

The layered structure of poly[[di- μ -chloro-bis[chloro(2-ethyltetrazole- κN^4)copper(II)]]-di- μ -2-ethyltetrazole- $\kappa^2 N^1:N^4$]

Alexander S. Lyakhov, Pavel N. Gaponik, Michail M. Degtyarik and Ludmila S. Ivashkevich*

Physico-Chemical Research Institute, Belarusian State University, Leningradskaya Str. 14, Minsk 220050, Belarus
Correspondence e-mail: iva@bsu.by

Received 27 March 2003

Accepted 14 April 2003

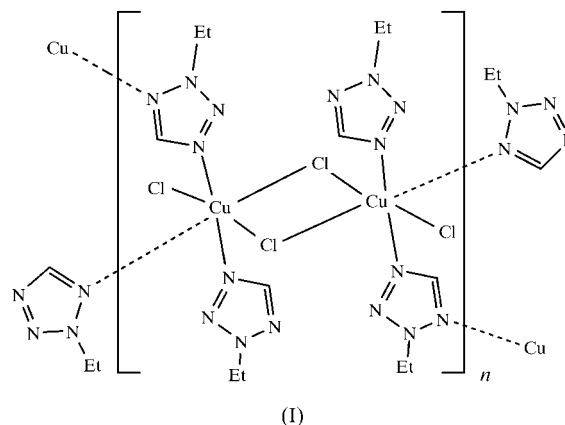
Online 10 May 2003

In the polymeric title complex, $[\text{CuCl}_2(\text{C}_3\text{H}_6\text{N}_4)_2]_n$, there are two ligands in the asymmetric unit. The Cu atom adopts an elongated octahedral geometry, with two 2-ethyltetrazole ligands $[\text{Cu}-\text{N} = 2.0037(16)$ and $2.0136(16)$ Å] and two Cl atoms $[\text{Cu}-\text{Cl} = 2.2595(6)$ and $2.2796(6)$ Å] in equatorial positions. A Cl atom and a symmetry-related 2-ethyltetrazole molecule $[\text{Cu}-\text{Cl} = 2.8845(8)$ Å and $\text{Cu}-\text{N} = 2.851(2)$ Å] lie in the axial positions of the octahedron. One of the two 2-ethyltetrazole ligands of the asymmetric unit exhibits bidentate binding to two Cu atoms through two N atoms of the tetrazole ring, whereas the other ligand is coordinated in a monodentate fashion *via* one tetrazole N atom. The Cu-atom octahedra form dimer entities by sharing edges with equatorial and axial Cl atoms. The dimers are linked together through the 2-ethyltetrazole ligands to form one-dimensional polymeric zigzag chains extending along the *b* axis. The chains are connected into infinite layers parallel to the $(10\bar{1})$ plane *via* the 2-ethyltetrazole ligands.

Comment

This work forms part of a project dealing with the synthesis, structures and properties of complexes of copper(II) chloride with 2-monosubstituted tetrazoles. To date, only two such complexes have been structurally characterized, namely $[\text{CuCl}_2L]$, where *L* is 2-*tert*-butyltetrazole (Lyakhov, Gaponik, Degtyarik & Ivashkevich, 2003), and $[\text{Cu}_3\text{Cl}_6L_4]$, where *L* is 2-allyltetrazole (Lyakhov, Gaponik, Degtyarik, Matulis *et al.*, 2003). Only one 2-monosubstituted tetrazole complex, *viz.* $[\text{NiL}_6](\text{BF}_4)_2$, where *L* is 2-methyltetrazole (van den Heuvel *et al.*, 1983), exists in the Cambridge Structural Database (CSD; Version 5.24 of November 2002; Allen, 2002). A new complex of copper(II) chloride, *viz.* $[\text{CuCl}_2L_2]$, where *L* is 2-ethyltetrazole, (I) (Fig. 1), has been synthesized and investigated in

the present work. There are two 2-ethyltetrazole ligands in the asymmetric unit of (I), and these are denoted by *A* and *B*.



The geometric parameters of the tetrazole rings of the two 2-ethyltetrazole molecules in (I) are very similar (Table 1). Bond lengths and angles are comparable to those obtained previously for copper(II) chloride complexes with 2-*tert*-butyltetrazole (Lyakhov, Gaponik, Degtyarik & Ivashkevich, 2003) and 2-allyltetrazole (Lyakhov, Gaponik, Degtyarik, Matulis *et al.*, 2003), and also for nickel(II) tetrafluoroborate with 2-methyltetrazole (van den Heuvel *et al.*, 1983).

The tetrazole rings in (I) are planar within 0.002 (3) and 0.003 (3) Å for ligands *A* and *B*, respectively.

The Cu atom exhibits axially elongated octahedral coordination, with two 2-ethyltetrazole ligands $[\text{Cu1}-\text{N4A} = 2.0037(16)$ Å and $\text{Cu1}-\text{N4B} = 2.0136(16)$ Å] and two Cl atoms $[\text{Cu1}-\text{Cl1} = 2.2796(6)$ Å and $\text{Cu1}-\text{Cl2} = 2.2595(6)$ Å] in the equatorial positions. Atom Cl1 and a symmetry-related 2-ethyltetrazole molecule lie in the axial positions of the octahedron $[\text{Cu1}-\text{Cl1}^{\text{ii}} = 2.8845(8)$ Å and $\text{Cu1}-\text{N1A}^{\text{i}} = 2.851(2)$ Å; symmetry codes: (i) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$; (ii) $1 - x, -y, -z$]. Ligand *A* thus exhibits bidentate binding to two Cu atoms through atoms N4 and N1 of the tetrazole ring, whereas ligand *B* is coordinated in a monodentate fashion *via* atom N4.

In the crystal structure of (I), the Cu-atom octahedra form dimer entities, by sharing edges with symmetry-related Cl1

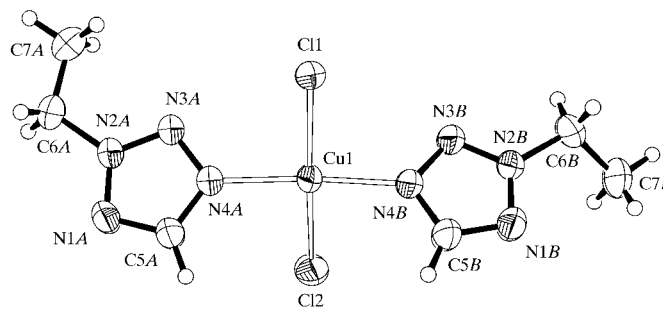
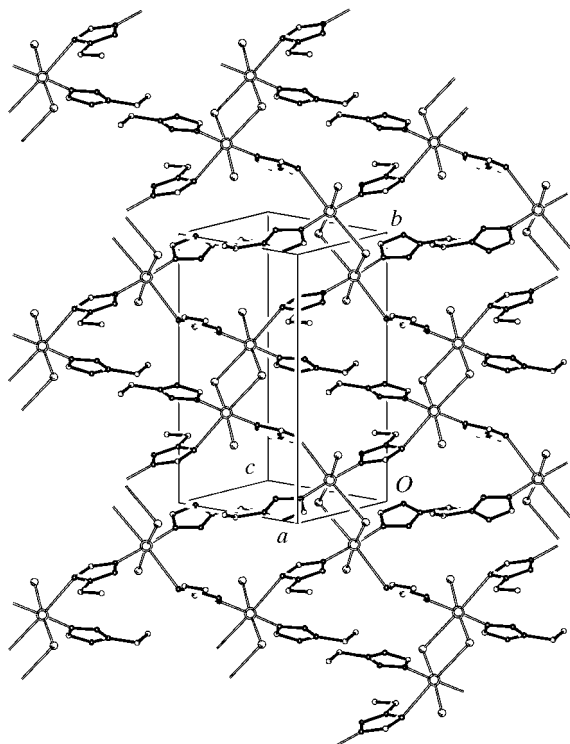


Figure 1

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.


Figure 2

A fragment of the crystal structure of (I), showing a polymeric sheet parallel to the $(10\bar{1})$ plane.

atoms (Fig. 2). The separation between the Cu atoms in the dimer is $3.6557(10)$ Å. The dimer entities are linked by ligand *A* to form one-dimensional polymeric zigzag chains extending along the *b* axis. The chains are connected into infinite layers parallel to the $(10\bar{1})$ plane via ligand *A*. Only van der Waals interactions exist between the sheets. Ligand *B* and atom Cl2 do not participate in the formation of the polymeric structure of (I).

Recently, we discussed an example of bidentate bridge coordination of the 2-allyltetrazole ligand via atoms N3 and N4 of the tetrazole ring in the complex $\text{Cu}_3\text{Cl}_6\text{L}_4$ (Lyakhov, Gaponik, Degtyarik, Matulis *et al.*, 2003). The structural data obtained for (I) revealed bidentate bridge coordination of the 2-ethyltetrazole ligand through atoms N4 and N1. By comparison with structures in the CSD containing 1-mono-substituted tetrazoles but having only N4-coordination, it can be concluded that 2-mono-substituted tetrazoles exhibit multidentate coordination more frequently than 1-mono-substituted tetrazoles. Further results on complexes of 2-mono-substituted tetrazoles will show how often bidentate coordination takes place for these ligands.

The bidentate bridge coordination of 2-mono-substituted tetrazoles is probably responsible for the difference in the crystal structures of the copper(II) chloride complexes with 1-ethyltetrazole (Virovets *et al.*, 1995) and 2-ethyltetrazole. These compounds are of the same composition; both have octahedrally coordinated Cu atoms and layered polymeric structures. However, whereas all the Cl atoms (and only these

atoms) participate in polymeric structure formation in the complex with 1-ethyltetrazole, only one Cl atom (Cl1) plays a bridging role in the polymeric structure of (I), but bidentate bridge coordination of ligand *A* makes it possible to form a two-dimensional polymeric network.

Experimental

The title complex was prepared by dissolving $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.0025 mol) in 2-ethyltetrazole (0.025 mol). The fine-grained complex that precipitated immediately was separated by decanting (yield 46%). Two months later, blue prismatic crystals of the title complex (0.35 g, 42%) were obtained from the decanted solution. Analysis calculated for $\text{C}_6\text{H}_{12}\text{Cl}_2\text{CuN}_8$: Cu 19.2, Cl 21.2%; found: Cu 19.3, Cl 21.1% (the results were identical for both obtained fractions).

Crystal data

$[\text{CuCl}_2(\text{C}_3\text{H}_6\text{N}_4)_2]$
 $M_r = 330.68$
 Monoclinic, $P2_1/n$
 $a = 10.234(2)$ Å
 $b = 13.690(4)$ Å
 $c = 10.478(2)$ Å
 $\beta = 119.174(15)^\circ$
 $V = 1281.9(5)$ Å³
 $Z = 4$

$D_x = 1.713$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 25 reflections
 $\theta = 22.0\text{--}24.1^\circ$
 $\mu = 2.11$ mm⁻¹
 $T = 293(2)$ K
 Prism, blue
 $0.60 \times 0.60 \times 0.52$ mm

Data collection

Nicolet R3m four-circle diffractometer
 $\omega/2\theta$ scans
 Absorption correction: ψ scan (North *et al.*, 1968)
 $T_{\min} = 0.298$, $T_{\max} = 0.333$
 4079 measured reflections
 3763 independent reflections
 3444 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.019$
 $\theta_{\text{max}} = 30.1^\circ$
 $h = 0 \rightarrow 14$
 $k = 0 \rightarrow 19$
 $l = -14 \rightarrow 12$
 3 standard reflections every 100 reflections
 intensity decay: none

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.034$
 $wR(F^2) = 0.098$
 $S = 1.09$
 3763 reflections
 156 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0535P)^2 + 0.5059P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.57$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.59$ e Å⁻³

Table 1

Selected intramolecular distances (Å).

Cu1—N4A	2.0037 (16)	N2A—N3A	1.308 (2)
Cu1—N4B	2.0136 (16)	N3A—N4A	1.326 (2)
Cu1—Cl2	2.2595 (6)	N4A—C5A	1.331 (2)
Cu1—Cl1	2.2796 (6)	N1B—C5B	1.319 (3)
Cu1—N1A ⁱ	2.851 (2)	N1B—N2B	1.325 (3)
Cu1—Cl1 ⁱⁱ	2.8845 (8)	N2B—N3B	1.313 (2)
N1A—N2A	1.328 (2)	N3B—N4B	1.317 (2)
N1A—C5A	1.328 (3)	N4B—C5B	1.333 (3)

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

H atoms were placed in calculated positions, with C—H distances in the range 0.93–0.97 Å, and were included in the refinement in a riding-model approximation, with $U_{\text{iso}}(\text{H})$ values equal to $1.5U_{\text{eq}}(\text{C})$ for the methyl group and $1.2U_{\text{eq}}(\text{C})$ for the other H atoms.

Data collection: *R3m Software* (Nicolet, 1980); cell refinement: *R3m Software*; data reduction: *OMNIBUS* (Galdecka, 2002); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997), *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1419). Services for accessing these data are described at the back of the journal.

References

Allen, F. H. (2002). *Acta Cryst.* **B58**, 380–388.

Altomare, A., Burla, M. C., Camalli, M., Cascarano, G. L., 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.

Galdecka, E. (2002). *J. Appl. Cryst.* **35**, 641–643.

Heuvel, E. J. van den, Franke, P. L., Verschoor, G. C. & Zuur, A. P. (1983). *Acta Cryst.* **C39**, 337–339.

Lyakhov, A. S., Gaponik, P. N., Degtyarik, M. M. & Ivashkevich, L. S. (2003). *Acta Cryst.* **E59**, m38–m40.

Lyakhov, A. S., Gaponik, P. N., Degtyarik, M. M., Matulis, V. E., Matulis, V. E. & Ivashkevich, L. S. (2003). *Acta Cryst.* **C59**, m90–m92.

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

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.

Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.

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

Virovets, A. V., Podberezhskaya, N. V., Lavrenova, L. G. & Bikzhanova, G. A. (1995). *Acta Cryst.* **C51**, 1084–1087.