

catena-Poly[[bis[μ -1,2-bis(1-methyl-tetrazol-5-yl)ethane- κ^2 N⁴:N^{4'}]-bis[chlorocopper(II)]]-di- μ -chloro]

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In the title compound, $[\text{Cu}_2\text{Cl}_4(\text{C}_6\text{H}_{10}\text{N}_8)_2]_n$, the ligand has C_2 symmetry, and the Cu and Cl atoms lie on a mirror plane. The coordination polyhedron of the Cu atom is a distorted square pyramid, with the basal positions occupied by two N atoms from two different ligands [$\text{Cu}-\text{N} = 2.0407$ (18) Å] and by the two Cl atoms [$\text{Cu}-\text{Cl} = 2.2705$ (8) and 2.2499 (9) Å], and the apical position occupied by a Cl atom [$\text{Cu}-\text{Cl} = 2.8154$ (9) Å] that belongs to the basal plane of a neighbouring Cu atom. The $[\text{CuCl}_2(\text{C}_6\text{H}_{10}\text{N}_8)_2]$ units form infinite chains extending along the a axis via the Cl atoms. Intermolecular $\text{C}-\text{H}\cdots\text{Cl}$ contacts [$\text{C}\cdots\text{Cl} = 3.484$ (2) Å] are also present in the chains. The chains are linked together by intermolecular $\text{C}-\text{H}\cdots\text{N}$ interactions [$\text{C}\cdots\text{N} = 3.314$ (3) Å].

Comment

Complexes of mononuclear N -alkyl- and N -alkenyltetrazoles with copper(II) chloride have been found to be low-temperature ferromagnets (Lavrenova *et al.*, 1993, 1996). For this reason, the crystal structures of such complexes have been studied intensively in the past few years (Ivashkevich *et al.*, 2001, 2002; Stassen *et al.*, 2002). However, the data on analogous complexes of N -substituted bistetrazoles are limited, and the crystal structures of only two chelate complexes of binuclear N -substituted tetrazoles with copper(II) chloride have been described so far, *viz.* $\text{Cu}(\text{btop})\text{Cl}_2$ and $\text{Cu}(\text{mtop})\text{Cl}_2$, where btop is 1,5-bis(2-*tert*-butyl-5-tetrazolyl)-3-oxopentane and mtop is 1,5-bis(1-methyl-5-tetrazolyl)-3-oxopentane (Voitekhovich *et al.*, 2002; Lyakhov *et al.*, 2001). In the present paper, we report the crystal structure of the coordination compound, (I), of copper(II) chloride with 1,2-bis(1-methyltetrazol-5-yl)ethane.

In the title compound, the ligand has crystallographically imposed C_2 symmetry (Fig. 1) and exhibits bidentate properties. The geometry of the tetrazole ring is close to that previously observed for 1,5-disubstituted tetrazoles (Cambridge Structural Database, Version 5.24 of November

2002; Allen, 2002). The ring is essentially planar, with the mean deviation of the tetrazole ring atoms from their least-squares plane being 0.0038 (12) Å.

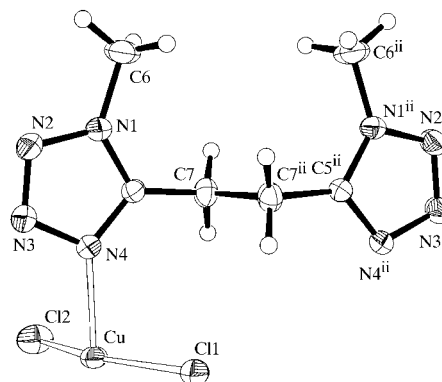
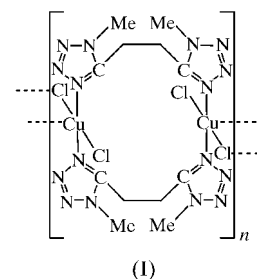


Figure 1

A view of (I), showing the atom-numbering scheme. Displacement ellipsoids have been plotted at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry code: (ii) $-x, -y, z$.]

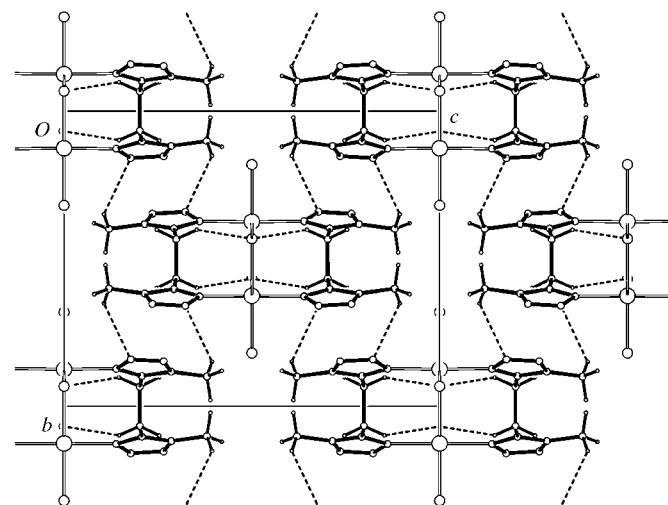


Figure 2

The crystal packing of (I), viewed along the a axis. Dashed lines show the $\text{C}-\text{H}\cdots\text{Cl}$ and $\text{C}-\text{H}\cdots\text{N}$ contacts presented in Table 2.

Cu—N = 2.0407 (18) Å] and by the two Cl atoms [Cu—Cl1 = 2.2705 (8) Å and Cu—Cl2 = 2.2499 (9) Å], and the apical position is occupied by atom Cl1ⁱⁱ [symmetry code: (ii) $-x, -y, z$; Cu—Cl = 2.8154 (9) Å], which belongs to the basal plane of a neighboring Cu atom.

The [CuCl₂(C₆H₁₀N₈)₂] units shown in the *Scheme* can be found in the structure of (I). The coordination polyhedra of Cu atoms of neighbouring units share edges with the Cl atoms, forming polymeric chains extending along the *a* axis. C7—H7B···Cl1ⁱⁱⁱ interactions [symmetry code: (iii) $1 - x, -y, z$; Table 2], with a C···Cl distance of 3.484 (2) Å, are also present in these chains. The chains are linked together by intermolecular C6—H6B···N3^{iv} interactions [symmetry code: (iv) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} - z$; Fig. 2], with a C···N distance of 3.314 (3) Å (Steiner, 1996).

Experimental

1,2-Bis(1-methyl-1*H*-tetrazol-5-yl)ethane was obtained according to the method described by Koren *et al.* (1995) for the selective synthesis of mononuclear 1,5-disubstituted tetrazoles from 5-substituted tetrazoles. *tert*-Butanol (2.2 ml, 23 mmol) was added dropwise with stirring to a solution of 1,2-bis(tetrazol-5-yl)ethane [1.83 g, 11 mmol; obtained from succinonitrile, sodium azide and ammonium chloride according to the method described by Finnegan *et al.* (1958)] in sulfuric acid (96%, 15 ml). The mixture was stirred at room temperature for 2 h, and the reaction mixture was then poured on to ice (50–70 g). The precipitate was filtered off, washed with cold water and dried *in vacuo*. Crystallization from diethyl ether/hexane (1:1) gave 1,2-bis(2-*tert*-butyl-1*H*-tetrazol-5-yl)ethane (2.3 g, 78%; m.p. 351–352 K). ¹H NMR [(CD₃)₂SO]: δ 1.69 (*s*, 18H, 6 × CH₃), 3.33 [*s*, 4H, 2 × CH₂C(tetrazole)]. A solution of 1,2-bis(2-*tert*-butyl-1*H*-tetrazol-5-yl)ethane (2.3 g, 8.2 mmol) and dimethyl sulfate (2.3 ml, 24.6 mmol) in acetonitrile or trichloromethane (5 ml) was stirred at room temperature for 4 d. Hydrochloric acid (36%, 40 ml) was added and the mixture was stirred for 1 h. The upper aqueous layer of the mixture was separated and heated on a water bath for 5 h. After neutralization of the reaction mixture with sodium hydroxide, the solvent was removed *in vacuo*. The residue was extracted with boiling ethanol, and the extract was cooled to 273–278 K. The precipitate obtained was recrystallized from water, yielding colorless crystals of 1,2-bis(1-methyl-1*H*-tetrazol-5-yl)ethane (0.98 g, 62%; total yield 46%; m.p. 426–427 K). ¹H NMR (100 MHz, CD₃CN): δ 3.44 (*s*, 4H, 2 × CH₂), 4.05 (*s*, 6H, 2 × CH₃); ¹³C NMR [25 MHz, (CD₃)₂SO]: δ 23.6 (2 × CH₂), 37.1 (2 × CH₃), 157.7 [2 × C(tetrazole)]. The title complex was prepared by the reaction of copper(II) chloride dihydrate (0.17 g, 1 mmol) and 1,2-bis(1-methyl-1*H*-tetrazol-5-yl)ethane (0.19 g, 1.0 mmol) in ethanol (20 ml) at room temperature. Single crystals were grown by slow evaporation (2–3 d) from the reaction mixture (0.19 g, yield 58%; decomposed at 484 K).

Crystal data

[Cu₂Cl₄(C₆H₁₀N₈)₂]
M_r = 657.32
 Orthorhombic, *Pnmm*
a = 6.7320 (10) Å
b = 11.500 (2) Å
c = 14.640 (3) Å
V = 1133.4 (3) Å³
Z = 2
D_x = 1.926 Mg m⁻³

Mo *K*α radiation
 Cell parameters from 25 reflections
 θ = 14.3–26.1°
 μ = 2.39 mm⁻¹
T = 293 (2) K
 Prism, blue
 0.58 × 0.32 × 0.24 mm

Data collection

Nicolet *R3m* four-circle diffractometer
 $\omega/2\theta$ scans
 Absorption correction: φ scan (North *et al.*, 1968)
 T_{\min} = 0.318, T_{\max} = 0.562
 1917 measured reflections
 1733 independent reflections
 1637 reflections with $I > 2\sigma(I)$

R_{int} = 0.013
 θ_{max} = 30.1°
 h = 0 → 9
 k = 0 → 16
 l = -1 → 20
 3 standard reflections every 100 reflections
 intensity decay: none

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)]$ = 0.031
 $wR(F^2)$ = 0.103
 S = 1.26
 1733 reflections
 83 parameters
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0501P)^2 + 0.7797P]$
 where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.55 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\text{min}} = -0.56 \text{ e } \text{Å}^{-3}$
 Extinction correction: *SHELXL97*
 Extinction coefficient: 0.064 (3)

Table 1

Selected geometric parameters (Å, °).

Cu—N4	2.0407 (18)	Cu—Cl1	2.2705 (8)
Cu—Cl2	2.2499 (9)	Cu—Cl1 ⁱⁱ	2.8154 (9)
N4 ⁱ —Cu—N4	174.24 (10)	Cl2—Cu—Cl1	160.54 (4)
N4 ⁱ —Cu—Cl2	89.85 (4)	N4 ⁱ —Cu—Cl1 ⁱⁱ	87.39 (5)
N4—Cu—Cl2	89.85 (4)	N4—Cu—Cl1 ⁱⁱ	87.39 (5)
N4 ⁱ —Cu—Cl1	91.10 (4)	Cl2—Cu—Cl1 ⁱⁱ	111.72 (3)
N4—Cu—Cl1	91.10 (4)	Cl1—Cu—Cl1 ⁱⁱ	87.74 (3)

Symmetry codes: (i) $x, y, -z$; (ii) $-x, -y, z$.

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>
C7—H7B···Cl1 ⁱⁱⁱ	0.97	2.61	3.484 (2)	150
C6—H6B···N3 ^{iv}	0.96	2.58	3.314 (3)	134

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

H atoms were included in idealized positions (C—H = 0.96 Å) and refined using a riding model, with $U_{\text{iso}}(\text{H})$ values equal to $1.5U_{\text{eq}}(\text{C})$ for methyl H atoms and $1.2U_{\text{eq}}(\text{C})$ for methylene H atoms.

Data collection: *R3m Software* (Nicolet, 1980); cell refinement: *R3m Software*; data reduction: *OMNIBUS* (Galdecka, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997), *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV1134). Services for accessing these data are described at the back of the journal.

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