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A Dinuclear Copper(II) Complex of Deprotonated *N*,*N*′-Bis(*N*-propylglycyl)ethylenediamine

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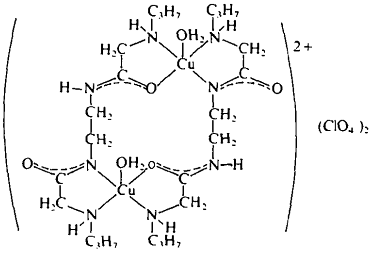
Abstract

In the title crystal of bis[μ-*N*,*N*′-bis(*N*-propylglycyl-κN)ethylenediaminato-κN:$\kappa O'$]bis[aquacopper(II)] diperchlorate, $[Cu_2(C_{12}H_{25}N_4O_2)_2(H_2O)_2](ClO_4)_2$, the cation exists as a dinuclear complex. Each Cu^{II} ion is pentacoordinated in a distorted square-pyramid conformation: two donor N atoms of one tetradentate ligand and one N atom and one O atom of the other ligand form a slightly distorted equatorial plane and a water O atom occupies the axial position.

Comment

In aqueous solution, the Cu^{II} ion reacts with a deprotonated diaminodiamide, $H_{-1}L$, to form the dinuclear chelate $[Cu_2(H_{-1}L)_2]^{2+}$ [(I), $H_{-1}L$ is deprotonated *N*,*N*′-bis(*N*-propylglycyl)ethylenediamine] (Bai & Martell, 1969; Smith & Martell, 1972; Muir & Rechani, 1974; Armani, Marchelli, Dossena, Casnati & Dallavalle, 1986). It is of interest to study the crystal structure of this type of dinuclear species.



(I)

The ligand was prepared as described by Goto, Okubo, Sawai & Yoshikawa (1970). After a solution of its dihydrochloride (3.31 g, 0.01 mol) in water (100 ml) was passed through an anion-exchange column (amberlite IR400, OH^- form), a solution of $Cu(ClO_4)_2.6H_2O$ (3.73 g, 0.01 mol) in water (100 ml) was added dropwise. The solution changed colour gradually from purple to blue during the dropwise addition and was stirred continuously for another 10 min whereupon green precipitates formed. On adding sodium hydroxide (0.8 g, 0.02 mol) in water (50 ml), the colour changed to dark red. The filtrate was recrystallized from methanol–water solution.

The coordination geometry about each Cu ion is distorted square pyramidal with a water O atom in an axial position, and two amine and one deprotonated amide N atom and an amide O atom in equatorial positions. The equatorial atoms about the Cu(2) atom lie in a plane, but the equatorial atoms about Cu(1) undergo a slight tetrahedral distortion with the largest deviation from the least-squares plane being 0.126 (9) Å. The deviation of Cu from the plane in the direction of the axial water O atom

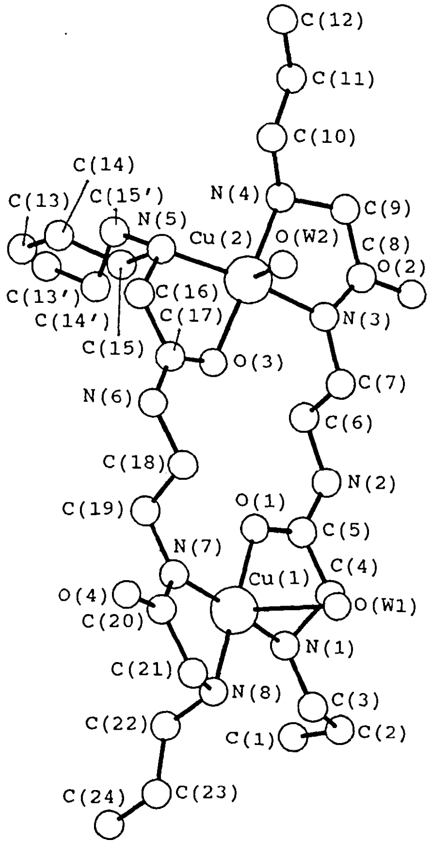


Fig. 1. A perspective view of the molecular structure of the title complex with the atom-numbering scheme excluding the H atoms and the perchlorate groups.

is 0.072 (3) Å for Cu(1) and 0.124 (3) Å for Cu(2). The Cu—O(water) distances are in good agreement with usual Cu—O(axial) distances in Cu^{II} complexes involving macrocyclic ligands. An analysis of the Cu—O distance in 166 Cu^{II} complexes in the Cambridge Structural Database shows that these distances are in the range 1.9–2.8 Å, with one sharp peak at about 1.9–2.0 Å for equatorial bonds and one wide peak with a maximum at about 2.4 Å for axial bonds. The sixth ligand site of Cu(1) is occupied by O(23) of a perchlorate anion at 2.98 Å distance, while that of Cu(2) is blocked by a disordered *N*-propyl group that has two conformations.

The Cu—N(amine) distances of 2.020 (6)–2.040 (5) Å, Cu—N(amide) distances of 1.917 (5)–1.929 (5) Å and Cu—O(amide) distances of 1.976 (4)–1.999 (4) Å are typical for Cu complexes (Lu, Chung & Ashida, 1991; Mitsui, Iitaka & Sakaguchi, 1976; Soldánová, Pavelčik & Majer, 1981). The C—O and C—N bond lengths in the amide groups are in the narrow ranges 1.264 (7)–1.271 (7) and 1.303 (8)–1.316 (8) Å, respectively. Each of the four amide groups is planar to within ±0.04 (1) Å. The compound has 1*RS*, 4*SR*, 5*SR*, 8*RS* configurations at the chiral N centres. The two five-membered chelate rings containing Cu(1) exhibit stable skew forms, but the two five-membered chelate rings containing Cu(2) have unstable distorted eclipsed forms. The distance between the two Cu^{II} ions is 7.020 (2) Å.

Experimental

Crystal data

$[Cu_2(C_{12}H_{25}N_4O_2)_2(H_2O)_2]$-
$(ClO_4)_2$
$M_r = 876.784$
Monoclinic
$P2_1/n$
$a = 9.454\ (1)$ Å
$b = 27.61\ (1)$ Å
$c = 14.762\ (3)$ Å
$\beta = 94.26\ (1)°$
$V = 3843\ (2)$ Å^3
$Z = 4$

$D_x = 1.516$ Mg m^{-3}
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 5.44$–$19.99°$
$\mu = 1.32$ mm^{-1}
$T = 298\ (3)$ K
Parallelepiped
0.50 × 0.45 × 0.38 mm
Blue-violet

Data collection

Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: empirical (North, Phillips & Mathews, 1968)
$T_{min} = 0.692$, $T_{max} = 0.695$
7012 measured reflections
6740 independent reflections

4465 observed reflections [$I \geq 2.5\sigma(I)$]
$R_{int} = 0.053$
$\theta_{max} = 24.9°$
$h = -11 \rightarrow 11$
$k = 0 \rightarrow 32$
$l = 0 \rightarrow 17$
3 standard reflections
frequency: 60 min
intensity variation: ±2%

Refinement

Refinement on F
$R = 0.058$
$wR = 0.061$
$S = 1.77$
4465 reflections
525 parameters
Only H-atom U's refined
Unit weights applied

$(\Delta/\sigma)_{max} = 0.938$
$\Delta\rho_{max} = 0.77$ e Å^{-3}
$\Delta\rho_{min} = -0.92$ e Å^{-3}
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)

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

	x	y	z	B_{eq}
Cu(1)	0.95915 (8)	0.14313 (4)	0.93332 (5)	3.31 (4)
Cu(2)	0.73817 (8)	0.08919 (3)	0.4800 (5)	2.83 (4)
Cl(1)	1.0435 (3)	0.03734 (9)	1.21825 (16)	5.34 (11)
Cl(2)	0.4172 (3)	0.20397 (11)	0.4214 (2)	6.85 (14)
O(1)	0.8217 (4)	0.1405 (2)	0.8258 (3)	3.8 (2)
O(2)	0.3534 (4)	0.0566 (2)	0.5571 (3)	4.0 (2)
O(3)	0.8779 (4)	0.1064 (2)	0.5833 (3)	3.6 (2)
O(4)	1.3548 (5)	0.1122 (2)	0.8793 (4)	5.3 (3)
O(*W*1)	0.8938 (7)	0.0573 (3)	0.9710 (5)	6.8 (4)
O(*W*2)	0.8408 (6)	0.0120 (3)	0.4789 (6)	6.9 (4)
O(11)	1.0171 (15)	0.0196 (3)	1.3002 (5)	13.5 (8)
O(12)	1.040 (2)	0.0847 (4)	1.2195 (8)	19.6 (13)
O(13)	1.1483 (13)	0.0182 (6)	1.1773 (10)	18.4 (10)
O(14)	0.9411 (15)	0.0209 (6)	1.1542 (8)	17.6 (11)
O(21)	0.4617 (16)	0.1812 (4)	0.3436 (8)	16.0 (9)
O(22)	0.5029 (17)	0.1937 (5)	0.4932 (8)	17.4 (10)
O(23)	0.4117 (18)	0.2509 (4)	0.4082 (8)	17.6 (11)
O(24)	0.2987 (17)	0.1888 (9)	0.4271 (19)	33 (2)
N(1)	0.7843 (5)	0.1636 (2)	0.9969 (4)	3.3 (3)
N(2)	0.5881 (6)	0.1313 (3)	0.7859 (4)	4.4 (3)
N(3)	0.5888 (5)	0.0748 (2)	0.5581 (4)	3.4 (3)
N(4)	0.5858 (6)	0.0800 (3)	0.3772 (4)	3.8 (3)
N(5)	0.8963 (6)	0.1139 (3)	0.4060 (4)	3.8 (3)
N(6)	1.1128 (5)	0.1016 (2)	0.6206 (4)	3.5 (3)
N(7)	1.1218 (5)	0.1366 (3)	0.8640 (4)	3.5 (3)
N(8)	1.1040 (5)	0.1429 (3)	1.0410 (4)	3.7 (3)
C(1)	0.6441 (17)	0.2360 (6)	1.12065 (11)	10.5 (9)
C(2)	0.6483 (9)	0.1832 (5)	1.1316 (6)	6.0 (5)
C(3)	0.7766 (8)	0.1590 (4)	1.0932 (5)	4.8 (4)
C(4)	0.6625 (7)	0.1408 (3)	0.9434 (5)	4.2 (4)
C(5)	0.6946 (7)	0.1372 (3)	0.8465 (5)	3.7 (3)
C(6)	0.5989 (7)	0.1277 (3)	0.6877 (5)	4.0 (4)
C(7)	0.6031 (7)	0.0762 (3)	0.6583 (5)	3.9 (4)
C(8)	0.4643 (6)	0.0651 (3)	0.5162 (4)	3.0 (3)
C(9)	0.4573 (6)	0.0611 (3)	0.4165 (4)	3.4 (3)
C(10)	0.6183 (7)	0.0565 (3)	0.2941 (5)	4.2 (4)
C(11)	0.5078 (9)	0.0535 (4)	0.2174 (6)	5.6 (5)
C(12)	0.5489 (12)	0.0281 (5)	0.1355 (7)	7.7 (7)
C(13)†	0.906 (4)	0.2564 (15)	0.344 (3)	6.6 (16)
C(13′)†	0.873 (3)	0.2489 (12)	0.377 (2)	7.4 (15)
C(14)†	0.943 (2)	0.2009 (10)	0.3440 (15)	5.3 (11)
C(14′)†	0.8843 (19)	0.2001 (7)	0.4275 (15)	5.7 (10)
C(15)†	0.857 (2)	0.1748 (10)	0.408 (2)	3.8 (12)
C(15′)†	0.8926 (15)	0.15863 (6)	0.3614 (10)	3.9 (7)
C(16)	1.0309 (7)	0.1057 (3)	0.4621 (4)	3.5 (3)
C(17)	1.0045 (6)	0.1046 (3)	0.5610 (4)	3.0 (3)
C(18)	1.1012 (7)	0.0960 (3)	0.7186 (5)	3.5 (3)
C(19)	1.1239 (7)	0.1435 (3)	0.7655 (5)	3.6 (3)
C(20)	1.2373 (7)	0.1219 (3)	0.9108 (5)	3.8 (4)
C(21)	1.2263 (7)	0.1152 (3)	1.0109 (5)	4.3 (4)
C(22)	1.1401 (8)	0.1927 (3)	1.0679 (6)	4.6 (4)
C(23)	1.2217 (10)	0.1976 (4)	1.1601 (6)	5.5 (4)
C(24)	1.2431 (14)	0.2507 (4)	1.1829 (9)	7.8 (6)

† Occupancies of 0.4 for C(13), C(14) and C(15), and 0.6 for C(13′), C(14′) and C(15′).

Table 2. *Selected bond lengths* (Å), *bond angles* (°) *and hydrogen-bond lengths* (Å)

Cu(1)—O(1)	1.976 (4)	N(4)—C(9)	1.480 (8)
Cu(1)—O(*W*1)	2.521 (7)	N(4)—C(10)	1.442 (9)
Cu(1)—N(1)	2.040 (5)	N(5)—C(15)	1.72 (3)
Cu(1)—N(7)	1.917 (5)	N(5)—C(15′)	1.40 (2)
Cu(1)—N(8)	2.020 (6)	N(5)—C(16)	1.483 (9)
Cu(2)—O(3)	1.999 (4)	N(6)—C(17)	1.303 (8)
Cu(2)—O(*W*2)	2.342 (7)	N(6)—C(18)	1.467 (9)
Cu(2)—N(3)	1.929 (5)	N(7)—C(19)	1.468 (9)
Cu(2)—N(4)	2.029 (6)	N(7)—C(20)	1.313 (9)
Cu(2)—N(5)	2.033 (6)	N(8)—C(21)	1.481 (9)
O(1)—C(5)	1.264 (7)	N(8)—C(22)	1.46 (1)
O(2)—C(8)	1.271 (7)	C(4)—C(5)	1.49 (1)
O(3)—C(17)	1.265 (7)	C(6)—C(7)	1.49 (1)
O(4)—C(20)	1.266 (8)	C(8)—C(9)	1.472 (9)
N(1)—C(3)	1.435 (9)	C(16)—C(17)	1.500 (9)
N(1)—C(4)	1.488 (9)	C(18)—C(19)	1.49 (1)
N(2)—C(5)	1.307 (9)	C(20)—C(21)	1.50 (1)
N(2)—C(6)	1.465 (9)	C(22)—C(23)	1.52 (1)
N(3)—C(7)	1.476 (9)	C(23)—C(24)	1.51 (2)
N(3)—C(8)	1.316 (8)		
O(1)—Cu(1)—O(*W*1)	89.2 (2)	O(1)—C(5)—N(2)	122.8 (6)
O(1)—Cu(1)—N(1)	82.7 (2)	O(1)—C(5)—C(4)	119.6 (6)
O(1)—Cu(1)—N(7)	94.2 (2)	N(2)—C(5)—C(4)	117.6 (6)
O(1)—Cu(1)—N(8)	177.3 (2)	N(2)—C(6)—C(7)	111.0 (7)
O(*W*1)—Cu(1)—N(1)	86.5 (2)	N(3)—C(7)—C(6)	108.4 (6)
O(*W*1)—Cu(1)—N(7)	104.4 (3)	O(2)—C(8)—N(3)	123.7 (6)
O(*W*1)—Cu(1)—N(8)	89.2 (3)	O(2)—C(8)—C(9)	118.9 (6)
N(1)—Cu(1)—N(7)	168.6 (3)	N(3)—C(8)—C(9)	117.2 (5)
N(1)—Cu(1)—N(8)	99.4 (2)	N(4)—C(9)—C(8)	112.8 (5)
N(7)—Cu(1)—N(8)	84.0 (2)	Cu(1)—O(1)—C(5)	112.9 (4)
O(3)—Cu(2)—O(*W*2)	88.3 (3)	Cu(2)—O(3)—C(17)	112.1 (4)
O(3)—Cu(2)—N(3)	93.7 (2)	Cu(1)—N(1)—C(3)	122.3 (5)
O(3)—Cu(2)—N(4)	172.9 (3)	Cu(1)—N(1)—C(4)	105.1 (4)
O(3)—Cu(2)—N(5)	81.9 (2)	C(3)—N(1)—C(4)	113.2 (6)
O(*W*2)—Cu(2)—N(3)	98.0 (3)	C(5)—N(2)—C(6)	125.4 (5)
O(*W*2)—Cu(2)—N(4)	98.8 (3)	Cu(2)—N(3)—C(7)	125.2 (4)
O(*W*2)—Cu(2)—N(5)	88.8 (3)	Cu(2)—N(3)—C(8)	115.5 (4)
N(3)—Cu(2)—N(4)	84.9{2)	C(7)—N(3)—C(8)	119.2 (5)
N(3)—Cu(2)—N(5)	171.8 (3)	Cu(2)—N(4)—C(9)	108.0 (4)
N(4)—Cu(2)—N(5)	98.6 (2)	Cu(2)—N(4)—C(10)	120.6 (4)
C(9)—N(4)—C(10)	114.0 (6)	N(5)—C(16)—C(17)	110.4 (5)
Cu(2)—N(5)—C(16)	106.5 (4)	O(3)—C(17)—N(6)	122.6 (6)
C(17)—N(6)—C(18)	124.1 (5)	O(3)—C(17)—C(16)	118.8 (6)
Cu(1)—N(7)—C(19)	126.0 (4)	N(6)—C(17)—C(16)	118.6 (5)
Cu(1)—N(7)—C(20)	114.6 (4)	N(6)—C(18)—C(19)	110.3 (6)
C(19)—N(7)—C(20)	119.3 (5)	N(7)—C(19)—C(18)	109.6 (6)
Cu(1)—N(8)—C(21)	105.3 (4)	O(4)—C(20)—N(7)	126.2 (7)
Cu(1)—N(8)—C(22)	109.9 (5)	O(4)—C(20)—C(21)	117.6 (6)
C(21)—N(8)—C(22)	113.2 (6)	N(7)—C(20)—C(21)	116.2 (6)
N(1)—C(4)—C(5)	109.4 (5)	N(8)—C(21)—C(20)	110.1 (6)
D—H···*A*	*D*···*A*	*D*—H···*A*	*D*···*A*
O(*W*1)—H(*W*11)···O(13^{i})	3.03 (2)	N(2)—H(N2)···O(4^{v})	2.736 (7)
O(*W*1)—H(*W*12)···O(14)	2.89 (1)	N(4)—H(N4)···O(21)	3.06 (1)
O(*W*2)—H(*W*22)···O(2^{ii})	2.663 (8)	N(6)—H(N6)···O(2^{vi})	2.813 (7)
O(*W*2)—H(*W*21)···O(*W*2^{iii})	3.10 (1)	N(8)—H(N8)···O(12)	3.18 (1)
N(1)—H(N1)···O(23^{iv})	2.99 (1)		

Symmetry codes: (i) $2 - x, -y, 2 - z$; (ii) $1 - x, -y, 1 - z$; (iii) $2 - x, -y, 1 - z$; (iv) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$; (v) $x - 1, y, z$; (vi) $1 + x, y, z$.

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

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Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71490 (15 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AS1044]

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Tris(2-pyridinethiolato)(*p*-tolyl)tin(IV), $[Sn(C_5H_4NS)_3(C_7H_7)]$

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Abstract

In the title compound three bidentate 2-pyridinethiolato ligands (2-SPy) together with *p*-tolyl form a distorted pentagonal bipyramid around Sn. Two S atoms and three N atoms form the pentagonal plane. One S and the C(*p*-tolyl) atom are in the axial positions. The distortion of the molecule is explicated by the axial S—Sn—C angle of 156.0 (3)° and by the distance of 0.635 (7) Å of one of the N atoms from the pentagonal plane. The Sn—S distances in the plane are longer [2.571 (3) Å] than the axial Sn—S bond [2.486 (3) Å]. The Sn—N distances are in the range 2.468 (8) ± 0.024 Å. Intermolecular distances shorter than the sum of the van der Waals radii do not exist.

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