

A redetermination of bis(*N*-methylethylenediamine- κ^2N,N')bis(perchlorato- κO)-copper(II)Takashi Akitsu* and
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Key indicators

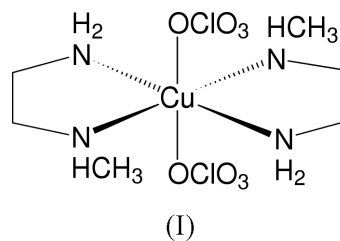
Single-crystal X-ray study
 $T = 297\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.003\text{ \AA}$
 R factor = 0.024
 wR factor = 0.068
Data-to-parameter ratio = 15.7For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

In the title compound, $[\text{Cu}(\text{ClO}_4)_2(\text{C}_3\text{H}_{10}\text{N}_2)_2]$, the Cu atom is located at a center of symmetry. Despite asymmetric introduction of *N*-methyl groups into the ethylenediamine moieties, a second-order Jahn–Teller effect produces a typical semi-coordination *trans*- $[\text{CuN}_4(\text{O}_2)]$ environment with long axial Cu–O bonds of 2.569 (2) Å. The Cu–N bond distances are 2.004 (2) and 2.057 (2) Å.

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Comment

Since synchrotron spectroscopic measurements have made remarkable advances recently, detailed studies of structures and the electronic properties of functional transition metal complexes, including intercalated hybrid materials (Choy *et al.*, 2002) and thermochromic (Narayanan & Bhadbhade, 1998) or photochromic (Takahashi *et al.*, 2002) complexes, have become a matter of great importance. It is well known that copper(II) complexes having ethylenediamine (en) ligands show flexibility of their coordination environment and adopt semi-coordination with tetragonal distortion (Hathaway, 1984). Indeed, redetermination of the structure of bis(ethylenediamine-*N,N'*)copper(II) perchlorate was reported by Maxcy *et al.* (1999), with emphasis on the Halden gap and magnetic behavior. However, the previous report of bis(*N*-methylethylenediamine)bis(perchlorato)copper(II), (I), did not include H atoms (Luukkonen *et al.*, 1970). Hence, we redetermined the structure of (I) in order to obtain detailed structural information for understanding the semi-coordination as a result of a second-order Jahn–Teller effect and the spectroscopic interpretation.



Complex (I) is centrosymmetric and atom Cu1 is located at the center of inversion (Fig. 1 and Table 1). Complex (I) adopts a tetragonal distorted *trans*- $[\text{CuN}_4(\text{O}_2)]$ environment, with long axial semi-coordination Cu1–O4 bonds of 2.569 (2) Å. This value is comparable to 2.579 (4) Å in the en complex (Maxcy *et al.*, 1999), and 2.594 (3) Å in the *N*-ethylethylenediamine (*N*-Eten) complex (Grenthe *et al.*, 1979). The axial perchlorate ions have normal geometric parameters, and intramolecular hydrogen bonds (Table 2) between amino H

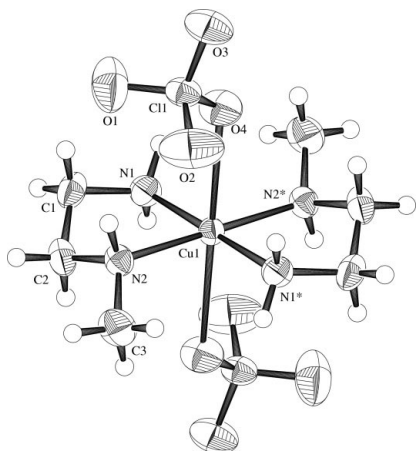


Figure 1
The molecular structure of (I), showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level. Atoms marked with an asterisk (*) are at the symmetry-generated position ($2 - x, -y, 2 - z$).

atoms also play an important role in stabilizing the axial semi-coordination. The complexes are linked by N—H \cdots O hydrogen bonds, forming a three-dimensional network.

The Cu1—N2 (NHMe side) bond distance of 2.057 (2) Å is longer than that of Cu1—N1, 2.004 (2) Å. The former is slightly longer than 2.031 (3) Å for the *N*-Eten complex, though the methyl group is less bulky than the ethyl group. The latter is quite similar to values of 2.012 (2) and 2.019 (2) Å for the en complex (Maxcy & Turnbull, 1999) and 2.013 (3) Å for the *N*-Eten complex (Grenthe *et al.*, 1979). It is well known that electron donation from in-plane Cu—N bonds results in elongation of the axial Cu—O bonds. Moreover, the Cu—N lengths, having σ -bonding character, are much longer than those of π -bonding ligands, but both Cu—N bond lengths of (I) are slightly shorter than that of common σ -bonding amine ligands. Each diamine ligand, with an N—Cu—N chelate angle of 84.58 (7)°, adopts a conformation similar to the mixed-ligand complexes (Akitsu & Komorita, 2002); one of the chelate rings is in the δ conformation and the other is in the λ conformation.

To describe the stereochemistry of copper(II) complexes, $T = R_S/R_L$, where R_S and R_L denote short in-plane Cu—N and long axial Cu—O bond lengths, respectively, has been commonly employed as a measure of the degree of tetragonal distortion caused by a Jahn–Teller effect (Hathaway & Billing, 1970). Although the difference in T values [0.790 for (I), 0.781 for the en, and 0.780 for the *N*-Eten complex] is quite small, the Cu—N bond distances are more sensitive to the steric effects of *N*-substituted groups than the axial Cu—O bond distances. Consequently, individual Cu—N and Cu—O coordination bond distances can be regarded as informative criteria for tetragonal distortion in itself, when one uses spectroscopic methods which can detect not only totally electronic states of copper(II) ions but also individual bond distances or coordination bonding features. Synchrotron spectroscopic studies (soft X-ray absorption spectroscopy) for the semi-coordination complexes are now in progress to

obtain detailed results, for example the direct detection of light-induced excitation.

Experimental

Crystals of (I) were prepared from a methanol solution (10 ml) of $\text{Cu}(\text{ClO}_4)_2$ (1.01 mmol) and *N*-methylethylenediamine (2.03 mmol) at room temperature. Blue prismatic crystals were obtained after a few days.

Crystal data

$[\text{Cu}(\text{ClO}_4)_2(\text{C}_3\text{H}_{10}\text{N}_2)]$
 $M_r = 410.71$
 Monoclinic, $P2_1/a$
 $a = 8.436$ (3) Å
 $b = 11.857$ (4) Å
 $c = 8.352$ (3) Å
 $\beta = 113.96$ (3)°
 $V = 763.4$ (5) Å³
 $Z = 2$

$D_x = 1.787$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 25 reflections
 $\theta = 10.1$ – 15.0 °
 $\mu = 1.82$ mm⁻¹
 $T = 297.2$ K
 Prism, blue
 0.40 × 0.30 × 0.30 mm

Data collection

Rigaku AFC-7R diffractometer
 ω - 2θ scans
 Absorption correction: ψ scan
 (North *et al.*, 1968)
 $T_{\min} = 0.524$, $T_{\max} = 0.579$
 2072 measured reflections
 1749 independent reflections
 1538 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.008$
 $\theta_{\text{max}} = 27.5$ °
 $h = -10 \rightarrow 4$
 $k = 0 \rightarrow 15$
 $l = -9 \rightarrow 10$
 3 standard reflections
 every 150 reflections
 intensity decay: 0.2%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.024$
 $wR(F^2) = 0.068$
 $S = 1.08$
 1538 reflections
 98 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0348P)^2 + 0.3309P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.002$
 $\Delta\rho_{\text{max}} = 0.33$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.29$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Cu1—O4	2.569 (2)	Cl1—O4	1.435 (2)
Cu1—N1	2.004 (2)	N1—C1	1.482 (3)
Cu1—N2	2.057 (2)	N2—C2	1.481 (3)
Cl1—O1	1.422 (2)	N2—C3	1.470 (3)
Cl1—O2	1.409 (2)	C1—C2	1.493 (3)
Cl1—O3	1.421 (2)		
N1—Cu1—O4	89.72 (7)	Cu1—N2—C2	105.6 (1)
N2—Cu1—O4	95.51 (7)	Cu1—N2—C3	119.0 (1)
N1—Cu1—N2	84.58 (7)		
N1—C1—C2—N2	56.2 (2)		

Table 2

Hydrogen-bonding geometry (Å, °).

$D\cdots H\cdots A$	$D\cdots H$	$H\cdots A$	$D\cdots A$	$D\cdots H\cdots A$
N1—H1 \cdots O4	0.95	3.01	3.250 (3)	96
N2—H7 \cdots O1	0.96	2.64	3.460 (3)	144
N2—H7 \cdots O2	0.96	2.66	3.376 (4)	132
N2—H7 \cdots O4	0.96	3.06	3.442 (2)	106
N1—H2 \cdots O3 ⁱ	0.95	2.49	3.206 (2)	132
N1—H1 \cdots O3 ⁱⁱ	0.95	2.31	3.158 (2)	148
N1—H1 \cdots O4 ⁱⁱ	0.95	2.70	3.347 (2)	126

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

All the H atoms were placed at calculated positions (C–H and C–N = 0.95–0.97 Å), and allowed for as riding, 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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