metal-organic compounds

[1,5-Bis(1-methyl-1H-tetrazol-5-yl-κN)-3-oxopentane-κO]-dichlorocopper(II)

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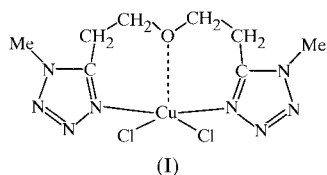Correspondence e-mail: lyakhov@fhp.bsu.unibel.by

The title compound, $[CuCl_2(C_8H_{14}N_8O)]$, is the first structurally characterized molecular chelate complex of a binuclear N-substituted tetrazole. The Cu atom is five-coordinate, with an approximately square-pyramidal geometry. The equatorial positions of the pyramid are occupied by two Cl atoms and two N atoms from the ligand molecule; the O atom of the ligand lies in the axial position. Each complex is connected to four others via weak C—H···Cl and C—H···N interactions, forming sheets parallel to the (010) plane.

Comment

Binuclear N-substituted tetrazoles are of interest as potential chelating ligands (Downard *et al.*, 1995). Some molecular complexes of binuclear substituted tetrazoles have been reported in the literature (Gaponik *et al.*, 1990; Lavrenova *et al.*, 1991; Downard *et al.*, 1995; van Koningsbruggen *et al.*, 2001). An inspection of the Cambridge Structural Database (April 2001 release; Allen & Kennard, 1993) with respect to binuclear N-substituted tetrazole complexes revealed only a

(I)

thallium(III) organometallic compound with 1,2-bis(tetrazol-5-yl)benzene as the ligand molecule (Bhandari *et al.*, 2000). The crystal structure of a non-chelate complex of 1,2-bis-(tetrazol-1-yl)propane with iron(II) perchlorate has also been reported (van Koningsbruggen *et al.*, 2000). In this paper, we present the molecular and crystal structures of the title copper(II) complex with 1,5-bis(1-methyl-1H-tetrazol-5-yl)-3-oxopentane, (I).

In compound (I), the coordination polyhedron of the Cu atom is somewhat distorted from a perfect square pyramid, as is apparent from the observed τ value of 0.3 (values of 0 and 1 are indicative of idealized square-pyramidal and trigonal-bipyramidal geometries, respectively; Addison *et al.*, 1984). The equatorial positions of the pyramid are occupied by atoms Cl1 and Cl2 [Cu1—Cl1 2.2557 (7) and Cu1—Cl2 2.2464 (7) Å], and by atoms N4 and N4′ of the ligand molecule [Cu—N4 2.002 (2) and Cu—N4′ 2.003 (2) Å]. These Cu—Cl and Cu—N distances are in the normal ranges observed previously for Cu^{II} complexes. Atom O1 of the ligand molecule lies in the axial position of the pyramid. The Cu1—O1 distance of 2.499 (2) Å is significantly longer than the usual bonding distance (Orpen *et al.*, 1989), representing a weak Cu—O interaction.

The ligand molecule is tridentate. Both tetrazole rings of the ligand in (I) have very similar geometries. They are both planar, to within 0.006 (2) Å for the ring with primed atom numbering, and to within 0.003 (2) Å for the ring numbered without primes (Fig. 1). The bond distances and angles in the tetrazole fragments of (I) are consistent with those previously observed for tetrazole rings. The dihedral angle between the planes of the two tetrazole rings in the ligand molecule is 18.86 (7)°.
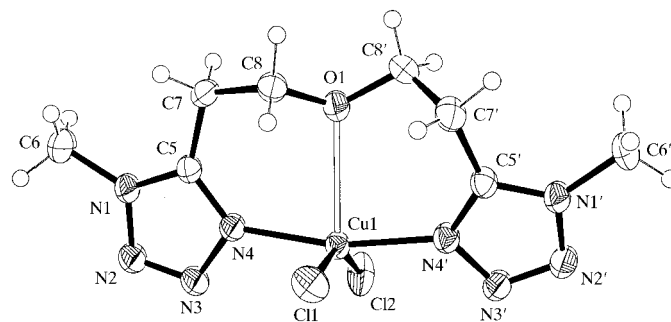

Figure 1
The molecular view of (I) with displacement ellipsoids drawn at the 50% probability level. H atoms are shown as small spheres of arbitrary radii.

Inspecting the packing structure of (I), the following peculiarities may be discerned. There are no classical hydrogen bonds in the structure, but the intermolecular contacts C7—H7A···Cl2[i] and C7′—H7′B···N3[ii] may be noted [symmetry codes: (i) $x - 1, y, z$; (ii) $x - \frac{1}{2}, \frac{1}{2} - y, z - \frac{1}{2}$]. Taking these weak interactions into account, two types of infinite one-dimensional chains may be seen in the structure of (I). Chains of the first type are formed by C7—H7A···Cl2[i] interactions and run parallel to the *a* axis. Chains of the second type are due to C7′—H7′B···N3[ii] contacts and are oriented along the [101] direction. The connection of each complex with four others via these interactions leads to sheets parallel to the (010) plane. No pronounced interaction could be found between these sheets.

Experimental

1,5-Bis(1-methyl-1*H*-tetrazol-5-yl)-3-oxopentane was synthesized by methylation of 1,5-bis(*tert*-butyl-1*H*-tetrazol-5-yl)-3-oxopentane, followed by de-*tert*-butylation of the intermediate tetrazolium salt according to the method previously described by Gaponik *et al.* (2000). The title complex was prepared by the reaction of copper(II) chloride dihydrate with 1,5-bis(1-methyl-1*H*-tetrazol-5-yl)-3-oxopentane in ethanol. Single crystals of (I) were grown by slow crystallization from the reaction mixture.

Crystal data

$[CuCl_2(C_8H_{14}N_8O)]$
$M_r = 372.71$
Monoclinic, $P2_1/n$
$a = 8.566 (2)$ Å
$b = 13.611 (3)$ Å
$c = 12.633 (3)$ Å
$\beta = 108.54 (2)°$
$V = 1396.5 (6)$ Å^3
$Z = 4$

$D_x = 1.773$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 13.7–19.8°$
$\mu = 1.96$ mm^{-1}
$T = 293 (2)$ K
Prism, blue
$0.56 \times 0.38 \times 0.08$ mm

Data collection

Nicolet *R*3*m* four-circle diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.407$, $T_{max} = 0.859$
4477 measured reflections
4095 independent reflections
3547 reflections with $I > 2\sigma(I)$

$R_{int} = 0.020$
$\theta_{max} = 30.1°$
$h = 0 \rightarrow 12$
$k = 0 \rightarrow 19$
$l = -17 \rightarrow 16$
3 standard reflections
  every 100 reflections
  intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.092$
$S = 1.06$
4095 reflections
183 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0509P)^2 + 0.6526P]$
  where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.59$ e Å^{-3}
$\Delta\rho_{min} = -0.56$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—N4	2.002 (2)	Cu1—Cl1	2.2557 (7)
Cu1—N4′	2.003 (2)	Cu1—O1	2.499 (2)
Cu1—Cl2	2.2464 (7)		
N4—Cu1—N4′	166.77 (7)	Cl2—Cu1—Cl1	148.75 (3)
N4—Cu1—Cl2	91.29 (5)	N4—Cu1—O1	81.73 (6)
N4′—Cu1—Cl2	90.79 (5)	N4′—Cu1—O1	85.31 (6)
N4—Cu1—Cl1	92.97 (5)	Cl2—Cu1—O1	110.75 (5)
N4′—Cu1—Cl1	92.02 (5)	Cl1—Cu1—O1	100.50 (4)

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

$D—H\cdots A$	$D—H$	$H\cdots A$	$D\cdots A$	$D—H\cdots A$
C7—H7A$\cdots$Cl2^i	0.97	2.79	3.697 (2)	156
C7′—H7′B$\cdots$N3^{ii}	0.97	2.59	3.484 (3)	154

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

The H atoms were included in geometrically calculated positions, with C—H = 0.96–0.97 Å, and refined using a riding model, with $U_{iso}(H)$ equal to $1.2U_{eq}$ of the corresponding C atom ($1.5U_{eq}$ for methyl groups).

Data collection: *R*3*m Software* (Nicolet, 1980); cell refinement: *R*3*m Software*; data reduction: *R*3*m Software*; program(s) used to solve structure: *SIR*97 (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1997); software used to prepare material for publication: *SHELXL*97.

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