

Bis[*N*-(isopropylidene)propane-1,3-diamine- κ^2N]-
(perchlorato- κO)copper(II) perchlorateNeil F. Curtis^{a*} and Ward T. Robinson^b^aSchool of Chemical and Physical Sciences, Victoria University of Wellington, Box 600, Wellington, New Zealand, and ^bChemistry Department, University of Canterbury, Christchurch, New Zealand

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Key indicators

Single-crystal X-ray study

T = 106 K

Mean $\sigma(C-C) = 0.003 \text{ \AA}$

R factor = 0.038

wR factor = 0.109

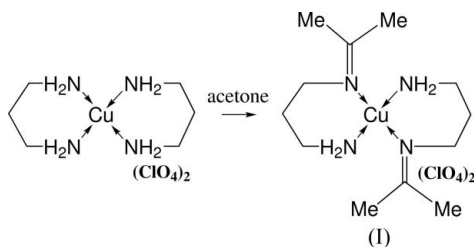
Data-to-parameter ratio = 27.2

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

The title compound, $[\text{Cu}(\text{C}_{10}\text{H}_{28}\text{N}_4)(\text{ClO}_4)]\text{ClO}_4$, is formed by the reaction of bis(propane-1,3-diamine)copper(II) perchlorate with acetone. It has copper(II) ions coordinated by two bidentate ligands, *N*-(isopropylidene)propane-1,3-diamine, with *N*-isopropylidene imine and primary amine donor groups, the former resulting from the combination of the amine with acetone. The N_4 group is tetrahedrally twisted [r.m.s. displacement of N atoms from the N_4 plane = $0.252(1) \text{ \AA}$], with the Cu displaced from the plane by $0.113(1) \text{ \AA}$, towards an O atom of an axially coordinated perchlorate ion [mean $\text{Cu}-\text{N}_{\text{amine}} = 2.029(3) \text{ \AA}$, mean $\text{Cu}-\text{N}_{\text{imine}} = 1.993(3) \text{ \AA}$ and $\text{Cu}-\text{O} = 2.474(2) \text{ \AA}$].

Comment

When $[\text{Cu}(\text{tmd})_2](\text{ClO}_4)_2$, or $[\text{Ni}(\text{tmd})_3](\text{ClO}_4)_2$, (tmd = propane-1,3-diamine, trimethylenediamine) is dissolved in acetone the solutions change colour over a period of minutes and deposit blue or yellow crystals, respectively (House & Curtis, 1964; Curtis, 1968; Cook & Curtis, 1973). These are of composition $[M(\text{C}_{10}\text{H}_{28}\text{N}_4)](\text{ClO}_4)_2$, with ligands formed by combination of two amine and two acetone residues with loss of two moles of water. If the reacting mixtures are allowed to stand the crystals slowly redissolve as further reactions occur, leading ultimately to azamacrocycle compounds. The rapid formation of the initial compounds, and their relatively facile hydrolysis, support their formulation as ligands with simple imine functions (see the scheme). The structure of the title compound, (I) (Fig. 1), formed by the reaction of $[\text{Cu}(\text{tmd})_2](\text{ClO}_4)_2$ with acetone, is now reported.



The asymmetric unit consists of one cation and two perchlorate anions, one weakly coordinated. The cation has copper(II) ions in square-pyramidal coordination by two *N*-(isopropylidene)propane-1,3-diamine ligands, with the imine functions coordinated *trans*. The N_4 group is tetrahedrally twisted [r.m.s. displacements of N atoms from the N_4 plane = $0.252(1) \text{ \AA}$], with the Cu atom displaced from this plane by $0.113(1) \text{ \AA}$. Both *N*-isopropylidene groups are almost planar and tilted to the side of the N_4 'plane' opposite to the Cu ion,

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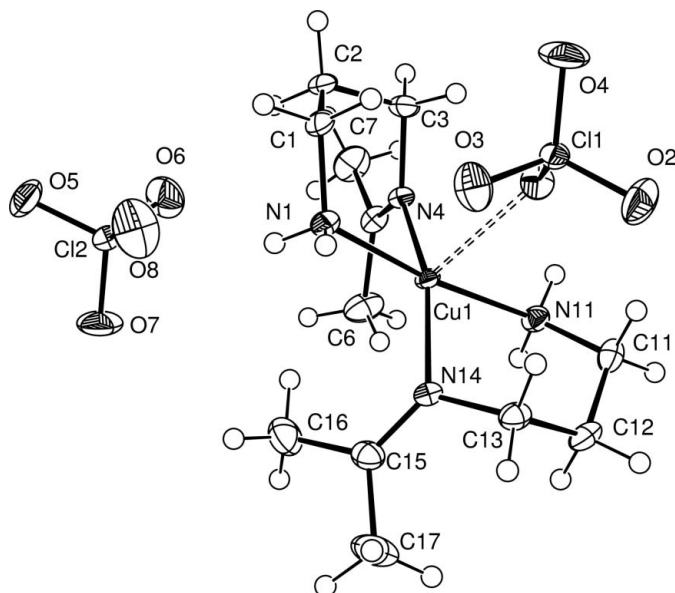


Figure 1

The asymmetric unit of $[\text{Cu}(\text{tmdac})_2](\text{OCIO}_3)(\text{ClO}_4)$, drawn with displacement ellipsoids at the 50% probability level, with H atoms shown as circles of arbitrary radii. The weak coordination interaction to the perchlorate anion is drawn as a dashed bond.

which has the perchlorate O atom, O11, weakly coordinated in an apical position. The Cu–N_{imine} distances are shorter than the Cu–N_{amine} distances, as is usual (Table 1).

The two chelate rings have chair conformations; the displacements (Å) of C atoms from the relevant CuN₂ plane are as follows: C1, 0.975 (3); C2, 0.874 (4); C3, 1.135 (3); C5, –0.957 (3); C6, –2.162 (3); C7, –1.011 (5); C11, 0.967 (3); C12, 0.808 (4); C13, 1.079 (3); C15, –0.950 (3); C16, –2.088 (3); C17, –0.993 (5).

The anions and cations are linked by a hydrogen-bond network (Table 2).

While it would be anticipated that amine compounds of labile metal ions would react readily with acetone to form compounds with *N*-isopropylidene imine ligands, these are seldom isolated. The first isolable products when ethane-1,2-diamine compounds of copper(II) and nickel(II) react with acetone have β -aminoketone ligands, formed by aldol-like reactions of the *N*-isopropylidene imine group with acetone (Curtis, 1972; Hay *et al.*, 1996; Curtis *et al.*, 2003). These undergo intramolecular imine formation reactions with coordinated amino groups to form β -amino-imine ligands. A nickel(II) compound of this type with a residual *N*-isopropylidene imine group, which is quite resistant to hydrolysis, has been structurally characterized. This also has Ni–N_{imine} = 1.894 (4) Å shorter than N–N_{amine} = 1.915 (4) Å (Curtis *et al.*, 2003). Structures have been described of compounds with an *N*-isopropylidene-imine-containing ligand with Cu^{II} (Dietz *et al.*, 1999) and Ni^{II} (Zimmermann *et al.*, 2001).

Experimental

The title compound was prepared by dissolving tris(propene-1,3-diamine)copper(II) perchlorate in acetone (1 g in 10 ml); the product

crystallized within minutes (see the scheme) (Curtis *et al.*, 2003). CAUTION: Although no problems were encountered in this work, perchlorate compounds are potentially explosive. They should be prepared in small amounts and handled with care.

Crystal data

$[\text{Cu}(\text{C}_{12}\text{H}_{28}\text{N}_4)(\text{ClO}_4)]\text{ClO}_4$
 $M_r = 490.82$
 Monoclinic, $P2_1/c$
 $a = 11.1939$ (4) Å
 $b = 14.8324$ (5) Å
 $c = 12.4020$ (4) Å
 $\beta = 104.241$ (2)°
 $V = 1995.86$ (12) Å³

$Z = 4$
 $D_x = 1.633$ Mg m^{–3}
 Mo $K\alpha$ radiation
 $\mu = 1.41$ mm^{–1}
 $T = 106$ (2) K
 Plate, blue
 $0.7 \times 0.5 \times 0.04$ mm

Data collection

Bruker SMART CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Bruker, 1997)
 $T_{\min} = 0.675$, $T_{\max} = 0.945$

23993 measured reflections
 6737 independent reflections
 5036 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.040$
 $\theta_{\text{max}} = 32.9^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.038$
 $wR(F^2) = 0.109$
 $S = 1.05$
 6737 reflections
 248 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0591P)^2 + 0.52P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta\sigma)_{\text{max}} = 0.008$
 $\Delta\rho_{\text{max}} = 1.03$ e Å^{–3}
 $\Delta\rho_{\text{min}} = -0.74$ e Å^{–3}

Table 1

Selected geometric parameters (Å, °).

Cu1–N4	1.991 (2)	Cu1–O1	2.474 (2)
Cu1–N14	1.995 (2)	N4–C5	1.274 (3)
Cu1–N1	2.024 (2)	N14–C15	1.282 (3)
Cu1–N11	2.033 (2)		
N4–Cu1–N14	158.87 (7)	C5–N4–Cu1	124.95 (14)
N4–Cu1–N1	88.15 (7)	C3–N4–Cu1	113.57 (13)
N14–Cu1–N1	94.68 (7)	N4–C5–C6	119.67 (19)
N4–Cu1–N11	91.79 (7)	N4–C5–C7	125.5 (2)
N14–Cu1–N11	88.27 (7)	C15–N14–C13	119.22 (18)
N1–Cu1–N11	171.96 (7)	C15–N14–Cu1	125.15 (15)
N4–Cu1–O1	97.11 (6)	C13–N14–Cu1	114.72 (12)
N14–Cu1–O1	103.83 (6)	N14–C15–C16	121.1 (2)
N1–Cu1–O1	89.83 (6)	N14–C15–C17	123.7 (2)
N11–Cu1–O1	82.20 (6)	C16–C15–C17	115.2 (2)
C5–N4–C3	120.75 (18)	C11–O1–Cu1	133.06 (9)

Table 2

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1–H1A \cdots O8	0.90	2.33	3.173 (3)	155
N1–H1B \cdots O3 ⁱ	0.90	2.22	3.093 (3)	163
N11–H11A \cdots O5 ⁱⁱ	0.90	2.20	3.077 (2)	165
N11–H11B \cdots O6 ⁱⁱⁱ	0.90	2.25	3.110 (3)	161

Symmetry codes: (i) $-x, -y + 2, -z + 1$; (ii) $x, -y + \frac{3}{2}, z + \frac{1}{2}$; (iii) $-x + 1, y + \frac{1}{2}, -z + \frac{3}{2}$.

All H atoms were positioned geometrically and refined using a riding model with C–H = 0.97 Å, $U_{\text{iso}} = 1.2U_{\text{eq}}$ (C) for CH₂ atoms, C–H = 0.96 Å, $U_{\text{iso}} = 1.5U_{\text{eq}}$ (C) for CH₃ atoms, and N–H = 0.90 Å,

$U_{\text{iso}} = 1.2U_{\text{eq}}(\text{N})$ for the NH_2 groups. The maximum and minimum electron-density peaks in the final difference map lie 0.74 and 0.82 Å, respectively, from atom Cu1.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINTE* (Bruker, 1997); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997a); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997a); molecular graphics: *ORTEP-3.2* (Farrugia, 1997); software used to prepare material for publication: *SHELXTL* (Sheldrick, 1997b).

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