Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71752 (11 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AB1092]

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A Binuclear Copper(II) Complex of the Deprotonated Anion of *N*,*N*′-Diglycylethylenediamine

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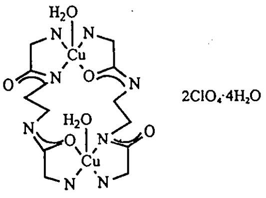
Abstract

The title compound, diaquabis[μ-*N*,*N*′-diglycylethylenediaminato(1 −)]-1κ^2*N*,*N*″:2κ*N*′,κO′;1κ*N*′,-κ*O*′:2κ^2*N*,*N*″-dicopper(II) diperchlorate tetrahydrate, $[Cu_2(C_6H_{13}N_4O_2)_2(H_2O)_2]2ClO_4.4H_2O$, in which only one of the two amide protons of each *N*,*N*′-diglycylethylenediamine is released in solution, exists as a binuclear complex with inversion symmetry in the solid state. Each Cu^{II} ion is five-coordinate with a distorted square-pyramidal geometry. Two donar N atoms of one tetradentate ligand and one N atom and one O atom of the other ligand form a slightly distorted plane and a water O atom occupies the axial position. Hydrogen bonds help stabilize the crystal structure.

Comment

It has been shown by potentiometric and spectrophotometric methods (Bai & Martell, 1969; Smith & Martell, 1972; Muir & Rechani, 1974; Armani, Marchelli, Dossena, Casasti & Dallavalle, 1986) that in solution the Cu^{II} ion reacts with deprotonated diaminodiamide, $H_{-1}L$, to form the binuclear chelate $[Cu_2(H_{-1}L)_2]^{2+}$. Previously, we have studied the binuclear complex formed by Cu with a diaminodiamide ligand containing terminal propyl groups (Tahirov, Lu, Shu & Chung, 1994). In order to study the steric effects governing the differences between the two crystal structures, we prepared the title binuclear complex (I), the structure of which has been predicted by Smith & Martell (1972).



(I)

The ligand, *N*,*N*′-diglycylethylenediamine, was prepared as described by Goto, Okubo, Sawai & Yoshikawa (1970). A solution of $Cu(ClO_4)_2.6H_2O$ (0.01 mol in 100 ml water) was added dropwise to an aqueous solution of the ligand (0.01 mol in 100 ml water). The solution changed gradually from purple to blue and was stirred continuously for another 10 min. After adding sodium hydroxide (0.02 mol in 50 ml water), the solution changed from blue to dark red and was then filtered. The dark red filtrate was evaporated to dryness and recrystallized from an aqueous methanol solution.

The coordination geometry about each of the two Cu^{II} ions is a distorted square pyramid with a water O atom in the axial position, and two amine N atoms, one deprotonated amide N atom and an amide O atom in equatorial positions. The Cu^{II} ion deviates by 0.14 Å from the equatorial best plane towards the axial water O atom. Cu–water O-atom distances are 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.

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The Cu–ligand bond distances are typical for copper complexes (Lu, Chung & Ashida, 1991). 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. This binuclear compound has an inversion symmetry. The two five-membered chelate rings containing the Cu atom exhibit skew forms. The distance between the two Cu^{II} ions is far too large for bonding interactions. All three water molecules, two amino groups, one NH group, one carbonyl O atom and three perchlorate O atoms participate in forming the hydrogen bonds which help stabilize the crystal structure.

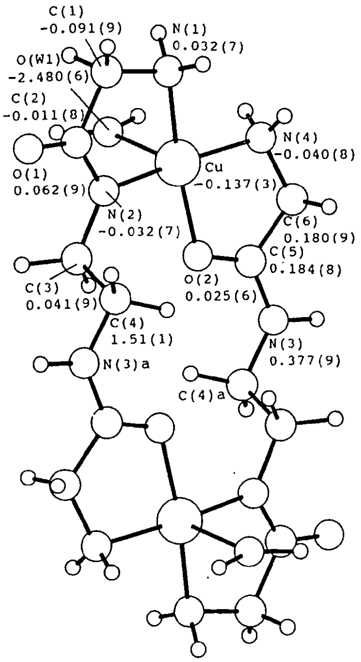

Fig. 1. A perspective view of the molecular structure with the atom-numbering scheme, excluding the perchlorate groups and the non-bonded water molecules. The displacements (Å) from the best planes formed by the atoms O(2), N(1), N(2) and N(4) for the molecule around one nucleus are indicated. The other nucleus is centrosymmetrically related to the one labeled.

Experimental

Crystal data

$[Cu_2(C_6H_{13}N_4O_2)_2(H_2O)_2]$-$(ClO_4)_2.4H_2O$
M_r = 780.47
Monoclinic
$P2_1/n$
a = 7.321 (1) Å
b = 9.786 (1) Å
c = 20.803 (2) Å
β = 90.63 (1)°
V = 1490.3 (3) Å^3
Z = 2

D_x = 1.739 Mg m^{-3}
Mo $K\alpha$ radiation
λ = 0.7107 Å
Cell parameters from 25 reflections
θ = 7.46 - 18.49°
μ = 1.70 mm^{-1}
T = 298 (3) K
Rectangular parallelepiped
0.26 × 0.25 × 0.22 mm
Blue

Data collection

Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: empirical (North, Phillips & Mathews, 1968)
T_{min} = 0.927, T_{max} = 0.998
2358 measured reflections
2358 independent reflections

1424 observed reflections [$I \geq 2.5\sigma(I)$]
θ_{max} = 29.9°
h = 0 → 10
k = 0 → 13
l = 0 → 29
3 standard reflections
frequency: 60 min
intensity variation: ±0.5%

Refinement

Refinement on F
R = 0.038
wR = 0.038
S = 0.64
1424 reflections
191 parameters
H-atom parameters not refined
Unit weights applied
$(\Delta/\sigma)_{max}$ = 0.041

$\Delta\rho_{max}$ = 0.24 e Å^{-3}
$\Delta\rho_{min}$ = −0.27 e Å^{-3}
Extinction correction: Zachariasen (1967)
Extinction coefficient: 0.36 (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)

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

	x	y	z	B_{eq}
Cu	0.35272 (11)	0.74669 (7)	0.10924 (3)	2.56 (3)
Cl	0.5919 (3)	0.06513 (18)	0.20691 (11)	3.84 (9)
O(1)	0.7749 (6)	0.5102 (4)	0.0582 (2)	3.2 (2)
O(2)	0.3056 (6)	0.9064 (4)	0.0534 (2)	2.9 (2)
O(3)	0.5081 (10)	0.1314 (6)	0.1545 (3)	8.4 (5)
O(4)	0.7582 (9)	0.1252 (7)	0.2198 (3)	7.8 (4)
O(5)	0.4859 (13)	0.0788 (7)	0.2627 (4)	7.1 (6)
O(6)	0.6172 (13)	−0.0748 (6)	0.1918 (4)	9.4 (7)
O(*W*1)	0.1401 (7)	0.6001 (5)	0.0600 (3)	4.8 (3)
O(*W*2)	0.9166 (7)	0.2851 (4)	0.1163 (3)	4.5 (3)
O(*W*3)	0.2251 (8)	0.3226 (5)	0.2004 (3)	5.5 (3)
N(1)	0.4288 (7)	0.6054 (4)	0.1740 (2)	2.9 (2)
N(2)	0.5546 (7)	0.6782 (4)	0.0588 (2)	2.3 (2)
N(3)	0.1546 (7)	1.1069 (4)	0.0459 (3)	2.8 (2)
N(4)	0.1608 (8)	0.8327 (4)	0.1653 (3)	3.1 (3)
C(1)	0.5669 (10)	0.5158 (6)	0.1448 (3)	3.3 (3)
C(2)	0.6409 (8)	0.5704 (5)	0.0824 (3)	2.5 (3)
C(3)	0.6201 (9)	0.7343 (5)	−0.0010 (3)	3.0 (3)
C(4)	0.7618 (9)	0.8470 (5)	0.0127 (3)	3.0 (3)
C(5)	0.1957 (8)	0.9904 (5)	0.0753 (3)	2.6 (3)
C(6)	0.1025 (9)	0.9646 (5)	0.1382 (3)	3.1 (3)

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

Cu—O(2)	1.975 (3)	N(2)—C(2)	1.322 (6)
Cu—O(*W*1)	2.344 (4)	N(2)—C(3)	1.446 (9)
Cu—N(1)	2.005 (4)	N(3)—C(4^{i})	1.44 (1)
Cu—N(2)	1.941 (6)	N(3)—C(5)	1.327 (6)
Cu—N(4)	2.019 (7)	N(4)—C(6)	1.470 (6)
O(1)—C(2)	1.254 (9)	C(1)—C(2)	1.51 (1)
O(2)—C(5)	1.240 (8)	C(3)—C(4)	1.538 (8)
N(1)—C(1)	1.474 (9)	C(5)—C(6)	1.50 (1)

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.

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

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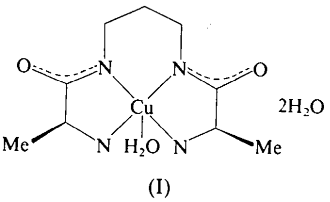
Abstract

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)

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