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Di-μ-chloro-bis({2-[*N*,*N*-bis(2-aminoethyl)amino-κ^3N]ethylaminium}-copper(II)) bis(naphthalene-1,5-disulfonate) pentahydrate

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The title compound, $[Cu_2(C_6H_{19}N_4)_2Cl_2](C_{10}H_6O_6S_2)_2\cdot5H_2O$, is comprised of discrete $[Cu_2(tren)_2Cl_2]^{2+}$ dimers {tren is 2-[*N*,*N*-bis(2-aminoethyl)amino]ethylaminium} and naphthalene-1,5-disulfonate anions. Two Cl^- anions bridge two Cu^{II} ions, each of which is also coordinated by two of the primary and the tertiary amino N atoms of the tren ligand, giving each metal atom a distorted square-pyramidal coordination geometry. The cation lies about an inversion centre and the asymmetric unit also has two independent anions lying about inversion centres.

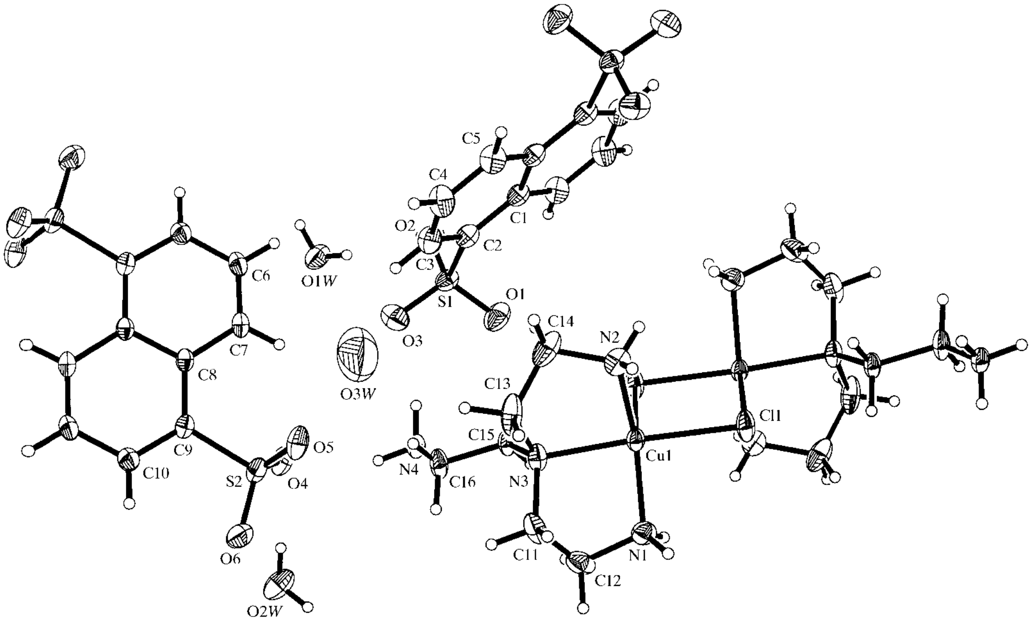
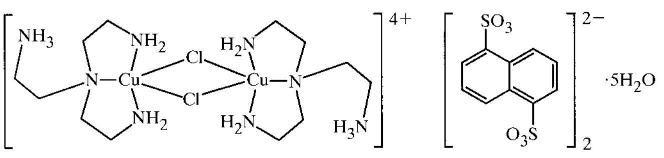


Figure 1
The molecular structure of (I) shown with 30% probability displacement ellipsoids. H atoms are shown as small spheres of arbitrary radii and only the unique portions are labelled. Only three of the five water molecules are shown.

Comment

Copper(II) complexes with the formula $[Cu_2(tren)_2X_2](BPh_4)_2$, where X is CN^-, NCO^-, NCS^- or Cl^-, have been studied from both structural and magnetic points of view (Duggan & Hendrickson, 1974*a*,*b*; Duggan *et al.*, 1974; Laskowski *et al.*, 1975). Each Cu^{II} ion in these compounds is five-coordinate in a trigonal-bipyramidal geometry, with tren as a tetradentate ligand and the X^- anion in an axial position. These $[Cu_2(tren)_2\text{-}\ X_2]^{2+}$ ions dimerize *via* a hydrogen bond between the X group and a primary amine of tren coordinated to the second Cu^{II} ion. We report herein a novel dimeric Cu^{II} cation with the same basic formula as the above but with a different structure, *viz*. $[Cu_2(tren)_2Cl_2](1,5\text{-nds})_2\cdot5H_2O$, (I) (1,5-nds is naphthalene-1,5-disulfonate).



(I)

Crystals of (I) are comprised of discrete $[Cu_2(tren)_2Cl_2]^{2+}$ cations, 1,5-nds anions and water molecules, as shown in Fig. 1. Two Cl^- anions bridge two Cu^{II} ions, each of which is also coordinated by two of the primary and the tertiary amino N atoms of the tren ligands, leaving two free ethylamine arms. A search of the Cambridge Structural Database (April 2001 release; Allen & Kennard, 1993) indicates no previous observation of this kind of coordination mode of tren with Cu^{II}.

The coordination geometry of Cu^{II} in (I) can be described as a distorted square pyramid, as ascertained by Reedijk's τ factor (Addison *et al.*, 1984) of 0.313 for Cu1 and 0.331 for Cu1*A* (τ = 0 for a square pyramid and 1 for a trigonal bipyramid). Atoms N1, N2 and N3 of the tren ligand and atom Cl1 are nearly coplanar, constituting the base of one pyramid, while Cl1*A* occupies the apical position. As a result, the geometry of the complex consists of two square pyramids sharing one common base-to-apex edge, with the two bases nearly parallel to each other (dihedral angle 1.6°).

The reported geometry of Cu^{II} dimers with the general formula $[N_3Cu(\mu\text{-}Cl)_2CuN_3]$ has been classified into three types (Rodríguez & Llobet, 1999). The arrangement in (I) belongs to type II. The Cu—N distances are

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1.975 (3), 1.983 (2) and 2.081 (2) Å. Obviously, the Cu—N bonds in which N is *cis* to the basal Cl are slightly shorter than that in which N is *trans* to the basal Cl. This phenomenon is different from that in $[Cu_2(dien)_2Cl_2](ClO_4)_2$ (dien is diethylenetriamine; Hoffmann *et al.*, 1984), with the same geometry and N_3Cl_2 coordination environment, but similar to that in $[Cu_2(dpt)_2Cl_2]Cl_2$ (dpt is dipropylenetriamine; Rodríguez & Llobet, 1999).

With regard to the $[Cu(\mu\text{-}Cl)_2Cu]$ core of (I), the dimeric unit has unsymmetrical Cu—Cl bridging distances of 2.2819 (7) and 2.6320 (7) Å. The bridging Cu—Cl—Cu angle is 91.46 (3)° and Cl—Cu—Cl is 88.54 (3)°. All of the bond distances and angles are close to those found in $[Cu_2(dien)_2Cl_2](ClO_4)_2$ (Hoffmann *et al.*, 1984). The Cu···Cu separation is 3.5269 (8) Å, which is slightly shorter than the values reported in analogous compounds (Hoffmann *et al.*, 1984; Rodríguez & Llobet, 1999).

The coordination mode of tren, the mode of dimerization and the coordination geometry in (I) are quite different from those in $[Cu_2(tren)_2Cl_2](BPh_4)_2$, (II) (Laskowski *et al.*, 1975), although the two compounds have the same cation formula, *i.e.* $[Cu_2(tren)_2Cl_2]^{2+}$. In (II), each Cu^{II} centre is coordinated by a Cl^- ligand and all four amino N atoms of tren, and the Cu^{II} centres are dimerized by two complementary hydrogen bonds between Cl^- and a primary amine of tren. Moreover, the local copper environment in (II) is a distorted trigonal bipyramid (N_4Cl), while in (I), it is a distorted square pyramid (N_3Cl_2).

Experimental

Disodium naphthalene-1,5-disulfonate (0.17 g, 0.5 mmol) was added to an aqueous solution of cupric chloride (0.09 g, 0.5 mmol). The solution was then treated with tris(2-aminoethyl)amine (0.076 g, 0.5 mmol). The resulting solution was allowed to stand at room temperature. After 10 d, blue block-shaped crystals of (I) were collected in 10% yield.

Crystal data

$[Cu_2(C_6H_{19}N_4)_2Cl_2]$-
$(C_{10}H_6O_6S_2)_2 \cdot 5H_2O$
$M_r = 1155.10$
Triclinic, $P\overline{1}$
$a = 9.9348$ (15) Å
$b = 11.5498$ (17) Å
$c = 11.9637$ (17) Å
$\alpha = 71.806$ (3)°
$\beta = 75.622$ (3)°
$\gamma = 66.844$ (2)°
$V = 1186.6$ (3) Å^3

$Z = 1$
$D_x = 1.616$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 843 reflections
$\theta = 2.3$–26.4°
$\mu = 1.26$ mm^{-1}
$T = 293$ (2) K
Block, blue
0.25 × 0.25 × 0.10 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Blessing, 1995)
$T_{min} = 0.743$, $T_{max} = 0.884$
7629 measured reflections

4786 independent reflections
4259 reflections with $I > 2\sigma(I)$
$R_{int} = 0.017$
$\theta_{max} = 26.4°$
$h = -12 \rightarrow 12$
$k = -14 \rightarrow 13$
$l = -14 \rightarrow 14$

Refinement

Refinement on F^2
$R(F) = 0.041$
$wR(F^2) = 0.118$
$S = 1.01$
4786 reflections
301 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0786P)^2 + 0.7132P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 1.08$ e Å^{-3}
$\Delta\rho_{min} = -0.52$ e Å^{-3}

Table 1
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O1W—H1WA···O2^{i}	0.86	2.12	2.975 (3)	172
O1W—H1WB···O2	0.83	2.07	2.883 (3)	165
O2W—H2WA···O4	1.09	1.98	3.009 (4)	156
O2W—H2WB···O5^{ii}	0.85	2.28	3.025 (3)	146
O2W—H2WB···O6^{ii}	0.85	2.56	3.238 (4)	138
N1—H1A···O1W^{iii}	0.90	2.10	2.982 (4)	167
N1—H1B···O2W^{iv}	0.90	2.20	2.945 (4)	140
N2—H2A···O4^{iv}	0.90	2.48	3.226 (4)	141
N2—H2B···O1W^{iv}	0.90	2.11	2.977 (4)	160
N4—H4B···O4	0.89	2.11	2.941 (3)	154
N4—H4C···O1^{iii}	0.89	2.00	2.879 (3)	170
N4—H4D···O3	0.89	1.98	2.845 (4)	164

Symmetry codes: (i) $-x, -1-y, -z$; (ii) $-1-x, -y, 1-z$; (iii) $-1-x, -y, -z$; (iv) $x-1, y, z$.

The H atoms of the tren ligands and the 1,5-nds anions were placed in idealized positions (N—H = 0.90 and 0.89 Å for NH_2 and NH_3, respectively, and C—H = 0.97 and 0.93 Å for CH_2 and CH, respectively) and refined as riding atoms. The H atoms of water molecules O1W and O2W were located from a difference Fourier map and not refined and those of the O3W water molecule were not located.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SMART*; data reduction: *SAINT-Plus* (Bruker, 1999); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1998).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DA1201). Services for accessing these data are described at the back of the journal.

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