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Bis(*N*,*N*-dimethylethylenediamine-κ^2N,N')-bis(perchlorato-κO)copper(II)

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Key indicators

Single-crystal X-ray study
T = 297 K
Mean σ(C–C) = 0.005 Å
R factor = 0.031
wR factor = 0.113
Data-to-parameter ratio = 17.7

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

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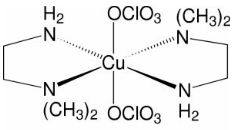
In the title compound, $[Cu(ClO_4)_2(C_4H_{12}N_2)_2]$, the Cu atom is located at a center of symmetry. It adopts an elongated octahedral *trans*-$[CuN_4O_2]$ coordination geometry, which is a typical feature of the pseudo-Jahn–Teller effect. The axial Cu—O bond length is 2.605 (4) Å, while the in-plane Cu—N bond lengths are 1.987 (2) and 2.098 (2) Å.

Comment

Because of the bright prospect of developing photo-controlling materials, copper(II) complexes having ethylenediamine derivatives are important not only as candidates for these materials but also as their building blocks. Indeed, intercalated hybrid materials (Choy *et al.*, 2002), thermochromism (Narayanan & Bhadbhade, 1998), and photochromism (Takahashi *et al.*, 2002) have been reported so far. The characteristic stereochemistry of copper(II) complexes, for example, flexible distortion (Simmons, 1993) or semi-coordination (Hathaway, 1984), may be explained by the Jahn–Teller effect (Murphy & Hathaway, 2003). The pseudo-Jahn–Teller effect predicts that only appropriately elongated axial bonds may be effective for thermally accessible distortion, and these systems may be very important for designing photo-controlling materials. The structures of semi-coordinated copper(II) complexes having *N*-substituted ethylenediamine ligands have been systematically investigated, *viz*. ethylenediamine (en; Maxcy & Turnbull, 1999), *N*-methylethylenediamine (*N*-Meen; Akitsu & Einaga, 2003), and *N*-ethylethylenediamine (*N*-Eten; Grenthe *et al.*, 1979). We have determined the crystal structure of bis(*N*,*N*-dimethylethylenediamine-κ^2N,N')bis(perchlorato-κO)copper(II), (I), and discuss here its structural features.



(I)

Complex (I) is centrosymmetric, with atom Cu1 located at a center of inversion (Fig. 1 and Table 1). Complex (I) adopts a tetragonally distorted (*i.e.* elongated) *trans*-$[CuN_4O_2]$ coordination environment. The axial Cu1—O1 semi-coordination bond distance is 2.605 (4) Å. The corresponding Cu—O bond lengths are 2.579 (4), 2.569 (2) and 2.594 (3) Å for the en, *N*-Meen and *N*-Eten complexes, respectively. The axial bond length of (I) is comparable to the largest value in the analogous complexes. The geometric parameters in the axial perchlorate ions are unremarkable. Intramolecular hydrogen

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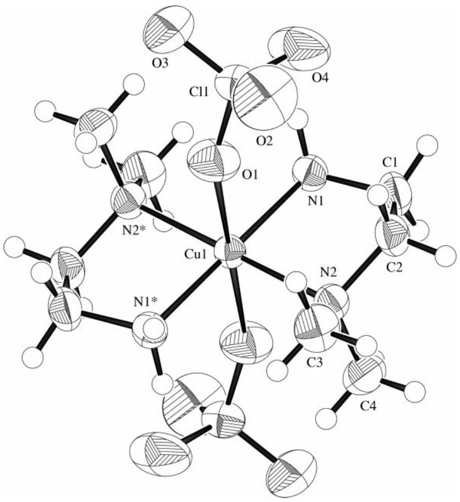

Figure 1
The molecular structure of (I), showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level. Atoms marked with an asterisk (*) are at the symmetry positions (2 − x, −y, 2 − z).

bonds (Table 2) are observed between amino H atoms and perchlorate O atoms. These hydrogen bonds also contribute to the stabilization of the axial semi-coordination. Moreover, the complexes are linked by N—H⋯O hydrogen bonds to form a three-dimensional network in the crystal structure.

The Cu1—N1 (NH_2) and Cu1—N2 (NMe_2) bond distances in (I) are 1.987 (2) and 2.098 (2) Å, respectively. Apparently, a characteristic structural feature of (I), *viz.* the difference in the Cu—N bond distances, may be attributed to the steric hindrance of the methyl groups. The corresponding Cu—N (NH_2) bond distances are 2.012 (2) and 2.019 (2) Å for the en, 2.004 (2) Å for the *N*-Meen and 2.013 (3) Å for the *N*-Eten complex. The Cu—N (NHR) bond distances are 2.057 (2) and 2.031 (3) Å for the *N*-Meen and *N*-Eten complexes, respectively. The number of substituent groups (*R*) at N is more effective in elongating the Cu—N bond than the length of the group. The N1—Cu1—N2 bond angle of the chelate ligands is 85.40 (8)°, which is slightly larger than that of the *N*-Meen complex [84.58 (7)°]. The N1—C1—C2—N2 torsion angle [50.5 (3)°] is similar to that of related complexes involving mixed ligands (Akitsu & Komorita, 2002).

The *T* value, which is defined as the ratio of (in-plane) Cu—N to (axial) Cu—O bond lengths, is the usual criterion for the degree of tetragonal distortion caused by the Jahn–Teller effect (Hathaway & Billing, 1970). The values of *T* are 0.78, 0.78, 0.78 and 0.79 for the *N*-Eten, en, (I), and *N*-Meen complexes, respectively. On the other hand, individual *T* values Cu—N (NH_2)/Cu—O are 0.78, 0.78, 0.76 and 0.78, and Cu—N (NR_2)/Cu—O are 0.78, none, 0.81 and 0.80 for the *N*-Eten, en, (I) and *N*-Meen complexes, respectively. The maximum *T* value of Cu1—N2/Cu1—O1 in (I) suggests that the steric effect of the present *N*,*N*-dimethyl substitution results in no elongation of specific bonds but elongation of both types of coordination bonds. Thermal and photo-response, and soft X-ray absorption spectroscopic studies of the series of related complexes are now in progress to elucidate detailed correlations between the structures and the electronic states.

Experimental

Crystals of (I) were prepared from a methanol solution (10 ml) of $Cu(ClO_4)_2$ (1.01 mmol) and *N*,*N*-dimethylethylenediamine (2.00 mmol) at room temperature. Blue prismatic crystals were obtained after a few days.

Crystal data

$[Cu(ClO_4)_2(C_4H_{12}N_2)_2]$
$M_r = 438.76$
Triclinic, $P\overline{1}$
$a = 7.978$ (4) Å
$b = 8.593$ (4) Å
$c = 7.797$ (8) Å
$\alpha = 111.01$ (6)°
$\beta = 104.91$ (6)°
$\gamma = 61.65$ (3)°
$V = 436.7$ (6) Å^3

$Z = 1$
$D_x = 1.668$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 17 reflections
$\theta = 11.2$–$12.4°$
$\mu = 1.60$ mm^{-1}
$T = 297.2$ K
Prism, blue
0.30 × 0.30 × 0.20 mm

Data collection

Rigaku AFC-7*R* diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.625$, $T_{max} = 0.726$
2269 measured reflections
2007 independent reflections
1894 reflections with $I > 2\sigma(I)$

$R_{int} = 0.061$
$\theta_{max} = 27.5°$
$h = -10 \rightarrow 10$
$k = -11 \rightarrow 10$
$l = -4 \rightarrow 10$
3 standard reflections every 150 reflections intensity decay: 2.5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.031$
$wR(F^2) = 0.113$
$S = 0.91$
1894 reflections
107 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0348P)^2 + 0.3309P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.41$ e Å^{-3}
$\Delta\rho_{min} = -0.48$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0234

Table 1
Selected geometric parameters (Å, °).

Cu1—O1	2.605 (4)	Cl1—O4	1.421 (3)
Cu1—N1	1.987 (2)	N1—C1	1.482 (3)
Cu1—N2	2.098 (2)	N2—C2	1.487 (4)
Cl1—O1	1.433 (4)	N2—C3	1.480 (4)
Cl1—O2	1.404 (4)	N2—C4	1.485 (4)
Cl1—O3	1.416 (3)	C1—C2	1.501 (4)
O1—Cu1—N1	90.9 (1)	Cu1—N2—C3	115.3 (1)
O1—Cu1—N2	85.65 (9)	Cu1—N2—C4	111.7 (2)
N1—Cu1—N2	85.40 (8)		
N1—C1—C2—N2	50.5 (3)		

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

D—H⋯*A*	*D*—H	H⋯*A*	*D*⋯*A*	*D*—H⋯*A*
N1—H1⋯O2^{i}	0.96	2.26	3.057 (5)	140

Symmetry code: (i) $1 + x, y, z$.

Since the intensity of diffraction was considerably weak, not all of the independent reflections were used for refinement. All H atoms were positioned geometrically (N—H = 0.95, C—H = 0.95–0.96 Å) and refined as riding, with $U_{iso}(H) = 1.2U_{eq}$(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: *SIR*92 (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *TEXSAN*.

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