O(2)—Cu—O(*W*1)	96.7 (2)	C(2)—N(2)—C(3)	117.4 (6)
O(2)—Cu—N(1)	170.4 (2)	C(4^{i})—N(3)—C(5)	124.2 (6)
O(2)—Cu—N(2)	94.9 (2)	Cu—N(4)—C(6)	110.2 (5)
O(2)—Cu—N(4)	83.8 (2)	N(1)—C(1)—C(2)	113.4 (4)
O(*W*1)—Cu—N(1)	92.9 (2)	O(1)—C(2)—N(2)	126.8 (7)
O(*W*1)—Cu—N(2)	93.3 (2)	O(1)—C(2)—C(1)	117.9 (4)
O(*W*1)—Cu—N(4)	92.6 (2)	N(2)—C(2)—C(1)	115.3 (6)
N(1)—Cu—N(2)	85.3 (2)	N(2)—C(3)—C(4)	110.0 (4)
N(1)—Cu—N(4)	95.1 (2)	N(3^{i})—C(4)—C(3)	111.1 (5)
N(2)—Cu—N(4)	174.1 (2)	O(2)—C(5)—N(3)	123.0 (7)
Cu—O(2)—C(5)	114.7 (4)	O(2)—C(5)—C(6)	120.7 (5)
Cu—N(1)—C(1)	108.7 (4)	N(3)—C(5)—C(6)	116.3 (6)
Cu—N(2)—C(2)	116.0 (5)	N(4)—C(6)—C(5)	110.4 (6)
Cu—N(2)—C(3)	126.6 (3)		

Symmetry code: (i) $1 - x, 2 - y, -z$.

The structure was solved by direct and Fourier methods and refined by full-matrix least-squares techniques. H atoms were located by difference Fourier methods. *NRCVAX* (Gabe, Le Page, White & Lee, 1987) was used for all calculations.

The authors thank the National Science Council for support under grants NSC82-0208-M007-119 and NSC82-0208-M007-032. They are also indebted to Ms Shu-Fang Tung for collecting the X-ray diffraction data.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and bond distances and angles involving H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71690 (7 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AS1061]

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Acta Cryst. (1994). C**50**, 710–712

A Copper(II) Complex of the Deprotonated Anion of (2*R*,10*R*)-*N*,*N'*-Dialanylpropylenediamine

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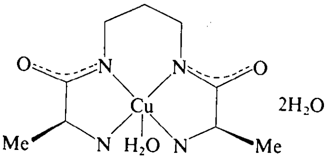
Abstract

The title compound, aqua[(2*R*,10*R*)-*N*,*N'*-dialanyl-κ^2N',N''-propylenediaminato(2 −)-κ^2N,N']copper(II) dihydrate, $[Cu(C_9H_{18}N_4O_2)(H_2O)].2H_2O$, in which two amide protons of (2*R*,10*R*)-*N*,*N'*-dialanylpropylenediamine are released, exists as a monomeric complex. The Cu^{II} ion is five-coordinate with distorted square-pyramidal geometry; the water O atom is in an axial position and two amine and two deprotonated amide N atoms are in equatorial positions. All three water molecules, two amine groups and two carbonyl O atoms participate in forming hydrogen bonds.

Comment

Potentiometric and spectrophotometric methods (Bai & Martell, 1969; Smith & Martell, 1972; Muir & Rechani, 1974; Armani, Marchelli, Dossena, Casasti & Dallavalle, 1986) have shown that in aqueous solution the Cu^{II} ion reacts with deprotonated diaminodiamide, $H_{-2}L$, to form the monomer chelate $[Cu(H_{-2}L)]$. Fawcett *et al.* (1980) have reported the crystal structure of $[Cu(2,3,2\text{-tet})(ClO_4)_2]$ (2,3,2-tet = 1,4,8,11-tetraazaundecane). In order to study the differences between amino and amide N atoms in the internal coordination center of 2,3,2-type structures, we prepared the title complex (I), the structure of which has been predicted by Armani, Marchelli, Dossena, Casasti & Dallarelle (1986).



(I)

The ligand (2*R*,10*R*)-*N*,*N*′-dialanylpropylenediamine was prepared as described by Armani, Marchelli, Dossena, Casasti & Dallaralle (1986). A solution of $Cu(ClO_4)_2.6H_2O$ (0.01 mol in 100 ml H_2O) was added dropwise to an aqueous solution of the ligand (0.01 mol in 200 ml H_2O). The solution changed gradually from purple to blue and was stirred continuously for another 10 min. After the addition of a solution of sodium hydroxide (0.02 mol in 50 ml H_2O), a green participate formed which was then filtered off. The resulting dark red filtrate was passed through an anion exchange column (amberlite IR400, OH^- form) and evaporated to dryness. The single crystal was recrystallized from aqueous solution.

The coordination geometry about the Cu^{II} ions is a distorted square pyramid with the bonded water O atom in an axial position and the two amine and deprotonated amide N atoms in equatorial positions. The Cu–water O atom distance is in good agreement with the usual Cu–axial O-atom distances in Cu^{II} complexes with macrocyclic ligands. An analysis of the Cu—O distances in 166 Cu^{II} complexes using the Cambridge Structural Database (Allen, Kennard & Taylor, 1983) shows that these distances are within the wide range 1.9–2.8 Å, with one sharp peak at *ca* 1.9–2.0 Å for equatorial bonds and one wide peak with a maximum at 2.4 Å for axial bonds.

The Cu—N(amine) and Cu—N(amide) distances of 1.945 (7)–2.014 (7) Å are typical for copper complexes (Lu, Chung & Ashida, 1991). The Cu—N(deprotonated amide) distances are slightly shorter than the Cu—N(amine) distances. The difference between Cu—N(amine) and Cu—N(deprotonated amide) distances has been seen in earlier reports (Diaddario, Robinson & Margerum, 1983; Belokon *et al.*, 1985). The C—O and C—N bond lengths in the amide groups span narrower ranges. The two five-membered chelate rings exhibit skew forms. Thus, the crystal consists of two kinds of Cu^{II} complex, which differ only by the conformation of the central six-membered chelate ring. In the molecule containing the propylene C atom at position C(5), this chelate ring is in a distorted boat form while in the molecule containing the propylene C atom at position C(5′), this chelate ring is in a distorted chair form. The structure of the title complex consists of a five-coordinate Cu^{II} monomer with a four N and one O-atom ligand donor set, while $[Cu(2,3,2\text{-tet})(ClO_4)_2]$ consists of a six-coordinate monomer with a four N and two O-atom ligand donor set. Owing to the existence of the resonance form of the internal amide group, the *trans* N—Cu—N angles and the bond lengths of the title complex are significantly less than those of $[Cu(2,3,2\text{-tet})(ClO_4)_2]$. All three water molecules, the two amino groups and the two carbonyl O atoms participate in forming hydrogen bonds.

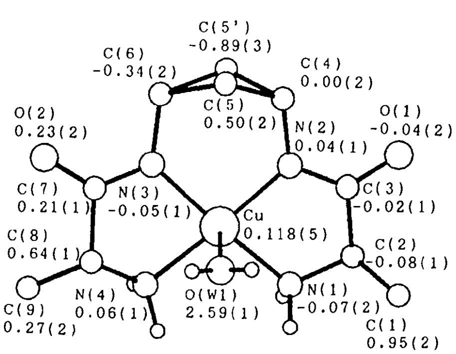


Fig. 1. A perspective view of the molecular structure with the atom-numbering scheme, excluding the non-bonded water molecules and the H atoms attached to the C atoms. The displacements (Å) from the best planes formed by the atoms N(1), N(2), N(3) and N(4) are indicated.

Experimental

Crystal data

$[Cu(C_9H_{18}N_4O_2)(H_2O)].2H_2O$
M_r = 331.86
Orthorhombic
$P2_12 2_1$
a = 7.656 (3) Å
b = 12.020 (2) Å
c = 15.890 (1) Å
V = 1462.3 (6) Å^3
Z = 4
D_x = 1.507 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.7107 Å
Cell parameters from 25 reflections
θ = 6.33 - 15.2°
μ = 1.52 mm^{-1}
T = 298 (3) K
Hexagonal plate
0.34 × 0.31 × 0.25 mm
Reddish violet

Data collection

Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: empirical (North, Phillips & Mathews, 1968)
T_{min} = 0.916, T_{max} = 0.998
2428 measured reflections
2428 independent reflections

1615 observed reflections $[I \geq 2.5\sigma(I)]$
θ_{max} = 29.9°
$h = 0 \rightarrow 10$
$k = 0 \rightarrow 16$
$l = 0 \rightarrow 22$
3 standard reflections
frequency: 60 min
intensity variation: ±0.5%

Refinement

Refinement on F
R = 0.043
wR = 0.047
S = 0.74
1615 reflections
191 parameters
H-atom parameters not refined
Unit weights applied
$(\Delta/\sigma)_{max}$ = 0.133

$\Delta\rho_{max}$ = 0.58 e Å^{-3}
$\Delta\rho_{min}$ = −0.36 e Å^{-3}
Extinction correction: Zachariasen (1967)
Extinction coefficient: 0.48 (2)
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$

	Occupancy	*x*	*y*	*z*	B_{eq}
Cu	1.0	0.67671 (11)	0.24621 (9)	0.23119 (4)	2.65 (3)
O(1)	1.0	0.6742 (10)	0.5579 (4)	0.3253 (4)	3.9 (3)
O(2)	1.0	0.7507 (8)	−0.0618 (4)	0.3243 (4)	3.3 (2)
O(*W*1)	1.0	0.9884 (7)	0.2475 (6)	0.1890 (3)	4.5 (3)
O(*W*2)	1.0	0.6861 (12)	−0.1365 (5)	0.4856 (4)	4.6 (3)
O(*W*3)	0.6	0.632 (3)	−0.3737 (11)	0.4831 (11)	6.4 (8)
O(*W*3′)	0.4	0.784 (3)	−0.3511 (15)	0.4749 (14)	5.5 (10)
N(1)	1.0	0.6105 (15)	0.3684 (6)	0.1511 (5)	4.8 (4)
N(2)	1.0	0.6924 (11)	0.3675 (5)	0.3119 (5)	2.6 (3)
N(3)	1.0	0.6955 (12)	0.1264 (5)	0.3130 (5)	2.8 (3)
N(4)	1.0	0.6439 (13)	0.1170 (5)	0.1521 (4)	3.1 (3)
C(1)	1.0	0.7304 (17)	0.5584 (8)	0.1434 (7)	5.4 (5)
C(2)	1.0	0.6182 (10)	0.4781 (6)	0.1896 (5)	2.9 (3)
C(3)	1.0	0.6653 (11)	0.4686 (6)	0.2830 (5)	2.7 (3)
C(4)	1.0	0.7244 (17)	0.3542 (8)	0.4016 (6)	3.7 (4)
C(5)	0.6	0.8080 (18)	0.2530 (14)	0.4253 (6)	3.7 (5)
C(5′)	0.4	0.626 (2)	0.254 (2)	0.4347 (9)	3.3 (7)
C(6)	1.0	0.6953 (19)	0.1395 (7)	0.4058 (6)	3.8 (4)
C(7)	1.0	0.7248 (11)	0.0271 (6)	0.2834 (5)	2.6 (3)
C(8)	1.0	0.7423 (10)	0.0225 (5)	0.1871 (4)	2.6 (3)
C(9)	1.0	0.6847 (16)	−0.0883 (6)	0.1496 (5)	3.7 (3)

Table 2. *Selected geometric parameters* (Å, °)

Cu—O(*W*1)	2.479 (5)	N(3)—C(7)	1.303 (9)
Cu—N(1)	2.008 (8)	N(4)—C(8)	1.47 (1)
Cu—N(2)	1.946 (7)	C(1)—C(2)	1.49 (1)
Cu—N(3)	1.945 (7)	C(2)—C(3)	1.53 (1)
Cu—N(4)	2.014 (7)	C(4)—C(5)	1.43 (2)
O(1)—C(3)	1.269 (9)	C(4)—C(5′)	1.51 (3)
O(2)—C(7)	1.267 (9)	C(5)—C(6)	1.64 (2)
N(1)—C(2)	1.46 (1)	C(5′)—C(6)	1.55 (3)
N(2)—C(3)	1.315 (9)	C(7)—C(8)	1.54 (1)
N(2)—C(4)	1.46 (1)	C(8)—C(9)	1.52 (1)
N(3)—C(6)	1.48 (1)		
O(*W*1)—Cu—N(1)	93.8 (4)	N(1)—C(2)—C(1)	113.9 (7)
O(*W*1)—Cu—N(2)	96.6 (3)	N(1)—C(2)—C(3)	110.4 (6)
O(*W*1)—Cu—N(3)	96.6 (3)	C(1)—C(2)—C(3)	113.0 (7)
O(*W*1)—Cu—N(4)	87.5 (3)	O(1)—C(3)—N(2)	126.0 (8)
N(1)—Cu—N(2)	83.4 (3)	O(1)—C(3)—C(2)	117.6 (6)
N(1)—Cu—N(3)	169.6 (4)	N(2)—C(3)—C(2)	116.4 (7)
N(1)—Cu—N(4)	97.9 (3)	N(2)—C(4)—C(5)	115.4 (8)
N(2)—Cu—N(3)	96.3 (3)	N(2)—C(4)—C(5′)	110.2 (9)
N(2)—Cu—N(4)	175.7 (4)	C(4)—C(5)—C(6)	115 (1)
N(3)—Cu—N(4)	81.7 (3)	C(4)—C(5′)—C(6)	116 (1)
Cu—N(1)—C(2)	112.7 (5)	N(3)—C(6)—C(5)	106.0 (8)
Cu—N(2)—C(3)	116.9 (6)	N(3)—C(6)—C(5′)	113.0 (8)
Cu—N(2)—C(4)	125.0 (5)	O(2)—C(7)—N(3)	127.9 (7)
C(3)—N(2)—C(4)	118.1 (7)	O(2)—C(7)—C(8)	117.9 (6)
Cu—N(3)—C(6)	125.9 (5)	N(3)—C(7)—C(8)	114.0 (6)
Cu—N(3)—C(7)	116.7 (6)	N(4)—C(8)—C(7)	107.7 (6)
C(6)—N(3)—C(7)	117.2 (7)	N(4)—C(8)—C(9)	112.2 (7)
Cu—N(4)—C(8)	107.2 (5)	C(7)—C(8)—C(9)	113.3 (6)

The structure was solved by direct and Fourier methods and refined by full-matrix least-squares techniques. H atoms were located by difference Fourier methods. Eight H atoms attached to C(4), C(5), C(5′), C(6), O(*W*3) and O(*W*3′) could not be located because of disorder. *NRCVAX* (Gabe, Le Page, White & Lee, 1987) was used for all calculations.

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Trichloro(1,4,7-trithiacyclononane-*S*,*S*′,*S*″)iron(III), $[FeCl_3(C_6H_{12}S_3)]$

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Abstract

The crystal structure of red trichloro(1,4,7-trithiacyclononane-*S*,*S*′,*S*″)iron(III), $[FeCl_3(C_6H_{12}S_3)]$, containing a distorted octahedral high-spin $[Fe^{III}Cl_3S_3]$ core, is reported. The structure of $[FeCl_3(C_6H_{12}S_3)]$ consists of discrete molecules containing six-coordinate Fe atoms. The three chlorides range in distance from the Fe atom from

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