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Poly[μ_4-sulfido-tris(thiocyanato-κN)-tris(μ_3-1,2,4-triazolato-κ^3N^1:N^2:N^4)-tetrazinc(II)]: a three-dimensional zinc sulfide coordination polymer

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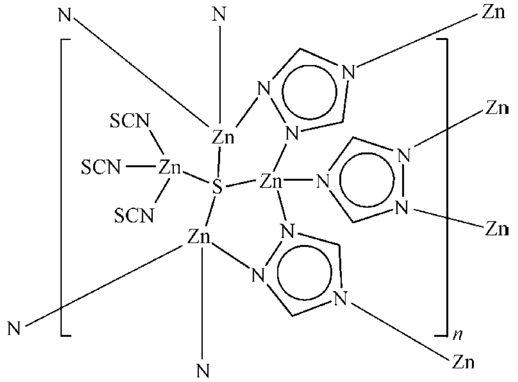
The title compound, $[Zn_4(C_2H_2N_3)_3(NCS)_3S]_n$, is a three-dimensional coordination polymer consisting of tetrahedral SZn_4 clusters bridged by triazole ligands. In the tetrahedral unit, three Zn atoms are connected to six bridging triazolate ligands, whereas the fourth Zn atom (site symmetry $3m$) is bonded to three terminal thiocyanate anions that protrude into the void space created by the Zn–triazolate network. The network prototype is simple cubic, but a strong distortion along a body diagonal and the imposition of a polar direction by the arrangement of the molecular constituents lead to the trigonal space group $R3m$. This study demonstrates the use of the 3-mercapto-1,2,4-triazole ligand as an effective source for sulfide ions in the synthesis of sulfide-based coordination polymers.

Comment

Research into organic–inorganic hybrid solids has resulted in a tremendous number of new and interesting structures in recent years (Cheetham *et al.*, 2006; Férey, 2008; Suh *et al.*, 2008). Many of these have been investigated for potential applications in gas storage, catalysis, magnetism, luminescence, *etc.* (Maspoch *et al.*, 2007; Morris & Wheatley, 2008). While a wide variety of organic ligands are available for the construction of coordination polymers, polyazaheterocyclic compounds, such as pyrazole, imidazole and triazole, have been extensively applied as organic linkers due to their ability to form multidimensional frameworks through multiple metal-binding sites. For example, a new class of zeolitic imidazolate frameworks (ZIFs) have recently been found to have exceptional stability and structrual similarities to traditional zeolites (Huang *et al.*, 2006; Park *et al.*, 2006; Hayashi *et al.*, 2007). There are also a number of compounds containing triazole-type ligands (Haasnoot, 2000; Zhang & Chen, 2006; Park *et al.*, 2007; Ouellette *et al.*, 2006, 2007). The ZnF(AmTAZ) (AmTAZ = 3-amino-1,2,4-triazole) coordination polymer forms an especially interesting hollow tubular architecture (Su *et al.*, 2004).

In addition to their fascinating framework architectures, polyazaheterocycle-based compounds are of interest as functional materials, since they can possess interesting photoluminescence properties when d^{10} metal ions such as Cu^+, Zn^{2+} and Cd^{2+} are present (Ouellette *et al.*, 2007; Zhao *et al.*, 2008). Although there are many known sulfide-based inorganic frameworks, coordination polymers based on metal–sulfur linkages are still quite uncommon. Recent developments by Feng and co-workers have resulted in a number of transition metal–sulfide clusters linked by organic ligands (Xie *et al.*, 2005; Zhang, Lin *et al.*, 2008; Zhang, Liu *et al.*, 2008). These materials contain tetrahedral M_4S (M = Zn or Cd) units which are connected to each other *via* substituted phenylthiolates in order to create a three-dimensional open framework. The single-crystal growth of these materials depends on the slow release of sulfide from the decomposition of thiourea. There is only one example of a sulfide-based metal–triazolate complex known in the literature to date (Schlueter *et al.*, 2006). In that case, the sulfide is generated by the slow thermal decomposition of thiocyanate. The basic building block for the $(H_3O)[Zn_6(AmTAZ)_6S_2](NO_3)_3{\cdot}xH_2O$ structure is a sulfide-centered triangle of Zn atoms. The assembly of eight of these building units results in the formation of a three-dimensional cage structure. In this report, we describe a new zinc triazole–thiolate coordination polymer, (I). To our knowledge, the crystallization of (I) is the first example whereby 3-mercapto-1,2,4-trizole undergoes a gradual *in situ* dethiolation process to generate both the triazolate ligand and the sulfide anion during the solvothermal reaction.



(I)

The atom-numbering scheme of (I) is shown in Fig. 1. The structure is based on the $[SZn_3(\text{triazole})_3]^+$ secondary building unit (SBU) which has a Zn_3S core. The central S2 sulfide ion (site symmetry $3m$) of the $[SZn_3(\text{triazole})_3]^+$ SBU is bonded to three Zn1 atoms and Zn2 of the $[Zn(NCS)_3]^-$ anion. Atom Zn1 is further bound to one N2 atom and two N3 atoms of three triazolate ligands. Atom N2 is at the 4-position of the triazole ring, while the N3 atoms are at the 1,2-positions. The Zn1—N3 bonds complete the trimeric $[SZn_3(\text{triazole})_3]^+$ SBU. A three-dimensional cage structure is formed by linking eight $[SZn_3(\text{triazole})_3]^+$ SBUs through Zn1—N2 bonds. The Zn1—

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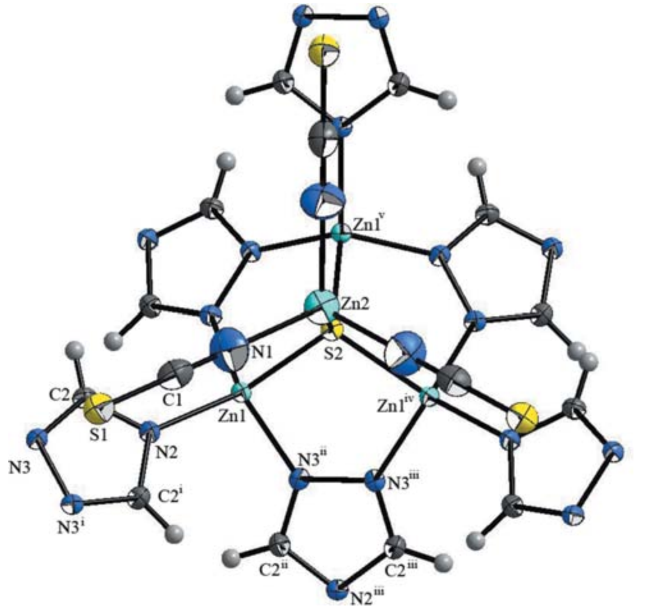

Figure 1
The structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry codes: (i) $-x + y, y, z$; (ii) $\frac{2}{3} - y, \frac{1}{3} - x, \frac{1}{3} + z$; (iii) $\frac{2}{3} - y, \frac{1}{3} + x - y, \frac{1}{3} + z$; (iv) $-x + y, -x, z$; (v) $-y, x - y, z$.]

N bond lengths are in the range 1.995 (2)–2.0310 (13) Å, which is consistent with the values reported for similar tetrahedral Zn^{2+} coordination polymers (Park *et al.*, 2007; Ouellette *et al.*, 2007). The resulting environment around Zn1 is a distorted tetrahedron, with N—Zn—N and N—Zn—S bond angles varying from 107.45 (5) to 125.05 (7)°. Distorted tetrahedral coordination about the S2 sulfide center is completed by coordination to the Zn2 atom of the $[Zn(NCS)_3]^-$ anion [Zn2—S2 = 2.3580 (11) Å]. Atom Zn2 is also coordinated to the N atoms of three thiocyanate anions, with Zn2—N distances of 1.952 (3) Å, resulting in a stretched tetrahedral coordination.

The thiocyanate anion shows a typical linear geometry, with an N—C—S angle of 178.8 (3)°. The C≡N bond length is 1.151 (5) Å, and the C—S bond distance is 1.624 (4) Å. The resulting structure (Fig. 2) is a three-dimensional distorted (6,4) simple cubic net with pore dimensions of approximately 3.5 × 3.5 Å, taking the van der Waals radii into account. However, the porosity of the structure is removed as the bulky thiocyanate ligands protrude into the void space.

In conclusion, a new sulfide-based three-dimensional Zn–triazolate coordination polymer has been prepared. This work demonstrates that the slow decomposition of 3-mercapto-1,2,4-triazole provides an effective source of sulfide ions for the crystallization of novel sulfide-based coordination complexes and framework materials. In contrast with the crystallization of $(H_3O)[Zn_6(AmTAZ)_6S_2](NO_3)_3{\cdot}xH_2O$, where the sulfide is formed from the slow thermal decomposition of thiocyanate, in the case of (I), the sulfide is formed from the thermal decompositon of 3-mercapto-1,2,4-triazole, while the thiocyanate is incorporated into the crystal structure.

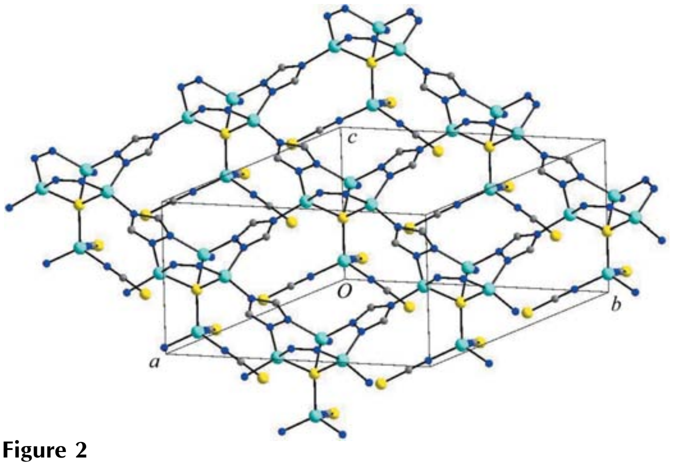

Figure 2
Ball-and-stick representation of the distorted (6,4) nets formed by $[SZn_3(triazole)_3]^+$ SBUs. The $[Zn(NCS)_3]^-$ groups occupy the void space.

Experimental

The title compound was prepared under mild solvothermal conditions. Zinc nitrate hexahydrate $[Zn(NO_3)_2{\cdot}6H_2O$; 0.594 g, 2 mmol], 3-mercapto-1,2,4-triazole (0.202 g, 2 mmol) and potassium thiocyanate (KSCN; 0.194 g, 2 mmol) were added to a solvent mixture of water (6.0 ml) and ethanol (4.0 ml) in a 23 ml Teflon-lined stainless steel autoclave. The sealed reaction vessel was heated at 423 K for 3 d. After cooling to room temperature, the product was filtered off, washed with deionized water and dried in air. Colorless block-shaped crystals of (I) were recovered.

Crystal data

$[Zn_4(C_2H_2N_3)_3(NCS)_3S]$
$M_r = 672.10$
Hexagonal, *R*3*m*
$a = 13.9947$ (4) Å
$c = 8.4249$ (3) Å
$V = 1428.97$ (8) Å^3
$Z = 3$
Mo $K\alpha$ radiation
$\mu = 5.44$ mm^{-1}
$T = 298$ (2) K
0.30 × 0.22 × 0.22 mm

Data collection

Siemens SMART CCD area-detector diffractometer
Absorption correction: integration (*SADABS*; Sheldrick, 2001)
$T_{min} = 0.201$, $T_{max} = 0.442$
4682 measured reflections
871 independent reflections
865 reflections with $I > 2\sigma(I)$
$R_{int} = 0.026$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.014$
$wR(F^2) = 0.034$
$S = 1.13$
871 reflections
56 parameters
1 restraint
H-atom parameters constrained
$\Delta\rho_{max} = 0.23$ e Å^{-3}
$\Delta\rho_{min} = -0.31$ e Å^{-3}
Absolute structure: Flack (1983), with 421 Friedel pairs
Flack parameter: 0.032 (10)

Table 1
Selected geometric parameters (Å, °).

Zn1—N2	1.995 (2)	Zn2—N1	1.952 (3)
Zn1—$N3^{i}$	2.0309 (13)	Zn2—S2	2.3580 (11)
Zn1—S2	2.3185 (6)		
N2—Zn1—$N3^{i}$	107.45 (5)	$N3^{ii}$—Zn1—S2	100.51 (4)
$N3^{i}$—Zn1—$N3^{ii}$	116.40 (8)	$N1^{iii}$—Zn2—N1	110.83 (14)
N2—Zn1—S2	125.05 (7)	N1—Zn2—S2	108.07 (14)

Symmetry codes: (i) $-y + \frac{2}{3}, -x + \frac{1}{3}, z + \frac{1}{3}$; (ii) $-x + y - \frac{1}{3}, -x + \frac{1}{3}, z + \frac{1}{3}$; (iii) $-x + y, -x, z$.

H atoms were positioned geometrically and treated as riding, with C—H = 0.93 Å and $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C). The correct orientation of the structure with respect to the polar-axis direction was established by means of the Flack *x* parameter (Flack, 1983).

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2003).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD3237). Services for accessing these data are described at the back of the journal.

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