

Bis(acetone- κ O)bis(*N,N'*-dimethylethylenediamine- κ^2N,N')copper(II) diperchlorate

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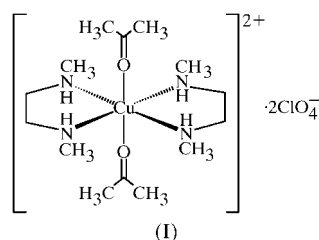
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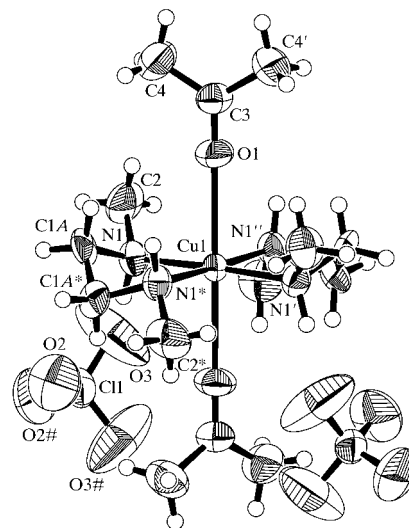
The title compound, $[\text{Cu}(\text{C}_4\text{H}_{12}\text{N}_2)_2(\text{C}_3\text{H}_6\text{O})_2](\text{ClO}_4)_2$, is the first structurally characterized Cu^{II} complex having acetone as axial ligands. The complex adopts an elongated octahedral *trans*- $[\text{CuN}_4\text{O}_2]$ coordination geometry, with the Cu atom having 222 site symmetry. The axial Cu—O(acetone) and in-plane Cu—N bond lengths are 2.507 (5) and 2.041 (3) Å, respectively.

Comment

One of the most promising strategies for development of optical switching materials of metal complexes is to investigate candidates exhibiting thermal phase transition or having physical properties described by bistable potentials. Since there have been reports on intercalated hybrid materials (Choy *et al.*, 2002), thermochromism (Narayanan & Bhadbhade, 1998) and photochromism (Takahashi *et al.*, 2002), Cu^{II} complexes incorporating ethylenediamine derivatives have been of interest as candidates for such functional materials.



The varied stereochemistry of the Cu^{II} complexes, for instance, distortion (Simmons, 1993) and semi-coordination (Hathaway, 1984), has been studied mainly in view of a Jahn–Teller effect (Murphy & Hathaway, 2003). Strictly speaking, a pseudo-Jahn–Teller effect can be applied to systems involving non-equivalent ligands, such as *trans*- $[\text{CuA}_4\text{B}_2]$, with D_{4h} symmetry. Mixing of non-degenerated ground states and excited states through spin-orbit vibronic coupling results in


Figure 1

The molecular structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. One of the two possible conformations of the disordered ethylenediamine moiety has been omitted for clarity. Atoms marked with a prime ('), asterisk (*), double prime (") or hash (#) are at the symmetry-related positions $(x, \frac{1}{2} - y, \frac{1}{2} - z)$, $(1 - x, \frac{1}{2} - y, z)$, $(-x, y, \frac{1}{2} - z)$ and $(\frac{1}{2} - x, 1 - y, z)$, respectively.

stabilization of potential energy by a pseudo-Jahn–Teller effect.

So far, the structures of a number of semi-coordinated Cu^{II} complexes with *N*-substituted ethylenediamine ligands have been investigated: ethylenediamine (en) by Maxcy & Turnbull (1999), *N*-methylethylenediamine (N-Meen) by Akitsu & Einaga (2003), *N*-ethylethylenediamine (N-Eten) by Grenthe *et al.* (1979) and *N,N*-dimethylethylenediamine (N-Me₂en) by Akitsu & Einaga (2004). We have determined the crystal structure of bis(acetone- κ O)bis(*N,N'*-dimethylethylenediamine- κ^2N,N')copper(II) diperchlorate, (I), which is the first structurally characterized example of a Cu^{II} complex incorporating acetone as axial ligands.

Complex (I) adopts an elongated octahedral *trans*- $[\text{CuN}_4\text{O}_2]$ coordination geometry, where atom Cu1 lies on a site of 222 symmetry (Fig. 1 and Table 1). The axial Cu1—O1 bond length of 2.507 (5) Å is in the range of semi-coordination (2.22–2.89 Å for H₂O; Hathaway, 1973) caused by a Jahn–Teller effect. As for the above-mentioned analogous Cu^{II} complexes with axial perchlorate ligands, the corresponding Cu—O(perchlorate) bond lengths are 2.579 (4), 2.569 (2), 2.594 (3) and 2.605 (4) Å for the en, N-Meen, N-Eten and N-Me₂en complexes, respectively. Interestingly, the axial Cu—O(acetone) bond in (I) is shorter than the Cu—O(perchlorate) bond, regardless of the acetone ligands being neutral; however, it is considerably longer than corresponding values for dimeric Cu^{II} complexes having acetone ligands, which range from 2.1379 (5) (Agterberg *et al.*, 1997) to 2.206 (3) Å (Castellari *et al.*, 1999). Furthermore, in these similar complexes, the Cu—O=C(acetone) bond angles are bent (133°; Steward *et al.*, 1996), whereas the Cu—O—C bond

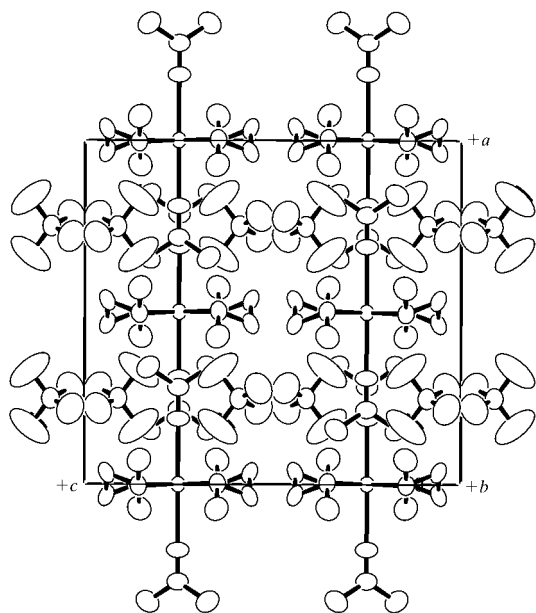


Figure 2
The crystal structure of (I).

angles are 180° in (I). The Cu1–N1 bond length of 2.041 (3) Å in (I) is comparable to that of 2.057 (2) Å in the N-Meen complex. Indeed, the number of groups substituted on the N atom is reflected in the Cu–N bond distance for a series of these complexes: Cu–N(H₂) = 2.012 (2) Å for the en, Cu–N(HMe) = 2.057 (2) Å for the N-Meen, Cu–N(HEt) = 2.031 (3) Å for the N-Eten and Cu–N(Me₂) = 2.098 (2) Å for the N-Me₂en complex. The *T* values, *i.e.* the Cu–N(in-plane)/Cu–O(axial) bond-length ratio (Hathaway *et al.*, 1973) of 0.81 for (I) is comparable or slightly larger than the *T* values of the perchlorate complexes (0.76–0.81).

The N1–Cu1–N1ⁱ [symmetry code: (i) $1 - x, \frac{1}{2} - y, z$] chelate angle of $84.7 (1)^\circ$ is almost the same as that of the N-Meen complex [$84.58 (7)^\circ$]. The perchlorate ion lies on a twofold axis and has normal geometric parameters. N–H...O hydrogen bonds are formed between the complex cation and the perchlorate ions (Table 2). The crystal packing of (I) is illustrated in Fig. 2. The *trans*-O–Cu–O axial bonds lie on twofold axes parallel to the *a* axis. Each complex cation is linked to four perchlorate anions and each perchlorate anion is linked to two cations *via* hydrogen bonds. The complex cations and perchlorate anions are aligned alternately along the *a* axis, forming networks of two-dimensional sheets.

The crystal structures of metal complexes having two acetone ligands at axial sites, *i.e.* having *trans*-O–M–O axial bonds, have been reported for the Mn^{III} (Zhang *et al.*, 1990), Zn^{II} (Bench, Beveridge *et al.*, 2002) and Co^{II} (Bench, Brennessel *et al.*, 2002) complexes. Despite the *trans*-coordination mode, the acetone ligands are inclined in the Mn^{III}, Zn^{II} and Co^{II} complexes, whereas they are coordinated in a linear fashion in (I) as a result of the symmetry of the crystal structure.

Experimental

To a methanol solution (20 ml) of Cu(ClO₄)₂ (0.375 g, 1.01 mmol), *N,N'*-dimethylethylenediamine (0.176 g, 2.00 mmol) was added dropwise at 298 K, giving rise to blue precipitates of the precursor bis(*N,N'*-dimethylethylenediamine)copper(II) diperchlorate. Blue prismatic crystals of (I) suitable for X-ray analysis were grown from an acetone–methanol solution (4:1 *v/v*) at 298 K over a period of a few days.

Crystal data

[Cu(C₄H₁₂N₂)₂(C₃H₆O)₆](ClO₄)₂
M_r = 554.92
 Orthorhombic, *Ccca*
a = 13.145 (5) Å
b = 13.333 (4) Å
c = 14.332 (4) Å
V = 2511.9 (14) Å³
Z = 4
D_x = 1.467 Mg m^{−3}

Mo *K*α radiation
 Cell parameters from 25 reflections
 $\theta = 11.1$ – 12.3°
 $\mu = 1.13 \text{ mm}^{-1}$
T = 297.2 K
 Prismatic, blue
 0.30 × 0.30 × 0.30 mm

Data collection

Rigaku AFC-7R diffractometer
 ω – 2θ scans
 Absorption correction: ψ scan
 (North *et al.*, 1968)
 $T_{\text{min}} = 0.712$, $T_{\text{max}} = 0.719$
 1525 measured reflections
 1449 independent reflections
 747 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.008$

$\theta_{\text{max}} = 27.5^\circ$
 $h = -17 \rightarrow 0$
 $k = 0 \rightarrow 17$
 $l = 0 \rightarrow 18$
 3 standard reflections
 every 150 reflections
 intensity decay: 87.2%

Refinement

Refinement on F^2
 $R(F) = 0.055$
 $wR(F^2) = 0.180$
 $S = 1.08$
 747 reflections
 83 parameters
 H-atom parameters not refined

$w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.010$
 $\Delta\rho_{\text{max}} = 0.44 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\text{min}} = -0.46 \text{ e } \text{Å}^{-3}$

Table 1

Selected geometric parameters (Å, °).

Cu1–O1	2.507 (5)	N1–C2	1.488 (5)
Cu1–N1	2.041 (3)	C1A–C1A ⁱ	1.48 (2)
O1–C3	1.203 (5)	C1B–C1B ⁱ	1.46 (2)
N1–C1A	1.530 (8)	C3–C4	1.471 (5)
N1–C1B	1.503 (9)		
O1–Cu1–N1	91.11 (7)	N1–Cu1–N1 ⁱ	84.7 (1)
N1–Cu1–N1 ⁱⁱ	177.8 (1)	N1–Cu1–N1 ⁱⁱⁱ	95.3 (1)
N1–C1A–C1A ⁱ –N1 ⁱ	70.2 (8)	N1–C1B–C1B ⁱ –N1 ⁱ	−47 (1)

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

Table 2

Hydrogen-bonding geometry (Å, °).

<i>D</i> –H... <i>A</i>	<i>D</i> –H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> –H... <i>A</i>
N1–H1A...O2	0.97	2.46	3.362 (4)	154
N1–H1B...O2	0.97	2.65	3.362 (4)	130
N1–H1A...O3	0.97	2.37	3.177 (5)	140
N1–H1B...O3	0.97	2.30	3.177 (5)	150

Despite the use of an epoxy coating to retain the solvent, the crystal used for analysis was seriously damaged by the X-ray radiation during the data collection. There is a positional disorder of atom C1 over two equally occupied sites. It was assumed that the ethylenediamine moiety has two possible conformations, namely N1(H1A)—C1A(H2A/H3A)—C1Aⁱ(H2Aⁱ/H3Aⁱ) and N1(H1B)—C1B(H2B/H3B)—C1Bⁱ(H2Bⁱ/H3Bⁱ) [symmetry code: (i) $1 - x, \frac{1}{2} - y, z$]. In an approximation, positional disorder of atom C2 was not taken into account, because the ratio of its maximum/minimum principal r.m.s. displacements was fairly small (1.14) and there was no remarkable peak in the difference map. All H-atom positional parameters were calculated geometrically and fixed with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{parent atom})$.

Data collection: *WinAFC Diffractometer Control Software* (Rigaku, 1999); cell refinement: *WinAFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 2001); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *TEXSAN*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OB1168). Services for accessing these data are described at the back of the journal.

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