Hong-Shan He

Department of Applied Chemistry, Huaqiao University, Quanzhou 362011, People's Republic of China, and Department of Chemistry, Biochemistry and Molecular Biology, North Dakota State University, Fargo, ND 58105, USA

Correspondence e-mail:
hongshan.he@ndsu.edu

A second polymorph of {tris[2-(5-methylimidazol-4-ylmethylimino)ethyl]amino}copper(II) diperchlorate

The crystal structure of the title compound, $[Cu(C_{21}H_{30}N_{10})](ClO_4)_2$, has recently been reported to crystallize in $P2_1/c$ [Brewer, Brewer, Butcher & Carpenter (2006). *Inorg. Chim. Acta*, **359**, 1263–1268]. The structure of a second polymorph crystallizes in $P2_1$ with different cell dimensions. In the crystal structure, the Cu^{II} complex cations are bridged by perchlorate anions through N—H···O hydrogen bonds.

Comment

Tris(2-ethylamino)amine (tren)-based tripodal ligands have attracted considerable interest in recent years owing to their easy modification for the building of model complexes of different metalloenzymes and the design of new materials with excellent physical properties (Brewer *et al.*, 1998; Katsuki *et al.*, 2000; Mohamadou & Gerard, 2001; Paul *et al.*, 2000; Schatz *et al.*, 2001; Su *et al.*, 2001; Wang *et al.*, 1997; Yang *et al.*, 2000). Previously, we reported the structures of Mg^{II} complexes, where the Mg^{II} atoms are coordinated by 4-methyl-5-imidazole and 2-thiazole-modified tren (He & Rodgers, 2004; He *et al.*, 2004). The results showed that the metal ions were six-coordinate. In order to explore the application of Cu^{II} complexes as potential inhibitors for metalloenzymes, several copper complexes have been prepared, and reported here is the crystal structure of the Cu^{II} complex, (I), of tris[2-(5-methylimidazol-4ylmethyliminoethyl]amine, (I). During the preparation of this manuscript, the structure of a polymorph of the title compound that crystallizes in $P2_1/c$ has been reported by Brewer *et al.* (2006).

(I)
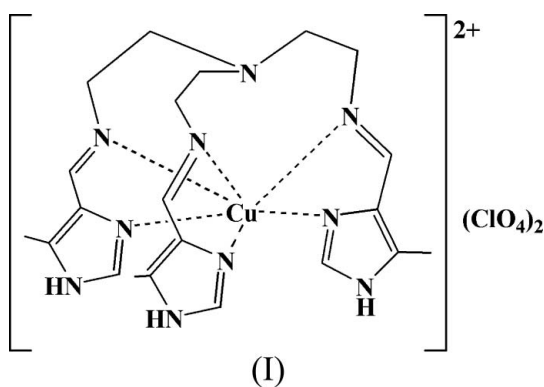
The structure determined in the present study crystallizes in the monoclinic space group $P2_1$. The copper ion is coordinated by three N atoms from 4-methyl-5-imidazole groups and three N atoms from imine groups (Fig. 1). The coordination geometry is distorted octahedral. The Cu—N bond lengths
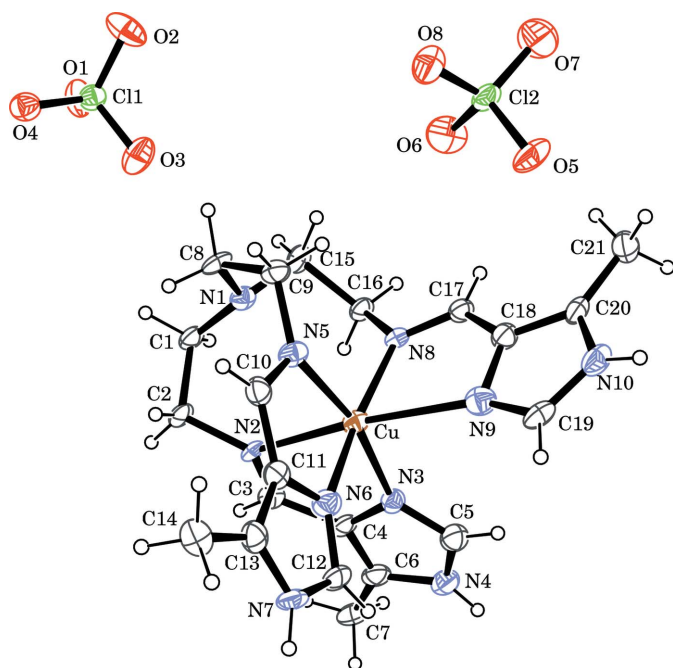
Figure 1
The asymmetric unit of (I). Displacement ellipsoids are drawn at the 30% probability level.
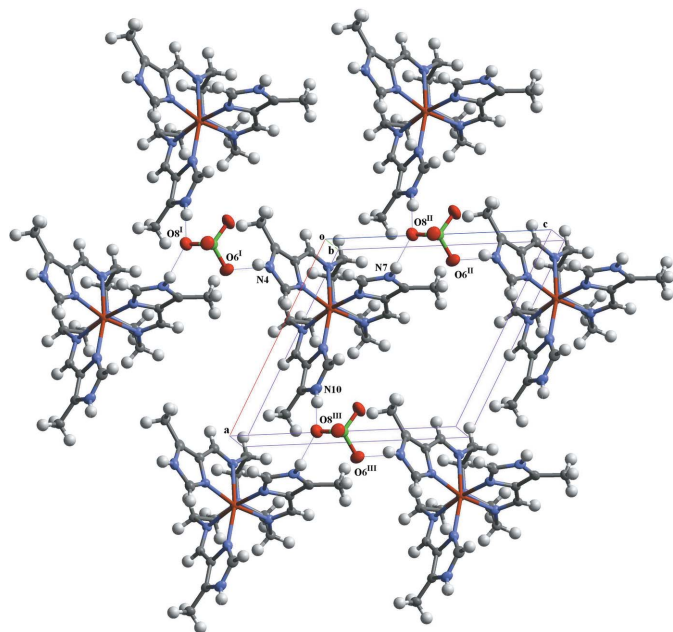

Figure 2
A packing diagram of (I), showing N—H···O hydrogen bonds (light blue lines) . Symmetry codes are as given in Table 2.

and the bond angles at Cu are given in Table 1. The distance between atoms Cu and N1 is 3.254 (8) Å, indicating that there is no bond formation between them. Each Cu^{II} complex is linked to six neighboring complexes through perchlorate ions, which are connected to the complexes by N—H···O hydrogen bonds (Table 2 and Fig. 2).

Experimental

A solution of tris(2-ethylamino)amine (1.0 mmol) in MeOH (6 ml) was treated with 4-methyl-5-imidazolecarboxaldehyde (3.0 mmol) in MeOH (5 ml). The resulting solution was refluxed under nitrogen for 4 h, then $Cu(ClO_4)_2 \cdot 6H_2O$ (1.0 mmol) in MeOH (2 ml) was added. The mixture was refluxed further for 4 h, then cooled to room temperature. The precipitate was collected by filtration and was washed with MeOH three times. Single crystals suitable for X-ray diffraction were obtained by slow evaporation of an acetonitrile solution at room temperature for one week.

Crystal data

$[Cu(C_{21}H_{30}N_{10})](ClO_4)_2$	$Z = 2$
$M_r = 684.99$	$D_x = 1.560$ Mg m^{-3}
Monoclinic, $P2_1$	Mo $K\alpha$ radiation
$a = 10.7278$ (6) Å	$\mu = 1.00$ mm^{-1}
$b = 13.8859$ (6) Å	$T = 293$ (2) K
$c = 11.1108$ (7) Å	Thin plate, green
$\beta = 118.220$ (2)°	$0.23 \times 0.11 \times 0.04$ mm
$V = 1458.39$ (14) Å^3	

Data collection

Nonius KappaCCD diffractometer	6006 measured reflections
φ and ω scans	5771 independent reflections
Absorption correction: multi-scan	4982 reflections with $I > 2\sigma(I)$
(DENZO; Otwinowski & Minor, 1997)	$R_{int} = 0.049$
$T_{min} = 0.804$, $T_{max} = 0.961$	$\theta_{max} = 27.0°$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.1344P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.082$	$+ 6.0122P]$
$wR(F^2) = 0.244$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.09$	$(\Delta/\sigma)_{max} < 0.001$
5771 reflections	$\Delta\rho_{max} = 2.16$ e Å^{-3}
382 parameters	$\Delta\rho_{min} = -0.94$ e Å^{-3}
H-atom parameters constrained	Absolute structure: Flack (1983), 2461 Friedel pairs
	Flack parameter: 0.06 (3)

Table 1
Selected geometric parameters (Å, °).

Cu—N2	2.377 (7)	Cu—N6	2.022 (8)
Cu—N3	2.040 (7)	Cu—N8	2.041 (7)
Cu—N5	2.062 (8)	Cu—N9	2.426 (9)
N2—Cu—N3	75.3 (3)	N3—Cu—N9	94.3 (3)
N2—Cu—N5	94.5 (3)	N5—Cu—N6	80.2 (3)
N2—Cu—N6	92.6 (3)	N5—Cu—N8	96.6 (3)
N2—Cu—N8	98.1 (3)	N5—Cu—N9	96.3 (3)
N2—Cu—N9	168.8 (3)	N6—Cu—N8	169.0 (3)
N3—Cu—N5	166.7 (3)	N6—Cu—N9	92.0 (3)
N3—Cu—N6	91.6 (3)	N8—Cu—N9	77.9 (3)
N3—Cu—N8	93.3 (3)		

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

D—H···A	D—H	H···A	D···A	D—H···A
N4—NH4···O6^i	0.86	2.09	2.930 (13)	165
N7—NH7···O8^{ii}	0.86	2.12	2.937 (14)	157
N10—NH10···O8^{iii}	0.86	2.14	2.993 (14)	172

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

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H atoms were positioned geometrically (N—H = 0.86 Å and C—H = 0.93–0.97 Å) and refined as riding with $U_{iso}(H) = 1.2U_{eq}(C,N)$ or $1.5U_{eq}$(methyl C). The highest residual density peak is 1.05 Å from the Cu atom.

Data collection: *COLLECT* (Hooft, 1998); cell refinement: *DENZO* (Otwinowski & Minor, 1997); data reduction: *DENZO*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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