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catena-Poly[[[*cis*-bis(1-phenyltetrazole-κN^4)copper(II)]-di-μ-chloro] hemi(1-phenyltetrazole)]

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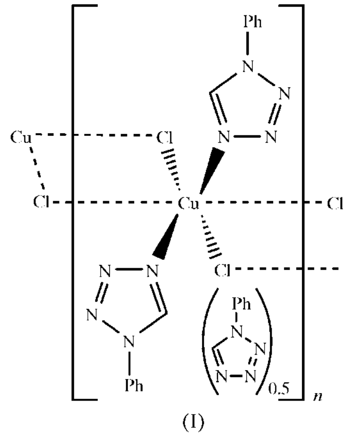
The title compound, {[CuCl$_2$(PhTz)$_2$]·0.5PhTz}$_n$ (PhTz is 1-phenyltetrazole, C$_7$H$_6$N$_4$), has a polymeric structure, with uncoordinated disordered PhTz molecules in the cavities. The coordination polyhedron of the Cu atom is a highly elongated octahedron. The equatorial positions are occupied by two Cl atoms [Cu—Cl = 2.2687 (9) and 2.2803 (7) Å] and two N atoms of the PhTz ligands [Cu—N = 2.0131 (19) and 2.0317 (18) Å]. The more distant axial positions are occupied by two Cl atoms [Cu—Cl = 3.0307 (12) and 2.8768 (11) Å] that lie in the equatorial planes of two neighbouring Cu octahedra. The [CuCl$_2$(PhTz)$_2$] units are linked by Cu—Cl bridges into infinite chains extending parallel to the *a* axis. The chains are linked into two-dimensional networks by intermolecular C—H···N interactions between the phenyl and tetrazole fragments, and by face-to-face π–π interactions between symmetry-related phenyl rings. These two-dimensional networks, which lie parallel to the *ac* plane, are connected by intermolecular π–π stacking interactions between phenyl rings, thus forming a three-dimensional network.

Comment

This work continues our X-ray studies of transition metal complexes with bulky 1-alkyl- and 1-aryltetrazole ligands. Previously, we reported the structures of CuCl$_2$ complexes with 1-*tert*-butyl- (Ivashkevich *et al.*, 2002) and 1-(2,4,6-trimethylphenyl)tetrazole (Ivashkevich *et al.*, 2003). The present paper is concerned with the crystal structure determination of a new complex, *catena*-poly[[*cis*-bis(4-phenyltetrazole-κN^1)-copper(II)]-di-μ-chloro], which crystallizes as the 2:1 adduct, (I), with 1-phenyltetrazole; the asymmetric unit of (I) contains two 1-phenyltetrazole ligands (*A* and *B*) and an uncoordinated 1-phenyltetrazole molecule (*C*; see Fig. 1).

The tetrazole rings of ligands *A* and *B* have very similar geometries, close to those previously observed for 1-substituted tetrazoles [Cambridge Structural Database (CSD); Version 5.25 of November 2003; Allen, 2002]. These rings are essentially planar, with mean deviations of the tetrazole ring atoms from their least-squares planes of 0.004 (3) and 0.003 (2) Å for ligands *A* and *B*, respectively.



(I)

The interplanar angle between the phenyl and tetrazole rings is 15.23 (14)° for ligand *A* and 21.67 (16)° for ligand *B*. The N1—C6 bond lengths [1.439 (3) and 1.430 (3) Å for ligands *A* and *B*, respectively] are typical of N—C$_{\text{aromatic}}$ single bonds with cyclic pseudo-aromatic nitrogen. A search of the CSD gives a mean bond length of 1.426 (18) Å for such bonds.

The bond lengths of ligands *A* and *B* are similar to those of the free 1-phenyltetrazole molecule (Matsunaga *et al.*, 1999); all of the corresponding values fall within the 3σ range. The corresponding bond angles differ slightly more, but fall within the 5σ range. The most important difference is observed in the interplanar angle between the tetrazole and phenyl rings; the value of 11.8 (1)° for the 1-phenyltetrazole molecule differs from those of ligands *A* and *B*.

The coordination polyhedron of the Cu atom is a highly elongated octahedron (Table 1). The equatorial positions are occupied by the two Cl atoms [Cu—Cl1 = 2.2687 (9) Å and

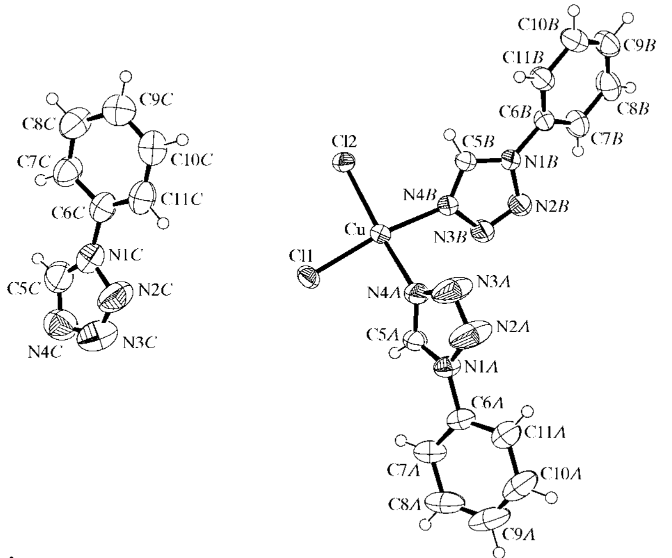


Figure 1
The structure of the components of (I). The monomeric unit is shown. Displacement ellipsoids are plotted at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

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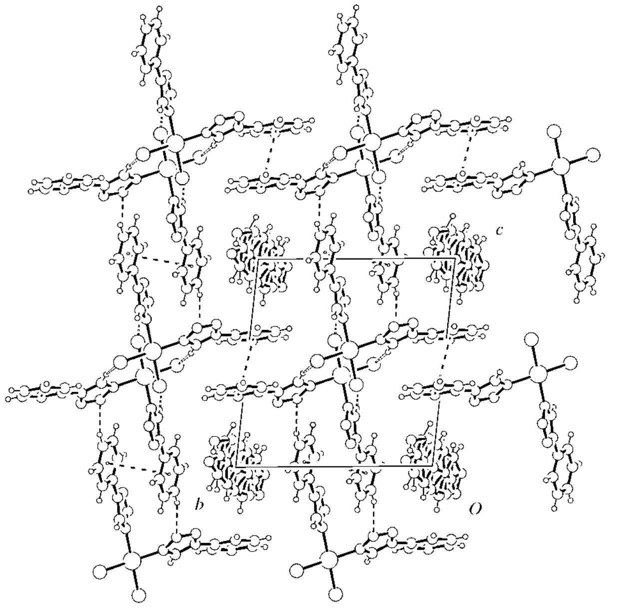

Figure 2
A projection of the structure of (I) along the *a* axis, showing the three-dimensional network. Dashed lines denote hydrogen bonds and π–π interactions. Disorder of the uncoordinated 1-phenyltetrazole molecule, *C*, is also shown.

Cu—Cl2 = 2.2803 (7) Å] and the two N-4 atoms of the 1-phenyltetrazole ligands [Cu—N4*A* = 2.0131 (19) Å and Cu—N4*B* = 2.0317 (18) Å]. The ligands are coordinated in a *cis* orientation. The Cu—Cl distances for the axial $\mathrm{Cl1^{ii}}$ and $\mathrm{Cl2^{i}}$ atoms are 3.0307 (12) and 2.8768 (11) Å, respectively (the symmetry codes are as in Table 1).

The coordination polyhedra of adjacent Cu atoms share edges, forming a one-dimensional polymeric structure, $[\mathrm{CuCl_2(C_7H_6N_4)_2}]_n$. These infinite chains extend parallel to the *a* axis (Fig. 2). C5*B*—H5*B*$\cdots$$\mathrm{Cl1^{i}}$ and C5*A*—H5*A*$\cdots$$\mathrm{Cl2^{ii}}$ hydrogen bonds (Steiner, 1996) are observed within the polymeric chains (Table 2).

In view of the lack of classical hydrogen bonds in the structure of (I), the packing structure is determined by weaker interactions. The infinite chains are linked into two-dimensional networks by C9*A*—H9*A*$\cdots$N3B^{iii} hydrogen bonds and by face-to-face π–π interactions between symmetry-related phenyl rings of ligands *A* [symmetry code: (iii) $1 - x$, $1 - y$, $2 - z$], with an intercentroid distance of 3.704 (2) Å and an offset value of *ca* 1.48 Å. These two-dimensional networks, which are parallel to the *ac* plane, are linked by intermolecular π–π stacking interactions between symmetry-related benzene rings of ligands *B* (symmetry code: $2 - x$, $-y$, $1 - z$), with an intercentroid distance of 4.055 (2) Å and an offset value of *ca* 1.93 Å, thus forming a three-dimensional network (Fig. 2).

This three-dimensional network contains a potential 'solvent-accessible area', with a volume of *ca* 230 $\mathrm{Å^3}$ and a possible electron count of 75 per unit cell (Spek, 2003), which is consistent with the presence of one 1-phenyltetrazole molecule. Analysis of a ΔF map indeed showed that the 'solvent-accessible area' contained molecule *C*. This molecule is associated with the $\bar{1}$ Wyckoff position, the C6*C* atom being displaced from the inversion centre by *ca* 0.08 Å. As a consequence, the molecule is disordered over two positions, each with an occupancy of 0.5 (Fig. 2).

Comparison of the structure of (I) with those of previously investigated $\mathrm{CuCl_2}L_2$ complexes, where *L* is 1-*tert*-butyl- (Ivashkevich *et al.*, 2002) and 1-(2,4,6-trimethylphenyl)-tetrazole (Ivashkevich *et al.*, 2003), shows that they all form one-dimensional polymeric chains with a copper–chlorine skeleton. However, the polymeric chains in (I) are linked by intermolecular C—H$\cdots$N and π–π interactions, forming a three-dimensional network, while the polymeric chains in the previously investigated $\mathrm{CuCl_2}L_2$ complexes, which contain no guest molecules, are connected only by van der Waals interactions.

Experimental

1-Phenyltetrazole was prepared by the heterocyclization of aniline with ethyl orthoformate and sodium azide in acetic acid (Gaponik *et al.*, 1985). The title compound was prepared by adding $\mathrm{CuCl_2{\cdot}2H_2O}$ (0.46 g) to a heated solution (303 K) of 1-phenyltetrazole (0.73 g) in ethanol (20 ml) with stirring. The reaction mixture was heated on a water bath for 5–7 min. Single crystals were grown by slow evaporation of the reaction mixture at 289–291 K over a period of one month (0.8 g, yield 32%).

Crystal data

$[\mathrm{CuCl_2(C_7H_6N_4)_2}]{\cdot}0.5\mathrm{C_7H_6N_4}$
$M_r = 499.84$
Triclinic, $P\bar{1}$
$a = 7.264$ (2) Å
$b = 11.669$ (4) Å
$c = 12.745$ (3) Å
$\alpha = 95.91$ (2)°
$\beta = 104.37$ (2)°
$\gamma = 92.93$ (3)°
$V = 1037.6$ (5) $\mathrm{Å^3}$
$Z = 2$
$D_x = 1.600$ Mg $\mathrm{m^{-3}}$
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 20.5$–22.3°
$\mu = 1.34$ $\mathrm{mm^{-1}}$
$T = 293$ (2) K
Prism, green
0.56 × 0.30 × 0.20 mm

Data collection

Nicolet *R*3*m* four-circle diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min} = 0.521$, $T_{\max} = 0.776$
5185 measured reflections
4804 independent reflections
4296 reflections with $I > 2\sigma(I)$
$R_{\mathrm{int}} = 0.056$
$\theta_{\max} = 27.6°$
$h = 0 \rightarrow 9$
$k = -15 \rightarrow 15$
$l = -16 \rightarrow 16$
3 standard reflections every 100 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.037$
$wR(F^2) = 0.111$
$S = 1.04$
4804 reflections
325 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0695P)^2 + 0.4065P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.57$ e $\mathrm{Å^{-3}}$
$\Delta\rho_{\min} = -0.72$ e $\mathrm{Å^{-3}}$

Table 1
Selected interatomic distances (Å).

Cu—N4*A*	2.0131 (19)	Cu—Cl2	2.2803 (7)
Cu—N4*B*	2.0317 (18)	Cu—$\mathrm{Cl2^{i}}$	2.8768 (11)
Cu—Cl1	2.2687 (9)	Cu—$\mathrm{Cl1^{ii}}$	3.0307 (12)

Symmetry codes: (i) $2 - x, 1 - y, 1 - z$; (ii) $1 - x, 1 - y, 1 - z$.

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C5A—H5A···Cl2^{ii}	0.93	2.52	3.446 (2)	173
C5B—H5B···Cl1^{i}	0.93	2.55	3.454 (2)	164
C9A—H9A···N3B^{iii}	0.93	2.61	3.521 (4)	167

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

H atoms were included in idealized positions (C—H = 0.93 Å) using a riding model [$U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C)]. The disordered 1-phenyltetrazole molecule was treated using an appropriate series of restraints; details are included in the supplementary material.

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: *SHELXS*97 (Sheldrick, 1997) and *PLATON* (Spek, 2003); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997) and *PLATON*; software used to prepare material for publication: *SHELXL*97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1625). Services for accessing these data are described at the back of the journal.

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