

Fig. 1. ORTEP drawing of the molecule in the general position, with thermal ellipsoids at 50% probability level.

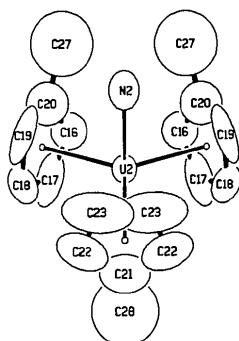


Fig. 2. ORTEP drawing of the molecule on the mirror plane, with thermal ellipsoids at 50% probability level.

compound has a U—N distance similar to that found in the dimethylaminopyridine adduct, consistent with their similar steric nature. This is in marked contrast to the quinuclidine complex. Solution-based competition studies further reflect this difference: the ammonia and dimethylaminopyridine complexes are similar in their

coordinative affinity for uranium, and both are better Lewis bases than quinuclidine (Brennan, 1985; Rosen, 1988).

The average Cp—U—Cp and Cp—U—N angles also reflect the steric differences between these ligands, although the differences are small. In $(\text{MeC}_5\text{H}_4)_3\text{U}\cdot\text{NH}_3$, these angles are 118 and 97°, respectively, while in $(\text{MeC}_5\text{H}_4)_3\text{U}\cdot 4\text{-NC}_5\text{H}_4(\text{NMe}_2)$ and $(\text{MeC}_5\text{H}_4)_3\text{U}\cdot\text{N}(\text{CH}_2\text{CH}_2)_3\text{CH}$ the Cp—U—Cp angles are 117 and 116° and the Cp—U—N angles are 100 and 101°. Thus, the title compound shows a slightly greater tendency towards an idealized geometry of trigonal pyramidal, suggesting that ammonia is slightly less bulky than either of these other ligands. Although these values are consistent with the solution equilibrium studies, they are not significant crystallographically.

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Structure of *trans*-Bis(DL- α -alaninato)copper(II) Monohydrate

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Abstract. $[\text{Cu}\{\text{NH}_2\text{CH}(\text{CH}_3)\text{COO}\}_2]\cdot\text{H}_2\text{O}$, $[\text{Cu}(\text{C}_3\text{H}_6\text{NO}_2)_2]\cdot\text{H}_2\text{O}$, $M_r = 257.76$, monoclinic, $C2/c$, $a =$

$12.074(2)$, $b = 9.567(2)$, $c = 8.944(1)$ Å, $\beta = 110.87(1)^\circ$, $V = 965.3(5)$ Å³, $Z = 4$, $D_x = 1.790$ Mg m⁻³, $\lambda(\text{Mo K}\alpha) = 0.71073$ Å, $\mu = 2.35$ mm⁻¹, $F(000) = 532$, $T = 295$ K. Conventional R factor: 0.053 for 1825 unique reflections. The Cu^{II} ion

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Table 1. Fractional atomic coordinates ($\times 10^4$, hydrogen $\times 10^3$) and isotropic or equivalent isotropic temperature factors ($\times 10^2 \text{ \AA}^2$)

U_{eq} calculated from u_i , the m.s. displacement along the principal axis: $U_{eq} = (u_1^2 + u_2^2 + u_3^2)^{1/3}$.

	x	y	z	U_{eq}/U_{iso}
Cu	0	0	$\frac{1}{2}$	2.7
C(1)	2146 (1)	1280 (2)	6465 (2)	2.8
C(2)	2385 (2)	227 (2)	5317 (3)	2.9
C(3)	3640 (2)	-335 (3)	5948 (4)	4.3
N	1471 (1)	-869 (1)	4947 (2)	2.7
O(1)	1096 (1)	1305 (1)	6476 (1)	3.1
O(2)	2939 (1)	2078 (1)	7265 (1)	3.7
O(3)	0	1538 (2)	$\frac{1}{2}$	3.7
C(2B)	2607 (16)	87 (22)	1010 (29)	2.0 (4)
C(3b)	3426 (18)	212 (23)	5133 (27)	2.9 (6)
H(1)	166 (2)	-152 (2)	563 (3)	4.8 (6)
H(2)	136 (2)	-123 (2)	394 (3)	4.6 (6)
H(3)	222 (2)	74 (2)	431 (3)	3.5 (5)
H(4)	382 (2)	-74 (3)	695 (3)	7.6 (10)
H(5)	382 (2)	-96 (3)	520 (3)	6.6 (8)
H(6)	417 (2)	50 (3)	609 (3)	5.8 (7)
H(7)	55 (2)	208 (2)	265 (3)	6.0 (7)

is octahedrally coordinated to N and O atoms belonging to alaninate ligands and to two water molecules. These polyhedra are linked through water O atoms to form infinite chains, the water molecules providing hydrogen-bond bridging between the alaninate ligands. The NH_2 protons are also involved in hydrogen bonds. Disorder was observed as a result of the arrangement of the alaninate ligands: approximately 8% of the D and L forms of the ligand are interchanged.

Introduction. The structure determination of the title compound was undertaken as part of a project focused on spectroscopic and structural studies of hydrogen-bonded systems, particularly crystal hydrates. The compound trans-bis(DL-alaninato)copper(II) monohydrate has previously been studied within the project by IR spectroscopy (Eriksson, Lindgren & Stojanoski, 1986). Single crystals of this copper complex have also been investigated earlier by low-temperature NMR spectroscopy (Sandreczki, Ondercin & Kreilick, 1979). It was anticipated that this present study would serve to equip this earlier work with a firm structural foundation.

Experimental. Compound prepared as reported by Segnini, Curran & Quagliano (1960); slow recrystallization from aqueous solution; crystal dimensions $0.22 \times 0.17 \times 0.14$ mm. CAD-4 diffractometer with graphite-monochromatized $\text{Mo K}\alpha$ radiation; ω -scan mode. Cell parameters from 25 reflections ($8 < \theta < 17^\circ$). 1895 reflections collected, 1825 unique, for $(\sin \theta)/\lambda < 0.766 \text{ \AA}^{-1}$; $0 \leq h \leq 17$, $0 \leq k \leq 14$, $-13 \leq l \leq 12$. Five standard reflections decreased by less than 3% during the data collection. Intensities and their standard deviations corrected accordingly (McCand-

lish, Stout & Andrews, 1975). Data corrected for Lorentz, polarization and absorption effects (transmission range: 59–75%); f , f' and f'' from *International Tables for X-ray Crystallography* (1974). Possible space groups Cc and $C2/c$ from systematic absences; $C2/c$ confirmed by structural determination. Structure solved using *MULTAN80* (Main *et al.*, 1980). Disorder was detected in the alaninate ligand during refinement and subsequently included in the model. All H atoms located in the difference Fourier maps. Full-matrix least-squares refinement based on F^2 with weights $w = \sigma^{-2}$; anisotropic thermal parameters used for non-H atoms and isotropic for all H atoms. 1825 reflections gave $R(F^2) = 0.046$, $wR(F^2) = 0.069$, conventional $R(F) = 0.053$, $S = 1.66$, all shifts $< 0.1\sigma$. Max. and min. in final difference Fourier maps 0.39 and -0.85 e \AA^{-3} . No extinction correction needed. All programs described by Lundgren (1982). The final positional parameters are given in Table 1.*

Discussion. A view of the region around the Cu^{II} ion is given in Fig. 1 (the atom-labelling scheme is also shown). Fig. 2 illustrates the packing of the molecules in the unit cell. The Cu atom is at a centre of symmetry and is octahedrally coordinated by two bidentate alaninate ligands and two crystallographically equivalent water molecules. The two N atoms and the two O(1) atoms from the alaninate residues form a square-planar arrangement at distances 1.977 (1) and 1.951 (1) \AA from the Cu^{II} ions. The two O(3) atoms from the water molecules are situated 2.677 (1) \AA above and below this plane. These values compare well with average values found in previously determined structures of similar copper chelate complexes (Freeman, 1967; Gillard, Mason, Payne & Robertson, 1969).

The water molecule lies on a twofold axis which is inclined approximately 33° to the plane formed by the two N and two O(1) atoms around Cu. In this compound, the water O atom occupies both apical positions in the coordination octahedron, as in the structure of copper proline dihydrate (Mathieson & Welsh, 1952). It serves to provide the linkage for the octahedra. The water molecule is also hydrogen bonded to O atoms of the carboxylate group. The Cu complexes are thus linked to form infinite chains. The configuration around the water molecule is tetrahedral, comprising two Cu and two O atoms.

The bond lengths and angles of the alaninate residues (Table 2) agree with the values found in many copper chelates of amino acids, *e.g.* in bis(D-alaninato)-

*Lists of structure factors and anisotropic displacement parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51793 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

copper(II) (Gillard *et al.*, 1969) and bis(L-phenylalaninato)copper(II) (van der Helm, Lawson & Enwall, 1971). The N atom is tetrahedrally coordinated, linked by two weak hydrogen bonds to carboxyl O atoms [O(1) and O(2)] of the neighbouring molecules.

Equations for the three dominant planes in the structure are given in Table 3, along with corresponding perpendicular distances. The latter show that the carboxyl group is planar, while the chelate ring is not. Such a result compares well with previously reported experience.

During the structure refinement, a degree of disorder was found to affect the asymmetric C(2) atom, the H(3) atom bonded to it, and the C(3) and H(4) atoms of the methyl group. This is presumably the result of 'mistakes' occurring in the choice of site for the racemic molecules during crystallization; it is known that racemic compounds can sometimes crystallize with isomers occupying centrosymmetrically related sites (Barnes, Forsyth & Schroth, 1986). In the present case, the calculated occupancy for the major component was 0.919 (7), with 0.081 (7) for the isomer in which the D

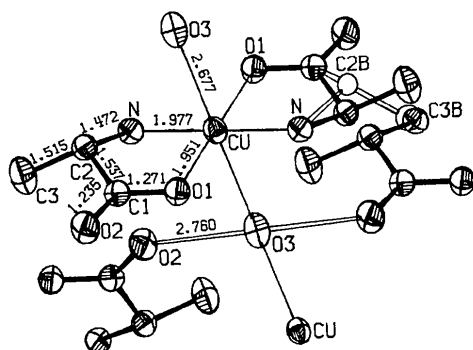


Fig. 1. Perspective view and atom labelling of *trans*-bis-(DL- α -alaninato)copper(II) monohydrate.

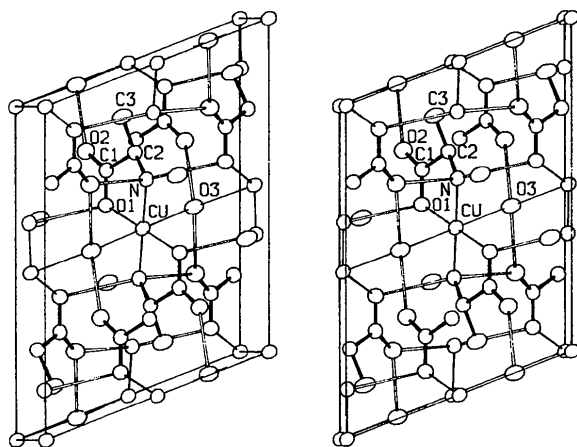


Fig. 2. A stereoview of the molecular packing of *trans*-bis-(DL- α -alaninato)copper(II) monohydrate in the unit cell, viewed down *b*.

Table 2. *Interatomic distances* (Å) *and angles* (°)

(a) Coordination polyhedra			
Cu-N	1.977 (1)	N-Cu-O(1)	83.48 (5)
Cu-O(1)	1.951 (1)	O(3)-Cu-N	86.77 (6)
Cu-O(3)	2.677 (1)	O(3)-Cu-O(1)	90.67 (5)
(b) Alaninate ligand			
C(1)-O(1)	1.271 (2)	Cu-O(1)-C(1)	114.9 (1)
C(1)-O(2)	1.235 (2)	O(1)-C(1)-C(2)	116.2 (1)
C(1)-C(2)	1.536 (3)	O(1)-C(1)-O(2)	123.5 (2)
C(1)-C(2B)	1.531 (22)	O(2)-C(1)-C(2)	120.1 (2)
C(2)-N	1.472 (2)	C(1)-C(2)-N	108.3 (2)
C(2)-C(2B)	0.654 (23)	C(1)-C(2)-C(3)	112.6 (2)
C(2)-C(3)	1.515 (3)	C(3)-C(2)-N	113.7 (2)
C(2)-C(3B)	1.325 (24)	C(2)-N-Cu	107.6 (1)
C(3)-C(3B)	0.858 (22)	C(1)-C(2B)-N	104 (1)
C(3)-C(2B)	1.290 (22)	C(1)-C(2B)-C(3B)	110 (2)
C(2B)-N	1.555 (18)	C(3B)-C(2B)-N(1)	112 (2)
C(2B)-C(3B)	1.492 (37)	H(1)-N-H(2)	109 (2)
C(2)-H(3)	0.982 (22)	H(4)-C(3)-H(5)	111 (2)
C(3)-H(4)	0.934 (29)	H(4)-C(3)-H(6)	107 (2)
C(3)-H(5)	0.979 (27)	H(5)-C(3)-H(6)	107 (2)
C(3)-H(6)	1.000 (25)		
N-H(1)	0.847 (22)		
N-H(2)	0.928 (22)		
O(3)-H(7)	0.815 (21)		
(c) Hydrogen bonding			
O(3)-O(2 ⁱⁱ)	2.760 (2)	O(3)-H(7)...O(2 ⁱⁱ)	162 (2)
N-O(1 ⁱⁱ)	3.002 (2)	N-H(2)...O(1 ⁱⁱ)	160 (2)
N-O(2 ⁱⁱⁱ)	3.052 (2)	N-H(1)...O(2 ⁱⁱⁱ)	168 (2)

Symmetry code: (i) $\frac{1}{2}-x, \frac{1}{2}-y, 1-z$; (ii) $\frac{1}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z$; (iii) $x, -y, z-\frac{1}{2}$.

Table 3. *Some least-squares planes in the structure, and distances from the corresponding planes*

The equations for the planes are expressed in the form: $Ax + By + Cz + D = 0$, where x, y and z are fractional coordinates. Underlined atoms were used in the calculation of the least-squares planes.

Plane		<i>A</i>	<i>B</i>	<i>C</i>	<i>D</i>
(1)	Cu, N, O(1), C(1), C(2)	0.6014	5.5577	-6.9483	3.6183
(2)	O(1), O(2), C(1), C(2)	-0.0966	6.4775	-6.1244	3.1367
(3)	N, C(1), O(1), O(2)	0.7987	5.2009	-7.2034	3.8835

	$\Delta(1)$ (Å)	$\Delta(2)$ (Å)	$\Delta(3)$ (Å)
Cu	0.144	O(1) 0.005 (1)	N -0.014 (1)
N	-0.213 (1)	O(2) 0.005 (1)	C(1) 0.064 (2)
O(1)	-0.090 (1)	C(1) -0.014 (2)	O(1) -0.015 (1)
C(1)	-0.033 (2)	<u>C(2)</u> -0.004 (2)	O(2) -0.034 (1)
C(2)	0.193 (2)	Cu 0.074	<u>C(2)</u> 0.362 (2)
C(2B)	0.193 (2)	N -0.470 (1)	C(2B) -0.283 (23)
C(3)	-0.481 (3)		C(3) -0.284 (3)
C(3B)	0.375 (22)		C(3B) 0.570 (22)

form of the alaninate group is replaced by the L form. The positions for the atoms expected to be most affected by this kind of disorder [C(2B) and C(3B)] in the second isomer are reasonable; bond angles, distances and deviations from plane (3) also have expected values (see Tables 2 and 3). Once the disorder in the structure had been identified, it was possible to explain the presence of the strong peaks close to C(2) and C(3) in the difference map; the large temperature factors for these atoms [as well as for H(3) and H(4)] became more reasonable, and the whole structure could be refined more satisfactorily.

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Structure of 1-(4-Pyridyl)pyridinium trans-Tetrachlorodi(pyridine)molybdate(III)*

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Abstract. $C_{10}H_9N_2^+[MoCl_4(C_5H_5N)_2]^-$, $C_{10}H_9N_2^+ = pyp^+$, $C_5H_5N = py$, $M_r = 553.15$, triclinic, PI , $a = 7.669$ (1), $b = 8.949$ (1), $c = 16.455$ (2) Å, $\alpha = 86.77$ (1), $\beta = 83.20$ (1), $\gamma = 84.30$ (1)°, $V = 1114.7$ (1) Å³, $Z = 2$, $D_m = 1.63$ (2), $D_x = 1.648$ Mg m⁻³, $Mo K\alpha$, $\lambda = 0.71069$ Å, $\mu = 1.08$ mm⁻¹, $F(000) = 554$, $T = 293$ K, $R = 0.037$ for 2893 reflections. The unit cell contains two independent *trans*-[$MoCl_4py_2$]⁻ octahedral anions situated on centers of symmetry and two symmetry-related *pyp*⁺ cations. Average Mo–Cl and Mo–N(pyridine) bond lengths are 2.442 and 2.195 Å. The two rings of the cation are linked by a C–N bond of length 1.446 (9) Å.

Introduction. Mo^{III} coordination compounds of the type $M^I MoX_4L_2$ are still rare. The crystal structures of two members of this family, $(PPh_4)MoCl_4(THF)_2$ (Hill, Leigh, Hutchinson & Zubieta, 1985) and $(PPh_4)MoCl_4(bipy)$, *bipy* = bipyridine (Richards, Shortman, Povey & Smith, 1987), were published recently. The only structural information about the *pyp*⁺ cation comes from the crystal structure of *pypH*MoCl₅·H₂O (Brenčič, Čeh & Leban, 1988) where 1-(4-pyridyl)pyridinium (*pyp*⁺) is protonated. One of the reasons for this structural work was therefore to compare the

dimensions of the unprotonated *pyp*⁺ cation with those in protonated *pypH*²⁺.

Experimental. Yellow plates were obtained from a solution of *pyH*[$MoCl_4py_2$] (Brenčič, Čeh & Leban, 1986) in conc. ammonia solution to which excess *pypHCl*₂ dissolved in water was added. The low solubility of (*pyp*) $MoCl_4py_2$ required low concentrations of the reactants. The crystal density was determined by flotation in a mixture of organic solvents.

Crystal approximated by square plate, dimensions 0.32 × 0.16 × 0.4 mm. The unit-cell dimensions were calculated from 75 reflections ($17 < 2\theta < 27^\circ$) measured on the diffractometer at 293 (1) K. The data were collected at the same temperature with an Enraf–Nonius CAD-4 diffractometer; graphite-monochromatized *Mo Kα* radiation, ω – 2θ scans, $\theta_{min} = 1^\circ$, $\theta_{max} = 28^\circ$, θ scan width = $(0.8 + 0.3 \tan \theta)^\circ$, a horizontal counter aperture = $(2.4 + 0.9 \tan \theta)$ mm, variable scan rate, maximum scan time = 45 s. 5077 independent reflections ($-9 < h < 10$, $-11 < k < 11$, $0 < l < 21$) were measured, 2893 with $I > 2\sigma(I)$ were used for the solution and refinement of the structure. Three standard reflections $\bar{2}32$, $20\bar{6}$, $\bar{2}1\bar{6}$ showed no decay during data collection and no reorientation of the crystal was necessary.

Structure factors on a relative scale were calculated by applying Lorentz, polarization and absorption corrections (transmission factors were in the range

* For a preliminary account see Brenčič, Čeh, Golič & Leban (1988).