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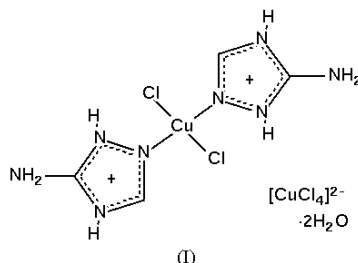
Key indicators

Single-crystal X-ray study
 $T = 100\text{ K}$
Mean $\sigma(\text{N}-\text{C}) = 0.002\text{ \AA}$
 R factor = 0.018
 wR factor = 0.046
Data-to-parameter ratio = 17.0For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.***trans*-Bis(3-amino-1,2,4-triazolium- κN^1)-
dichlorocopper(II) tetrachlorocuprate(II)
dihydrate**

The title compound, *trans*-[CuCl₂(tzH)₂][CuCl₄] \cdot 2H₂O (tz is 3-amino-1,2,4-triazolium, C₂H₅N₄), was obtained by the decomposition of a 1,2,4-triazolo-[1,5-*a*]pyrimidine derivative in concentrated hydrochloric acid in the presence of Cu^{II}. The two Cu^{II} ions occupy crystallographic inversion centres and display square-planar (or tetragonally very elongated) geometries. The complex cation of this salt is an example of a positively charged species (protonated 3-amino-1,2,4-triazole) coordinated to a metal atom.

Comment

The coordination chemistry of 1,2,4-triazolo-[1,5-*a*]pyrimidine derivatives has been extensively studied by our group and others (Salas *et al.*, 1999). These compounds are generally fairly stable in aqueous solution at different pH values, although the 5,7-dioxo derivative readily decomposes in acidic medium, the acidity of this compound being enough to promote its spontaneous decomposition if the solution is concentrated enough (Orihuela *et al.*, 1997). One of the products of such decomposition is 3-amino-1,2,4-triazole (tz), which is also the starting material for the synthesis of bicyclic heterocycles. If the decomposition takes place in the presence of Cu^{II}, the resulting tzH⁺ cation is attached to the metal atom, giving rise to the formation of the title compound, *trans*-bis(3-amino-1,2,4-triazolium- N^1)dichlorocopper(II) tetrachlorocuprate(II) dihydrate, (I) (Fig. 1). The same compound is obtained from the decomposition of other 1,2,4-triazolo[1,5-*a*]pyrimidine derivatives in concentrated hydrochloric acid in the presence of Cu^{II}, for example, by refluxing the compound [CuCl₂(HmtpO)₂] (HmtpO is 4,7-dihydro-5-methyl-7-oxo-1,2,4-triazolo[1,5-*a*]pyrimidine) in concentrated HCl.



Compound (I) is built up from *trans*-[CuCl₂(tzH)₂]²⁺ cations and [CuCl₄]²⁻ anions plus interstitial water molecules. Both copper ions lie on crystallographic inversion centres and the environment around the metal atoms is square planar (Table 1). Both Cu atoms also display weak interactions in the axial direction [Cu1—O1W = 2.630 (2) Å and Cu2—Cl1 = 3.0068 (3) Å], so the coordination polyhedra could be alternatively described as ‘tetragonally very elongated octa-

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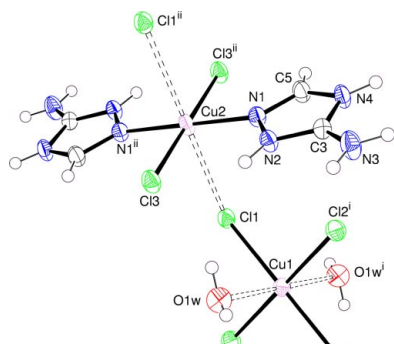


Figure 1
View of the atomic connectivity in (I), with the non-H atoms represented by 50% probability ellipsoids and the long axial Cu1—O1W and Cu2—Cl1 bonds (see text) indicated by dashed lines. [Symmetry codes: (i) $1 - x, 1 - y, -z$; (ii) $1 - x, 1 - y, 1 - z$.]

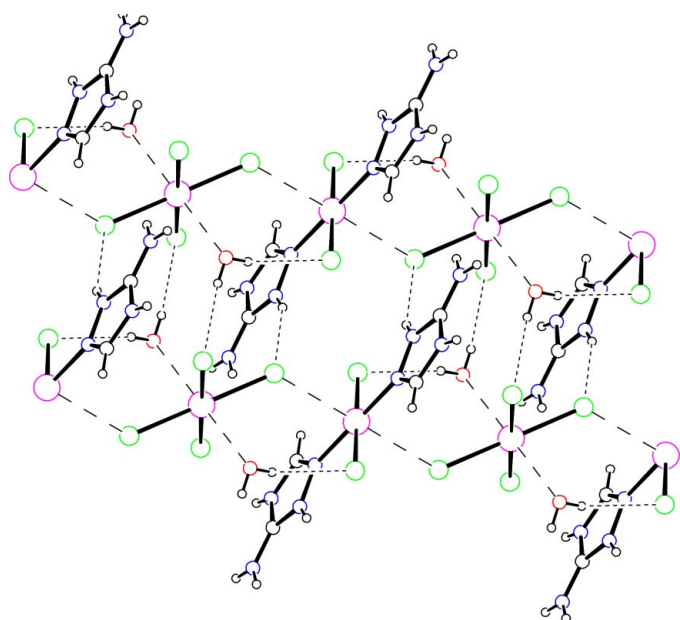


Figure 2
Intermolecular interactions in (I) viewed in projection on the *ac* plane. Long-dashed lines indicate long axial Cu...L interactions and short-dashed lines indicate hydrogen bonds.

hedra', with atom Cl1 asymmetrically bridging both metal atoms, thus building infinite chains along the *c* axis.

The most outstanding feature of this compound is probably the fact that the ligating organic moiety is also protonated. H atoms are clearly attached to both atom N2 and atom N4, as could be seen in the ΔF maps, and these atoms are hydrogen bonded to neighbouring chloride ions (see Table 2). Distances and angles within this ligand are not significantly different from those in other structures containing the tzH^+ cation as an independent species (Smith *et al.*, 1996).

Electrostatic repulsion does not favour the formation of a coordination bond between a positively charged heterocycle and a metallic cation, but the stability of such a bond may be able to overcome this. Thus, examples have been published with protonated purines such as adeninium (Abdus Salam & Aoki, 2000) or 9-ethyl-guaninium (Sindellari *et al.*, 1990); regarding single-ring heterocycles, there is the example of 2-amino-pyrimidinium (Masaki *et al.*, 2002).

The water molecule is attached to the rest of the structure as a hydrogen-bond acceptor from the amine group and as a hydrogen-bond donor to chloride ions (Table 2 and Fig. 2), as well as its weak coordination to Cu1.

Experimental

The heterocyclic compound 4,5,6,7-tetrahydro-5,7-dioxo-1,2,4-triazolo[1.5-*a*]pyrimidine (H_2tpO_2) was prepared, according to the published method (Orihuela *et al.*, 1997), from 3-amino-1,2,4-triazole and diethyl malonate in EtOH/EtONa. The title compound was prepared as follows: $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.269 g, 2 mmol) was dissolved in the minimum amount of concentrated HCl; this solution was added to another containing H_2tpO_2 (4 mmol) in concentrated HCl (3 ml). The reaction mixture was stirred for 1 h and allowed to stand at room temperature. Green crystals were obtained after 48 h, collected by filtration and air dried. Analysis found: C 8.86, H 2.77, N 20.53, Cu 23.41%; calculated for $\text{C}_4\text{H}_{14}\text{Cl}_6\text{Cu}_2\text{N}_8\text{O}_2$: C 8.79, H 2.56, N 20.51, Cu 23.25%.

Crystal data

$[\text{CuCl}_2(\text{C}_2\text{H}_5\text{N}_4)_2][\text{CuCl}_4] \cdot 2\text{H}_2\text{O}$
 $M_r = 546.01$
 Triclinic, $P\bar{1}$
 $a = 6.1505$ (6) Å
 $b = 7.6367$ (8) Å
 $c = 9.7197$ (10) Å
 $\alpha = 95.0132$ (15)°
 $\beta = 99.9045$ (15)°
 $\gamma = 110.2812$ (14)°
 $V = 416.47$ (7) Å³

$Z = 1$
 $D_x = 2.177$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 3558 reflections
 $\theta = 3.6\text{--}28.0^\circ$
 $\mu = 3.53$ mm⁻¹
 $T = 100$ (2) K
 Prism, green
 $0.26 \times 0.25 \times 0.22$ mm

Data collection

Bruker SMART APEX CCD diffractometer
 ω and φ scans
 Absorption correction: multi-scan (SADABS; Bruker, 1999)
 $T_{\min} = 0.380$, $T_{\max} = 0.460$
 4759 measured reflections

1867 independent reflections
 1800 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.015$
 $\theta_{\max} = 28.3^\circ$
 $h = -8 \rightarrow 8$
 $k = -10 \rightarrow 10$
 $l = -12 \rightarrow 12$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.018$
 $wR(F^2) = 0.046$
 $S = 1.08$
 1867 reflections
 110 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.02P)^2 + 0.2P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.30$ e Å⁻³
 $\Delta\rho_{\min} = -0.33$ e Å⁻³
 Extinction correction: SHELXL97
 Extinction coefficient: 0.079 (2)

Table 1

Selected geometric parameters (Å, °).

Cu1—Cl2	2.2467 (4)	N1—N2	1.3749 (18)
Cu1—Cl1	2.3695 (4)	N2—C3	1.330 (2)
Cu2—N1	2.0233 (13)	C3—N3	1.312 (2)
Cu2—Cl3	2.2691 (4)	C3—N4	1.349 (2)
N1—C5	1.295 (2)	N4—C5	1.355 (2)
Cl2—Cu1—Cl1	89.901 (15)	N3—C3—N2	127.60 (15)
N1—Cu2—Cl3	90.53 (4)	N3—C3—N4	126.81 (15)
C5—N1—N2	104.80 (13)	N2—C3—N4	105.58 (13)
C5—N1—Cu2	131.20 (11)	C3—N4—C5	107.61 (13)
N2—N1—Cu2	124.00 (10)	N1—C5—N4	111.03 (14)
C3—N2—N1	110.98 (13)		

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

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$N2-H2 \cdots C1^{iii}$	0.86	2.46	3.2084 (14)	146
$N3-H32 \cdots O1W^{iv}$	0.86	2.05	2.892 (2)	168
$N4-H4 \cdots C1^{iv}$	0.86	2.34	3.1899 (14)	170
$O1W-H1W \cdots C13$	0.828 (16)	2.529 (18)	3.3078 (15)	157 (2)
$O1W-H2W \cdots C12^{iv}$	0.806 (16)	2.475 (17)	3.2728 (15)	171 (2)

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

H atoms of the organic moiety were positioned geometrically and treated as riding ($C-H = 0.93 \text{ \AA}$ and $N-H = 0.86 \text{ \AA}$). Those of the water molecule were located in difference maps and refined with restrained $O-H$ distances [$0.828 (16)$ and $0.806 (16) \text{ \AA}$]. Isotropic displacement parameters of all H atoms were fixed at $1.2U_{eq}$ of their parent atoms.

Data collection: *SMART* (Bruker, 1999); cell refinement: *SMART*; data reduction: *SAINTE* (Bruker, 1999); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *Xtal_GX* (Hall & du Boulay, 1997) and *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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