Blue crystals of the complex separated as fairly large platelets (Found: C, 30.50; H, 6.25; N, 6.75. Calc. for $C_{10}H_{14}CuN_2O_6{\cdot}4H_2O$: C, 30.35; H, 6.05; N, 7.10%).

Complex (**2**). Blue single crystals were obtained from slow vapour diffusion of ethanol into an aqueous solution (10 cm^3) containing copper(II) acetate (0.0015 mol) and D-allohydroxyproline (0.003 mol). No recrystallization was needed (Found: C, 32.90; H, 5.05; N, 7.50. Calc. for $C_{10}H_{14}CuN_2O_6{\cdot}2.5H_2O$: C, 32.35; H, 5.65; N, 7.55%).

Crystal Data.—X-ray measurements were made using an Enraf-Nonius CAD4 diffractometer and graphite monochromatized Mo-K_α radiation (λ = 0.710 69 Å). Orientation matrices and cell dimensions were obtained by least-squares refinement of setting angles for 25 automatically centred reflections for $16.0 \leqslant \theta \leqslant 18.0°$ in the case of complex (**1**) and $12.0 \leqslant \theta \leqslant 15.0°$ for complex (**2**).

Crystallographic details are listed in Table 1. Both sets of data were corrected for Lorentz and polarization effects. Empirical absorption corrections were applied.[15]

The two structures were solved by Patterson methods and all non-hydrogen atoms were successively located from Fourier difference syntheses. For complex (**1**) full-matrix least-squares refinement was used with all non-hydrogen atoms refining anisotropically. Some hydrogen atoms were found in the difference map and allowed to refine isotropically while the remainder were inserted in idealized positions and assigned a common refined isotropic thermal parameter. A weighting scheme $w = 0.718/[\sigma^2(F) + 0.0022(F)^2]$ was used to give satisfactory agreement.

For complex (**2**) block-diagonal least-squares refinement was used with all non-hydrogen atoms anisotropic. All the hydrogens attached to carbon and nitrogen atoms were inserted in idealized positions and allowed group-refined U_{iso} values. A weighting scheme $w = 0.700/[\sigma^2(F) + 0.0030(F)^2]$ was used in the final stage of refinement.

The main calculations were made using SHELX 76.[16]

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix-xxii.

Table 1. Crystallographic data

Complex	(**1**)	(**2**)
Formula	$C_{10}H_{14}CuN_2O_6 \cdot 4H_2O$	$C_{10}H_{14}CuN_2O_6 \cdot 2.5H_2O$
M	393.71	366.71
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1$	$P2_12_12_1$
a/Å	10.209(6)	8.678(5)
b/Å	8.071(3)	17.737(4)
c/Å	9.698(3)	18.686(7)
β/°	100.33(4)	
U/Å^3	786.1(6)	2 879(3)
Z	2	8
D_c/g cm^{-3}	1.66	1.69
$F(000)$	414	1 368
μ(Mo-K_α)/cm^{-1}	14.5	15.6
N	2 565	2 912
N (unique)	2 438	2 555
$N [I \geqslant 1.5\sigma(I)]$	2 248	2 207
$R(\Sigma\lvert F_o - F_c\rvert/\Sigma\lvert F_o\rvert)$	0.037	0.045
$R'(\Sigma w\lvert F_o - F_c\rvert^2/\Sigma\lvert F_o\rvert 2)^{\frac{1}{2}}$	0.054	0.058
Largest peak in final Fourier difference map/e Å^{-3}	0.78	0.44

Table 2. Fractional atomic co-ordinates (× 10^4) for *cis*-bis(L-hydroxyprolinato)copper(II) tetrahydrate (**1**)

Atom	*x*	*y*	*z*
Cu	−692.7(3)	−2 500	−2 563.9(4)
N(1)	−2 003(3)	−3 851(4)	−3 904(3)
O(1)	649(2)	−3 524(4)	−3 473(3)
C(1)	220(4)	−4 482(5)	−4 512(4)
C(2)	−1 258(4)	−4 827(5)	−4 813(4)
O(2)	929(4)	−5 141(7)	−5 246(6)
C(3)	−1 867(4)	−4 343(8)	−6 320(4)
C(4)	−3 279(4)	−3 842(6)	−6 242(4)
O(3)	−4 054(3)	−5 298(5)	−6 225(5)
C(5)	−3 098(4)	−2 938(4)	−4 835(4)
N(2)	−2 018(3)	−1 150(4)	−1 761(3)
O(4)	634(2)	−1 403(4)	−1 153(3)
C(6)	184(3)	−508(5)	−259(4)
C(7)	−1 311(4)	−189(5)	−526(4)
O(5)	877(3)	118(5)	786(4)
C(8)	−1 955(4)	−713(8)	707(4)
C(9)	−3 352(4)	−1 222(6)	38(4)
C(10)	−3 121(3)	−2 080(4)	−1 286(4)
O(6)	−4 151(3)	231(4)	−278(4)
Ow(1)	3 469(3)	−1 440(5)	−259(4)
Ow(2)	−6 493(4)	−3 618(5)	−3 397(4)
Ow(3)	−6 473(3)	−3 779(5)	−6 312(3)
Ow(4)	−4 180(4)	−5 757(5)	−2 648(4)

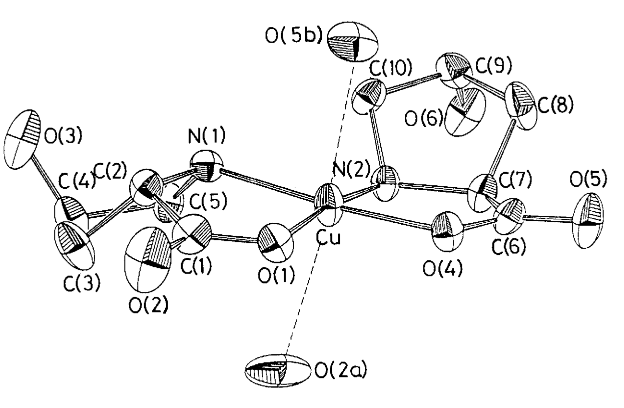

Figure 1. ORTEP II[17] drawing of *cis*-bis(L-hydroxyprolinato)copper(II) tetrahydrate showing the atomic labelling scheme. Thermal ellipsoids are drawn at 50% probability level. The water molecules are not shown

Drawings were made with ORTEP II.[17] Atomic scattering factors were taken from ref. 18. Final atomic parameters for non-hydrogen atoms are listed in Table 2 for complex (**1**) and in Table 3 for complex (**2**).

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

Results and Discussion

The structure of the *cis*-bis(L-hydroxyprolinato)copper(II) unit is shown in Figure 1 whilst selected bond distances and angles are given in Table 4.

The complex has the copper atom in the usual square-planar configuration with a distorted six-fold co-ordination achieved by weak Cu ··· O interactions with oxygen atoms O(2) and O(5), from carboxylate groups of symmetry-related molecules. This is also observed in the structures of the bis(L-serinato),[19] bis(*S*-methyl-L-cysteinato),[20] bis(glycinato),[6] bis(D-alaninato),[7] and bis(L-alaninato)[8] complexes.

Both L-hydroxyproline residues chelate *via* the carboxy oxygen and the nitrogen atom of the pyrrolidine ring, such that the O,O and the N,N atom pairs adopt a *cis* configuration. On co-ordination to the copper ion the nitrogen atom becomes chiral, thus stereoselectively creating an extra asymmetric centre on the molecule.[21–23]

The two chelate rings are planar with maximum deviations of 0.038(4) and 0.059(4) Å, making a dihedral angle of 10.8(1)°. Thus the N_2O_2 group shows a distortion toward tetrahedral with the four co-ordinating atoms deviating ±0.116(7) Å from their best least-squares plane. The copper atom is 0.012(1) Å away in the direction of O(4) and N(1) and towards O(5b).

The geometries of the two anionic L-hydroxyproline residues are similar and comparable to that observed in the free molecule[24] which is zwitterionic with the acid proton bonded to the nitrogen. The pyrrolidine rings, with their intracycle angles of 105(2)° and a mean C–C distance of 1.522(8) and C–N of 1.494(5) Å are comparable to the corresponding values in the free molecule [105(2)°, 1.523(3) and 1.49(8) Å]. The rings are in the 'envelope' conformation with C(4) and C(9) lying +0.561(5) and +0.559(4) Å out of the plane defined by N(1)C(3)C(5)C(2) and N(2)C(7)C(8)C(10) respectively, values comparable to 0.516 Å found for L-hydroxyproline.[24a]

The dihedral angle between the planes N(1)C(3)C(5)C(2) and C(3)C(4)C(5) is 36.6(3)° while the equivalent angle between

Table 3. Fractional atomic co-ordinates (× 10^4) for *trans*-bis(D-allohydroxyprolinato)copper(II)–water(2/5) (**2**)

Atom	*x*	*y*	*z*
Cu	−1 696(1)	−1 605(1)	−4 113(1)
O(1)	−2 695(7)	−2 576(3)	−4 184(3)
O(2)	−4 597(8)	−3 186(3)	−4 769(4)
O(3)	−4 458(9)	−1 120(5)	−3 483(3)
O(4)	−676(6)	−641(3)	−4 073(3)
O(5)	1 321(7)	−38(3)	−3 595(3)
O(6)	−1 452(8)	−603(4)	−2 329(4)
N(1)	−3 157(8)	−1 266(4)	−4 857(3)
N(2)	−361(8)	−1 880(4)	−3 295(3)
C(1)	−3 869(10)	−2 599(4)	−4 615(4)
C(2)	−4 384(9)	−1 866(4)	−4 941(4)
C(3)	−5 802(9)	−1 543(5)	−4 544(5)
C(4)	−5 209(10)	−873(5)	−4 135(5)
C(5)	−3 979(10)	−555(5)	−4 636(5)
C(6)	484(10)	−606(5)	−3 653(4)
C(7)	919(9)	−1 309(5)	−3 235(4)
C(8)	1 087(11)	−1 164(6)	−2 418(5)
C(9)	−603(11)	−1 233(5)	−2 142(5)
C(10)	−1 179(12)	−1 915(5)	−2 584(4)
Cu(1′)	−4 584(1)	−4 304(1)	−3 869(1)
O(1′)	−2 483(7)	−4 651(3)	−3 996(4)
O(2′)	−1 096(7)	−5 600(4)	−4 389(4)
O(3′)	−5 360(9)	−5 632(4)	−3 162(4)
O(4′)	−6 656(6)	−3 925(3)	−3 731(3)
O(5′)	−7 973(8)	−3 031(4)	−3 199(4)
O(6′)	−6 158(8)	−4 457(4)	−2 048(3)
N(1′)	−5 140(8)	−5 104(4)	−4 572(4)
N(2′)	−4 041(8)	−3 634(4)	−3 057(4)
C(1′)	−2 347(10)	−5 278(5)	−4 319(5)
C(2′)	−3 802(10)	−5 633(5)	−4 616(5)
C(3′)	−4 268(10)	−6 333(5)	−4 168(5)
C(4′)	−5 762(10)	−6 072(5)	−3 787(5)
C(5′)	−6 479(10)	−5 565(5)	−4 344(5)
C(6′)	−6 782(9)	−3 368(4)	−3 310(4)
C(7′)	−5 347(10)	−3 107(5)	−2 915(5)
C(8′)	−5 553(12)	−3 121(5)	−2 087(4)
C(9′)	−5 004(11)	−3 904(6)	−1 885(5)
C(10′)	−3 650(10)	−4 041(5)	−2 366(5)
Ow(1)	−65(9)	−4 245(5)	−3 134(4)
Ow(2)	−4 240(12)	−1 110(5)	−8 346(5)
Ow(3)	−4 733(15)	−3 089(5)	−10 042(5)
Ow(4)	−2 170(13)	−8 005(5)	−4 439(6)
Ow(5)	−8 081(23)	−7 788(9)	−4 024(8)

Table 4. Selected molecular dimensions (lengths in Å, angles in °) for complex (**1**) *

N(1)–Cu	2.011(5)	O(1)–Cu	1.942(5)
N(2)–Cu	2.000(5)	O(4)–Cu	1.956(5)
O(2a)–Cu	2.831(6)	O(5b)–Cu	2.612(6)
O(1)–Cu–N(1)	85.2(2)	N(2)–Cu–N(1)	97.4(2)
N(2)–Cu–O(1)	171.9(1)	O(4)–Cu–N(1)	174.0(1)
O(4)–Cu–O(1)	93.1(2)	O(4)–Cu–N(2)	85.0(2)
N(1)–Cu–O(2a)	85.5(2)	O(1)–Cu–O(2a)	85.3(2)
N(2)–Cu–O(2a)	87.3(2)	O(4)–Cu–O(2a)	100.1(2)
N(1)–Cu–O(5b)	84.8(2)	O(1)–Cu–O(5b)	97.3(2)
N(2)–Cu–O(5b)	90.6(2)	O(4)–Cu–O(5b)	89.7(2)
O(2a)–Cu–O(5b)	169.8(3)		
Non-bonded distances			
Intramolecular			
Ow(4) ··· N(1)	3.125(5)	Ow(1) ··· O(4)	2.869(4)
Ow(1) ··· O(5)	3.252(5)	Ow(3) ··· Ow(2)	2.834(5)
Ow(4) ··· Ow(2)	2.912(6)	Ow(3) ··· O(3)	2.746(5)
Intermolecular			
O(2) ··· N(1c)	3.343(6)	O(5) ··· N(1d)	3.149(5)
Ow(2) ··· O(1e)	2.907(5)	O(2) ··· O(1e)	3.299(6)
Ow(2) ··· O(2e)	3.154(6)	Ow(2) ··· O(3f)	2.775(6)
O(5) ··· N(2d)	3.306(5)	Ow(3) ··· N(2g)	2.913(5)
O(5) ··· O(4d)	3.254(5)	Ow(1) ··· O(6i)	2.781(5)
Ow(4) ··· Ow(1h)	2.837(5)	Ow(1) ··· O(6b)	2.802(5)
Ow(4) ··· Ow(3g)	2.766(5)	Ow(3) ··· O(2e)	3.208(6)

* Key to symmetry operations relating designated atoms to reference atoms at (x, y, z): (a) $-x, \frac{1}{2} + y, -1 - z$; (b) $-x, -\frac{1}{2} + y, -z$; (c) $-x, -\frac{1}{2} + y, -1 - z$; (d) $-x, \frac{1}{2} + y, -z$; (e) $-1 + x, y, z$; (f) $-1 - x, \frac{1}{2} + y, -1 - z$; (g) $-1 - x, -\frac{1}{2} + y, -1 - z$; (h) $-x, -\frac{1}{2} + y, -z$; (i) $1 + x, y, z$.

planes N(2)C(7)C(8)C(10) and C(8)C(9)C(10) is 36.8(3)° (33.5° for the ligand). The torsion angle C(5)N(1)C(2)C(3) is 4.9(4)° while on the other pyrrolidine ring the corresponding angle C(10)N(2)C(7)C(8) is 5.0(4)°. The angles of fold at the ring junctions are 44.3(1) and 54.2(4)° respectively. This geometrical arrangement is analogous to that found in the *trans*-diaqua(D,L-prolinato)copper(II) complex.[25]

The complex and water molecules are held together by a large number of hydrogen bonds. The strongest interactions are listed in Table 4.

The structure of *trans*-bis(D-allohydroxyprolinato)copper(II) contains two independent molecules per asymmetric unit. In each the copper ion is approximately square planar, co-ordinated by two chelating ligands bonding *via* the pyrrolidine nitrogen and carboxylate oxygen, with *trans* arrangements of the O,O and N,N pairs. The nitrogen atom becomes a new asymmetric centre as well.

In both molecules distorted octahedral six-fold co-ordination is achieved *via* the formation of weak Cu ··· O interactions, but in two different ways. In each case one 'axial' site is occupied by the hydroxyl oxygen of one ligand of the molecule. In molecule B the second axial site is occupied by a free carboxylate oxygen O(2) of molecule A. The remaining site in molecule A is occupied also by oxygen O(2), but from a symmetry-related molecule A(a). This oxygen is therefore three-co-ordinate.

In most other amino acid copper complexes the apical interactions are provided by carboxyl oxygen atoms from symmetry-related molecules[6–8,19,20] or oxygen atoms from different molecules (*e.g.* water[10,26,27] or acetate[13]) or mixed situations.[5] Relevant bond lengths and angles are presented in Table 5. The molecular diagram with atomic labelling is shown in Figure 2.

In both independent molecules chelating rings are close to planar with the maximum deviation of 0.178(9) Å in the plane Cu(1′)N(1′)O(1′)C(1′)C(2′). Dihedral angles between both chelating rings are 5.8(2)° in molecule A and 11.2(2)° in molecule B. The two 'N_2O_2' planes show a fairly even distortion of the shallow tetrahedral type with maximum deviations of ±0.075(7) and ±0.094(7) Å respectively in molecules A and B. In molecule A the copper atom is 0.027(2) Å away in the direction of the two basal oxygens and towards O(2a); the Cu(1′) atom is 0.060(1) Å out of the plane, also in the direction of the two oxygens and towards O(2), the shorter apical interaction. The distances and angles in the D-allohydroxyproline residues are in general comparable to those in complex (**1**) and in the free L-hydroxyproline molecule.[24]

The pyrrolidine rings are in a slightly distorted 'envelope' form. Fold angles at the ring junctions are 63.9(3) and 58.6(3)°

Table 5. Selected molecular dimensions (lengths in Å, angles in °) for complex (**2**)*

O(1)–Cu(1)	1.932(7)	O(4)–Cu(1)	1.926(7)
N(1)–Cu(1)	1.976(8)	N(2)–Cu(1)	1.979(9)
O(3)–Cu(1)	2.805(9)	O(2a)–Cu(1)	2.796(9)
O(1′)–Cu(1′)	1.939(8)	O(4′)–Cu(1′)	1.937(8)
N(1′)–Cu(1′)	1.993(9)	N(2′)–Cu(1′)	1.983(9)
O(3′)–Cu(1′)	2.784(9)	O(2)–Cu(1′)	2.600(9)
O(4)–Cu(1)–O(1)	178.2(2)	N(1)–Cu(1)–O(1)	86.3(4)
N(1)–Cu(1)–O(4)	93.0(3)	N(2)–Cu(1)–O(1)	95.5(4)
N(2)–Cu(1)–O(4)	85.4(3)	N(2)–Cu(1)–N(1)	173.9(3)
O(3)–Cu(1)–N(1)	69.7(4)	O(3)–Cu(1)–N(2)	104.5(4)
O(3)–Cu(1)–O(1)	85.3(4)	O(3)–Cu(1)–O(4)	95.9(4)
O(2a)–Cu(1)–N(1)	86.2(4)	O(2a)–Cu(1)–N(2)	99.4(4)
O(2a)–Cu(1)–O(1)	97.1(4)	O(2a)–Cu(1)–O(4)	81.3(4)
O(3)–Cu(1)–O(2a)	155.6(4)	O(2)–Cu(1′)–O(3′)	162.1(4)
O(2)–Cu(1′)–O(1′)	79.5(4)	O(2)–Cu(1′)–O(4′)	99.6(4)
O(2)–Cu(1′)–N(1′)	92.2(4)	O(2)–Cu(1′)–N(2′)	96.6(4)
O(3′)–Cu(1′)–O(1′)	90.3(4)	O(3′)–Cu(1′)–O(4′)	91.0(4)
O(3′)–Cu(1′)–N(1′)	101.6(4)	O(3′)–Cu(1′)–N(2′)	68.7(4)
O(4′)–Cu(1′)–O(1′)	178.1(2)	N(1′)–Cu(1′)–O(1′)	85.4(4)
N(1′)–Cu(1′)–O(4′)	96.3(3)	N(2′)–Cu(1′)–O(1′)	93.5(4)
N(2′)–Cu(1′)–O(4′)	84.9(4)	N(2′)–Cu(1′)–N(1′)	171.2(3)

Non-bonded distances

Intramolecular

N(2′) ··· O(1)	3.052(9)	O(4′) ··· O(2)	2.945(9)
N(2′) ··· O(2)	3.330(9)	Ow(1) ··· O(1′)	2.742(9)

Intermolecular

O(4) ··· O(2a)	3.145(8)	N(1) ··· O(2a)	3.313(9)
O(3′) ··· O(3c)	3.197(9)	O(6′) ··· O(3c)	3.16(1)
Ow(2) ··· O(4d)	3.39(1)	N(1′) ··· O(4b)	2.894(8)
Ow(2) ··· O(5d)	2.76(1)	O(3′) ··· O(6c)	2.91(1)
O(6′) ··· O(6c)	3.128(9)	Ow(1) ··· O(6f)	2.88(1)
O(4′) ··· N(1b)	2.961(8)	O(5′) ··· N(2e)	2.915(9)
Ow(3) ··· O(2′h)	2.72(1)	Ow(1) ··· O(4′g)	3.211(9)
Ow(1) ··· O(5′g)	2.82(1)	Ow(2) ··· O(6′a)	2.95(1)
Ow(2) ··· Ow(1b)	2.92(1)	Ow(4) ··· Ow(2j)	2.85(1)
Ow(5) ··· Ow(2k)	3.290(8)	Ow(4) ··· Ow(3j)	2.78(1)
Ow(5) ··· Ow(3k)	3.105(8)	Ow(4) ··· Ow(3l)	2.861(9)
Ow(5) ··· Ow(3l)	3.049(8)	Ow(5) ··· Ow(4i)	3.295(9)

* Key to symmetry operations relating designated atoms to reference atoms at (x, y, z): (a) $\frac{1}{2} + x, -\frac{1}{2} - y, -1 - z$; (b) $-\frac{1}{2} + x, -\frac{1}{2} - y, -1 - z$; (c) $-1 - x, -\frac{1}{2} + y, -\frac{1}{2} - z$; (d) $-\frac{1}{2} - x, -y, -\frac{1}{2} + z$; (e) $-1 + x, y, z$; (f) $-x, -\frac{1}{2} + y, -\frac{1}{2} - z$; (g) $1 + x, y, z$; (h) $-\frac{1}{2} - x, -1 - y, -\frac{1}{2} + z$; (i) $-\frac{1}{2} + x, -\frac{3}{2} - y, -1 - z$; (j) $-\frac{1}{2} - x, -1 - y, \frac{1}{2} + z$; (k) $-\frac{3}{2} - x, -1 - y, \frac{1}{2} + z$; (l) $-1 - x, -\frac{1}{2} + y, -1.5 - z$.

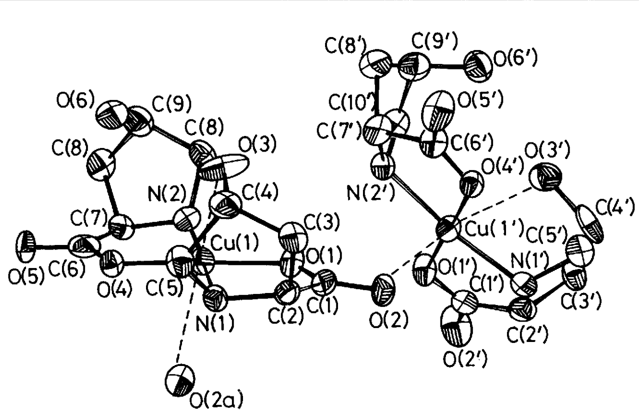

Figure 2. ORTEP II[17] drawing of *trans*-bis(D-allohydroxyprolinato)copper(II)–water(2/5), thermal ellipsoids at 50% probability level. The two molecules in the asymmetric unit, the distorted octahedral co-ordination around each copper, and the atomic labelling are shown

in molecule A and 62.1(3) and 56.6(3)° in molecule B. The two complex molecules and the five water molecules are connected to each other by a complex series of hydrogen bonds; important ones are listed in Table 5.

A significant feature in the two complexes studied is the different orientation of the pyrrolidine rings. In the *cis* complex (**1**) the two rings are on opposite sides of the main co-ordination plane (N_2O_2), while in the *trans* complex (**2**) they are both on the same side. This is a consequence of the optical configuration of the amino acids.[21]

In L-hydroxyproline the imine (and carboxylate) functions are *trans* to the hydroxyl group, hence apical co-ordination of the copper(II) ion by the OH group is impossible. The situation is entirely different in the D-allohydroxyprolinato complex; the *cis* arrangement of the potentially co-ordinating groups in D-allohydroxyproline makes apical co-ordination by the hydroxyl oxygen atom feasible. A *cis* arrangement of the ligands in the latter complex could have led to a molecular structure involving a 'CuN_2O_4' core. Presumably one of the reasons that this complex precipitates as a *trans* isomer involves the polymerization of the complex *via* the vacant co-ordination site in copper(II), a site group in the corresponding *cis* isomer.

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