

Tetrakis(2-amino-5-methyl-1,3,4-thiadiazole-*N*³)chlorocopper(II) chloride monohydrate and tetrakis(2-amino-5-ethyl-1,3,4-thiadiazole-*N*³)chlorocopper(II) chloride

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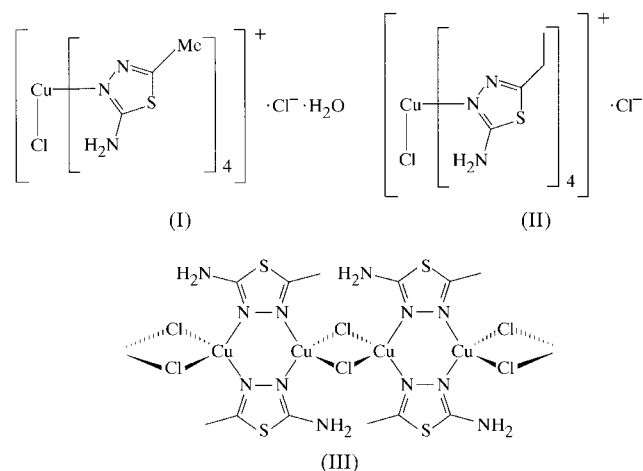
The structures of the title compounds, $[\text{CuCl}(\text{C}_3\text{H}_5\text{N}_3\text{S})_4]\text{Cl}\cdot\text{H}_2\text{O}$, (I), and $[\text{CuCl}(\text{C}_4\text{H}_7\text{N}_3\text{S})_4]\text{Cl}$, (II), comprise square-pyramidal Cu centres with four N-bound organic ligands filling the base positions, a Cl atom in the apical position and a Cl^- as a free counter-ion. The cation and free chloride ion in (II) have fourfold crystallographic symmetry. Hydrogen-bonding associations from the 2-amino H atoms dominate both structures, with the principal acceptors being the chlorides, although in (I), the N4 atoms are also involved. Furthermore, (I) is a hydrate, with the water molecule participating in the hydrogen-bonding network.

Comment

2-Amino-1,3-thiazoles have many applications in both human and veterinary medicine, as well as materials science (Lynch *et al.*, 1999). The mode of action for several 2-aminothiazole derivatives depends on metal–ligand binding, such as in the case of 2-amino-4,5-dihydro-1,3-thiazole, which possibly induces the transformation of tumour cells (Kubiak *et al.*, 1983; Kubiak & Glowiak, 1984). 2-Aminothiazoles contain three donor sites available for coordination to a metal species, *i.e.* the amine N and the heterocyclic N and S atoms. However, structural studies of metal complexes containing 2-aminothiazoles have shown that the predominant point for metal attachment is at the heterocyclic N atom. As a derivative of 2-aminothiazoles, 2-amino-1,3,4-thiadiazoles contain two heterocyclic N atoms available for metal complexation and have been studied as corrosion inhibitors (Downie *et al.*, 1972), for potential antiviral activity (Saramet, 1975; Tonew & Limki, 1974) and as inhibitors of carbonic anhydrase (Pedregosa *et al.*, 1993).

Four structural examples of metal complexes of substituted 2-amino-1,3,4-thiadiazoles are known and they display varying coordination geometries. The copper(I) chloride complex of 2-amino-5-methyl-1,3,4-thiadiazole (Neverov *et al.*, 1986)

forms linear polymers with planar units of two Cu atoms bridged by two thiadiazole molecules which then propagate *via* two bridging Cl atoms to the next Cu atom, (III). For the thiadiazoles in this structure, Cu atoms bind both heterocyclic N atoms. However, in the known metal(II) halide complexes of thiadiazole derivatives (Mn: Fabretti *et al.*, 1993; Zn: Khusenov *et al.*, 1997; Hg: Antolini *et al.*, 1988), only one N atom is involved in metal coordination. In each case, there are two thiadiazoles per metal and for the ZnCl_2 and HgBr_2 complexes, the geometry is tetrahedral, whereas the addition of two water molecules in the MnCl_2 complex results in octahedral geometry. We have instigated a series of studies covering the syntheses of metal halide complexes of substituted 2-amino-1,3,4-thiadiazoles to determine the role, if any, of the exocyclic N atom in determining the metal coordination and/or the overall packing structure. If this N atom is not metal-bound it is still available for hydrogen-bonding interactions if considering the presence of the 2-amino groups. For this particular study, we chose to use the same thiadiazole derivative, as well as the ethyl analogue, that produced the Neverov *et al.* (1986) structure. However, complexation of 2-amino-5-methyl-1,3,4-thiadiazole and 2-amino-5-ethyl-1,3,4-thiadiazole with CuCl_2 yielded square-pyramidal Cu complexes (I) and (II), respectively, containing four bound thiadiazoles, one bound Cl and the other in the lattice as a counter-ion. Complex (I) was characterized as a hydrate.



The structures of (I) and (II) are shown in Figs. 1 and 2, respectively, while selected bonds involving copper for both complexes are listed in Tables 1 and 3, and hydrogen-bonding geometries are given in Tables 2 and 4. For any 2-aminothiazole derivative, (I) and (II), are the first examples of five-coordinate square-pyramidal geometry. In both (I) and (II), the thiadiazoles are singly bound at N3 and occupy the four square-planar positions, but differences between the two structures occur in the specific orientations of the organic ligands. In the structure of (I), there are four unique heterocycles, with ligand *A* opposing the similar orientations of groups *B*, *C* and *D*, whereas for (II), all four thiadiazoles are symmetry related around the Cu atom. In both complexes, the amino groups are orientated in the same direction as the Cu–Cl1 bond such that all, except for ligand *A* in (I), are involved

in $N-H \cdots Cl$ hydrogen-bonding associations. The Cl2 atoms also participate in $N-H \cdots Cl$ associations, but only in (I) are the N4 atoms used as hydrogen-bonding acceptors. The rotation of the *A* moiety in (I) is interesting because if it were orientated the same as thiadiazoles *B–D* then it would associate with Cl1. Instead, N21A associates with O1W and N4B, while the second N21B H atom, from an adjacent molecule, slots in to associate with Cl1 (Fig. 3). The availability of the N4 atoms for hydrogen bonding, combined with the presence of Cl2, creates five free acceptor elements, in

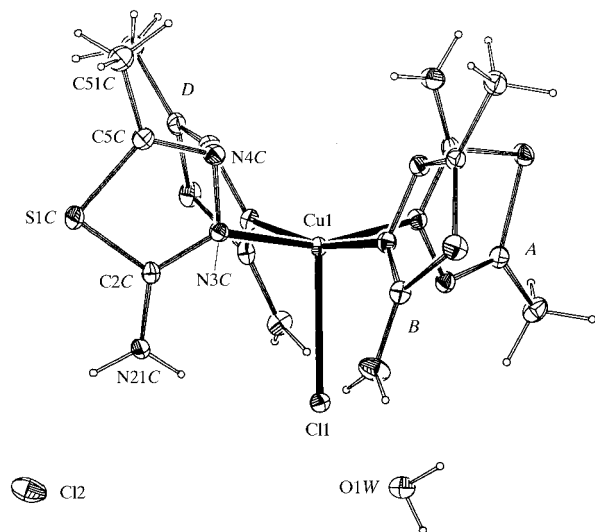


Figure 1
The molecular configuration and atom-numbering scheme for (I), showing 50% probability ellipsoids.

comparison to the four free 2-amino H atoms, but a water molecule is still required to complete the hydrogen-bonding network, most probably because Cl2 is a multi-point hydrogen-bonding acceptor. For (II), the unique position of Cl2 satisfies the hydrogen-bonding requirements of the second 2-amino H atom; thus, in this structure, all hydrogen-bonding elements are either complemented or structurally hindered (Fig. 4).

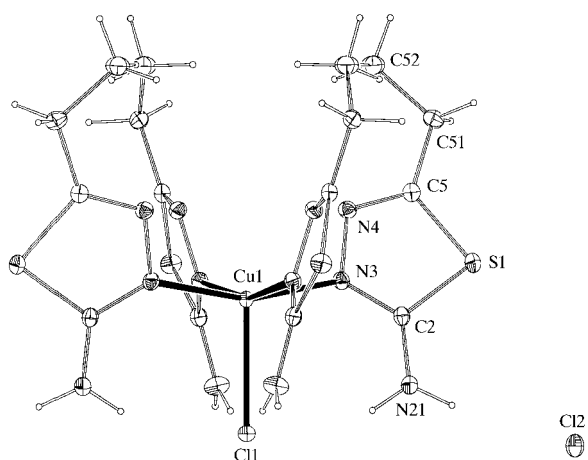


Figure 2
The molecular configuration and atom-numbering scheme for (II), showing 50% probability ellipsoids.

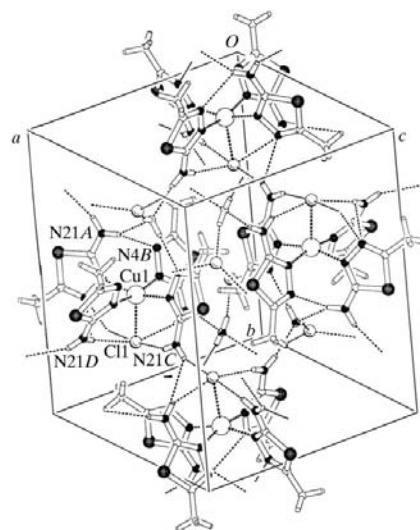


Figure 3
Packing diagram showing the unit cell of (I). Hydrogen-bonding interactions are shown as dotted lines.

The general conformations of the Cu complexes in (I) and (II) are such that the S atom in each thiadiazole ring faces outwards, away from the metal centre. This specific ligand orientation generates several $S \cdots Cl$ and $S \cdots S$ short contacts. In (I), the $S1A \cdots Cl2(x, \frac{1}{2} - y, \frac{1}{2} + z)$ distance is 3.351 (3) Å, the $S1B \cdots Cl2(1 - x, -\frac{1}{2} y, \frac{1}{2} - z)$ distance is 3.534 (3) Å, the $S1C \cdots Cl1(x, \frac{1}{2} - y, \frac{1}{2} + z)$ distance is 3.476 (3) Å, and the $S1A \cdots S1D(-x, -y, 1 - z)$ distance is 3.465 (3) Å, while the slightly longer contacts are $S1A \cdots S1B(1 - x, -y, 1 - z)$ of 3.626 (3) Å and $S1C \cdots S1D(-x, -y, -z)$ of 3.760 (3) Å. In

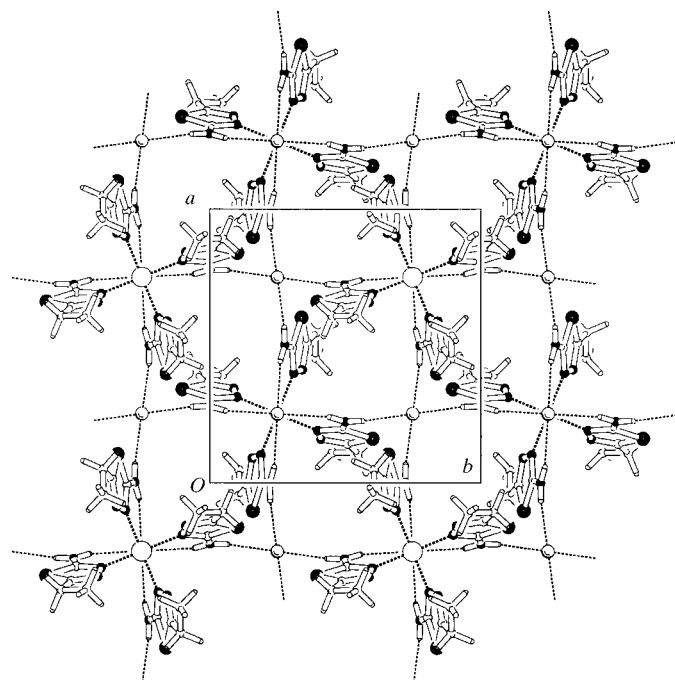


Figure 4
Packing diagram showing the unit cell of (II), viewed down the *c* axis

(II), the $S1 \cdots S1(\frac{1}{2} + y, 1 - x, -z)$ distance is 3.633 (2) Å. A Cambridge Structural Database (CSD) search (Fletcher *et al.*, 1996) on five-coordinate Cu complexes with at least one bound Cl atom gave 315 hits, of which 286 were for Cu^{II} . Of the Cu^{II} complexes, only one of these was found with four separate N-bound ligands and, similar to complexes (I) and (II), the two conformations of tetrakis(pyridine-*N*)chloro-(chlorotetrapyrrolinecopper)dotriacontaoxodecatungsten pyridine solvate trihydrate (Gongdu *et al.*, 1987) were square pyramidal. Analysis of the angle between the four pyridine rings and the Cu–Cl bonds gave values of 22.5 (6), 23.4 (6), 31.5 (6) and 50.9 (6)°, and 16.1 (6), 29.1 (6), 29.4 (6) and 49.8 (6)° for the two conformations. For comparison, these same values in (I) and (II) are 15.9 (1), 8.6 (1), 26.0 (1), 19.9 (1) and 15.5 (2)°, respectively. Given the CSD search parameters, complexes (I) and (II) have proved to be novel in their specific molecular construction, whereas complex (II) is certainly unique with respect to its existence in a high symmetry space group given the near identical similarity of the thiadiazole in complex (I).

Experimental

Complexes (I) and (II) were prepared by mixing boiling solutions of 50/50 aqueous ethanol separately containing $CuCl_2$ and either 2-amino-5-methyl-1,3,4-thiadiazole, (I), or 2-amino-5-ethyl-1,3,4-thiadiazole, (II). Upon cooling, the mixtures were filtered and allowed to evaporate to dryness. Crystals of (I) and (II) were separated from the resultant mass that also included crystals of the unreacted starting materials.

Compound (I)

Crystal data

$[CuCl(C_3H_5N_3S)_4]Cl \cdot H_2O$
 $M_r = 613.15$
 Monoclinic, $P2_1/c$
 $a = 12.7183$ (2) Å
 $b = 15.3106$ (3) Å
 $c = 12.8865$ (2) Å
 $\beta = 90.4820$ (9)°
 $V = 2509.23$ (7) Å³
 $Z = 4$

$D_x = 1.623$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 8104 reflections
 $\theta = 2.9$ – 27.5°
 $\mu = 1.45$ mm⁻¹
 $T = 150$ (2) K
 Prism, green
 $0.25 \times 0.18 \times 0.05$ mm

Data collection

Enraf–Nonius KappaCCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SORTAV; Blessing, 1995)
 $T_{\min} = 0.714$, $T_{\max} = 0.931$
 19695 measured reflections

5620 independent reflections
 4500 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.050$
 $\theta_{\max} = 27.5^\circ$
 $h = -16 \rightarrow 15$
 $k = -19 \rightarrow 19$
 $l = -14 \rightarrow 16$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.039$
 $wR(F^2) = 0.105$
 $S = 0.85$
 5620 reflections
 302 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0629P)^2 + 3.8292P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.003$
 $\Delta\rho_{\max} = 0.73$ e Å⁻³
 $\Delta\rho_{\min} = -0.77$ e Å⁻³
 Extinction correction: *SHELXL*
 Extinction coefficient: 0.0028 (4)

Table 1
 Selected bond lengths (Å) for (I).

Cu1–N3A	2.019 (2)	Cu1–N3D	2.029 (2)
Cu1–N3B	2.014 (2)	Cu1–Cl1	2.5744 (7)
Cu1–N3C	2.033 (2)		

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

<i>D</i> –H \cdots <i>A</i>	<i>D</i> –H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> –H \cdots <i>A</i>
N21A–H21A \cdots O1W ⁱ	0.88	2.14	2.953 (3)	154
N21A–H21A \cdots N4B	0.88	2.57	3.049 (3)	115
N21A–H22A \cdots Cl2 ⁱⁱ	0.88	2.31	3.134 (2)	156
N21B–H21B \cdots Cl1	0.88	2.35	3.152 (3)	151
N21B–H22B \cdots O1W	0.88	1.97	2.835 (3)	167
N21C–H21C \cdots Cl1	0.88	2.44	3.269 (2)	158
N21C–H22C \cdots Cl1 ⁱⁱⁱ	0.88	2.53	3.348 (2)	155
N21C–H22C \cdots N4A ⁱⁱⁱ	0.88	2.55	3.102 (3)	122
N21D–H21D \cdots Cl1	0.88	2.47	3.257 (2)	149
N21D–H21D \cdots N4A	0.88	2.62	3.059 (3)	112
N21D–H22D \cdots Cl2 ^{iv}	0.88	2.39	3.169 (2)	148
O1W–H1W \cdots N4C ^v	0.83 (5)	2.10 (5)	2.921 (3)	170 (4)
O1W–H2W \cdots Cl2 ^v	0.88 (5)	2.21 (5)	3.075 (3)	167 (4)

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

Compound (II)

Crystal data

$[CuCl(C_4H_7N_3S)_4]Cl$
 $M_r = 651.23$
 Tetragonal, $P4/ncc$
 $a = 12.3273$ (17) Å
 $c = 17.705$ (4) Å
 $V = 2690.5$ (7) Å³
 $Z = 4$
 $D_x = 1.608$ Mg m⁻³

Mo $K\alpha$ radiation
 Cell parameters from 6958 reflections
 $\theta = 2.9$ – 27.5°
 $\mu = 1.35$ mm⁻¹
 $T = 150$ (2) K
 Plate, green
 $0.30 \times 0.15 \times 0.08$ mm

Data collection

Enraf–Nonius KappaCCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SORTAV; Blessing, 1995)
 $T_{\min} = 0.687$, $T_{\max} = 0.905$
 15487 measured reflections

1531 independent reflections
 1303 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.051$
 $\theta_{\max} = 27.5^\circ$
 $h = -15 \rightarrow 15$
 $k = -15 \rightarrow 15$
 $l = -22 \rightarrow 21$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.032$
 $wR(F^2) = 0.088$
 $S = 1.04$
 1531 reflections
 84 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0565P)^2 + 0.8119P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.54$ e Å⁻³
 $\Delta\rho_{\min} = -0.65$ e Å⁻³

Table 3
 Selected geometric parameters (Å, °) for (II).

Cu1–N3	2.0171 (15)	Cu1–Cl1	2.5013 (10)
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Table 4

Hydrogen-bonding geometry (Å, °) for (II).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N21—H21 \cdots Cl1	0.88	2.42	3.2396 (16)	155
N21—H22 \cdots Cl2	0.88	2.42	3.2928 (16)	171

All H atoms, except for the water H atoms, were included in the refinement at calculated positions as riding models with C—H set to either 0.98 (CH₃) or 0.99 Å (CH₂) and N—H set to 0.88 Å. The two water H atoms were located on difference syntheses and both the positional and displacement parameters were refined. The OW—H distances are 0.83 and 0.89 Å.

For both compounds, data collection: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT* (Hooft, 1998); cell refinement: *DENZO* and *COLLECT*; data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 1997); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG1063). Services for accessing these data are described at the back of the journal.

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