

(4,4,12,12-Tetramethyl-5,8,11-triazapenta-2,14-dione 2-oxime 14-oximato- κ^5N)copper(II) perchlorate: a copper(II) compound with a pentadentate triamino-oxime-oximate ligand

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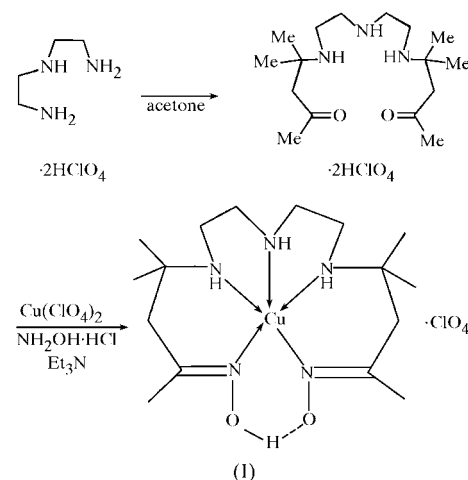
The title compound, $[\text{Cu}(\text{C}_{16}\text{H}_{34}\text{N}_5\text{O}_2)]\text{ClO}_4$, has discrete square-pyramidal (triamino-oxime-oximate)copper(II) cations and perchlorate anions. The cations have very approximate mirror symmetry, with the oxime $[\text{Cu}-\text{N} = 2.066 (2) \text{ \AA}]$, oximate $[\text{Cu}-\text{N} = 2.087 (2) \text{ \AA}]$ and amine N atoms $[\text{Cu}-\text{N} = 2.138 (2) \text{ and } 2.095 (2) \text{ \AA}]$ in the tetrahedrally twisted basal plane, and the 'central' amine N atom coordinated axially $[\text{Cu}-\text{N} = 2.183 (2) \text{ \AA}]$. The oxime and oximate groups are linked by an $\text{O}-\text{H}\cdots\text{O}$ hydrogen bond, forming a pseudo-cyclic pentadentate ligand, with an $\text{O}\cdots\text{O}$ distance of $2.395 (3) \text{ \AA}$.

Comment

The structure of the title copper(II) compound, (I), with a pentadentate triamino-oxime-oximate ligand, is reported. The ligand is the mono-deprotonated dioxime of the triamino-diketone 4,4,12,12-tetramethyl-5,8,11-triazapenta-2,14-dione, which is formed (as the dihydroperchlorate salt) by reaction of 3-azapentane-1,5-diamine dihydroperchlorate with acetone (see scheme) (Morgan *et al.*, 1982).

Compound (I) has discrete cations, with Cu^{II} in a square-pyramidal coordination (Fig. 1), and perchlorate anions. Oxime atom N2, oximate atom N14, and secondary amine atoms N5 and N11, are coordinated in the tetrahedrally twisted basal plane, with the bond to the axially coordinated secondary amine atom N8 being significantly longer. Displacements from the mean-square plane defined by atoms N2, N5, N11 and N14 are: N2 0.154, N5 -0.158 , N11 0.158, N14 -0.154 , Cu 0.100, N8 2.213, O2 0.793 and O14 0.082 \AA (s.u. 0.003 \AA), and the *trans* angles are $\text{N2}-\text{Cu}-\text{N11} = 175.75 (8)^\circ$ and $\text{N14}-\text{Cu}-\text{N5} = 165.87 (8)^\circ$. The five-membered chelate

rings both have asymmetrical *gauche* conformations [displacements of atoms from the Cu/N5/N8 plane: C6 0.145 and C7 0.697 \AA ; from the Cu/N8/N11 plane: C9 0.035 and C10 0.683 \AA], while the six-membered chelate rings have 'half-chair' conformations, with methyl substituents C41 and C121 axially oriented [displacements from the Cu/N2/N5 plane: C2 0.052, C3 0.445, C4 0.948, C41 -2.323 and C42 1.050 \AA ; from the Cu/N11/N14 plane: C12 0.984, C121 2.355, C122 1.039, C13 0.590 and C14 0.263 \AA].



Atom O2 of the oxime and O14 of the oximate group are linked by a short hydrogen bond (Table 2), as is common for oxime-oximate compounds, forming a pseudo-macroyclic ligand. The cations are linked into a one-dimensional chain, with base vector 001, by weak intramolecular hydrogen bonding. The perchlorate ion shows rotational disorder which was not modelled.

The structures of a number of copper(II) compounds with tetradentate diaza-oxime-oximate ligands with short $\text{O}-\text{H}\cdots\text{O}$ hydrogen-bonded 14- to 16-membered pseudo-cyclic structures have been reported. These generally have square-pyramidal coordination, with water (Nunes *et al.*, 1999; Anderson & Packard, 1979; Lee *et al.*, 1990; Pal *et al.*, 1986; Kiani *et al.*, 2002) or an anion (Tahirov *et al.*, 1993, 1995; Jiang *et al.*, 1993; Nunes *et al.*, 1999; Gavel & Schlemper, 1979; Lee *et al.*, 1991; Liss *et al.*, 1975; Schlemper *et al.*, 1981) coordinated axially, or have dinuclear (Tahirov *et al.*, 1993; Fraser *et al.*,

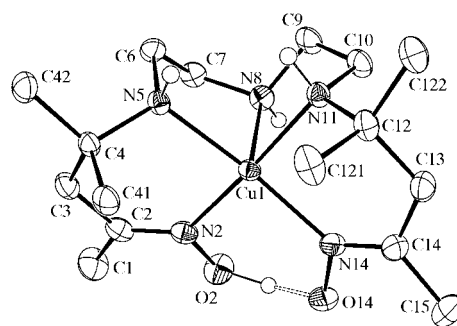


Figure 1

The cation of (I), drawn with displacement ellipsoids at the 50% probability level. H atoms bonded to C atoms have been omitted for clarity, and H atoms bonded to N or O atoms are shown as circles of arbitrary radii.

1972; Timmons *et al.*, 1981; Kiani *et al.*, 2002; Pal *et al.*, 1986; Fun *et al.*, 1993) or chain polymeric structures (Bertrand *et al.*, 1977) with an oximate O atom bridging to the axial site. The work presented here is the first report of a triaza-oxime-oximate compound in which the pentadentate ligand donor atoms occupy all five coordination sites about the copper(II).

Experimental

The starting material, 4,4,12,12-tetramethyl-5,8,11-triazapenta-2,14-dione dihydroperchlorate, was prepared by reaction of 3-azapentane-1,5-diamine (diethylenetriamine) dihydroperchlorate with acetone (Morgan *et al.*, 1982). The title compound was prepared by reaction of the starting material with $[\text{Cu}(\text{H}_2\text{O})_6](\text{ClO}_4)_2$, hydroxylamine hydrochloride and triethylamine in a 1:1:2:5 molar ratio in methanol. The green product which crystallized on addition of propan-2-ol was recrystallized by dissolving in methanol, adding propan-2-ol until just turbid, and allowing the solvent to evaporate.

Crystal data

$[\text{Cu}(\text{C}_{16}\text{H}_{34}\text{N}_5\text{O}_2)]\text{ClO}_4$	$D_x = 1.455 \text{ Mg m}^{-3}$
$M_r = 491.47$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 9707 reflections
$a = 10.8307 (7) \text{ \AA}$	$\theta = 2.1\text{--}28.4^\circ$
$b = 23.9974 (15) \text{ \AA}$	$\mu = 1.13 \text{ mm}^{-1}$
$c = 8.6318 (6) \text{ \AA}$	$T = 160 (2) \text{ K}$
$\beta = 90.058 (2)^\circ$	Plate, green
$V = 2243.5 (3) \text{ \AA}^3$	$0.62 \times 0.28 \times 0.10 \text{ mm}$
$Z = 4$	

Data collection

Siemens SMART CCD area-detector diffractometer	4845 independent reflections
ω rotation scans with narrow frame	4392 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (Blessing, 1995)	$R_{\text{int}} = 0.035$
$T_{\text{min}} = 0.540$, $T_{\text{max}} = 0.895$	$\theta_{\text{max}} = 28.4^\circ$
12 927 measured reflections	$h = -10 \rightarrow 14$
	$k = -26 \rightarrow 30$
	$l = -11 \rightarrow 11$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0379P)^2 + 3.1169P]$
$R[F^2 > 2\sigma(F^2)] = 0.040$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.100$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.12$	$\Delta\rho_{\text{max}} = 0.64 \text{ e \AA}^{-3}$
4845 reflections	$\Delta\rho_{\text{min}} = -0.70 \text{ e \AA}^{-3}$
271 parameters	
H atoms treated by a mixture of independent and constrained refinement	

Table 1

Selected geometric parameters (\AA , $^\circ$).

Cu1—N2	2.067 (2)	N2—C2	1.285 (3)
Cu1—N14	2.088 (2)	N2—O2	1.420 (3)
Cu1—N11	2.096 (2)	C14—N14	1.292 (3)
Cu1—N5	2.138 (2)	N14—O14	1.426 (3)
Cu1—N8	2.182 (2)		
N2—Cu1—N14	93.32 (9)	O2—N2—Cu1	113.9 (2)
N2—Cu1—N11	175.79 (8)	N2—C2—C3	122.7 (2)
N14—Cu1—N11	89.90 (8)	C1—C2—C3	118.1 (2)
N2—Cu1—N5	89.33 (8)	C2—C3—C4	121.8 (2)
N14—Cu1—N5	165.85 (8)	C14—C13—C12	122.3 (2)
N11—Cu1—N5	88.20 (8)	N14—C14—C15	118.9 (3)
N2—Cu1—N8	93.82 (8)	N14—C14—C13	122.8 (2)
N14—Cu1—N8	110.13 (8)	C15—C14—C13	118.2 (2)
N11—Cu1—N8	82.52 (8)	C14—N14—O14	113.6 (2)
N5—Cu1—N8	83.53 (7)	C14—N14—Cu1	129.3 (2)
C2—N2—O2	113.4 (2)	O14—N14—Cu1	117.1 (2)
C2—N2—Cu1	130.4 (2)		

Table 2

Hydrogen-bonding geometry (\AA , $^\circ$).

$D\text{—}H\cdots A$	$D\text{—}H$	$H\cdots A$	$D\cdots A$	$D\text{—}H\cdots A$
O2—H2 \cdots O14	1.14 (4)	1.27 (4)	2.395 (3)	171 (4)
O2—H2 \cdots N14	1.14 (4)	2.16 (4)	3.044 (3)	132 (3)
N5—H5 \cdots O5	0.93	2.34	3.257 (4)	167
N8—H8 \cdots O14 ⁱ	0.93	2.12	3.009 (3)	160
N11—H11 \cdots O4	0.93	2.58	3.437 (4)	154

Symmetry code: (i) $x, \frac{1}{2} - y, \frac{1}{2} + z$.

For atom H2, the positional coordinates were refined, with $U_{\text{iso}} = 1.5U_{\text{eq}}(\text{O2})$. All other H atoms were treated as riding atoms, with N—H distances of 0.93 \AA and C—H distances of 0.98 or 0.99 \AA , and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N})$ or $1.5U_{\text{eq}}(\text{C})$.

Data collection: SMART (Siemens, 1995); cell refinement: local programs; data reduction: SAINT (Siemens, 1995); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEP-3 (Farrugia, 1997); software used to prepare material for publication: SHELXL97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1308). Services for accessing these data are described at the back of the journal.

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