

catena-Poly[[tetrakis(2-allyltetrazole- κ N⁴)-tetra- μ -chloro-tricopper(II)]-di- μ -chloro]

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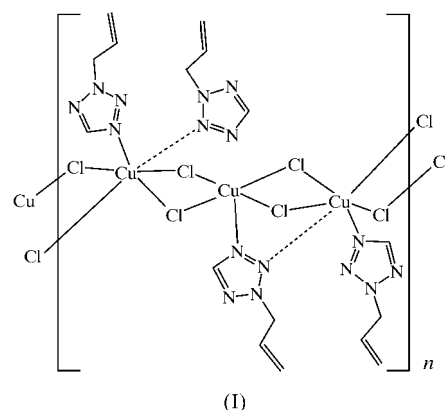
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In the crystal structure of the title compound, $[\text{Cu}_3\text{Cl}_6(\text{C}_4\text{H}_6\text{N}_4)_4]_n$, there are three Cu atoms, six Cl atoms and four 2-allyltetrazole ligands in the asymmetric unit. The polyhedron of one Cu atom adopts a flattened octahedral geometry, with two 2-allyltetrazole ligands in the axial positions [Cu–N4 = 1.990 (2) and 1.991 (2) Å] and four Cl atoms in the equatorial positions [Cu–Cl = 2.4331 (9)–2.5426 (9) Å]. The polyhedra of the other two Cu atoms have a square-pyramidal geometry, with three basal sites occupied by Cl atoms [Cu–Cl = 2.2487 (9)–2.3163 (8) and 2.2569 (9)–2.3034 (9) Å] and one basal site occupied by a 2-allyltetrazole ligand [Cu–N4 = 2.028 (2) and 2.013 (2) Å]. A Cl atom lies in the apical position of either pyramid [Cu–Cl = 2.8360 (10) and 2.8046 (9) Å]. The possibility of including the tetrazole N3 atoms in the coordination sphere of the two Cu atoms is discussed. Neighbouring copper polyhedra share their edges with Cl atoms to form one-dimensional polymeric chains running along the *a* axis.

Comment

Isomeric 1- and 2-monosubstituted tetrazoles are different in their physicochemical properties (boiling and melting points, dipole moments, electron-density distribution in the tetrazole ring *etc.*) and in their ability to form complexes with transition metal salts (Butler, 1996; Gaponik, 1998). 1-Monosubstituted tetrazoles easily form complexes with copper(II) chloride, with CuCl_2L_2 complexes usually being produced. In contrast, special conditions are needed to obtain crystalline complexes with 2-monosubstituted tetrazoles (Gaponik, 2000), and hence the structures and properties of these complexes have barely been investigated. Only one complex of copper(II) chloride with 2-substituted tetrazole has been structurally characterized, namely CuCl_2L_2 , where *L* is 2-*tert*-butyltetrazole (Lyakhov *et al.*, 2003). Moreover, an inspection of the Cambridge Structural Database (Version 5.23 of September

2002; Allen, 2002) with respect to 2-substituted tetrazole complexes revealed only one complex, namely $[\text{NiL}_6](\text{BF}_4)_2$, where *L* is 2-methyltetrazole (van den Heuvel *et al.*, 1983).



A new complex of copper(II) chloride, (I), with the unusual composition $\text{Cu}_3\text{Cl}_6\text{L}_4$, where *L* is 2-allyltetrazole (see Fig. 1), has been synthesized, and this complex is investigated in the present work. There are four 2-allyltetrazole ligands in the asymmetric unit of (I), and these are denoted by the suffixes *A*, *B*, *C* and *D*.

The geometric parameters of the tetrazole rings of the four 2-allyltetrazole molecules are very similar. The tetrazole rings are planar to within 0.002 (3), 0.003 (3), 0.003 (7) and 0.003 (3) Å for *A*, *B*, *C* and *D*, respectively. The lengths of the corresponding bonds in the tetrazole rings of (I) lie in the following ranges (Å): N1–N2 = 1.314 (4)–1.322 (4), N2–N3 = 1.287 (3)–1.308 (4), N3–N4 = 1.319 (3)–1.327 (3), N4–C5 = 1.313 (4)–1.338 (4) and N1–C5 = 1.314 (4)–1.326 (5). There is a reasonable agreement (within 3.2σ) between the corresponding bond distances of the rings.

There are three Cu atoms in the asymmetric unit of (I), namely Cu1, Cu2 and Cu3. Atom Cu3 adopts a distorted flattened octahedral geometry (Table 1 and Fig. 2), with two 2-allyltetrazole ligands in the axial positions [Cu3–N4A = 1.990 (2) Å and Cu3–N4B = 1.991 (2) Å]. Four Cl atoms occupy the equatorial positions, with Cu3–Cl distances in the range 2.4431 (9)–2.5426 (9) Å (Table 1).

Atoms Cu1 and Cu2 may be considered to be five-coordinated, with square-pyramidal geometry (Table 1). For either pyramid, three basal sites are occupied by Cl atoms [Cu1–Cl = 2.2487 (9)–2.3163 (8) Å and Cu2–Cl = 2.2569 (9)–2.3034 (9) Å] and one basal site is occupied by a 2-allyltetrazole ligand [Cu1–N4D = 2.028 (2) Å and Cu2–N4C = 2.013 (2) Å]. Cl atoms lie in the apical positions of the pyramids [Cu1–Clⁱ = 2.8360 (10) Å and Cu2–Clⁱⁱ = 2.8046 (9) Å; symmetry codes: (i) 1 + *x*, *y*, *z*; (ii) *x* – 1, *y*, *z*].

Note that, within a range of 3.0 Å, atoms Cu1 and Cu2 adopt an octahedral geometry, with additional N3 atoms in axial positions [Cu1–N3A = 2.898 (3) Å and Cu2–N3B = 2.926 (3) Å]. These long contacts are shown by dashed lines in the *Scheme* and in Figs. 1–3. However, according to the accepted point of view, the nucleophilic reactivity of 2-substituted tetrazoles is only due to the N4 atoms, and hence

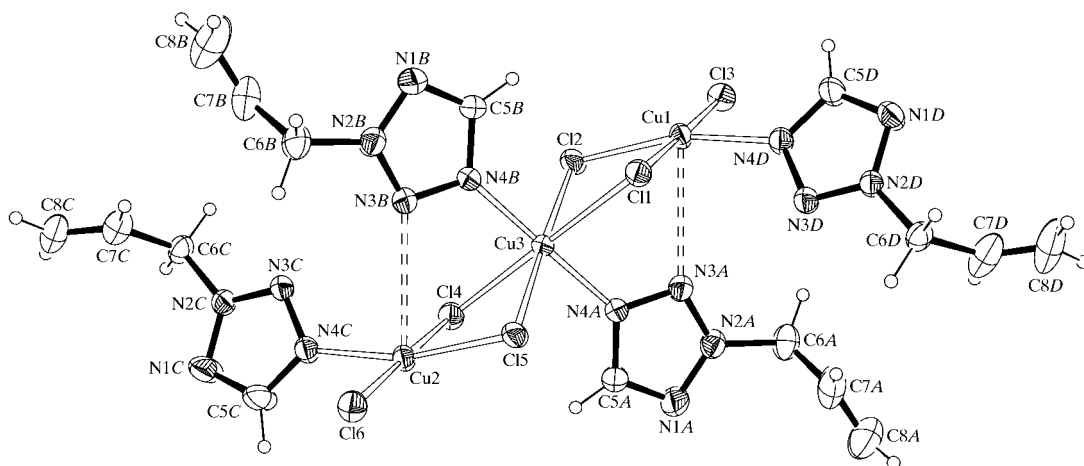


Figure 1

An ORTEP-3 (Farrugia, 1997) plot of the asymmetric unit of (I). Displacement ellipsoids are drawn at the 50% probability level, and H atoms are shown as spheres of arbitrary radii.

the N3 atoms should not be included in the Cu-atom coordination sphere. Nevertheless, since Cu1 and Cu2 are surrounded symmetrically in the structure of (I), and because of the favourable orientation of the *A* and *B* tetrazole rings with reference to atoms Cu1 and Cu2, respectively, we can assume that atoms N3A and N3B may be included in the Cu1 and Cu2 octahedra. Note that all our attempts to synthesize CuCl_2L_2 and CuCl_2L complexes of copper(II) with 2-allyltetrazole failed because only (I) was crystallized. Additional Cu1–N3A and Cu2–N3B bonds may be responsible for the favourable formation of (I).

To investigate the Cu1–N3 and Cu2–N3 bonds in (I), density functional theory calculations of the crystal structure of (I), including the neighbouring Cu1 and Cu3 atoms with all their ligands, have been carried out within the B3LYP model (Becke, 1993) using the NWCHEM package (Harrison *et al.*, 2002). Because the surroundings of atoms Cu1 and Cu2 are similar, analogous calculations for atom Cu2 were not performed. Atoms Cu1 and Cu3 were described by the standard LANL2DZ double- ξ basis set, with the effective core potential given by Hay & Wadt (1985). The standard STO-3G

basis set (Hehre *et al.*, 1969) was used for the remaining atoms. Both singlet and triplet multiplicities have been considered for the fragment. The calculations showed that the triplet state energy was $31.5 \text{ kcal mol}^{-1}$ ($1 \text{ kcal mol}^{-1} = 4.184 \text{ kJ mol}^{-1}$) lower than that of the singlet. For the triplet state, the overlap population for the Cu1–N4D bond (0.237) is almost two times greater than that for the Cu1–N3A bond (0.132). Therefore, the Cu1–N3A interaction is considerably weaker than the Cu1–N4D interaction. However, the overlap population value of 0.132 is neither high enough to be meaningful nor too low to be negligible when resolving the problem of the coordination bond Cu1–N3A (and Cu2–N3B). In view of this ambiguity, these calculations may only be considered to give preliminary results. More detailed calculations will be the topic of future investigation.

As can be seen from Fig. 2, adjacent copper polyhedra share their edges with Cl atoms to form one-dimensional polymeric

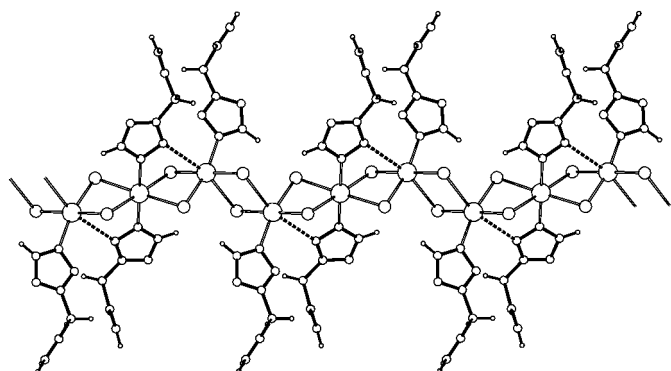


Figure 2

A fragment of the crystal structure of (I), showing a one-dimensional polymeric chain running along the *a* axis.

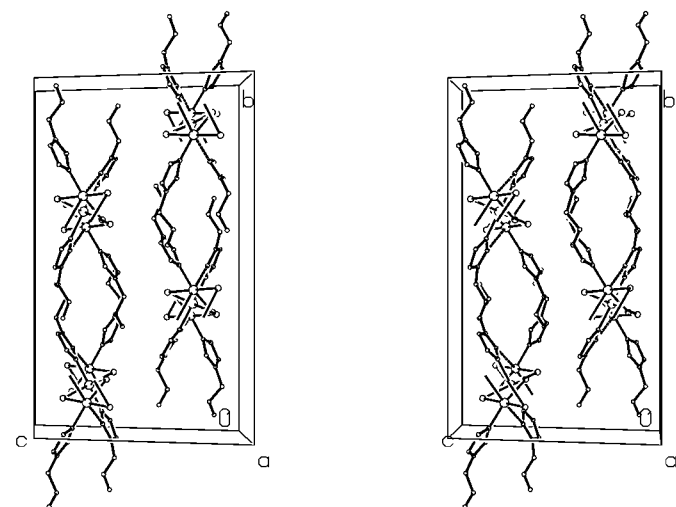


Figure 3

The crystal packing of (I), viewed along the *a* axis.

chains running along the *a* axis. The separations between the neighbouring Cu atoms in such a chain are listed in Table 1. Only van der Waals interactions exist between the chains, and there are no hydrogen bonds in the structure of (I). The packing structure of (I) is shown in Fig. 3.

Experimental

The complex CuCl_2L_2 , where *L* is 2-allyltetrazole, was prepared according to the method described by Degtyarik *et al.* (1985) and was used as the starting compound for the synthesis of (I). Dark-green single crystals of (I) were grown by the slow evaporation in air of a 2-propanol–butanol–ethyl orthoformate (*v/v* 2:2:1) solution of the starting complex at 288–291 K for 3 d.

Crystal data

$[\text{Cu}_3\text{Cl}_6(\text{C}_4\text{H}_6\text{N}_4)_4]$
 $M_r = 843.83$
 Monoclinic, $P2_1/c$
 $a = 9.7204(14) \text{ \AA}$
 $b = 23.495(2) \text{ \AA}$
 $c = 14.541(3) \text{ \AA}$
 $\beta = 107.578(14)^\circ$
 $V = 3165.8(9) \text{ \AA}^3$
 $Z = 4$

$D_x = 1.771 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 Cell parameters from 25 reflections
 $\theta = 20.0\text{--}22.4^\circ$
 $\mu = 2.54 \text{ mm}^{-1}$
 $T = 293(2) \text{ K}$
 Prism, green
 $0.48 \times 0.42 \times 0.36 \text{ mm}$

Data collection

Nicolet R3m four-circle diffractometer
 $\omega/2\theta$ scans
 Absorption correction: ψ scan (North *et al.*, 1968)
 $T_{\min} = 0.326$, $T_{\max} = 0.401$
 7987 measured reflections
 7316 independent reflections
 5828 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.017$
 $\theta_{\text{max}} = 27.6^\circ$
 $h = 0 \rightarrow 12$
 $k = 0 \rightarrow 30$
 $l = -18 \rightarrow 18$
 3 standard reflections every 100 reflections
 intensity decay: none

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.036$
 $wR(F^2) = 0.093$
 $S = 1.00$
 7316 reflections
 371 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0429P)^2 + 3.0438P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.73 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.39 \text{ e \AA}^{-3}$
 Extinction correction: *SHELXL97*
 Extinction coefficient: 0.00246 (15)

The H atoms were included in geometrically calculated positions, with C–H distances of 0.93–0.97 Å, and refined using a riding model, with $U_{\text{iso}}(\text{H})$ equal to $1.2U_{\text{eq}}$ of the corresponding C atom. The short C=C distances in the allyl groups [1.172(5)–1.260(5) Å] are the result of libration.

Data collection: *R3m Software* (Nicolet, 1980); cell refinement: *R3m Software*; data reduction: *R3m Software*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to

Table 1

Selected interatomic distances (Å).

Cu1–N4D	2.028 (2)	Cu2–Cl4	2.3034 (9)
Cu1–Cl3	2.2487 (9)	Cu2–Cl3 ⁱⁱ	2.8046 (9)
Cu1–Cl1	2.2863 (9)	Cu2–N3B	2.926 (3)
Cu1–Cl2	2.3163 (8)	Cu2···Cu3	3.3957 (6)
Cu1–Cl6 ⁱ	2.8360 (10)	Cu3–N4A	1.990 (2)
Cu1–N3A	2.898 (3)	Cu3–N4B	1.991 (2)
Cu1···Cu3	3.3992 (6)	Cu3–Cl2	2.4331 (9)
Cu1–Cu2 ⁱ	3.7334 (6)	Cu3–Cl5	2.4597 (9)
Cu2–N4C	2.013 (2)	Cu3–Cl4	2.5151 (10)
Cu2–Cl6	2.2569 (9)	Cu3–Cl1	2.5426 (9)
Cu2–Cl5	2.3031 (8)		

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

refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV1129). Services for accessing these data are described at the back of the journal.

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