

Fig. 1. Structure of the title compound showing the atomic numbering (four BF_4^- groups omitted).

is 8.07 (7) Å, and average Cu—N distances are Cu(1)—N(eq.) 2.03 (2), Cu(1)—N(ax1) 2.23 (2) Å and Cu(2)—N(eq.) 2.04 (2), Cu(2)—N(ax1) 2.25 (2) Å. Coordination around Cu takes the form of a distorted tetragonal pyramid. The dihedral angle between plane (1) [N(11), N(15), N(16), N(10)] and plane (2) [N(21), N(25), N(26), N(20)] is 62.8 (5)°. The distance of Cu(1) from plane (1) is -0.32 (2) Å and that of Cu(2) from plane (2) is $+0.31$ (2) Å.

It is interesting that, in contrast to the initial assumption, none of the BF_4^- ions are bonded to other atoms in the structure. The shortest intermolecular contacts are F(22)—H(20) 2.09 (2) and (between non-H atoms) F(22)—N(10) 3.00 (2) Å.

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Copper 1-Aminocyclohexanecarboxylate Monohydrate [Aquabis(1-aminocyclohexanecarboxylato)copper(II)]; Tetra- and Pentacoordinate Copper

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Abstract. $[\text{Cu}(\text{C}_7\text{H}_{12}\text{NO}_2)_2(\text{H}_2\text{O})]$, $M_r = 365.9$, monoclinic, $P2_1/c$, $a = 10.750$ (3), $b = 13.643$ (4), $c = 22.819$ (5) Å, $\beta = 100.51$ (2)°, $V = 3291$ (1) Å³, $Z = 8$, $D_x = 1.48$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 1.40$ mm⁻¹, $F(000) = 1544$, $T = 293$ (1) K, $R = 0.051$ for 4074 reflections. There are two chelated molecules in each of four asymmetric units, with two amino groups and two carboxyl groups coordinated to each Cu atom. The amino groups are in the axial

positions of the cyclohexane rings, the carboxyl groups in the equatorial positions. In one molecule the N atoms are in a *trans* position, and the configuration of the Cu atom is intermediate between that of a distorted pentacoordinate trigonal bipyramid and a distorted rectangular pyramid, with the O atom of a water molecule occupying the fifth position. In the second molecule the coordination is planar, with the N atoms in a *cis* position. A second

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uncoordinated water molecule is associated with this form. There are indications that the two water molecules act to form linkages between the two molecules of the asymmetric unit, and between ligands of molecules of adjacent asymmetric units. The copper—ligand distances are 2.005 (4) and 1.998 (4) Å for Cu—N and 1.957 (4) and 1.966 (4) Å for Cu—O in the *trans* form; 1.979 (4) and 1.983 (4) Å for Cu—N and 1.959 (4) and 1.930 (4) Å for Cu—O in the *cis* form.

Introduction. The structure analysis of the title compound is a continuation of the investigation of metal complexes of aromatic and heterocyclic amino acids (Boudreau & Haendler, 1986; Haendler, 1985, 1986). Copper(II) complexes of these amino acids have exhibited the ubiquitous square- or rectangular-planar coordination of the Cu atom, the Jahn–Teller octahedral distortion and the distorted trigonal-bipyramidal configuration associated with the Berry displacement. In this Cu complex both the planar and the bipyramidal structure (or its rectangular-pyramidal distortion) are observed in the two molecules of the asymmetric unit.

Experimental. Crystals of the monohydrate were grown by slow evaporation of an aqueous mixture of copper(II) acetate monohydrate and 1-aminocyclohexane carboxylic acid in a 1:2 ratio. The complex was first reported by Zelinsky & Stadnikoff (1906), and its composition has been reconfirmed by chemical analysis.

The crystal used was a blue, rectangular parallelepiped, 0.30 × 0.55 × 0.70 mm. Nicolet four-circle diffractometer, graphite-monochromatized Mo K α radiation. 15 reflections ($2\theta > 20^\circ$) for measurement of lattice parameters at 293 (1) K. Empirical absorption correction, using ψ scan with six reflections, range $4.9 < 2\theta < 32.4^\circ$, transmission factors 0.60–1.00. Maximum $\sin\theta/\lambda = 0.602 \text{ \AA}^{-1}$; h 0 to 16, l –27 to 27. Six check reflections, frequency 300, no indication of deterioration or alignment changes. 6006 reflections measured, 1582 unobserved with $I < 3\sigma(I)$. The VAX version of the *DIRDIF* system (Beurskens, Bosman, Doesburg, Gould, Van Den Hark, Prick, Noordik, Beurskens, Parthasarathi, Bruins Slot, Haltiwanger, Strumpel & Smits, 1985) was used to solve the structure. The two Cu atoms were located on the Patterson map, and the remaining 42 non-H atoms were found in a single pass. Least-squares refinement on F , block-diagonal approximation, isotropic and anisotropic thermal parameters. 44 (of 52) H atoms were located on a difference Fourier map or by superposition of a model on a scaled projection and were refined with the non-H atoms fixed. The remaining H atoms were then identified on a second difference map. Data did

Table 1. Fractional atomic coordinates and equivalent isotropic temperature factors

$$B_{\text{eq}} = (8\pi^2/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	$B_{\text{eq}}(\text{\AA}^2)$
Molecule (1)				
Cu(1)	0.68953 (7)	0.10414 (5)	0.24973 (3)	2.04
O(1)	0.6481 (4)	0.0174 (3)	0.3117 (2)	2.61
O(3)	0.6507 (3)	0.1985 (2)	0.1838 (2)	2.18
O(5)	0.6383 (4)	0.0095 (3)	0.4077 (2)	3.20
O(7)	0.5965 (4)	0.2088 (3)	0.0849 (2)	3.30
O(9)	0.9139 (3)	0.0892 (3)	0.2643 (2)	3.59
N(1)	0.6987 (4)	0.2082 (3)	0.3124 (2)	2.57
N(3)	0.6670 (4)	0.0036 (3)	0.1850 (2)	1.90
C(1)	0.6598 (5)	0.0563 (4)	0.3644 (3)	2.21
C(3)	0.6363 (5)	0.1613 (4)	0.1302 (2)	1.81
C(5)	0.7076 (5)	0.1625 (4)	0.3727 (2)	1.60
C(7)	0.6747 (5)	0.0530 (4)	0.1266 (2)	1.38
C(9)	0.8504 (4)	0.1571 (4)	0.4037 (2)	2.10
C(11)	0.9045 (5)	0.2580 (5)	0.4214 (3)	3.13
C(13)	0.8266 (5)	0.3146 (4)	0.4596 (3)	3.24
C(15)	0.6896 (5)	0.3223 (4)	0.4275 (3)	3.04
C(17)	0.6301 (5)	0.2196 (4)	0.4118 (3)	2.27
C(19)	0.8122 (4)	0.0544 (4)	0.1151 (2)	1.87
C(21)	0.8593 (5)	–0.0479 (4)	0.1032 (3)	2.66
C(23)	0.7702 (5)	–0.0978 (4)	0.0516 (3)	3.20
C(25)	0.6344 (5)	–0.1034 (4)	0.0634 (2)	2.58
C(27)	0.5858 (5)	0.0002 (4)	0.0744 (2)	2.27
Molecule (2)				
Cu(2)	0.54143 (6)	0.35907 (5)	0.19765 (3)	2.05
O(2)	0.4527 (3)	0.3258 (2)	0.2627 (2)	1.96
O(4)	0.6931 (3)	0.4042 (3)	0.2493 (2)	2.53
O(6)	0.2592 (3)	0.2995 (3)	0.2796 (2)	2.68
O(8)	0.8885 (3)	0.4612 (3)	0.2508 (2)	3.44
O(10)	0.0040 (4)	0.2743 (3)	0.2825 (2)	4.02
N(2)	0.3881 (4)	0.3090 (3)	0.1447 (2)	1.64
N(4)	0.6214 (4)	0.4110 (3)	0.1323 (2)	1.69
C(2)	0.3375 (5)	0.3020 (4)	0.2448 (2)	1.89
C(4)	0.7805 (5)	0.4406 (4)	0.2251 (3)	2.42
C(6)	0.2973 (4)	0.2656 (4)	0.1802 (2)	1.36
C(8)	0.7422 (5)	0.4627 (4)	0.1566 (2)	1.80
C(10)	0.3134 (5)	0.1528 (4)	0.1824 (3)	2.50
C(12)	0.2591 (6)	0.1052 (5)	0.1219 (3)	4.11
C(14)	0.1227 (5)	0.1368 (6)	0.0986 (3)	4.53
C(16)	0.1126 (5)	0.2454 (6)	0.0939 (3)	3.98
C(18)	0.1579 (5)	0.2948 (4)	0.1537 (3)	2.72
C(20)	0.7215 (5)	0.5742 (4)	0.1481 (3)	2.85
C(22)	0.6997 (6)	0.6056 (5)	0.0830 (3)	4.35
C(24)	0.8107 (6)	0.5656 (6)	0.0520 (3)	5.56
C(26)	0.8261 (6)	0.4579 (6)	0.0596 (3)	4.66
C(28)	0.8496 (5)	0.4272 (4)	0.1240 (3)	2.79

not permit unambiguous location of all H atoms. Final block-diagonal refinement, with H atoms fixed, using 4074 reflections (350 low-intensity reflections with $\Delta F/F > 0.3$ omitted), anomalous dispersion for Cu, and $B = 5.0 \text{ \AA}^2$ for H atoms, converged at $R = 0.051$, $w = 1/\sigma^2(F_o)$, $wR = 0.052$. $(\Delta/\sigma)_{\text{max}} = 0.24$, exclusive of H shifts. $S = 2.73$ for 4074 reflections with 397 variables. Final difference map showed max. and min. peaks of 0.77 and -0.57 e \AA^{-3} . No systematic errors as functions of $\sin^2\theta$ or F_o ; no significant correlations. Atomic scattering factors from *International Tables for X-ray Crystallography*

Table 2. Selected bond distances (Å) and angles (°)

Cu(1)—O(1)	1.957 (4)	Cu(2)—O(2)	1.959 (4)
Cu(1)—O(3)	1.966 (4)	Cu(2)—O(4)	1.930 (4)
Cu(1)—N(1)	2.005 (4)	Cu(2)—N(2)	1.979 (4)
Cu(1)—N(3)	1.998 (4)	Cu(2)—N(4)	1.983 (4)
O(1)—C(1)	1.299 (7)	O(2)—C(2)	1.273 (6)
O(3)—C(3)	1.307 (6)	O(4)—C(4)	1.274 (7)
O(5)—C(1)	1.233 (7)	O(6)—C(2)	1.259 (6)
O(7)—C(3)	1.229 (6)	O(8)—C(4)	1.234 (7)
C(1)—C(5)	1.537 (7)	C(2)—C(6)	1.541 (7)
C(3)—C(7)	1.540 (7)	C(4)—C(8)	1.571 (8)
C(5)—N(1)	1.498 (7)	C(6)—N(2)	1.499 (6)
C(7)—N(3)	1.509 (7)	C(8)—N(4)	1.493 (6)
Cu(1)—O(9)	2.383 (5)	O(6)···O(10)	2.778 (6)
O(9)···O(10)*	2.709 (6)	O(8)···O(10)	2.870 (6)
O(1)—Cu(1)—N(1)	84.3 (2)	O(2)—Cu(2)—N(2)	85.2 (2)
O(3)—Cu(1)—N(3)	84.5 (2)	O(4)—Cu(2)—N(4)	84.9 (2)
O(1)—Cu(1)—N(3)	96.1 (2)	O(2)—Cu(2)—N(4)	172.1 (2)
O(3)—Cu(1)—N(1)	93.3 (2)	O(4)—Cu(2)—N(2)	178.4 (2)
N(1)—Cu(1)—N(3)	175.7 (2)	N(2)—Cu(2)—N(4)	95.2 (2)
Cu(1)—N(1)—C(5)	110.3 (3)	Cu(2)—N(2)—C(6)	111.0 (3)
Cu(1)—N(3)—C(7)	109.1 (3)	Cu(2)—N(4)—C(8)	110.9 (3)
N(1)—C(5)—C(1)	108.4 (4)	N(2)—C(6)—C(2)	107.0 (4)
N(3)—C(7)—C(3)	108.8 (4)	N(4)—C(8)—C(4)	109.3 (4)
C(5)—C(1)—O(1)	118.2 (4)	C(6)—C(2)—O(2)	118.4 (4)
C(7)—C(3)—O(3)	115.8 (4)	C(8)—C(4)—O(4)	115.2 (5)
C(1)—O(1)—Cu(1)	115.2 (3)	C(2)—O(2)—Cu(2)	113.3 (3)
C(3)—O(3)—Cu(1)	115.7 (3)	C(4)—O(4)—Cu(2)	117.8 (3)
O(1)—C(1)—O(5)	122.0 (5)	O(2)—C(2)—O(6)	121.8 (5)
O(3)—C(3)—O(7)	123.1 (5)	O(4)—C(4)—O(8)	126.0 (5)
O(9)···H(1)···O(10)	176 (4)	O(10)—H(2)···O(6)	170 (4)
		O(10)—H(4)···O(8)	167 (4)

*The dotted line represents a bond between atoms in different molecules.

(1974). National Research Council of Canada programs (Ahmed, 1973) were used for most computations; ORTEPII (Johnson, 1976) for the thermal-ellipsoid plots.

Discussion. Final positional parameters of non-H atoms are given in Table 1,* and principal bond distances and angles in Table 2. One half of the unit cell is shown in projection in Fig. 1; the thermal-ellipsoid plots of each molecule in Fig. 2. Some H atoms are omitted for clarity.

The two ligands of each molecule are bidentate, coordinated to a Cu atom through the N atom of the amino group and the carboxyl oxygen. In molecule (1) the N atoms are in the *trans* position; in molecule (2), in the *cis* position. The Cu—N distances are greater in molecule (1), 1.988–2.005 Å, than in molecule (2), 1.979–1.983 Å, as are the Cu—O distances, 1.957–1.966 Å in (1) and 1.930–1.959 Å in (2). The Cu atom in molecule (1) is farther from the mean rectangular plane of the coordinated N and O atoms, 0.285 Å, than is the Cu atom from the corresponding plane of molecule (2), 0.057 Å. There are two water molecules in each asymmetric unit. One of these is centered on O(9), 2.383 Å from Cu(1), implying

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, ring-bond distances and angles, planes data and torsion angles and a stereoview have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52023 (77 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

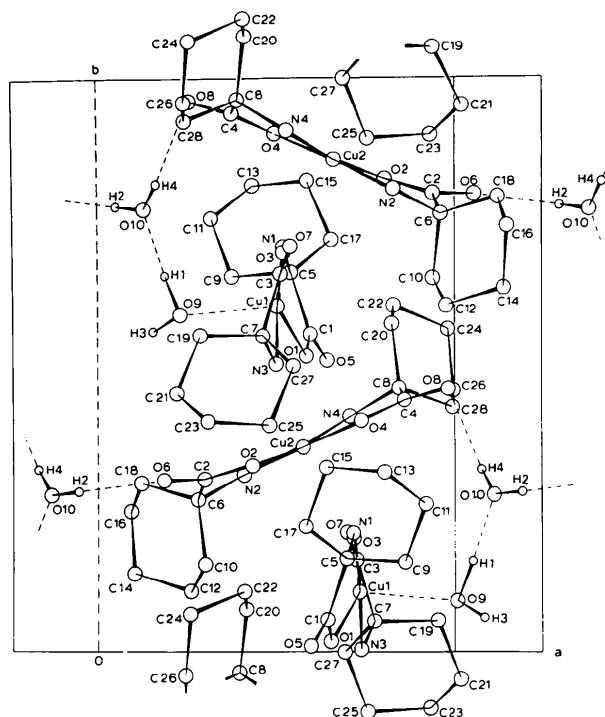


Fig. 1. Projection of one half of the unit cell of copper(II) 1-aminocyclohexanecarboxylate monohydrate, as viewed along the $c \sin \beta$ direction.

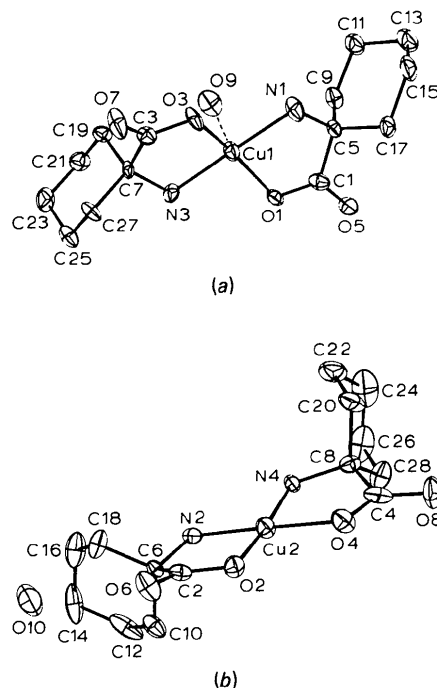


Fig. 2. (a) Thermal-ellipsoid plot of molecule (1) of copper(II) 1-aminocyclohexanecarboxylate monohydrate. (b) Thermal-ellipsoid plot of molecule (2) of copper(II) 1-aminocyclohexanecarboxylate monohydrate.

pentacoordination of the Cu atom in molecule (1). The second water molecule, centered on O(10), is not associated with Cu(2). There are indications that the two water molecules form hydrogen bonds between the two molecules of the asymmetric unit, at 2.709 Å, and one forms a bond between ligands of molecules of adjacent asymmetric units, at 2.778 and 2.870 Å, with O—H...O angles of 167 to 176° (see Fig. 1).

The displacement of the structure of molecule (1) from the rectangular pyramid (r.p.) towards the trigonal bipyramid (t.b.p.) is similar to that observed in copper quinaldinate monohydrate (Haendler, 1986). The transition characteristics and parameters for these systems, based on the Berry intramolecular ligand-exchange process, have been discussed by Holmes (1984) and Holmes & Deiters (1977). Unequal bond character (N vs O) favors axial-equatorial sites of t.b.p., and bidentate ligands permit some freedom of motion, in contrast to more rigid polydentate ligands. A comparison of the nine dihedral angles with idealized values places the complex on the Berry coordinate line, at 44% displacement from r.p. Table 3 lists the characterization parameters for the four atomic motions.

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Structure of Azido(1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane)cobalt(II) Perchlorate

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Abstract. [Co(N₃)(C₁₄H₃₂N₄)]ClO₄, *M_r* = 456.83, orthorhombic, *Pna*2₁, *a* = 14.223 (6), *b* = 15.252 (4), *c* = 9.514 (3) Å, *V* = 2064 Å³, *Z* = 4, *D_x* = 1.47 g cm⁻³, Mo *K*α radiation, λ = 0.71069 Å, μ = 9.92 cm⁻¹, *F*(000) = 964, *T* = 295 K, *R* = 0.049, *wR*

Table 3. Characteristic Berry ligand displacement motions (°)

	Observed	Expected
N(1)—Cu(1)—N(3)	175.7	< 180
O(3)—Cu(1)—O(1)	154.8	> 120
O(3)—Cu(1)—O(9)	103.4	< 120
O(9)—Cu(1)—O(1)	101.9	< 120
δ ₂₄ *	20.3	0 < δ < 53.0

*δ₂₄ is the dihedral angle between the two faces of the t.b.p. that convert to the basal plane of the r.p.

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= 0.047, 2541 unique reflections. The structure consists of discrete [Co(tetramethylcyclam)(N₃)]⁺ cations and ClO₄⁻ anions, the former containing five-coordinate cobalt(II) intermediate in geometry between trigonal bipyramidal and square pyramidal with the azide ion in the apical position of the distorted square pyramid.