

Copper(II) chloride and bromide complexes with 2-methyl-2H-tetrazol-5-amine: an X-ray powder diffraction study

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The complex *catena*-poly[[dibromidocopper(II)]-bis(μ -2-methyl-2H-tetrazol-5-amine)- $\kappa^2N^4:N^5;\kappa^2N^5:N^4$], [CuBr₂(C₂H₅N₅)₂]_n, (I), and the isotopic chloride complex *catena*-poly[[dichloridocopper(II)]-bis(μ -2-methyl-2H-tetrazol-5-amine)- $\kappa^2N^4:N^5;\kappa^2N^5:N^4$], [CuCl₂(C₂H₅N₅)₂]_n, (II), were investigated by X-ray powder diffraction at room temperature. The crystal structure of (I) was solved by direct methods, while the Rietveld refinement of (II) started from the atomic coordinates of (I). In both structures, the Cu atoms lie on inversion centres, adopting a distorted octahedral coordination of two halogen atoms, two tetrazole N atoms and two 5-amine group N atoms. Rather long Cu–N_{amine} bonds allow consideration of the amine group as semi-coordinated. The compounds are one-dimensional coordination polymers, formed as a result of 2-methyl-2H-tetrazol-5-amine ligands bridging *via* a tetrazole N atom and the amine N atom. In the polymeric chains, adjacent Cu atoms are connected by two such bridges.

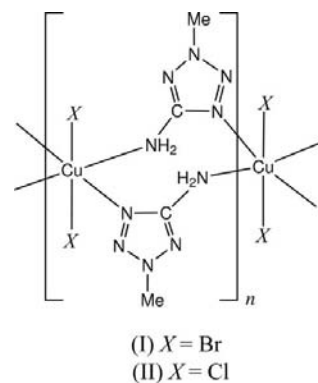
Comment

Aminotetrazoles are promising multifunctional ligands, with the amine group and the tetrazole ring N atoms able to be coordinated by metal atoms. This allows the formation of diverse coordination frameworks, resulting in coordination compounds with different structural motifs and properties.

A number of complexes of 5-aminotetrazole and its 1- and 2-substituted derivatives have been synthesized and characterized (see Voitekhovich *et al.*, 2009, and references therein; Gaponik *et al.*, 2006). Analysis of the structural data showed that in none of the compounds was the 5-amine group coordinated to the metal. In the case of 1-vinyltetrazol-5-amine, this fact was explained by the conjugation of the 5-amine group lone pair with the tetrazole π -ring, in accordance with quantum-chemical calculations (Lyakhov *et al.*,

2008). In most investigated complexes with 1,5-diaminotetrazole (Qi *et al.*, 2009; Cui, Zhang, Zhang, Yang, Hu & Zhang, 2008; Cui *et al.*, 2008*a,b*; Cui, Zhang, Zhang, Yang, Zhang & Shu, 2008), the 1-amine group does not participate in metal coordination; however, in the copper(II) chloride complex with this ligand (Gaponik *et al.*, 2005), the 1-amine N atom is bonded to Cu, showing the ability of the 1-amine group to be coordinated by a metal.

The present work is devoted to complexes of 2-substituted tetrazol-5-amines. To date, only structural data for copper(II), palladium(II) and platinum(II) chloride complexes with 2-*tert*-butyltetrazol-5-amine (Voitekhovich *et al.*, 2009), and for a silver complex of 2-methyltetrazol-5-amine (Karaghiosoff *et al.*, 2009) have been available. In these compounds, the 5-amine group adopts a geometry close to planar and is not included in the coordination environment of the metal atoms. We present here the structures of two Cu^{II} halogenide complexes with 2-methyl-2H-tetrazol-5-amine, *viz.* *catena*-poly[[dibromidocopper(II)]-bis(μ -2-methyl-2H-tetrazol-5-amine)- $\kappa^2N^4:N^5;\kappa^2N^5:N^4$], (I), and the isotopic chloride complex, (II). Because it was impossible to obtain single crystals suitable for X-ray analysis, both structures were determined by laboratory X-ray powder diffraction analysis.



Complexes (I) and (II) crystallize in the triclinic space group $P\bar{1}$ and are isotopic. The asymmetric units contain half a Cu atom, one Cl/Br atom and one molecule of 2-methyl-2H-tetrazol-5-amine (Fig. 1). The Cu atoms lie on inversion centres, whereas all other atoms are in general positions.

In both structures, the 2-methyl-2H-tetrazol-5-amine molecules reveal similar geometry (Tables 1 and 3). The formally single tetrazole ring N2–N3 bond is rather short, reflecting a tendency to be the shortest in the ring, as follows from previous structural investigations of 2-substituted tetrazoles and their complexes (Voitekhovich *et al.*, 2009; Karaghiosoff *et al.*, 2009; Lyakhov, Degtyarik *et al.*, 2005; Lyakhov, Gaponik *et al.*, 2005, and references therein).

In complexes (I) and (II), the Cu atoms coordinate four ligand molecules and two halogen atoms. Two of the four ligand molecules are bonded to the metal through the tetrazole ring N4 atoms, occupying together with two halogen atoms the equatorial sites of a distorted coordination octahedron. The two other ligand molecules of the Cu coordination environment are coordinated *via* the amine N7 atoms,

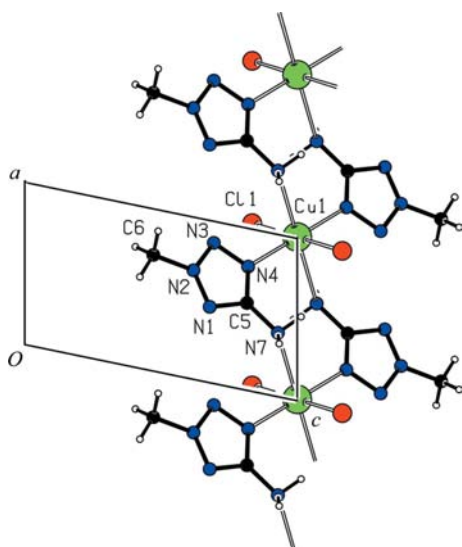


Figure 1
A polymeric chain in the crystal structure of complex (II). The atomic numbering for the asymmetric unit is the same for complex (I).

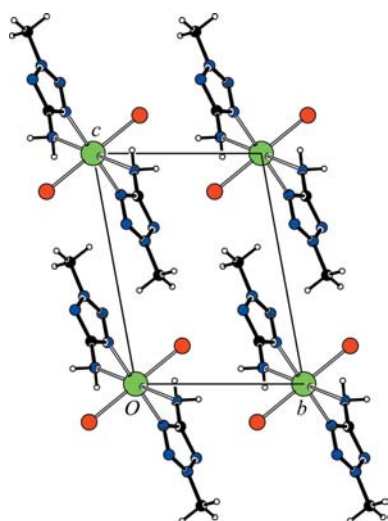


Figure 2
The crystal structure of complex (II), viewed along the *a* axis.

which are 2.783 (10) and 2.683 (6) Å from the metal in (I) and (II), respectively, and can be considered as semi-coordinated. Two 2-methyl-2*H*-tetrazol-5-amine molecules play the role of bridges between two adjacent Cu atoms in polymeric chains, running along the *a* axis (Figs. 1 and 2). Halogen atoms do not participate in building the coordination polymer.

In both structures, the amine group H atoms are involved in N—H···halogen hydrogen bonds (Tables 2 and 4). Two H atoms of the amine group are connected with two halogen atoms belonging to different polymeric chains (Fig. 3), to form polymeric layers parallel to the *ab* plane.

Thus, complexes (I) and (II) are the first examples of coordination of tetrazole ligands *via* the 5-amine group. Among complexes of tetrazol-5-amine and its 1-substituted derivatives, no such coordination has been observed. Probably, the amine groups of 2-substituted tetrazol-5-amines are

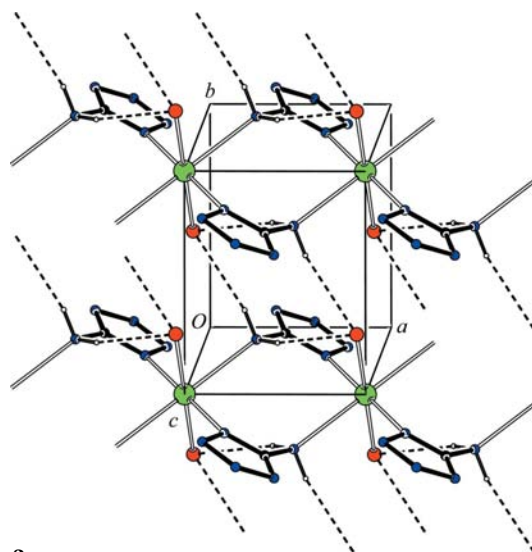


Figure 3
Coordination polymeric chains in (II), connected by hydrogen bonds to give polymeric layers parallel to the *ab* plane. The methyl groups have been omitted for clarity.

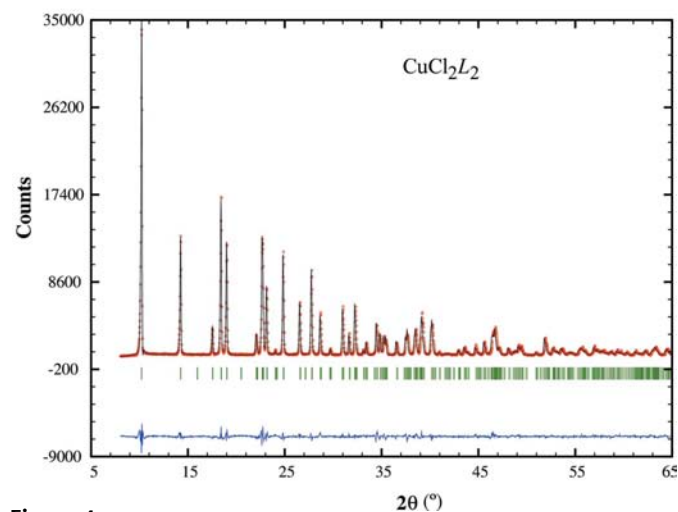
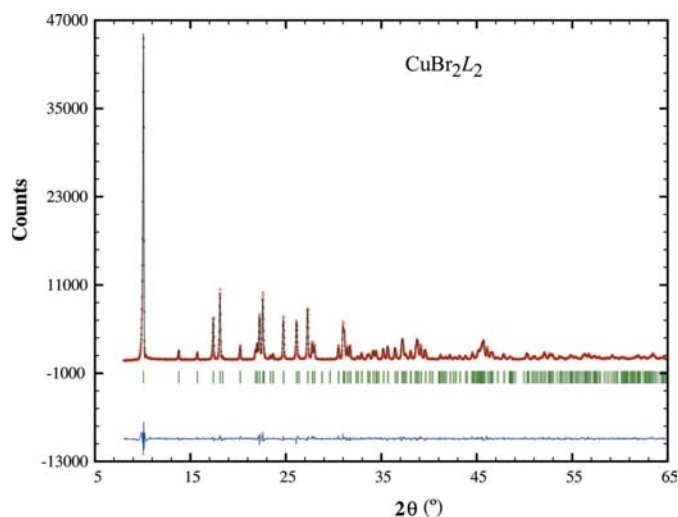


Figure 4
Experimental, calculated and difference powder patterns for complexes (I) (top) and (II) (bottom) in the range $2\theta = 5\text{--}65^\circ$. The positions of the Bragg reflections are marked by ticks.

conjugated with the tetrazole π -ring to a lesser extent than the 5-amine groups of 1-substituted analogues.

Experimental

For the synthesis of (I), CuBr_2 (0.44 g, 0.002 mol) was added with intensive stirring to a solution containing 2-methyl-2*H*-tetrazol-5-amine (0.4 g, 0.004 mol) in a methanol–hexane mixture (15 ml, 1:3 *v/v*). The resulting green precipitate, obtained simultaneously with the dissolution of copper(II) bromide, was filtered off, washed with diethyl ether (3 \times 5 ml) and dried in air [yield 0.68 g, 81%; m.p. 473 K (decomposition)]. Analysis calculated: Cu 15.1, Br 38.0%; found: Cu 15.4, Br 38.1%. IR (cm^{-1}): 3328 (*s*), 3262 (*s*), 3042 (*s*), 1600 (*sh*), 1524 (*s*), 1464 (*w*), 1436 (*s*), 1371 (*s*), 1351 (*w*), 1324 (*s*), 1199 (*s*), 107 (*s*), 1070 (*s*), 1020 (*s*), 818 (*s*), 765 (*s*), 706 (*s*), 638 (*s*), 520 (*s*), 467 (*s*).

For the synthesis of (II), a solution containing 2-methyl-2*H*-tetrazol-5-amine (0.4 g, 0.004 mol) in a mixture of methanol and diethyl ether (15 ml, 1:3 *v/v*) was added to a solution of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.34 g, 0.002 mol) in 10 ml of the same solvent mixture. After stirring the reaction mixture for 0.5 h, the resulting blue–green precipitate was filtered off, washed with diethyl ether (3 \times 5 ml) and dried in air [yield 0.53 g, 80%; m.p. 483 K (decomposition)]. Analysis calculated: Cu 19.1, Cl 21.4%; found: Cu 19.4, Cl 21.6%. IR (cm^{-1}): 3338 (*s*), 3267 (*s*), 3047 (*s*), 1600 (*sh*), 1524 (*s*), 1468 (*w*), 1436 (*s*), 1371 (*s*), 1351 (*sh*), 1323 (*s*), 1203 (*s*), 1109 (*w*), 1070 (*s*), 1017 (*s*), 818 (*s*), 765 (*m*), 709 (*s*), 640 (*s*), 540 (*m*), 481 (*s*).

Table 1
Selected bond lengths (\AA) for (I).

Cu1–Br1	2.4452 (18)	N2–N3	1.307 (13)
Cu1–N4	2.004 (8)	N2–C6	1.472 (12)
Cu1–N7 ⁱ	2.783 (10)	N3–N4	1.299 (11)
N1–N2	1.333 (12)	N4–C5	1.334 (16)
N1–C5	1.328 (15)	N7–C5	1.360 (14)

Symmetry code: (i) $x + 1, y, z$.

Table 2
Hydrogen-bond geometry ($\text{\AA}, ^\circ$) for (I).

$D\text{---}H\cdots A$	$D\text{---}H$	$H\cdots A$	$D\cdots A$	$D\text{---}H\cdots A$
N7–H7A \cdots Br1 ⁱⁱ	0.90	2.74	3.634 (11)	172
N7–H7B \cdots Br1 ⁱⁱⁱ	0.90	2.65	3.463 (9)	151

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

Table 3
Selected bond lengths (\AA) for (II).

Cu1–Cl1	2.305 (2)	N2–N3	1.287 (9)
Cu1–N4	2.101 (6)	N2–C6	1.465 (9)
Cu1–N7 ⁱ	2.683 (6)	N3–N4	1.344 (8)
N1–N2	1.317 (8)	N4–C5	1.318 (10)
N1–C5	1.332 (9)	N7–C5	1.376 (9)

Symmetry code: (i) $x + 1, y, z$.

Table 4
Hydrogen-bond geometry ($\text{\AA}, ^\circ$) for (II).

$D\text{---}H\cdots A$	$D\text{---}H$	$H\cdots A$	$D\cdots A$	$D\text{---}H\cdots A$
N7–H7A \cdots Cl1 ⁱⁱ	0.90	2.74	3.587 (8)	157
N7–H7B \cdots Cl1 ⁱⁱⁱ	0.90	2.49	3.323 (6)	154

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

Compound (I)

Crystal data

$[\text{CuBr}_2(\text{C}_2\text{H}_5\text{N}_5)_2]$
 $M_r = 421.57$
 Triclinic, $P\bar{1}$
 $a = 5.22187$ (19) \AA
 $b = 6.5081$ (2) \AA
 $c = 9.1165$ (3) \AA
 $\alpha = 99.0064$ (15) $^\circ$
 $\beta = 102.4480$ (15) $^\circ$
 $\gamma = 90.2997$ (18) $^\circ$
 $V = 298.56$ (2) \AA^3

$Z = 1$
 Cu $K\alpha$ radiation
 $T = 295$ K
 Specimen shape: flat sheet
 $30 \times 30 \times 1$ mm
 Specimen prepared at 100 kPa
 Specimen prepared at 295 K
 Particle morphology: finely ground powder, green

Data collection

HZG-4A (Carl Zeiss, Jena) diffractometer
 Specimen mounting: packed powder pellet

Specimen mounted in reflection mode
 Scan method: step
 $2\theta_{\min} = 8.0$, $2\theta_{\max} = 110.0$ $^\circ$
 Increment in $2\theta = 0.02$ $^\circ$

Refinement

$R_p = 0.037$
 $R_{wp} = 0.050$
 $R_{\text{exp}} = 0.029$
 $R_B = 0.043$
 $S = 1.74$
 Excluded region(s): none
 Profile function: pseudo-Voigt

822 reflections
 40 parameters
 7 restraints
 H-atom parameters constrained
 Preferred orientation correction: March–Dollase function (March, 1932; Dollase, 1986)

Compound (II)

Crystal data

$[\text{CuCl}_2(\text{C}_2\text{H}_5\text{N}_5)_2]$
 $M_r = 332.67$
 Triclinic, $P\bar{1}$
 $a = 5.16248$ (13) \AA
 $b = 6.32103$ (16) \AA
 $c = 8.9925$ (2) \AA
 $\alpha = 100.1652$ (13) $^\circ$
 $\beta = 101.4538$ (12) $^\circ$
 $\gamma = 90.4234$ (12) $^\circ$
 $V = 282.81$ (1) \AA^3

$Z = 1$
 Cu $K\alpha$ radiation
 $T = 295$ K
 Specimen shape: flat sheet
 $30 \times 30 \times 1$ mm
 Specimen prepared at 100 kPa
 Specimen prepared at 295 K
 Particle morphology: finely ground powder, blue-green

Data collection

HZG-4A (Carl Zeiss, Jena) diffractometer
 Specimen mounting: packed powder pellet

Specimen mounted in reflection mode
 Scan method: step
 $2\theta_{\min} = 8.0$, $2\theta_{\max} = 120.0$ $^\circ$
 Increment in $2\theta = 0.02$ $^\circ$

Refinement

$R_p = 0.030$
 $R_{wp} = 0.039$
 $R_{\text{exp}} = 0.025$
 $R_B = 0.045$
 $S = 1.56$
 Excluded region(s): none
 Profile function: pseudo-Voigt

896 reflections
 40 parameters
 7 restraints
 H-atom parameters constrained
 Preferred orientation correction: March–Dollase function (March, 1932; Dollase, 1986)

Powder diffraction patterns of complexes (I) and (II) were indexed using the program *TREOR90* (Werner *et al.*, 1985). As a result, triclinic unit cells were found for both compounds, with $a = 5.224$ \AA , $b = 6.512$ \AA , $c = 9.120$ \AA , $\alpha = 99.02$ $^\circ$, $\beta = 102.45$ $^\circ$ and $\gamma = 90.29$ $^\circ$ ($F_{20} = 118$, $M_{20} = 60$, $F_{30} = 111$ and $M_{30} = 45$) for complex (I), and $a = 5.164$ \AA , $b = 6.332$ \AA , $c = 9.002$ \AA , $\alpha = 100.09$ $^\circ$, $\beta = 101.47$ $^\circ$ and $\gamma = 90.41$ $^\circ$ ($F_{20} = 45$, $M_{20} = 26$, $F_{30} = 42$ and $M_{30} = 20$) for complex (II).

The similarity of the obtained unit cells as well as of the powder patterns of (I) and (II) allowed the assumption to be made that the compounds were isotopic. This prediction was supported later by the obtained results.

Structure solution was performed only for complex (I) using the program *EXPO* (Altomare *et al.*, 1999). Both possible space groups, *viz.* $P1$ and $P\bar{1}$, were tested, but $P\bar{1}$ was found to be appropriate, allowing a reasonable solution to be obtained. All non-H atoms were located by structure solution, with $R(F) = 0.124$. The solved structure of (I) was refined with the *FULLPROF* package (Rodrigues-Carvajal, 2001). The refined atomic positions in (I) were used as starting coordinates for (II).

Both structures were refined in the same way. The background was adjusted iteratively at each cycle by using a Fourier filtering technique as implemented in the *FULLPROF* program. The pseudo-Voigt profile function was used to fit the patterns. An asymmetry correction was applied according to the Bérar–Baldinozzi function (Bérar & Baldinozzi, 1993). A March–Dollase correction of intensities for the (001) preferred orientation of plate-like grains (March, 1932; Dollase, 1986) was used in the Rietveld refinement. The preferred orientation parameter G_1 refined to 0.7801 (13) for (I) and 0.9096 (18) for (II). For both compounds, the G_2 parameters were found to be practically equal to zero and were not included in the final refinement. The displacement parameters of all non-H atoms were refined isotropically and were constrained to be the same. The H atoms were placed in calculated positions (Sheldrick, 2008), with $C-H = 0.96 \text{ \AA}$, $N-H = 0.90 \text{ \AA}$ and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{iso}}(\text{C}, \text{N})$. Pyramidal geometry was assigned to the amine group in view of its coordination to the Cu atom. A set of suitable soft restraints on the bond lengths of the ligand molecule was introduced into the refinement. They were obtained as a result of analysis of bond lengths in copper(II), palladium(II) and platinum(II) chloride complexes with 2-*tert*-butyltetrazol-5-amine (Voitekhovich *et al.*, 2009), and a silver complex of 2-methyltetrazol-5-amine (Karaghiosoff *et al.*, 2009). The bonds were restrained to 1.32 (1) (N1–N2), 1.32 (1) (N1–C5), 1.30 (1) (N2–N3), 1.32 (1) (N3–N4), 1.33 (1) (N4–C5), 1.50 (1) (N2–C6) and 1.35 (1) Å (C5–N7). The final Rietveld refinement plots are shown in Fig. 4.

For both compounds, 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) for (I) only; program(s) used to refine structure: *FULLPROF*;

molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *FULLPROF* and *PLATON*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3362). Services for accessing these data are described at the back of the journal.

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