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Key indicators

Powder X-ray study
 $T = 293$ K
Mean $\sigma(\text{N}-\text{C}) = 0.016$ Å
 R factor = 0.054
 wR factor = 0.090

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

An X-ray powder diffraction study of catena-poly[[bis(1-methyl-1*H*-tetrazole- κ N⁴)copper(II)]-di- μ -bromo]

The crystal structure of the polymeric title complex, $[\text{CuBr}_2(\text{C}_4\text{H}_8\text{N}_8)_2]_n$, has been solved from X-ray powder data and refined with the Rietveld method using geometrical soft restraints. The Cu atom, lying on an inversion centre, has octahedral coordination, with two N atoms $[\text{Cu}-\text{N} = 2.090(13)$ Å] and two Br atoms $[\text{Cu}-\text{Br} = 2.432(4)$ Å] in the equatorial positions. The axial sites of the octahedron are occupied by two Br atoms, with Cu–Br distances of 3.101(4) Å. Each Br atom is a bridge between neighbouring Cu atoms, which is responsible for formation of polymeric layers parallel to the *bc* plane, with only van der Waals interactions between them.

Comment

Transition metal halide complexes with substituted tetrazoles are of interest because of their magnetic behaviour. This stimulates their structure determination to relate magnetic properties to structural peculiarities. Analysis of the available crystal data (Cambridge Structural Database, Version 5.25 of November 2003; Allen, 2002) for metal(II) halide complexes with 1-alkyltetrazoles showed that all the investigated complexes are of composition $M^{\text{II}}\text{Hal}_2L_2$, where M^{II} is a divalent metal, $L = 1$ -alkyltetrazole, and Hal is Cl or Br. Except for the CoCl_2L_2 complex, where L is 1-allyltetrazole (Shvedenkov *et al.*, 2003), all remaining investigated compounds are copper(II) complexes. Among these, most examples are copper(II) chloride compounds (Virovets *et al.*, 1995, 1996; Stassen *et al.*, 2002; Ivashkevich *et al.*, 2001, 2002, 2003, 2004). Two types of crystal structures are observed for the above cobalt(II) and copper(II) chloride complexes, *viz.* polymeric copper–chloride chains and polymeric copper–chloride layers. When 1-substituted tetrazoles with rather bulky substituents at the tetrazole ring atom N1 are used, structures of the first type are observed, otherwise structures of the second type are formed.

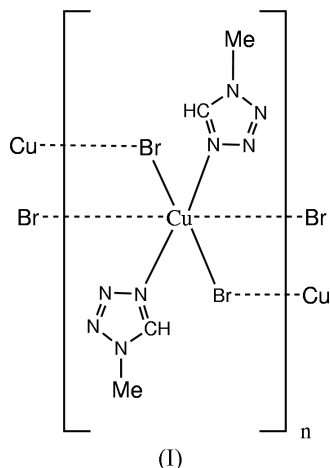
Only a few complexes of copper(II) bromide with 1-substituted tetrazoles have been structural characterized. These are CuBr_2L_2 , with $L = 1$ -(2-chloroethyl)tetrazole (Stassen *et al.*, 2002) and $L = 1$ -(2-methoxyethyl)tetrazole (Stassen *et al.*, 2003) (two isomeric complexes were reported with the last ligand). They are all layered coordination polymers. Structural peculiarities of analogous chloride and bromide complexes are expected to be the same; however, the larger bromide ion size may cause the structural features to be modified, which may be of importance for magnetic behaviour. From this point of view, it is of interest to enlarge the structural information on bromide complexes of 1-substituted tetrazoles.

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The aim of the present work was the structure determination of a new complex, (I), of copper(II) bromide with 1-alkyltetrazole, CuBr_2L_2 , where L is 1-methyltetrazole. It was impossible to grow single crystals suitable for structure analysis; X-ray powder diffraction was used for the crystal structure determination of (I).



In the crystal structure of (I), the Cu atom lies on an inversion centre and shows octahedral coordination (Fig. 1). The equatorial sites are occupied by two *trans* N4 and N4ⁱⁱ atoms of two ligand molecules [Cu–N distances of 2.090 (13) Å], and two Br atoms, Br and Brⁱⁱ [Cu–Br = 2.432 (4) Å]; atoms Brⁱ and Brⁱⁱⁱ are in axial positions and are essentially more distant from the Cu atom [Cu–Br = 3.101 (4) Å; symmetry codes: (i) $-x, y - \frac{1}{2}, \frac{1}{2} - z$; (ii) $-x, -y,$

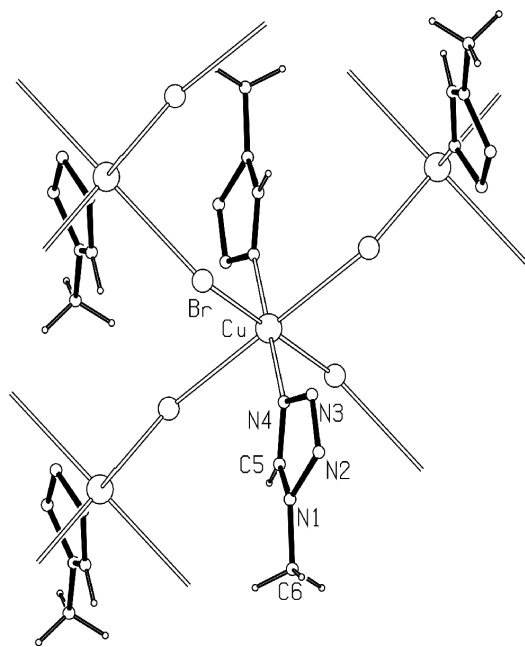


Figure 1

A fragment of the crystal structure of (I), showing the Cu atom environment, the formation of a polymeric layer and the atom numbering for the asymmetric unit.

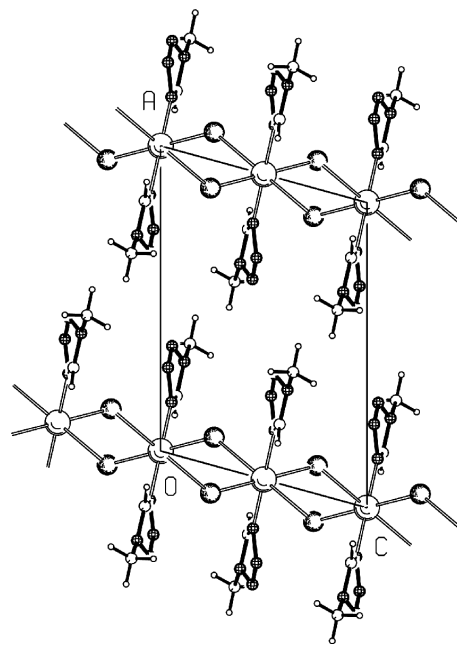


Figure 2

The layered structure of (I), viewed along the b axis.

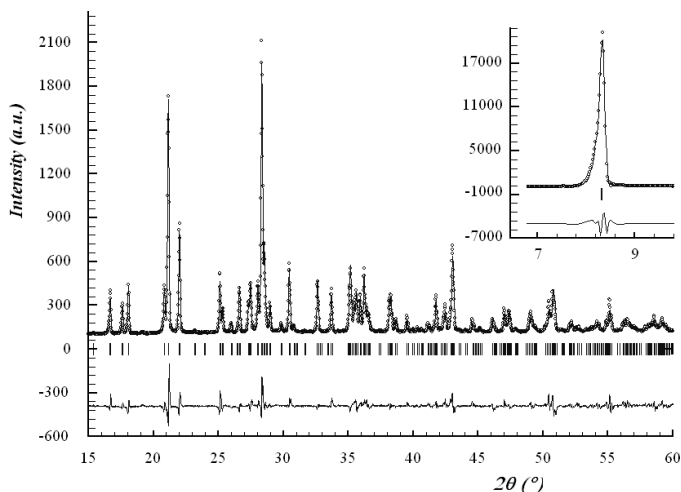


Figure 3

Two sections of Rietveld refinement final plots of (I): experimental diffraction pattern (circles), the pattern as calculated from the refined crystal structure (line), difference between these patterns (lower), and reflection positions (vertical lines).

$-z$; (iii) $x, \frac{1}{2} - y, z - \frac{1}{2}$]. Each Br atom is a bridge between neighbouring Cu atoms, forming two different Cu–Br bond lengths, with a Cu–Br–Cu angle of 137.05 (11)°. These bonds are responsible for the formation of polymeric layers parallel to the bc plane (Fig. 2). Within a layer, the shortest Cu··Cu distance is *ca* 5.15 Å, whereas between two neighbouring layers, the closest copper centres are separated by the cell length a . Only van der Waals interactions occur between the layers.

The structure of (I) is closely related to those of copper(II) chloride complexes CuCl_2L_2 , where $L = 1$ -ethyltetrazole (Virovets *et al.*, 1995), 1-(2-chloroethyl)tetrazole (Stassen *et al.*, 2002), 1-allyltetrazole (Virovets *et al.*, 1996), 1-(2-azidoethyl)tetrazole (Ivashkevich *et al.*, 2001), the cobalt(II)

chloride complex with $L = 1$ -allyltetrazole (Shvedenkov *et al.*, 2003), and the copper(II) bromide complex with 1-(2-chloroethyl)tetrazole (Stassen *et al.*, 2002). They all may be considered as, to a great extent, isostructural compounds. Surprisingly, complex CuBr_2L_2 with $L = 1$ -(2-methoxyethyl)-tetrazole (Stassen *et al.*, 2003) has essentially different coordination features, although it was expected that this structure would be similar in its coordination mode to the above complexes with non-bulky substituents at the tetrazole ring atom N1.

Experimental

CuBr_2 (1.12 g) was added to a solution of 1-methyltetrazole (0.89 g) in ethanol (20 ml) with stirring at room temperature. After keeping the mixture for 20 min at room temperature, the resulting brown crystals of (I) were filtered off, washed with ethanol and then diethyl ether, and air dried (1.57 g, yield 80%). Calculated (%): Cu 16.2, Br 40.8; found (%): Cu 16.0, Br 39.6.

Crystal data

$[\text{CuBr}_2(\text{C}_4\text{H}_8\text{N}_4)_2]$	$D_x = 2.317 \text{ Mg m}^{-3}$
$M_r = 391.53$	Cu $K\alpha$ radiation
Monoclinic, $P2_1/c$	$\mu = 10.98 \text{ mm}^{-1}$
$a = 11.0319 (5) \text{ \AA}$	$T = 293 \text{ K}$
$b = 6.8524 (4) \text{ \AA}$	Specimen shape: flat sheet
$c = 7.7018 (4) \text{ \AA}$	$30 \times 30 \times 1 \text{ mm}$
$\beta = 105.444 (3)^\circ$	Specimen prepared at 293 K
$V = 561.20 (5) \text{ \AA}^3$	Particle morphology: plate
$Z = 2$	Brown

Data collection

Carl Zeiss (Jena) HZG-4A diffractometer	Specimen mounted in reflection mode
$\theta/2\theta$ scans	Absorption correction: none
Specimen mounting: packed powder pellet	$2\theta_{\min} = 5$, $2\theta_{\max} = 110^\circ$
	Increment in $2\theta = 0.02^\circ$

Refinement

Refinement on I_{net}	$w = 1/\sigma^2$
$R_p = 0.054$	$(\Delta/\sigma)_{\max} = 0.016$
$R_{\text{wp}} = 0.090$	H-atom parameters constrained
$R_{\text{exp}} = 0.073$	Preferred orientation correction: Marsh–Dollase function (Marsh, 1932; Dollase, 1986)
$R_B = 0.049$	
Profile function: pseudo-Voigt	
44 parameters	

Table 1

Selected geometric parameters (\AA , $^\circ$).

Cu–Br	2.432 (4)	N1–C6	1.477 (16)
Cu–Br ⁱ	3.101 (4)	N2–N3	1.280 (16)
Cu–N4	2.090 (13)	N3–N4	1.361 (18)
N1–N2	1.356 (18)	N4–C5	1.308 (15)
N1–C5	1.33 (2)		
N2–N1–C5	94.9 (17)	N3–N4–C5	103.5 (15)
N2–N1–C6	128.4 (16)	N1–C5–N4	117.1 (17)
C5–N1–C6	133.0 (19)	N4–Cu–Br	88.1 (7)
N1–N2–N3	117.3 (16)	N4–Cu–Br ⁱ	89.1 (6)
N2–N3–N4	104.0 (16)	Br–Cu–Br ⁱ	91.2 (2)

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

The powder diffraction pattern was indexed using the *TREOR90* program (Werner *et al.*, 1985) ($F_{20} = 97$, $M_{20} = 57$, $F_{35} = 65$, $M_{35} = 34$).

Analysis of the systematic absences indicated Pc , $P2/c$ and $P2_1/c$ as possible space groups. All were used for crystal structure solution with the direct methods package *EXPO* (Altomare *et al.*, 1999). By testing the space groups, only $P2_1/c$ was found to be appropriate. All non-H atoms were located by structure solution, with $R_F = 0.186$. The solved structure was then refined against the full data set ($5-110^\circ 2\theta$), using the Rietveld method as implemented in *FULLPROF* (Rodrigues-Carvajal, 2001). A correction for profile asymmetry was made for reflections up to $2\theta = 40^\circ$. A Marsh–Dollase correction of intensities for [100] preferred orientation of plate-like grains in the sample (Marsh, 1932; Dollase, 1986) was applied and the refined value of the preferred orientation coefficient G_1 was 0.659 (2). The G_2 parameter was found to be practically equal to 0 and not included in the final refinement. Displacement parameters were refined isotropically, those for N and C atoms being refined as one parameter. H atoms were placed in calculated positions, with displacement parameters $U_{\text{iso}}(\text{H}) = 1.2U_{\text{iso}}(\text{C})$ for the tetrazole H atom and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{iso}}(\text{C})$ for the methyl group. The final structure was obtained as a result of refinement with soft restraints on interatomic distances and bond angles of the ligand molecule. The distance and angle restraints were based on a geometric analysis of a large number of 1-substituted tetrazoles (Cambridge Structural Database, Version 5.25 of November 2003; Allen, 2002).

Data collection: local program; cell refinement: *FULLPROF* (Rodrigues-Carvajal, 2001); data reduction: local program; program(s) used to solve structure: *EXPO* (Altomare *et al.*, 1999); program(s) used to refine structure: *FULLPROF*; molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *PLATON* (Spek, 2003); software used to prepare material for publication: *FULLPROF*.

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