

Coordination polymers formed by bridging 2-substituted tetrazole ligands: poly[[dichlorocopper(II)]-di- μ_2 -2-propyl-2*H*-tetrazole- κ^2 N¹:N⁴] and poly[[dichlorocopper(II)]-di- μ_2 -2-allyl-2*H*-tetrazole- κ^2 N¹:N⁴]

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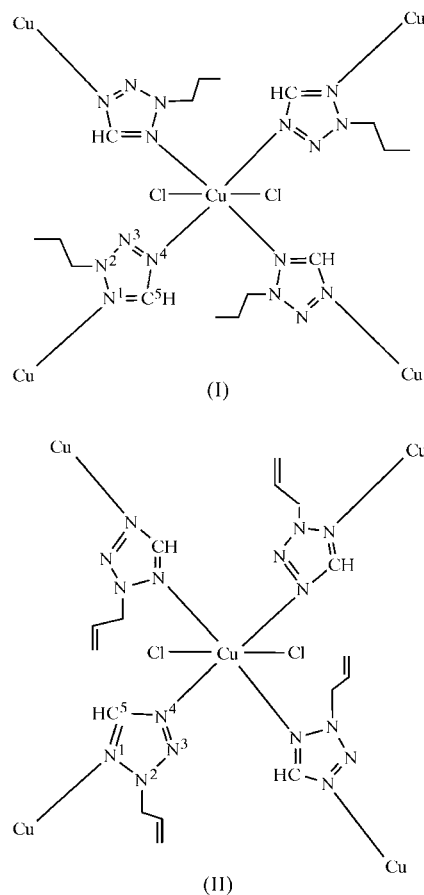
Two polymeric complexes, [CuCl₂L₂]_n, where *L* is 2-propyl-tetrazole (C₄H₈N₄) or 2-allyltetrazole (C₄H₆N₄), are the first coordination polymers of 2-substituted tetrazoles in which only the tetrazole rings bridge neighbouring Cu atoms. In both complexes, the Cu atoms lie on inversion centres and are six-coordinated in tetragonally distorted octahedral geometries, CuCl₂N₄, with two N¹ tetrazole ring atoms in the axial positions and two Cl atoms and two N⁴ tetrazole ring atoms in the equatorial sites. The Cl atoms do not participate in the polymeric layer formation.

Comment

We have recently reported the crystal structures of a number of copper(II) chloride complexes with 2-substituted tetrazoles (Lyakhov *et al.*, 2005, and references therein). Some of these complexes present chain coordination polymers with only Cl atoms as bridges between the neighbouring Cu atoms (Lyakhov *et al.*, 2003*a*, 2005). In other compounds, either chain coordination polymers (Lyakhov *et al.*, 2003) or layered polymers (Lyakhov *et al.*, 2003*b*), polymeric structures are formed through both Cl bridges and tetrazole ring coordination. We report here two complexes of copper(II) chloride with 2-substituted tetrazoles which are coordination polymers due only to the bridging coordination of the tetrazole rings. They are of the composition [CuCl₂L₂], where *L* is 2-propyl-tetrazole in (I) (Fig. 1) and 2-allyltetrazole in (II) (Fig. 2).

The tetrazole rings of the ligand molecules of complexes (I) and (II) are essentially planar, with mean deviations of the tetrazole ring atoms from their least-squares plane being 0.0007 (14) and 0.0010 (14) Å for (I) and (II), respectively. The ring geometries (Tables 1 and 3) are similar to those found previously for complexes of 2-substituted tetrazoles. For both

compounds, the shortest ring bond is the formal N²–N³ single bond of 1.308 (2) and 1.305 (2) Å for (I) and (II), respectively. The remaining ring bonds lie in the range 1.324 (2)–1.337 (3) Å for (I) and 1.318 (3)–1.345 (3) Å for (II).



In both compounds, the Cu1 atoms lie on inversion centres and have tetragonally distorted octahedral coordination (Tables 1 and 3). In both complexes, the equatorial positions of the octahedra are occupied by two N⁴ and two Cl¹ atoms, with two N¹ atoms lying in the axial sites. The Cu1–N⁴ distances are similar in (I) and (II), as are the Cu1–Cl¹ distances, while the Cu1–N¹ bond length in (I) is 0.175 (2) Å longer than that in (II).

Both compounds are layered coordination polymers in which only the ligand molecules act as bridges between neighbouring Cu atoms, through tetrazole ring atoms N⁴ and

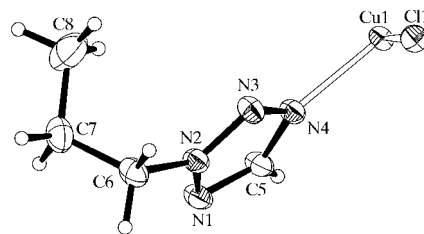


Figure 1
A view of the asymmetric unit of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

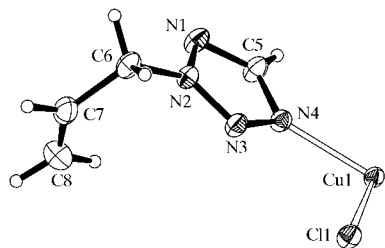


Figure 2

A view of the asymmetric unit of (II), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

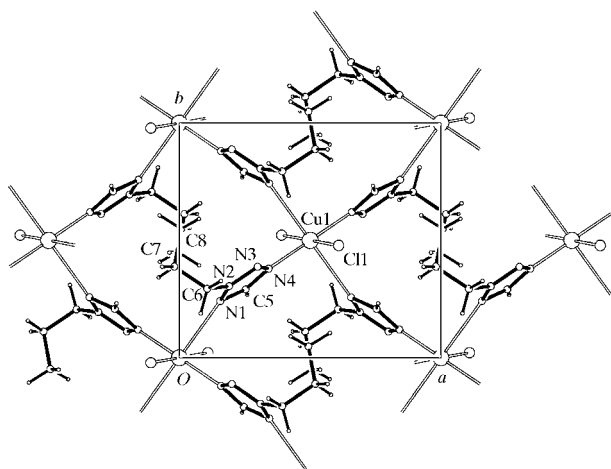


Figure 3

The atomic arrangement of the polymeric layer in complex (I), viewed parallel to the *ab* plane.

N1. The Cl atoms do not participate in the formation of polymeric layers. Figs. 3 and 4 show that the atomic arrangement of the polymeric layers is similar in both compounds. There are also differences within the layers of (I) and (II) with respect to the tetrazole ring orientations. The Cl1—Cu1—N4—C5 torsion angle is $-151.34(19)^\circ$ for (I) and $178.28(19)^\circ$ for (II), so that in the latter the tetrazole ring lies almost in the equatorial plane of the Cu octahedron.

In 2-substituted tetrazoles, the N¹ ring atoms may be the preferred metal binding site compared with the N³ atoms, based on the observed Cu—N¹ bond lengths of 2.7739 (17) Å in (I), 2.5987 (18) Å in (II) and 2.851 (2) Å in the related complex [CuCl₂L₂], where L is 2-ethyltetrazole (Lyakhov *et al.*, 2003b), and the Cu—N³ bond length of 2.926 (3) Å in the complex [Cu₃Cl₆L₄], where L is 2-allyltetrazole (Lyakhov *et al.*, 2003). Reliable conclusions about the electron-donating properties of the N¹ and N³ tetrazole ring atoms requires further experimental study, as well as verification by quantum-chemical calculations.

In the structures of (I) and (II), there are weak C5—H5...Cl hydrogen bonds (Tables 2 and 4), implemented inside the polymeric layers. In complex (II), there are also interlayer hydrogen bonds between the methylene H atom of the allyl substituent and a Cl atom of a neighbouring layer (Table 4). Because the propyl and allyl substituents at the N2 tetrazole ring atom of the ligand molecules are similar in size, it was

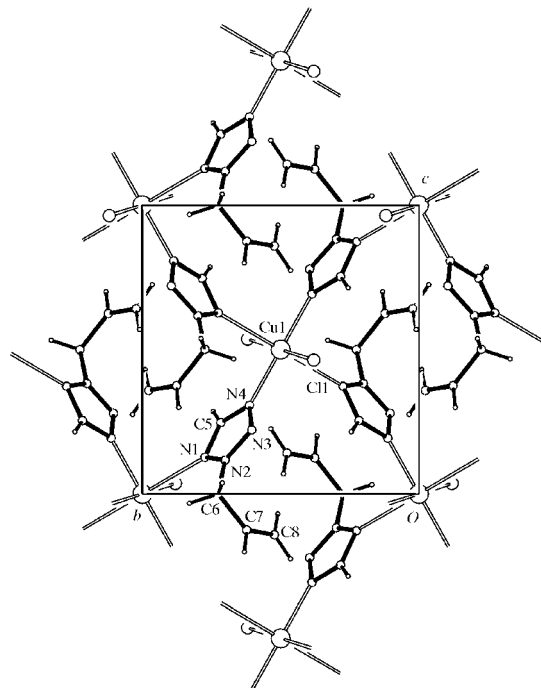


Figure 4

The atomic arrangement of the polymeric layer in complex (II), viewed parallel to the *bc* plane.

expected that complexes (I) and (II) would be isostructural. However, the present data show a similarity only in the atomic arrangement inside the polymeric layers.

Experimental

2-Propyltetrazole and 2-allyltetrazole were prepared according to the method described by Gaponik *et al.* (1980). For the synthesis of (I), 2-propyltetrazole (1.23 g, 0.011 mol) was added to a solution of CuCl₂·2H₂O (0.85 g, 0.005 mol) in methanol (10 ml). The mixture was stirred for 1 h at room temperature and then kept for about 20 d at room temperature in air. Green-blue crystals of (I) were obtained (yield 1.20 g, 67%). Analysis for (I) found: Cu 17.9, Cl 19.5%; C₈H₁₆Cl₂CuN₈ requires: Cu 17.7, Cl 19.8. For the synthesis of (II), CuCl₂·2H₂O (0.85 g, 0.005 mol) was added to a solution containing 2-allyltetrazole (1.21 g, 0.011 mol) in a methanol-diethyl ether mixture (50 ml, molar ratio 1:4). The resulting mixture was stirred for 1 h at room temperature. After removing about 35 ml of the solvent by heating the mixture at 353 K (water bath) for 30 min in air, it was cooled to room temperature and filtered. Green-blue crystals of (II) were obtained from the filtrate after 10 d (yield 0.91 g, 51%). Analysis for (II) found: Cu 17.6, Cl 19.5%; C₈H₁₂Cl₂CuN₈ requires: Cu 17.9, Cl 20.0%.

Compound (I)

Crystal data

[CuCl₂(C₄H₈N₄)₂]
M_r = 358.73
 Orthorhombic, *Pbca*
a = 9.885 (3) Å
b = 8.867 (2) Å
c = 17.092 (4) Å
V = 1498.1 (7) Å³
Z = 4
D_x = 1.590 Mg m⁻³

Mo Kα radiation
 Cell parameters from 24 reflections
 θ = 16.6–22.0°
 μ = 1.81 mm⁻¹
T = 292 (2) K
 Prism, green-blue
 0.58 × 0.54 × 0.40 mm

Data collection

Nicolet <i>R3m</i> four-circle diffractometer	$R_{\text{int}} = 0.027$
$\omega/2\theta$ scans	$\theta_{\text{max}} = 30.1^\circ$
Absorption correction: ψ scan (North <i>et al.</i> , 1968)	$h = 0 \rightarrow 13$
$T_{\text{min}} = 0.379$, $T_{\text{max}} = 0.483$	$k = 0 \rightarrow 12$
2477 measured reflections	$l = -24 \rightarrow 2$
2201 independent reflections	3 standard reflections
2024 reflections with $I > 2\sigma(I)$	every 100 reflections
	intensity decay: none

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0762P)^2 + 0.5691P]$
$R[F^2 > 2\sigma(F^2)] = 0.041$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.124$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.13$	$\Delta\rho_{\text{max}} = 0.67 \text{ e } \text{\AA}^{-3}$
2201 reflections	$\Delta\rho_{\text{min}} = -0.80 \text{ e } \text{\AA}^{-3}$
89 parameters	
H-atom parameters constrained	

Table 1

Selected interatomic distances (Å) for (I).

Cu1—N4	2.0196 (15)	N1—N2	1.328 (2)
Cu1—Cl1	2.2652 (6)	N2—N3	1.308 (2)
Cu1—N1 ⁱ	2.7739 (17)	N2—C6	1.464 (2)
Cu1···Cu1 ⁱⁱ	6.6396 (13)	N3—N4	1.324 (2)
N1—C5	1.324 (2)	N4—C5	1.337 (3)

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

Table 2

Hydrogen-bond geometry (Å, °) for (I).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C5—H5···Cl1 ⁱⁱⁱ	0.93	2.83	3.183 (2)	104

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

Compound (II)

Crystal data

[CuCl ₂ (C ₄ H ₆ N ₄) ₂]	Mo $K\alpha$ radiation
$M_r = 354.70$	Cell parameters from 25 reflections
Monoclinic, $P2_1/c$	$\theta = 17.9\text{--}23.6^\circ$
$a = 8.524$ (3) Å	$\mu = 1.95 \text{ mm}^{-1}$
$b = 8.855$ (3) Å	$T = 292$ (2) K
$c = 9.593$ (2) Å	Prism, green-blue
$\beta = 105.51$ (2)°	$0.40 \times 0.38 \times 0.26 \text{ mm}$
$V = 697.7$ (4) Å ³	
$Z = 2$	
$D_x = 1.688 \text{ Mg m}^{-3}$	

Data collection

Nicolet <i>R3m</i> four-circle diffractometer	$R_{\text{int}} = 0.062$
$\omega/2\theta$ scans	$\theta_{\text{max}} = 29.6^\circ$
Absorption correction: ψ scan (North <i>et al.</i> , 1968)	$h = 0 \rightarrow 11$
$T_{\text{min}} = 0.484$, $T_{\text{max}} = 0.600$	$k = 0 \rightarrow 12$
2066 measured reflections	$l = -13 \rightarrow 12$
1949 independent reflections	3 standard reflections
1824 reflections with $I > 2\sigma(I)$	every 100 reflections
	intensity decay: none

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0721P)^2 + 0.3127P]$
$R[F^2 > 2\sigma(F^2)] = 0.037$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.109$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.07$	$\Delta\rho_{\text{max}} = 0.69 \text{ e } \text{\AA}^{-3}$
1949 reflections	$\Delta\rho_{\text{min}} = -0.95 \text{ e } \text{\AA}^{-3}$
88 parameters	
H-atom parameters constrained	

Table 3

Selected geometric parameters (Å) for (II).

Cu1—N4	2.0615 (16)	N1—N2	1.326 (2)
Cu1—Cl1	2.2611 (8)	N2—N3	1.305 (2)
Cu1—N1 ⁱ	2.5987 (18)	N2—C6	1.468 (3)
Cu1—Cu1 ⁱ	6.5276 (13)	N3—N4	1.322 (2)
N1—C5	1.318 (3)	N4—C5	1.345 (3)

Symmetry code: (i) $-x + 2, y - \frac{1}{2}, -z + \frac{1}{2}$.

Table 4

Hydrogen-bond geometry (Å, °) for (II).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C5—H5···Cl1 ⁱⁱ	0.93	2.63	3.122 (2)	114
C6—H6B···Cl1 ⁱⁱⁱ	0.97	2.80	3.548 (2)	135

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

H atoms were included in geometrically calculated positions, with $C-H = 0.93\text{--}0.97$ Å, and refined using a riding model, with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for methyl and $1.2U_{\text{eq}}(\text{C})$ for other H atoms.

For both compounds, data collection: *R3m Software* (Nicolet, 1980); cell refinement: *R3m Software*; data reduction: *R3m Software*; structure solution: *SIR97* (Altomare *et al.*, 1999); structure refinement: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *PLATON* (Spek, 2003); publication software: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GA1097). Services for accessing these data are described at the back of the journal.

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