

An X-ray powder investigation of catena-poly[copper(II)-di- μ -chloro- κ^4 1:2Cl- μ -1,5-dimethyl-1*H*-tetrazole- κ^2 N³:N⁴]

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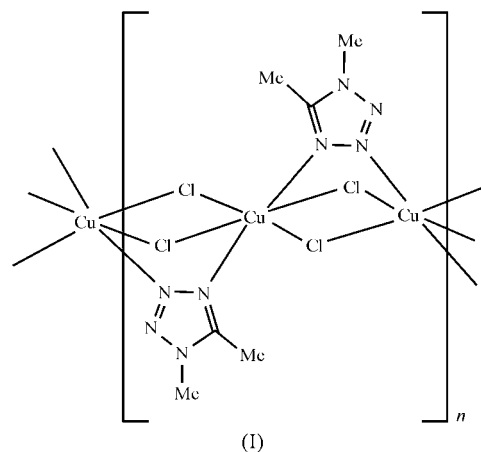
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The crystal structure of the polymeric title complex, $[\text{CuCl}_2(\text{C}_3\text{H}_6\text{N}_4)]_n$, has been solved from laboratory X-ray powder diffraction data collected at room temperature. The structural model obtained was refined with the Rietveld method using geometric soft restraints. There are two Cu atoms, two Cl atoms and one 1,5-dimethyltetrazole ligand in the asymmetric unit. Both Cu atoms lie on inversion centres and adopt essentially elongated octahedral coordination. Within the octahedra, the elongated axial positions are occupied by Cl atoms, while two Cl and two N atoms (N3 and N4 of the tetrazole ring) are in equatorial sites. Each Cl atom forms an asymmetric bridge between neighbouring Cu atoms, which are also bridged *via* the N3–N4 bond of the tetrazole ring. These bridges result in the formation of polymeric chains, running along the *a* axis, with weak C–H...Cl hydrogen bonds crosslinking the chains.

Comment

In the last decade, the crystal structures of metal halide complexes with substituted tetrazoles have been investigated intensively [Cambridge Structural Database (CSD), Version 5.27 of November 2005; Allen, 2002], because these compounds are potential molecular magnets. However, very little has appeared in the literature on Cu^{II} chloride complexes with 1,5-disubstituted tetrazoles. Only four such compounds have been structurally characterized to date, namely CuCl_2L complexes with *L* = 1,5-bis(1-methyl-1*H*-tetrazol-5-yl)-3-oxo pentane (Lyakhov *et al.*, 2001), *L* = *N,N*-dimethyl-1-(1-methyl-1*H*-tetrazol-5-yl)methanamine (Ivashkevich *et al.*, 2002) and *L* = 1,2-bis(1-methyltetrazol-5-yl)ethane (Ivashkevich *et al.*, 2003), and the CuCl_2L_2 complex with *L* = 1,5-diaminotetrazole (Gaponik *et al.*, 2005). In these complexes,

the ligand molecules may be considered as functionally substituted tetrazoles with additional electron-donor N and O atoms in the substituents [also including atom N4 of the tetrazole ring in bis(tetrazole) ligands]. In all these compounds, as they are molecular complexes (the first and the second compounds in the above list) or coordination polymers (the third and fourth compounds), only one tetrazole ring atom (N4) coordinates to the Cu atom, while additional coordination occurs through the amino N or O atom of the tetrazole ring substituents.



This paper presents the crystal structure of the title CuCl_2L complex, (I), where *L* is 1,5-dimethyltetrazole. This is the first structure of a metal(II) halide complex with a 1,5-disubstituted tetrazole containing simple alkyl substituents. The synthesis and some physicochemical properties of the complex have been described previously (Koren *et al.*, 1988). However, no structural data have appeared in the literature to date because of the difficulty in growing single crystals suitable for structural analysis. In the present paper, the structure of (I) was solved and refined from X-ray powder diffraction data.

Compound (I) crystallizes in the triclinic space group $P\bar{1}$ with two Cu atoms, two Cl atoms and one tetrazole ligand molecule in the asymmetric unit. Both Cu atoms, Cu1 and

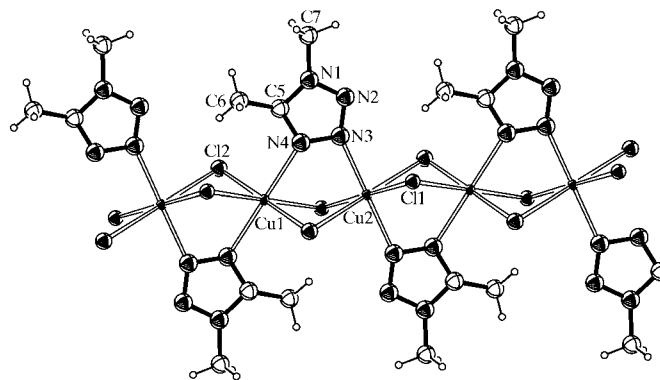


Figure 1

A fragment of the crystal structure of (I), showing the Cu-atom environment, the formation of a polymeric chain along the *a* axis and the atom numbering for the asymmetric unit. Displacement spheres are plotted at the 30% probability level.

Cu₂, lie on inversion centres, while all remaining atoms are in general positions.

The tetrazole ring geometry in (I) is normal for 1-mono and 1,5-disubstituted tetrazoles (CSD). The formal double bonds N2=N3 and N4=C5 are the shortest in the ring (Table 1), while the formal single bonds lie in the range 1.344 (8)–1.356 (8) Å.

The Cu atoms adopt essentially elongated octahedral coordination (Fig. 1 and Table 1). Within the octahedra, the elongated axial positions are occupied by Cl atoms, while two Cl and two N atoms (N3 and N4 of the tetrazole ring) are in equatorial sites. The axial Cu–Cl bonds are on average about 0.57 Å longer than the equatorial Cu–Cl bonds.

Each Cl atom belongs to two neighbouring Cu octahedra and lies in an axial position of one octahedron and in the equatorial plane of a neighbouring octahedron, thereby forming an asymmetric bridge between the Cu atoms. These metal atoms are also bridged *via* the N3–N4 bond of the tetrazole ring (see below). The bridges are responsible for the

existence of polymeric ribbon-like chains running along the *a* axis (Fig. 1), with the ribbon planes close to (011) (Fig. 2). Within the chains, the Cu···Cu distance is 3.4059 (2) Å.

There are weak C–H···Cl hydrogen bonds in the structure of (I) (Table 2). One H atom of the C6 methyl group interacts with atom Cl2 within a polymeric chain, while two H atoms of the C7 methyl group participate in interactions that serve to crosslink the chains.

In the structure of (I), the connection between neighbouring Cu atoms within the polymeric chains is realised not only through the Cl atoms, but also *via* the N3–N4 bridge of the tetrazole ring. This confirms the previously advanced hypothesis (Koren *et al.*, 1988) of the polymeric structure of (I) and the presence of additional linking between the Cu atoms *via* a tetrazole N–N bridge. More recently, this assumption was generalized in a review paper (Gaponik *et al.*, 2006) where, by analysing some experimental data and the results of quantum-chemical calculations concerned with disubstituted tetrazoles, a general conclusion was reached that 1,5-dialkyl-tetrazoles should be able to link metal atoms together through the N3–N4 bridge. To date, among the Cu^{II} complexes of 1,5-disubstituted tetrazoles, only complex (I) shows linking between the Cu atoms through the N3–N4 bridge. However, such a bridge was found in the complex of Ag^I nitrate with pentamethylenetetrazole, which is composed of [Ag(NO₃)-(C₁₂H₂₀N₈)]₂ dimers (Bonder & Popov, 1972). It should be noted that similar ring bridges are typical of 1,2,4-triazole complexes (Haasnoot, 2000), with iron(II) complexes incorporating 1,2,4-triazoles being spin-crossover compounds. Given the N3–N4 bridging in (I), one may expect that iron(II) complexes of 1,5-dialkyltetrazoles with such bridges may also reveal spin-crossover properties.

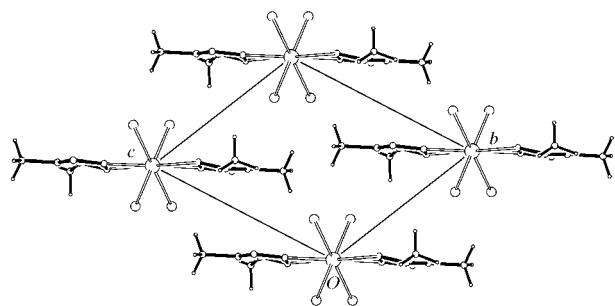


Figure 2
The crystal structure of (I), viewed along the *a* axis.

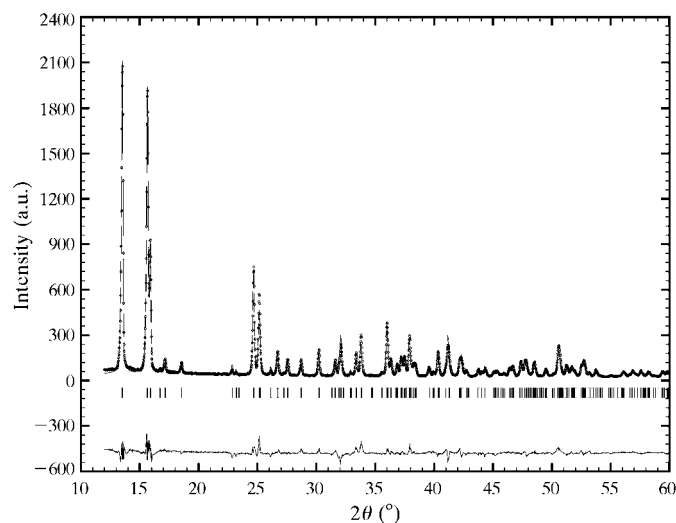


Figure 3
Final Rietveld refinement plots of (I). Circles denote the experimental diffraction pattern, the upper solid line indicates the pattern calculated from the refined crystal structure, the lower solid line indicates the difference between these patterns and vertical lines denote the reflection positions.

Experimental

A solution of CuCl₂·2H₂O (0.94 g, 0.0055 mol) in methanol (10 ml) was added to a solution of 1,5-dimethyltetrazole (1.10 g, 0.011 mol) in a mixture of methanol and diethyl ether (1:2 v/v, 30 ml) with stirring at room temperature. The reaction mixture was stirred for 0.5 h. The resulting green–blue crystals of (I) were filtered off, washed with a mixture of methanol and diethyl ether (1:3 v/v, 2 × 25 ml) and air dried (1.13 g, yield 89%). Analysis calculated (%): Cu 27.3; found (%): Cu 27.1.

Crystal data

[CuCl₂(C₃H₆N₄)]
M_r = 232.57
Triclinic, *P* $\bar{1}$
a = 6.8117 (4) Å
b = 7.4177 (4) Å
c = 8.6722 (4) Å
 α = 109.167 (2)°
 β = 105.528 (3)°
 γ = 103.121 (3)°
V = 374.15 (4) Å³

Z = 2
D_x = 2.064 Mg m^{−3}
Co *K*α radiation
 λ = 1.79021 Å
T = 295 K
Specimen shape: flat sheet
30 × 30 × 1 mm
Specimen prepared at 295 K
Particle morphology: needle,
green–blue

Data collection

Carl Zeiss HZG-4A diffractometer
Specimen mounting: packed powder
pellet
Specimen mounted in reflection
mode

Scan method: step
 $2\theta_{\min}$ = 12.0°, $2\theta_{\max}$ = 141.4°
Increment in 2θ = 0.02°

Refinement

Refinement on I_{net}	H-atom parameters constrained
$R_p = 0.078$	Weighting scheme based on measured s.u.'s
$R_{wp} = 0.104$	$(\Delta/\sigma)_{\text{max}} = 0.05$
$R_{\text{exp}} = 0.136$	Preferred orientation correction:
$R_B = 0.098$	Marsh–Dollase (Marsh, 1932;
$S = 0.76$	Dollase, 1986), for the [100]
Wavelength of incident radiation:	preferred orientation of needle-
1.79021 Å	like grains. The refined value of
Excluded region(s): none	coefficient G_1 is 1.076(3). The G_2
Profile function: pseudo-Voigt;	parameter was found to be prac-
refined value of the η -parameter	tically equal to 0 and was not
is 0.779 (14).	included in the final refinement.
973 reflections	
52 parameters	

Table 1

Selected geometric parameters (Å, °).

N1–N2	1.354 (10)	Cu1–N4	2.248 (10)
N1–C5	1.344 (8)	Cu1–Cl1 ⁱ	2.768 (5)
N2–N3	1.295 (16)	Cu2–Cl1	2.231 (5)
N3–N4	1.356 (8)	Cu2–N3	2.155 (12)
N4–C5	1.320 (10)	Cu2–Cl2 ⁱⁱ	2.829 (5)
Cu1–Cl2	2.233 (5)		
Cl2–Cu1–N4	93.6 (2)	Cl1–Cu2–Cl2 ⁱⁱ	84.71 (17)
Cl1 ⁱ –Cu1–Cl2	86.14 (16)	Cl2 ⁱⁱ –Cu2–N3	90.9 (2)
Cl1 ⁱ –Cu1–N4	99.7 (3)	Cu1 ⁱⁱ –Cl1–Cu2	85.17 (15)
Cl1–Cu2–N3	88.2 (3)	Cu1–Cl2–Cu2 ⁱ	83.69 (14)

Symmetry codes: (i) $x - 1, y, z$; (ii) $x + 1, y, z$.

Table 2

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C6–H6C [·] ··Cl2	0.96	2.47	3.243 (15)	137
C7–H7B [·] ··Cl2 ⁱⁱⁱ	0.96	2.47	3.406 (15)	165
C7–H7C [·] ··Cl2 ^{iv}	0.96	2.71	3.553 (18)	147

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

The *TREOR90* program (Werner *et al.*, 1985) was used to index the powder diffraction pattern to a triclinic cell ($F_{20} = 88$, $M_{20} = 50$, $F_{39} = 92$, $M_{39} = 35$). The possible space groups, $P1$ and $\bar{P}1$, were used for crystal structure solution with the direct methods package *EXPO* (Altomare *et al.*, 1999). Only $\bar{P}1$ was found to be appropriate. All non-H atoms were located by structure solution, with $R(F) = 0.105$.

The solved structure was then refined against the full data set using the Rietveld method as implemented in the *FULLPROF* program (Rodríguez-Carvajal, 2001). A correction for profile asymmetry was made for reflections up to $2\theta = 40^\circ$. A Marsh–Dollase correction of intensities for the [100] preferred orientation of needle-like grains in the sample (Marsh, 1932; Dollase, 1986) was applied. The refined value of the preferred orientation coefficient G_1 was 1.076 (3). The G_2 parameter was found to be practically equal to 0 and was not

included in the final refinement. The atomic displacement parameters were refined isotropically, those for N and C atoms being refined as one parameter. The H atoms were placed in calculated positions (C–H = 0.96 Å; Sheldrick, 1997), with displacement parameters $U_{\text{iso}}(\text{H}) = 0.05 \text{ Å}^2$, corresponding to the relationship $U_{\text{iso}}(\text{H}) = 1.5U_{\text{iso}}(\text{C})$ for the methyl group. The final structure was obtained as a result of refinement with soft restraints on the interatomic distances and bond angles of the ligand molecule. The distance and angle restraints were based on a geometric analysis of a large number of 1-mono and 1,5-disubstituted tetrazoles (CSD). The final Rietveld refinement plots are shown in Fig. 3.

Data collection: local program; cell refinement: *FULLPROF* (Rodríguez-Carvajal, 2001); data reduction: local program; program(s) used to solve structure: *EXPO* (Altomare *et al.*, 1999); program(s) used to refine structure: *FULLPROF*; molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *PLATON* (Spek, 2003); software used to prepare material for publication: *FULLPROF* and *PLATON*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN3024). Services for accessing these data are described at the back of the journal.

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