Aqua-di-μ_2-chloro-bis(diethylenetriamine)dicopper(II) dichloride

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Key indicators

Single-crystal X-ray study

$T = 293$ K

Mean σ(C–C) = 0.015 Å

R factor = 0.041

wR factor = 0.116

Data-to-parameter ratio = 22.0

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Reaction of $CuCl_2(H_2O)_2$ with diethylenetriamine (henceforth dien) in a 1:1 ratio has led to the formation of a non-centrosymmetric di-μ-chloro bibridged binuclear Cu^{II} species in which a water molecule is coordinated axially to one of the Cu^{II} ions. $[Cu_2Cl_2(C_4H_{13}N_3)_2(H_2O)]$ contains dinuclear $[(dien)_2Cu_2Cl_2(H_2O)]^{2+}$ cations and chloride ions. Both Cu^{II} ions in the dimer have a primary coordination sphere that is approximately planar, consisting of one dien molecule and one chloride ion. These monomeric units are linked via semi-coordinate Cu—Cl bonds to form dinuclear units. One Cu^{II} ion has a 4+1 coordination geometry while the second expands to a 4+2 geometry by the incorporation of a water molecule. The dinuclear cation has crystallographic reflection symmetry, the mirror plane containing the central Cu_2Cl_2 unit and the central N atom of each dien ligand.
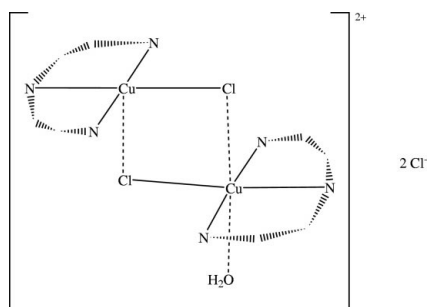
Comment

The crystal structure of the title compound, (I), consists of $[Cu_2(dien)_2Cl_2(H_2O)]^{2+}$ cations, as shown in Fig. 1, and Cl^- counter-ions; here dien is diethylenetriamine, a tridentate ligand.

(I)

Both Cu atoms have a pseudo-planar primary coordination sphere consisting of the three N atoms from a dien ligand and a Cl^- ion. Atom Cu(1) attains an expanded 4+1 coordination geometry by forming a semicoordinate apical bond of 2.676 (1) Å to the Cl^- ion bound to Cu(2). The deviation of the primary coordination sphere for Cu(1) is minimal, with Cl(2) displaced only 0.168 Å from the Cu(1)N$_3$ plane. In contrast, Cu(2) expands its coordination to a 4+2 geometry, with apical Cu—Cl and Cu—OH$_2$ bonds of 3.018 (1) and 2.608 (3) Å, respectively. In this case, considerable distortion from planarity occurs, with Cl(2) displaced by 0.847 Å from the Cu(2)N$_3$ plane. This distortion is associated with the difference in the apical Cu—Cl distances for the two Cu atoms. The 4+1 coordination for Cu(1) causes the apical Cu(1)—
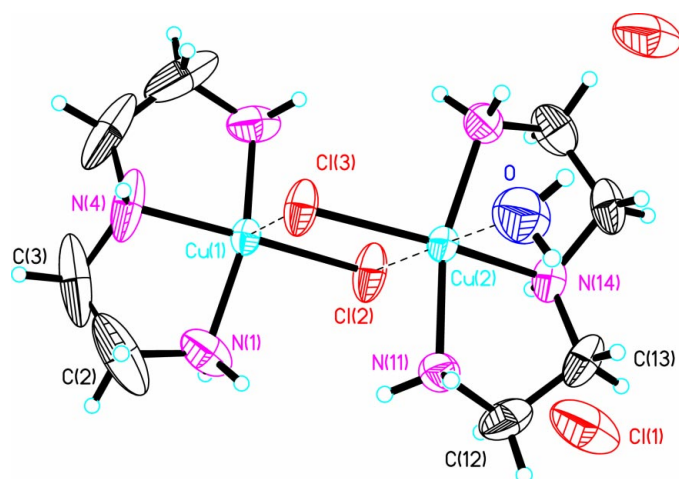
Figure 1
The asymmetric unit of (I) showing ellipsoids at the 50% probability level.

Cl(3) bond to be 0.342 Å shorter than the apical Cu(2)—Cl(2) bond. Because of this distortion, the two Cu—Cl—Cu bond angles differ by 8.5°. The 4+2 coordination for Cu(2) also imposes more rigidity on its dien ligand, as compared to the dien ligand for Cu(1). Here, with the absence of a coordinating ligand in the sixth position, the ethylene arms of the dien ligand show high anisotropic displacement parameters, indicative of unresolved disorder.

The crystal lattice is stabilized by O—H···Cl hydrogen bonds between the semicoordinated water molecule and the lattice chloride, pairs of N—H···Cl bonds between the terminal N atoms (N1 and N11) of the dien ligands and the lattice chloride, as well as N—H···Cl bonds between the central N atoms (N4 and N14) and the bridging Cl atoms of the dinuclear species. These hydrogen-bonding contacts range from 3.132 (O to Cl1) to 3.420 Å (N11 to Cl1).

A centrosymmetric $[Cu_2(dien)_2Cl_2]^{2+}$ dimer has been reported as the nitrate salt (Urtiaga *et al.*, 1996), while a monomeric $Cu(dien)I_2$ species has been described by Hodgson *et al.* (1991).

Experimental

Stoichiometric quantities of diethylenetriamine and $CuCl_2(H_2O)_2$ were dissolved in a minimum amount of water and a few drops of HCl were added to prevent hydrolysis of the aqueous Cu^{II} ions. The resultant solution was allowed to slowly evaporate at room temperature. Blue crystals were harvested by filtration and washing with cold ethanol.

Crystal data

$[Cu_2Cl_2(C_4H_{13}N_3)_2(H_2O)]$	$D_x = 1.624$ Mg m^{-3}
$M_r = 493.24$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/m$	Cell parameters from 34
$a = 6.7155$ (8) Å	reflections
$b = 14.6106$ (11) Å	$\theta = 5.9–15.0°$
$c = 10.3011$ (8) Å	$\mu = 2.65$ mm^{-1}
$\beta = 95.333$ (10)°	$T = 293$ (2) K
$V = 1006.34$ (16) Å^3	Parallelepiped, blue
$Z = 2$	$0.30 \times 0.25 \times 0.10$ mm

Data collection

Bruker $P4$ diffractometer	$R_{int} = 0.051$
ω scans	$\theta_{max} = 27.5°$
Absorption correction: empirical	$h = -1 \rightarrow 8$
($XEMP$; Siemens, 1990)	$k = -1 \rightarrow 18$
$T_{min} = 0.484$, $T_{max} = 0.861$	$l = -13 \rightarrow 13$
3012 measured reflections	3 standard reflections
2243 independent reflections	every 100 reflections
1948 reflections with $I > 2\sigma(I)$	intensity decay: <3%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0743P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.041$	$+ 0.9546P]$
$wR(F^2) = 0.116$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.03$	$(\Delta/\sigma)_{max} < 0.001$
2243 reflections	$\Delta\rho_{max} = 0.75$ e Å^{-3}
102 parameters	$\Delta\rho_{min} = -0.57$ e Å^{-3}
H-atom parameters constrained	Extinction correction: $SHELXTL$
	Extinction coefficient: 0.009 (3)

Table 1
Selected geometric parameters (Å, °).

Cu1—N1	1.989 (7)	Cu2—N11	2.005 (6)
Cu1—N1^i	1.990 (7)	Cu2—N14	2.006 (3)
Cu1—N4	2.000 (8)	Cu2—Cl3	2.278 (2)
Cu1—Cl2	2.269 (2)	Cu2—O	2.608 (2)
Cu1—Cl3	2.676 (2)	Cu2—Cl2	3.018 (2)
Cu2—N11^i	2.005 (6)		
N1—Cu1—N1^i	160.1 (4)	Cl2—Cu1—Cl3	93.84 (8)
N1—Cu1—N4	84.6 (2)	N11^i—Cu2—N11	162.6 (3)
N1^i—Cu1—N4	84.6 (2)	N11^i—Cu2—N14	84.40 (17)
N1—Cu1—Cl2	94.5 (2)	N11—Cu2—N14	84.40 (17)
N1^i—Cu1—Cl2	94.5 (2)	N11^i—Cu2—Cl3	97.00 (17)
N4—Cu1—Cl2	174.1 (2)	N11—Cu2—Cl3	97.00 (17)
N1—Cu1—Cl3	98.53 (18)	N14—Cu2—Cl3	166.53 (9)
N1^i—Cu1—Cl3	98.53 (18)	Cu2—Cl3—Cu1	94.77 (7)
N4—Cu1—Cl3	92.0 (2)	Cu2—Cl2—Cu1	86.27 (7)

Symmetry code: (i) $x, \frac{3}{2} - y, z$.

All H atoms were located from a difference Fourier and were refined as riding on their parent atoms, with displacement parameters set 20% larger than those of the attached atom.

Data collection: *XSCANS* (Siemens, 1996); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *XS* in *SHELXTL* (Bruker, 1998); program(s) used to refine structure: *XL* in *SHELXTL*; molecular graphics: *XP* in *SHELXTL*; software used to prepare material for publication: *XCIF* in *SHELXTL*.

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