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The neutral cluster amminehexa-μ_2-chlorido-μ_4-oxido-tris(1,4,6-triazabicyclo[3.3.0]oct-4-ene)tetracopper(II)

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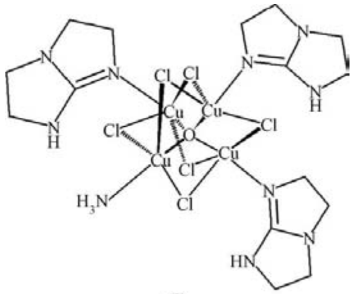
The title compound, [$Cu_4Cl_6O(C_5H_9N_3)_3(NH_3)$], is a neutral conformationally chiral cluster which crystallizes under the conditions described in this paper as a racemic conglomerate. It contains four Cu^{II} atoms in a tetrahedral coordination with a central O atom lying on a crystallographic threefold axis. Six chloride anions bridge the four Cu^{II} atoms. Three Cu^{II} atoms are bound by an N atom of a monodentate 1,4,6-triazabicyclo[3.3.0]oct-4-ene (Htbo) ligand and the remaining Cu^{II} atom is bound by a terminal ammine ligand. The geometry at each copper center is trigonal bipyramidal, produced by the bound N atom of Htbo or ammonia, the O atom in the axial position, and three chloride ions in the equatorial plane. The chloride anions form an octahedron about the oxygen center. The copper–ammonia bond lies along the crystallographic threefold axis, along which the molecules are packed in a polar head-to-tail fashion.

Comment

Clusters with four Cu^{II} atoms arranged tetrahedrally around an O atom have been studied for several years for their magnetic properties in materials science (Atria *et al.*, 1999; Reim *et al.*, 1995; Dickinson *et al.*, 1977), as well as in bioinorganic chemistry (El-Sayed *et al.*, 1992) and in anticorrosion studies (Skorda *et al.*, 2005). They have been reported to be good catalysts in the oxidation of aromatic compounds and in some biological systems (Sun *et al.*, 2004; Weinberger *et al.*, 1998).

Other nonbridging ligands may be attached to copper(II), such as halides (Jackson *et al.*, 1996; Belford *et al.*, 1972; Fu & Chivers, 2007; Harlow Simonsen, 1977), oxygen-bonded ligands (Churchill & Rotella, 1979; Bertrand & Kelley, 1966), nicotine (Haendler, 1990), oxoamines (Weinberger *et al.*, 1998), pyridine (Näther & Jess, 2002; Gill & Sterns, 1970; Duncan *et al.*, 1996; Kilbourn & Dunitz, 1967), imidazole (Zhang *et al.*, 2003; Norman *et al.*, 1989; Erdonmez *et al.*, 1990; Clegg *et al.*, 1988; Cortés *et al.*, 2006), pyrazole (Keij *et al.*, 1991; Liu *et al.*, 2003), triazole (Skorda *et al.*, 2005), tetrazole (Lyakhov *et al.*, 2004), azaindole (Poitras & Beauchamp, 1992), phosphine (Bertrand, 1967), thiazole (Bolos & Christidis, 2002), sulfimide (Kelly *et al.*, 1999), phosphite (Churchill *et al.*, 1975) or sulfoxide (Brownstein *et al.*, 1989; Guy *et al.*, 1988).

We report here the title compound, (I), an example of an oxo-centered cluster with an ammine and a guanidinate-type 1,4,6-triazabicyclo[3.3.0]oct-4-ene (Htbo) ligand. Although guanidinates are commonly found as deprotonated (anionic) bidentate ligands, in this cluster Htbo behaves as a terminal neutral ligand (see scheme). Only two other reported compounds have this terminal ligand feature (Khalaf *et al.*, 2008), both with the metal lithium. This is the first structure in which a transition metal atom is coordinated by a terminal Htbo ligand. Table 3 presents the C—N distances and N—C—N angles for Htbo in the present compound, in neutral unligated Htbo, and in previously reported bridging and terminal Htbo ligands.



(I)

When Htbo is a terminal ligand, there is a significant difference between the C1—N1 and C1—N3 bond lengths. This difference has been interpreted as being due to localization of the electron density from the double bond over the nonprotonated N1 atom (Khalaf *et al.*, 2008). The N1—C1—N3 angle is also noticeably larger for terminal Htbo, similar to the angle found in the free ligand.

In the cluster reported here, three Cu^{II} ions are bound by as many terminal Htbo ligands, with the fourth Cu^{II} atom bonded to ammonia. The result is a conformationally chiral compound which crystallizes in the space group *R*3 (Fig. 1). This can be contrasted with the formation of racemic crystals, which contain equal numbers of both enantiomers in the same unit cell and usually crystallize in a centrosymmetric space group (Li *et al.*, 2008). Since the preparation and crystallization of this compound involve no factor that would favor one conformational chirality sense, and since our refinement gave a clear indication of the absolute structure, we conclude that the bulk sample is a racemic conglomerate (Flack & Bernardinelli, 1999).

The structure contains intramolecular noncovalent interactions that could be described as hydrogen bonds. The N3—H3···Cl1 contact (Table 2) stabilizes the tilt of the Htbo ligand, which is ultimately responsible for the conformational chirality of the molecule. There are no intermolecular hydrogen bonds, but there are some short contacts between H atoms and chloride anions (Table 2; *vide infra*).

The central O atom has a slightly distorted tetrahedral coordination geometry [with unique Cu—O—Cu angles of 111.51 (14) and 107.34 (15)°]. The three Cl—Cu2—Cl angles, identical by symmetry, reveal only the slightest distortion from ideality in the equatorial plane of the trigonal-bipyramidal coordination about this metal (Table 1). The Cl—Cu—Cl angles at atom Cu1, however, reveal a degree of distortion. The Cu1—Cl distances also present significant differences (Table 1), varying over a range of about 0.18 Å. The unique Cu2—Cl2 distance is within the range covered by the Cu1—Cl distances. The Cu1 units are positioned out of the Cl2/Cl1/Cl1^{i} plane by 0.2162 (7) Å toward the Htbo ligand [symmetry code: (i) $-y+1, x-y, z$], while atom Cu2 is −0.166 (1) Å out of the $(Cl2)_3$ plane toward the ammine ligand.

The space group *R*3 not only accommodates an enantiopure molecular conformation, but being polar also hosts a purely head-to-tail packing arrangement (Fig. 2). All of the Cu2→N4 vectors point toward the negative *c* direction (the polar-axis direction is established by the absolute structure parameter). Three very well defined intermolecular N—H···Cl interactions, from the three symmetry-related N—H bonds of the ammine ligand to the three Cl1 congeners of the molecule at (x, y, $z-1$), mediate the polar organization of the structure. Thus, both the chirality and the polarity of the space group *R*3 play a role in enabling important features of this structure.

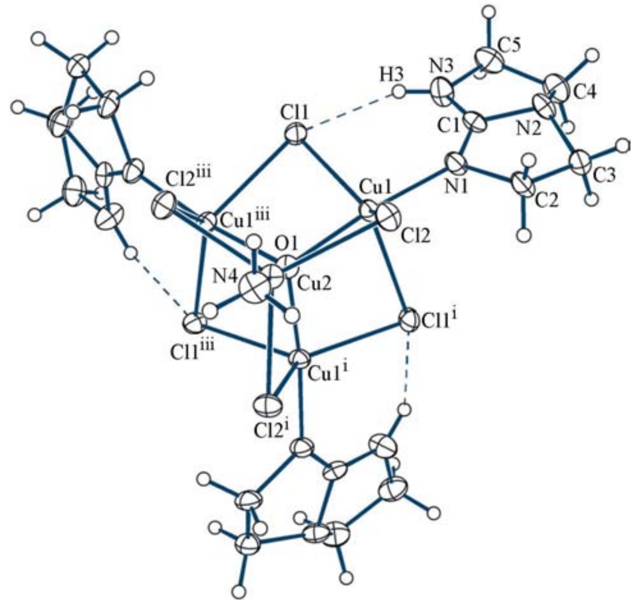


Figure 1
A molecule of (I), lying on a threefold axis, shown with 50% probability displacement ellipsoids for the non-H atoms. [Symmetry codes: (i) $-y+1$, $x-y$, z; (iii) $-x+y+1$, $-x+1$, z.]

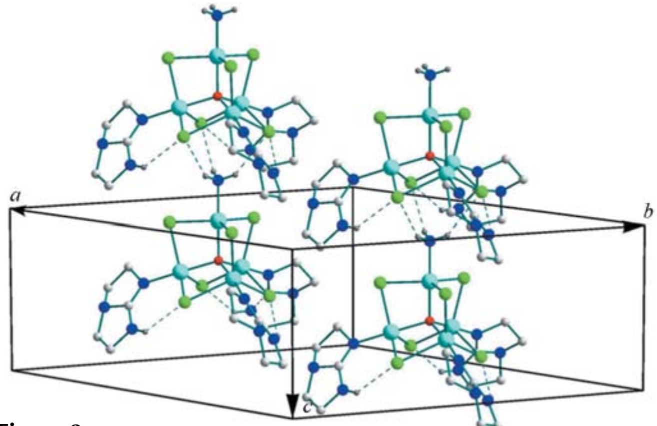


Figure 2
Head-to-tail packing in the extended crystal structure, showing the N—H···Cl contacts between molecules.

Experimental

The Htbo ligand was prepared according to the procedure described by Cotton *et al.* (2006). A solution of Htbo (0.057 g, 0.51 mmol) in tetrahydrofuran (THF, 20 ml) was placed in a 100 ml round-bottomed flask. Solid anhydrous copper(I) chloride (0.05 g, 0.51 mmol) was added. A condenser was fitted with a fritted drying tube containing magnesium carbonate and mounted on the reaction flask. The reaction mixture was refluxed for 48 h. After removing the condenser, the solution was evaporated to dryness by keeping the flask open and heated. After cooling, the solid product was extracted with THF and then the remaining solid was extracted with acetonitrile. The THF solution was layered with ether, rendering after one week deep-orange block-shaped crystals. The crystal used for data collection was mounted on a loop with Paratone oil. The THF fraction gave 0.050 g of product (0.060 mmol), a yield of 47%. The acetonitrile fraction was layered with ether but gave poor quality crystals of $(\mu_4\text{-O})(\mu_2\text{-Cl})_6(\text{CuHtbo})_4$ (structure not reported) in 20% yield. The remaining solid contained decomposition products.

Crystal data

$[Cu_4Cl_6O(C_5H_9N_3)_3(NH_3)]$
$M_r = 833.35$
Trigonal, *R*3
$a = 17.548\ (9)$ Å
$c = 7.898\ (4)$ Å
$V = 2106.2\ (17)$ Å^3
$Z = 3$
Mo *Kα* radiation
$\mu = 3.59$ mm^{-1}
$T = 110$ K
0.11 × 0.08 × 0.06 mm

Data collection

Bruker APEXII diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2006)
$T_{min} = 0.696$, $T_{max} = 0.811$
6295 measured reflections
1972 independent reflections
1772 reflections with $I > 2\sigma(I)$
$R_{int} = 0.061$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.063$
$S = 0.94$
1972 reflections
109 parameters
1 restraint
H-atom parameters constrained
$\Delta\rho_{max} = 0.42$ e Å^{-3}
$\Delta\rho_{min} = -0.31$ e Å^{-3}
Absolute structure: Flack (1983), 983 Friedel pairs
Flack parameter: −0.019 (19)

Table 1
Selected geometric parameters (Å, °).

Cu1—O1	1.9146 (18)	Cu1—Cl1^{i}	2.5423 (16)
Cu1—N1	1.930 (4)	Cu2—O1	1.916 (5)
Cu1—Cl1	2.3660 (15)	Cu2—N4	1.943 (7)
Cu1—Cl2	2.4046 (16)	Cu2—Cl2	2.4075 (16)
Cl1—Cu1—Cl2	126.57 (5)	Cl2—Cu1—Cl1^{i}	111.49 (5)
Cl1—Cu1—Cl1^{i}	119.56 (6)	Cl2—Cu2—Cl2^{i}	119.528 (8)

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

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Table 2
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H3···Cl1	0.86	2.54	3.210 (4)	135
N4—H4*B*···Cl1^{ii}	0.89	2.64	3.423 (5)	147

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

Table 3
Comparison of C—N distances (Å) and the N1—C1—N3 angle (°) in isolated Htbo and in Htbo acting as bridging and terminal ligands.

Compound	$C_1—N_1$	$C_1—N_3$	$C_1—N_2$	$N_1—C_1—N_3$
Neutral ligand alone				
Htbo[b]	1.2971 (18)	1.3455 (18)	1.3914 (16)	132.44 (13)
Bridging ligand				
$Mo_2(tbo)_4$[b]	1.318 (5)	1.322 (4)	1.394 (4)	128.0 (3)
	1.328 (4)	1.314 (5)	1.393 (4)	128.0 (3)
$Mo_2(tbo)_4Cl_2$[b]	1.315 (4)	1.312 (4)	1.374 (4)	128.0 (3)
	1.313 (4)	1.310 (4)	1.386 (4)	127.7 (3)
Terminal ligand				
$\{[Li(tbo)(VIII)(tboH)]_2\}_\infty$[c]	1.286 (3)	1.344 (3)	1.381 (2)	132.40 (18)
$Li_6(tbo)_6(Htbo)_3$[c]	1.291 (3)	1.340 (3)	1.388 (3)	132.49 (19)
	1.276 (3)	1.342 (3)	1.438 (4)	133.6 (2)
	1.308 (2)[a]	1.337 (2)	1.370 (2)	132.37 (17)
This work	1.286 (6)	1.336 (6)	1.377 (6)	134.0 (4)

Note: (*a*) nitrogen bridges two Li atoms. References: (*b*) Cotton *et al.* (2006); (*c*) Khalaf *et al.* (2008).

Since the crystal has a polar space group with a floating origin on *c*, *SHELXL97* (Sheldrick, 2008) automatically generated the appropriate restraint (Flack & Schwarzenbach, 1988). All H atoms were placed in calculated positions and were refined using a riding model. The C—H distances were fixed at 0.97 Å and the N—H distances at 0.86–0.89 Å. The U_{iso}(H) parameters were fixed at $1.2U_{eq}$(N,C). The H atoms of the ammine ligand are related to one another by the threefold axis; their positions were first established using a local difference map and rotating rigid group constraint (AFIX 137), and for the final refinement these H atoms were treated as riding (AFIX 3). Their final positions were checked with an omit map, using *PLATON* (Spek, 2009).

Data collection: *APEX2* (Bruker–Nonius, 2008); cell refinement: *APEX2*; data reduction: *APEX2*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXS97* (Sheldrick, 2008); molecular graphics: *X-SEED* (Barbour, 2001); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA3183). Services for accessing these data are described at the back of the journal.

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