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# *catena*-Poly[[(2-hexyl-2*H*-tetrazole-$\kappa N^4$)-copper(II)]-di-$\mu$-chloro]

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**Key indicators**

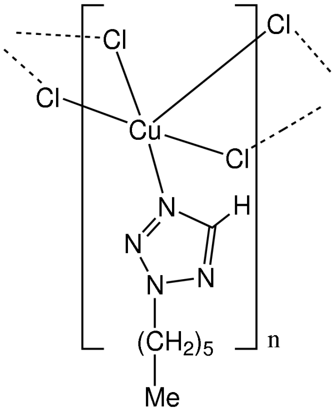
Single-crystal X-ray study
$T$ = 293 K
Mean $\sigma$(C–C) = 0.006 Å
Disorder in main residue
$R$ factor = 0.033
$wR$ factor = 0.095
Data-to-parameter ratio = 24.9

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

In the title polymeric complex, $[CuCl_2(C_7H_{14}N_4)]_n$, the Cu coordination polyhedron adopts the form of a distorted square pyramid. Basal sites of the pyramid are occupied by three Cl atoms [Cu—Cl = 2.2519 (7), 2.2842 (7) and 2.3114 (7) Å] and by the N atom of the 2-hexyl-2*H*-tetrazole ligand [Cu—N = 2.0068 (17) Å]. A Cl atom lies in the apical position, 2.6091 (6) Å from the Cu atom. Neighbouring polyhedra are linked by sharing their edges with Cl atoms to form polymeric chains running along the *a* axis. The $CH_3CH_2$– group at the end of the hexyl chain is positionally disordered.

## Comment

Copper(II) complexes with *N*-substituted tetrazole ligands are of great interest because of their magnetic properties (Gaponik, 1998; Shvedenkov *et al.*, 2003). A large majority of the papers on crystal structure determinations of these compounds are related to complexes with 1-substituted tetrazoles. Only a limited number of crystal structures of copper(II) salts with 2-alkyltetrazole ligands have been published.



(I)

With respect to copper(II) chloride complexes with 2-substituted tetrazoles, it was shown recently that 2-substituted tetrazoles form complexes of three types, namely Cu*L*Cl$_2$, Cu*L*$_2$Cl$_2$, and Cu$_3$*L*$_4$Cl$_6$, depending on initial component ratio and synthesis conditions; this is in contrast to 1-substituted tetrazoles, which give only Cu*L*$_2$Cl$_2$ complexes (Degtyarik *et al.*, 2003). Three representatives of copper(II) chloride complexes with 2-substituted tetrazoles have been structurally characterized. These are Cu*L*Cl$_2$ (*L* = 2-*tert*-butyltetrazole; Lyakhov *et al.*, 2003*a*), Cu$_3$*L*$_4$Cl$_6$ (*L* = 2-allyltetrazole; Lyakhov, Gaponik, Degtyarik, Matulis et al., 2003) and Cu*L*$_2$Cl$_2$ (*L* = 2-ethyltetrazole; Lyakhov *et al.*, 2003*b*). The

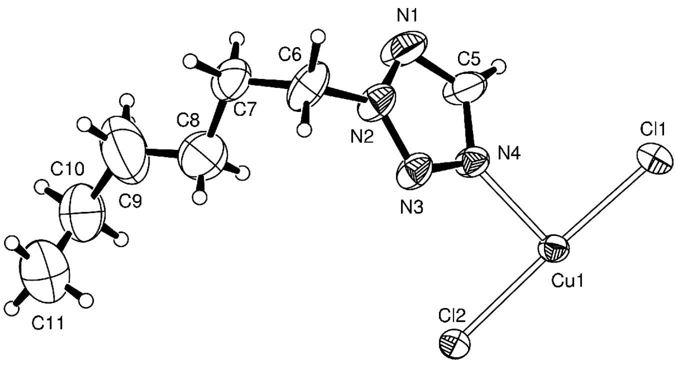


**Figure 1**
*ORTEP*-3 (Farrugia, 1997) plot of the asymmetric unit of (I). Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as spheres of arbitrary radii. Positional disorder in the hexyl fragment is not shown.

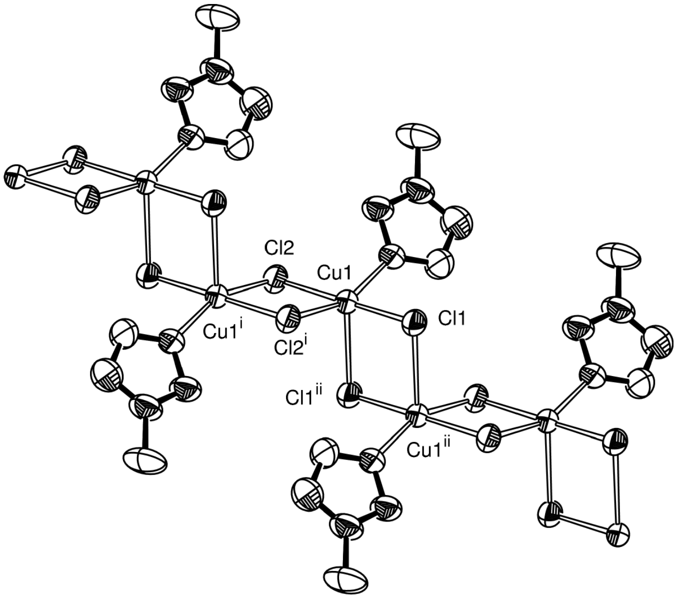


**Figure 2**
Fragment of the crystal structure of (I), showing a polymeric chain running along the *a* axis. For clarity, only the first atom of each hexyl fragment is shown. [Symmetry codes: (i) $2 - x, -y, -z$; (ii) $1 - x, -y, -z$.]

synthesis of these complexes is often accompanied by a side reaction giving tetranuclear complexes with the composition $Cu_4OCl_6L_4$. The crystal structure of such a complex with $L$ = 2-ethyltetrazole was reported recently (Lyakhov *et al.*, 2004). With the exception of the last complex, the remainder of the investigated compounds are coordination polymers.

This paper is part of our systematic investigation of transition metal complexes with 2-substituted tetrazoles. We describe here the crystal structure of a new compound, $[CuLCl_2]_n$ (where $L$ is 2-hexyltetrazole), (I) (Fig. 1).

The tetrazole ring of the 2-hexyltetrazole ligand is essentially planar, with a mean deviation of the tetrazole-ring atoms from their least-squares plane of 0.005 (2) Å. The ring geometry (Table 1) is similar to those found previously for complexes of 2-substituted tetrazoles (Cambridge Structural Database, Version 5.25, November 2003 release; Allen, 2002). The shortest ring bonds are formal single N2—N3 and N1—N2 bonds, with lengths of 1.303 (3) and 1.308 (3) Å, respectively. The three remaining bonds of the ring lie within the narrow range 1.319 (2)–1.321 (3) Å.

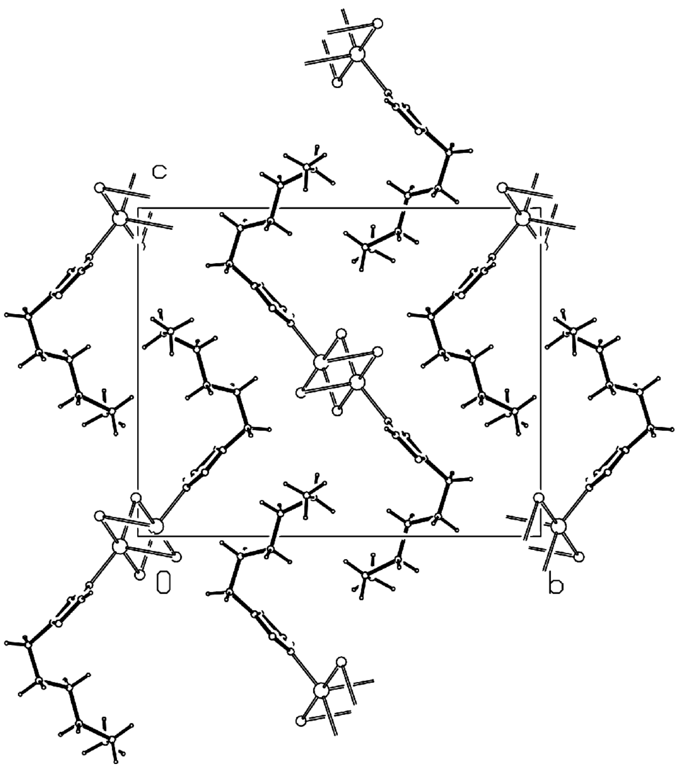


**Figure 3**
The crystal structure of (I), viewed along the *a* axis. Positional disorder in the hexyl fragment is not shown.

The structure of (I) exhibits positional disorder in the hexyl fragment (see *Experimental*). Atoms C10 and C11 are disordered over two positions, with site-occupancy factors 0.583 (14) and 0.417 (14).

In (I), the coordination environment of the Cu atom is essentially a distorted square pyramid, as is apparent from the observed $\tau$ descriptor of 0.36 (0 and 1 values are indicative of idealized square-pyramidal and trigonal-bipyramidal geometries, respectively; Addison *et al.*, 1984). The basal positions of the pyramid are occupied by three Cl atoms, *viz*. Cl1, Cl2 and symmetry-related $Cl2^i$ [symmetry code: (i) $2 - x, -y, -z$], with Cu1—Cl distances of 2.2519 (7), 2.2842 (7) and 2.3114 (7) Å, respectively, and by atom N4 of the tetrazole ligand, with a Cu1—N4 distance of 2.0068 (17) Å. Atom $Cl1^{ii}$ [symmetry code: (ii) $1 - x, -y, -z$] lies in the apical position, 2.6091 (6) Å from the Cu atom. As seen from Table 1, the N4—Cu1—$Cl2^i$ *trans* angle is significantly different from 180°, having a value of 155.22 (5)°. Neighbouring polyhedra share their edges with the Cl atoms to form a polymeric chain running along the *a* axis (Fig. 2). The linkage of atoms Cu1 and $Cu1^i$ is realised *via* Cl2 and $Cl2^i$, which are basal in polyhedra of both Cu atoms; the separation between Cu1 and $Cu1^i$ is 3.3700 (7) Å. The linkage of Cu1 and $Cu1^{ii}$ is implemented through Cl1 and Cl1$^{ii}$, each of which is apical in one polyhedron and basal in the other; the Cu1···Cu1$^{ii}$ separation is 3.4436 (8) Å. Together with the ligand molecules, chains of chloro-bridged Cu atoms form ribbons (Fig. 3), with only van der Waals interactions between them.

It is interesting to compare the crystal structure of (I) with that of the copper(II) chloride complex with 2-*tert*-butyltetrazole investigated previously (Lyakhov *et al.*, 2003*a*). Both compounds have the same composition, but crystallize in different space groups ($P\overline{1}$ in the case of the 2-*tert*-butyltetrazole complex), have different unit-cell dimensions (except for parameter *a*, where the values are close in both cases) and different *Z* values (2 for the 2-*tert*-butyltetrazole complex). However, both complexes show common structural features. Thus, in the two compounds, coordination polyhedra are distorted square pyramids [but the square pyramid in (I) is more distorted towards a trigonal bipyramid compared with the 2-*tert*-butyltetrazole complex]. In both compounds, copper polyhedra are linked together in the same manner to give polymeric chains in the form of ribbons running along the *a* axis. However, the packing of ribbons in the two structures is rather different. Whereas only one ribbon orientation in relation to the *c* and *b* axes exists in the structure of 2-*tert*-butyltetrazole complex, two different ribbon orientations are observed in the structure of (I). Because the two compounds differ only in the substituent attached to the tetrazole N2 atom, the above structural differences are probably caused by steric features of the substituents.

## Experimental

2-Hexyltetrazole was prepared by alkylation of 1*H*-tetrazole with 1-bromohexane (Gaponik, 2000). $CuCl_2·2H_2O$ (2.05 g, 0.012 mol) was added to a solution of 2-hexyltetrazole (1.8 g, 0.012 mol) in ethanol (7 ml). The mixture was stirred for 0.5 h at room temperature. After keeping the mixture about 100 h at room temperature, the resulting dark-green crystals of (I) were filtered off, washed with diethyl ether and air dried [yield 2.1 g (61%); m.p. 436 K (with decomposition)].

*Crystal data*

$[CuCl_2(C_7H_{14}N_4)]$
$M_r$ = 288.66
Monoclinic, $P2_1/c$
*a* = 5.9958 (13) Å
*b* = 15.891 (3) Å
*c* = 13.085 (3) Å
β = 97.49 (2)°
*V* = 1236.1 (5) Å$^3$
*Z* = 4

$D_x$ = 1.551 Mg m$^{-3}$
Mo *K*α radiation
Cell parameters from 25 reflections
θ = 15.5–20.0°
μ = 2.17 mm$^{-1}$
*T* = 293 (2) K
Prism, dark green
0.50 × 0.38 × 0.22 mm

*Data collection*

Nicolet *R*3*m* four-circle diffractometer
ω/2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min}$ = 0.394, $T_{max}$ = 0.621
4072 measured reflections
3639 independent reflections
2979 reflections with $I > 2\sigma(I)$

$R_{int}$ = 0.014
$\theta_{max}$ = 30.1°
*h* = 0 → 8
*k* = 0 → 22
*l* = −18 → 18
3 standard reflections every 100 reflections intensity decay: none

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)]$ = 0.033
$wR(F^2)$ = 0.095
*S* = 1.05
3639 reflections
146 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0545P)^2 + 0.229P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.30 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.74 e Å$^{-3}$

**Table 1**
Selected geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| Cu1—N4 | 2.0068 (17) | N1—N2 | 1.308 (3) |
| Cu1—Cl1 | 2.2519 (7) | N1—C5 | 1.321 (3) |
| Cu1—Cl2 | 2.2842 (7) | N2—N3 | 1.303 (3) |
| Cu1—Cl2$^{i}$ | 2.3114 (7) | N2—C6 | 1.476 (3) |
| Cu1—Cl1$^{ii}$ | 2.6091 (6) | N3—N4 | 1.319 (2) |
| Cu1—Cu1$^{i}$ | 3.3700 (7) | N4—C5 | 1.320 (3) |
| Cu1—Cu1$^{ii}$ | 3.4436 (8) | | |
| N4—Cu1—Cl1 | 91.28 (6) | Cl2—Cu1—Cl2$^{i}$ | 85.67 (3) |
| N4—Cu1—Cl2 | 90.60 (6) | N4—Cu1—Cl1$^{ii}$ | 106.12 (6) |
| Cl1—Cu1—Cl2 | 176.72 (2) | Cl1—Cu1—Cl1$^{ii}$ | 90.10 (2) |
| N4—Cu1—Cl2$^{i}$ | 155.22 (5) | Cl2—Cu1—Cl1$^{ii}$ | 91.96 (2) |
| Cl1—Cu1—Cl2$^{i}$ | 91.51 (3) | Cl2$^{i}$—Cu1—Cl1$^{ii}$ | 98.49 (2) |

Symmetry codes: (i) 2 − *x*, −*y*, −*z*; (ii) 1 − *x*, −*y*, −*z*.

The H atoms were included in geometrically calculated positions, with C—H = 0.93–0.97 Å, and refined using a riding model, with $U_{iso}$(H) equal to $1.5U_{eq}$ (for methyl group) and $1.2U_{eq}$ (for other H atoms) of the carrier C atom. During the refinement of (I), two hexyl atoms, C10 and C11, revealed very anisotropic atomic displacement parameters, so two sets of split sites were introduced for these atoms. In the subsequent refinement, the site-occupancy factors refined to 0.583 (14) and 0.417 (14) for C10*A*/C11*A* and C10*B*/C11*B*, respectively

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 *for Windows* (Farrugia, 1997) and *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL*97.

## References

Addison, A. W., Rao, T. N., Reedijk, J., van Rijn, J. & Verschoor, G. C. (1984). *J. Chem. Soc. Dalton Trans.* pp. 1349–1356.
Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.
Altomare, A., Burla, M. C., Camalli, M., Cascarano, G., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115–119.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Gaponik, P. N. (1998). *Chemical Problems of Development of New Materials and Technologies*, edited by V. V. Sviridov, pp. 185–214. Minsk: BSU Press.
Gaponik, P. N. (2000). Habilitational thesis, Belarusian State University, Minsk, Belarus.
Degtyarik, M. M., Gaponik, P. N., Ivashkevich, O. A. & Lyakhov A. S. (2003). *Proceedings of the XXIth International Chugaev's Conference on Coordination Chemistry*, Kiev, June 10–13, p. 241. (In Russian.)
Lyakhov, A. S., Gaponik, P. N., Degtyarik, M. M. & Ivashkevich, L. S. (2003*a*). *Acta Cryst.* E**59**, m38–m40.
Lyakhov, A. S., Gaponik, P. N., Degtyarik, M. M. & Ivashkevich, L. S. (2003*b*). *Acta Cryst.* C**59**, m204–m206.
Lyakhov, A. S., Gaponik, P. N., Degtyarik, M. M. & Ivashkevich, L. S. (2004). *Acta Cryst.* C**60**, m399-m401.
Lyakhov, A. S., Gaponik, P. N., Degtyarik, M. M., Matulis, V. E., Matulis, V. E. & Ivashkevich, L. S. (2003). *Acta Cryst.* C**59**, m90–m92.

*Acta Cryst.* (2005). E**61**, m183–m186 Alexander S. Lyakhov *et al.* • $[CuCl_2(C_7H_{14}N_4)]$ **m185**

Nicolet (1980). *R3m Software*. Nicolet XRD Corporation, Cupertino, California, USA.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.

Shvedenkov, Yu. G., Ikorskii, V. N., Romanenko, G. V., Lavrenova, L. G., Bogatikov, A. N., Voitekhovich, S. V. & Gaponik, P. N. (2003). *Proceedings of the XXIth International Chugaev's Conference on Coordination Chemistry*, Kiev, June 10–13, p. 416. (In Russian.)

Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.