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catena-Poly[[[bis(μ-4,5-dihydrothiazole-2-thiolato)-*tetrahedro*-tetracopper(I)]-di-μ-4,5-dihydrothiazole-2-thiolato] dihydrate]

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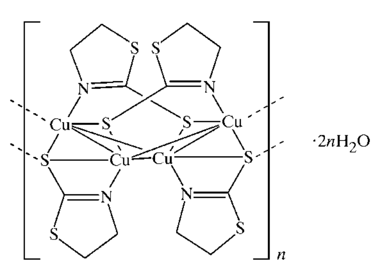
The title compound, $\{[Cu_4(C_3H_4NS_2)_4]\cdot 2H_2O\}_n$, was produced by diffusing a solution of 2-mercaptothiazoline in tetrahydrofuran into a solution of CuCl in CH_3CN at room temperature. The structure is characterized by self-assembled one-dimensional chains that are condensed from butterfly-like $[Cu(C_3H_4NS_2)]_4$ tetrameric units *via* double S-bridging at opposite ends. The Cu—Cu distances within the Cu_4 butterfly cluster are in the range 2.7103 (10)–2.9764 (10) Å, while the shortest Cu···Cu intercluster distance is 3.468 (1) Å, much longer than the sum of the van der Waals radii.

Comment

Polynuclear d^{10} metal complexes are potential luminescent sensor materials due to their interesting photochemical and photophysical properties (Ford *et al.*, 1999; Yam & Lo, 1999). In a recent effort to investigate the dependence of optical properties of coinage metal complexes on their molecular structures and metal–metal interactions (Zhou *et al.*, 2002), a variety of novel polynuclear compounds have been obtained through the selective use of different chelating ligands. Copper complexes with 2-mercaptothiazoline (or 2-thiazolidine-2-thione) ligands have been reported previously, *e.g.* mononuclear $[Cu(C_3H_5NS_2)_3Cl]$ (Zhao *et al.*, 1985) and $[(PPh_3)_2Cu(C_3H_4NS_2)]$ (Aslanidis *et al.*, 1998), as well as polymeric $[Cu(C_3H_4NS_2)]_4\cdot C_7H_8$, which was prepared electrochemically (Raper *et al.*, 1995). In this paper, we report the solution synthesis and single-crystal structure of the title compound, (I), which features similar tetracopper(I) chain structures but with different dimensions, due to solvation effects.



(I)

The marked structural feature of (I) is the formation of one-dimensional chains, built up from butterfly-like $[Cu(C_3H_4NS_2)]_4$ tetrameric units. As shown in Fig. 1, each building block consists of four Cu atoms divided into two categories, with atoms Cu1 and Cu2 in a distorted S_3N tetrahedral coordination geometry, and atoms Cu3 and Cu4 in a distorted S_2N triangle. The distance between atoms Cu1 and Cu2 on the 'wing-tip' [3.775 (1) Å] is much longer than that

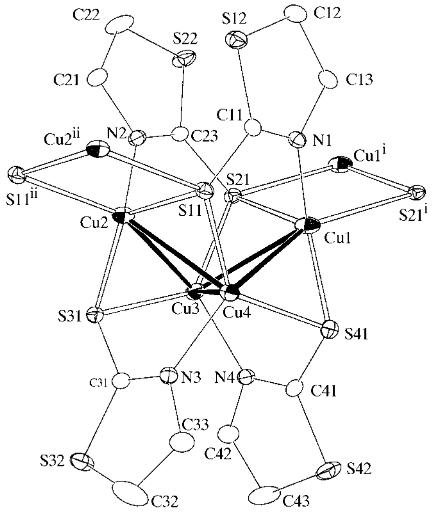


Figure 1
The tetrameric Cu^{I} building block in polymeric (I). Displacement ellipsoids are drawn at the 20% probability level, and H atoms and the hydrate water molecules have been omitted for clarity [symmetry codes: (i) $1 - x, 1 - y, -z$; (ii) $-x, 2 - y, -z$].

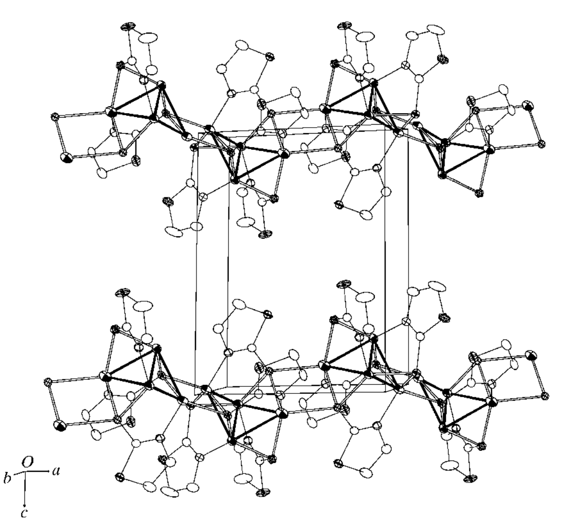


Figure 2
The one-dimensional chain in the polymer of (I). H and O atoms have been omitted for clarity and displacement ellipsoids are drawn at the 30% probability level.

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between the 'spinal' atoms Cu3 and Cu4 [2.9764 (10) Å], yielding a butterfly-like shape.

These butterfly-like tetramers link with neighbouring units through the wing-tip atoms Cu1 and Cu2 *via* S bridging atoms (S21 and S11) at opposite ends, leading to an infinite one-dimensional structure along the $[1\bar{1}0]$ direction (Fig. 2). The chain extension at both ends is actually generated through centrosymmetrically related Cu_2S_2 motifs. The intra-tetramer Cu···Cu distances are in the range 2.7103 (10)–2.9764 (10) Å, slightly longer than the range of 2.692 (4)–2.882 (5) Å reported in $[Cu(C_3H_4NS_2)]_4\cdot C_7H_8$ (Raper *et al.*, 1995).

The intercluster distances of 3.468 (1) Å for Cu1···Cu1^{i} and 3.487 (1) Å for Cu2···Cu2^{ii} (Fig. 1 and Table 1) are significantly longer than the intracluster distances, and are much longer than the sum of the van der Waals radii, implying no direct metal–metal interaction between tetramers. It is worth noting that the Cu—Cu distances around atom Cu3 are slightly longer than those around atom Cu4, presumably because 2-mercaptothiazoline is a very asymmetric bidentate ligand. Uncoordinated water molecules are located between the polymeric chains, producing efficient solvation and packing.

While each $C_3H_4NS_2$ moiety serves as a bidentate ligand through the N and thionate S atoms, the four ligands around the tetrameric Cu^{I}_4 unit are grouped into two types in accordance with the butterfly-like configuration. Ligands 3 and 4 are coordinated to only one tetramer, whereas ligands 1 and 2 form additional bridges to two neighbouring tetramers *via* the thionate S atoms. The bond distances associated with the centrosymmetrically related Cu_2S_2 units are Cu1—S21 2.4393 (14) and 2.6702 (14) Å, and Cu2—S11 2.4463 (14) and 2.5880 (14) Å, which are slightly shorter than those in $[Cu(C_3H_4NS_2)]_4\cdot C_7H_8$ [2.539 (3) and 2.790 (3) Å], presumably due to the presence of the water solvent molecules, which are smaller than toluene. The remaining Cu—S distances are in the range 2.2191 (13)–2.3163 (14) Å, with Cu—N distances ranging from 1.991 (4) to 2.021 (4) Å; both are in good agreement with those reported in $[Cu(C_3H_4NS_2)]_4\cdot C_7H_8$ (Raper *et al.*, 1995) and [Cu{1-methylimidazoline-2(3*H*)-thionate}]$_4$ (Raper *et al.*, 1991).

Experimental

Block-like pale-yellow crystals of (I) were obtained by diffusion of a solution of 2-mercaptothiazoline (0.160 g) in tetrahydrofuran (6 ml) into a solution of CuCl (0.033 g) in CH_3CN (6 ml) at room temperature over a period of four weeks.

Table 1
Selected interatomic distances (Å).

Cu1—N1	1.999 (4)	Cu2—Cu3	2.9041 (10)
Cu1—S41	2.2599 (15)	Cu3—N4	2.002 (4)
Cu1—S21	2.4393 (14)	Cu3—S21	2.2191 (13)
Cu1—S21^{i}	2.6702 (14)	Cu3—S31	2.2912 (13)
Cu1—Cu4	2.7390 (10)	Cu3—Cu4	2.9764 (10)
Cu1—Cu3	2.8120 (11)	Cu4—N3	1.991 (4)
Cu2—N2	2.021 (4)	Cu4—S11	2.2250 (13)
Cu2—S31	2.2796 (14)	Cu4—S41	2.3163 (14)
Cu2—S11	2.4463 (14)	S11—Cu2^{ii}	2.5880 (14)
Cu2—S11^{ii}	2.5880 (14)	S21—Cu1^{i}	2.6702 (14)
Cu2—Cu4	2.7103 (10)		

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

Crystal data

$[Cu_4(C_3H_4NS_2)_4]\cdot 2H_2O$
$M_r = 763.08$
Triclinic, $P\bar{1}$
$a = 9.8888$ (10) Å
$b = 10.7259$ (10) Å
$c = 13.1808$ (10) Å
$\alpha = 69.450$ (10)°
$\beta = 82.737$ (10)°
$\gamma = 70.075$ (10)°
$V = 1230.67$ (19) Å^3

$Z = 2$
$D_x = 2.059$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 1$–26°
$\mu = 4.11$ mm^{-1}
$T = 293$ (2) K
Block, yellow
0.32 × 0.30 × 0.30 mm

Data collection

Enraf-Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.287$, $T_{\max} = 0.292$
5061 measured reflections
4777 independent reflections
4208 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.014$
$\theta_{\max} = 26°$
$h = 0 \rightarrow 12$
$k = -12 \rightarrow 13$
$l = -16 \rightarrow 16$
3 standard reflections
frequency: 120 min
intensity decay: 0.6%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.045$
$wR(F^2) = 0.170$
$S = 0.88$
4777 reflections
272 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.1535P)^2 + 1.4219P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 1.60$ e Å^{-3}
$\Delta\rho_{\min} = -0.67$ e Å^{-3}

The ligand H atoms were located at geometrically calculated positions with constrained H-atom parameters (C—H = 0.97 Å). The aqua H atoms were not located. The highest and deepest residual peaks are located 0.59 Å from O1 and 0.80 Å from Cu3, respectively.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *XCAD*4 (Harms, 1996); data reduction: *XCAD*4; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OB1063). Services for accessing these data are described at the back of the journal.

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