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## Caesium 5-(2-cyanoethylthio)-2-thioxo-1,3-dithiole-4-thiolate

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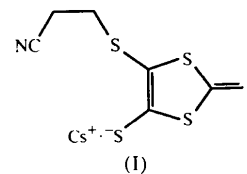
### Abstract

The crystal structure of the title compound,  $\text{Cs}^+ \cdot \text{C}_6\text{H}_4\text{-NS}_5^-$ , (I), shows that the Cs ion is eight-coordinated involving four thiolates, two neutral S atoms and two N atoms. The  $\text{Cs} \cdots \text{S}$  distances are in the range 3.474 (1)–3.810 (1) Å, and the  $\text{Cs} \cdots \text{N}$  distances are 3.317 (5) and 3.389 (5) Å. The three shortest  $\text{Cs} \cdots \text{S}$  distances probably contribute substantially to the unusual stability of (I) in solution and as a solid thiolate stored without special precautions.

### Comment

The 2-cyanoethyl group has been used extensively in our group as a versatile protecting group for 1,3-dithiole-4,5-dithiolates and tetrathiafulvalene (TTF) thiolates (Svenstrup *et al.*, 1994). These important building blocks can easily be incorporated into larger assemblies by the effective protection/deprotection methodology. Especially, the mono-deprotection of 2,3-bis-

(cyanoethylthio)tetrathiafulvalenes and 4,5-bis(2-cyanoethylthio)-1,3-dithiole-2-thiones (Becher *et al.*, 1994; Simonsen *et al.*, 1996) gives access to a variety of new tetrathiafulvalenes. The thiolates are generated *in situ* in a degassed solution of *N,N*-dimethylformamide under an inert atmosphere by addition of a methanolic solution of caesium hydroxide monohydrate. The caesium thiolates, which are stable in solution for at least 24 h, are normally not isolated, but subsequently realkylated with the electrophiles. In the DMIT salt series (DMIT is 2-thioxo-1,3-dithiole-4,5-dithiolate; Svenstrup & Becher, 1995), the van der Waals radius of the counter-ion seems to be the determining factor with regards to stabilization, rather than electronegativity considerations. In contrast to the caesium salts, the sodium and potassium salts have to be isolated using Schlenk techniques. Two stable caesium salts, caesium 5-(methoxycarbonylthio)-2-thioxo-1,3-dithiole-4-thiolate and caesium 3,6,7-tris(methoxycarbonyl)tetrathiafulvalene-2-thiolate, have been isolated and characterized by X-ray crystallography (Lau *et al.*, 1995; Simonsen *et al.*, 1996). In both cases, the neighboring electron-withdrawing methoxycarbonyl group stabilizes the thiolate by delocalization. Furthermore, the carbonyl group is situated in close proximity to the thiolate, resulting in a good bidentate ligand. It was therefore quite interesting that monothiolates bearing a 2-cyanoethylthio group in the  $\alpha$  position seem to be very stable in solution and especially that the title compound, (I), is stable as a microcrystalline powder for several months. The present structure determination has been undertaken to throw light on the unusual stability of (I).



The caesium ion is considered as eight-coordinated, bonding to four S4, one S3, one S5 and two N1 atoms. The  $\text{Cs} \cdots \text{S}$  contact distances are:  $\text{Cs} \cdots \text{S3/S5}^i$  3.810 (1)/3.701 (1) Å and  $\text{Cs} \cdots \text{S4}^{ii}/\text{S4}^{iii}/\text{S4/S4}^i$  3.474 (1)/3.497 (1)/3.526 (1)/3.762 (1) Å [symmetry codes: (i)  $1+x, \frac{3}{2}-y, -\frac{1}{2}+z$ ; (ii)  $1+x, y, z$ ; (iii)  $x, \frac{3}{2}-y, -\frac{1}{2}+z$ ]. The three shortest  $\text{Cs} \cdots \text{S}$  distances are significantly shorter than the  $\text{Cs} \cdots \text{S}$  distances found in the related compounds caesium 5-methoxycarbonyl-2-thioxo-1,3-dithiole-4-thiolate [ $\text{Cs} \cdots \text{S}$  3.636 (3) Å; Lau *et al.*, 1995] and caesium-3,6,7-tris(methoxycarbonyl)-tetrathiafulvalene-2-thiolate [ $\text{Cs} \cdots \text{S}$  3.62 (2) Å; Simonsen *et al.*, 1996]. We think that the three shortest  $\text{Cs} \cdots \text{S}$  contact distances contribute substantially to the stability of (I). The bond-valence parameters ( $s$ ) calculated for these bonds (Brown & Altermatt, 1985) are:  $\text{Cs} \cdots \text{S4}^{ii}/\text{S4}^{iii}/\text{S4}$ ,  $s = 0.099/0.093/0.086$ .

The Cs···O contact distances in caesium methylsulfonate are in the range 3.12(2)–3.34(2) Å (Brandon & Brown, 1967). The van der Waals radii for O/N are 1.40/1.50 Å according to Pauling (1970). Consequently, the observed Cs···N distances in (I) [3.317(5) and 3.389(5) Å] are considered as contact distances, although shorter Cs···N distances have been reported, e.g. in cyanoelpasolite [N(CH<sub>3</sub>)<sub>4</sub>]<sub>2</sub>CsCo(CN)<sub>6</sub> [3.255(8) and 3.258(11) Å; Peschel & Babel, 1994].

The five-membered ring of the anion constitutes a nearly planar system. Distances from a least-squares plane defined by the five atoms in the ring do not exceed 0.012(5) Å for the defining atoms and the attached atoms S1 and S4. Atoms S3 and C6 are 0.102(5) and 1.541(8) Å, respectively, from the least-squares plane.

In the crystal structure, the cations and anions form layers which stack perpendicular to the *b* axis.

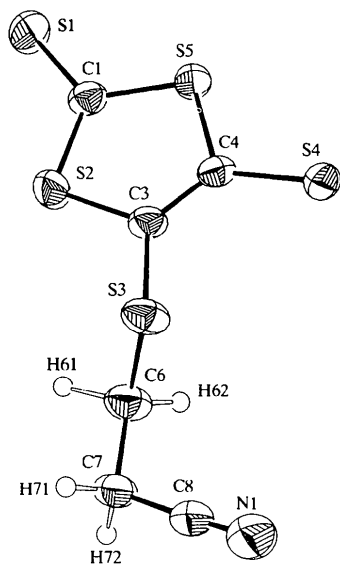


Fig. 1. Displacement ellipsoid plot of the anion in (I), with ellipsoids drawn at the 50% probability level. H atoms are drawn as spheres of arbitrary radii.

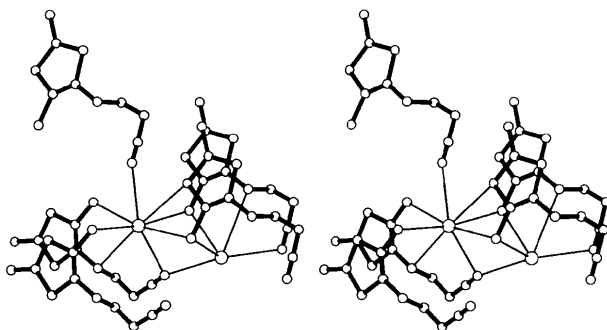


Fig. 2. Stereoview showing the coordinating atoms around the caesium ion.

## Experimental

The title compound, (I), was prepared as described by Simonsen *et al.* (1996). Single crystals were grown by vapour diffusion of diethyl ether into a solution of (I) in acetonitrile at room temperature.

### Crystal data

Cs<sup>+</sup>·C<sub>6</sub>H<sub>4</sub>NS<sub>5</sub><sup>-</sup>  
*M<sub>r</sub>* = 383.310  
 Monoclinic  
*P*2<sub>1</sub>/*c*  
*a* = 4.760(1) Å  
*b* = 26.181(5) Å  
*c* = 9.620(2) Å  
 $\beta$  = 92.8600(5)°  
*V* = 1197.4(4) Å<sup>3</sup>  
*Z* = 4  
*D<sub>x</sub>* = 2.126 Mg m<sup>-3</sup>  
*D<sub>m</sub>* not measured

Mo *K*α radiation  
 $\lambda$  = 0.71073 Å  
 Cell parameters from 2796 reflections  
 $\theta$  = 1.56–29.48°  
 $\mu$  = 3.866 mm<sup>-1</sup>  
*T* = 295 K  
 Needle (cut)  
 0.29 × 0.22 × 0.20 mm  
 Clear yellow–brown

### Data collection

Siemens SMART-CCD diffractometer  
 $\omega$  scans  
 Absorption correction: empirical (SADABS in SMART-CCD Software; Siemens, 1996)  
*T<sub>min</sub>* = 0.354, *T<sub>max</sub>* = 0.462

8064 measured reflections  
 3048 independent reflections  
 2796 reflections with *I* > 2.5σ(*I*)  
*R<sub>int</sub>* = 0.019  
 $\theta_{\text{max}}$  = 29.48°  
*h* = -6 → 6  
*k* = -35 → 33  
*l* = -13 → 12

### Refinement

Refinement on *F*<sup>2</sup>  
*R* = 0.033  
*wR* = 0.044  
*S* = 1.189  
 2796 reflections  
 134 parameters  
 All H atoms refined  
 $w = 1/[3\sigma^2(F) + 0.001F^2]$

( $\Delta/\sigma$ )<sub>max</sub> = 0.016  
 $\Delta\rho_{\text{max}}$  = 0.608 e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}}$  = -1.045 e Å<sup>-3</sup>  
 (1.5 Å from Cs1)  
 Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

The dimensions of the C—H bonds are within the range 0.92(7)–1.16(5) Å.

Data collection: SMART-CCD Software (Siemens, 1996). Cell refinement: SMART-CCD Software. Data reduction: SMART-CCD Software and Xtal3.2 ADDREF SORTRF (Hall *et al.*, 1992). Program(s) used to solve structure: Xtal3.2 FC FOURR PEKPIK MODEL. Program(s) used to refine structure: Xtal3.2 CRYLSQ. Molecular graphics: Xtal3.2 ORTEP and ATOMS2.2 (Dowty, 1992). Software used to prepare material for publication: Xtal3.2 ATABLE BONDLA CIFIO LISTFC LSQPL.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OS1038). Services for accessing these data are described at the back of the journal.

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## Tetrakis(tetrabutylammonium) tetrakis-[(*p*-cyanophenyl)trioxoarsonato]-tetratriacontaoxododecamolybdate(4-)

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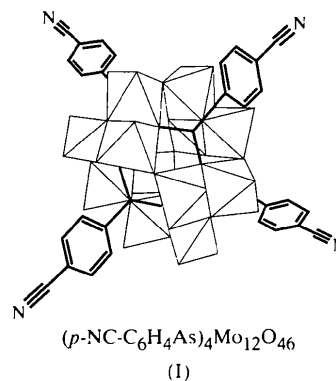
### Abstract

Crystals of the title compound,  $(C_{16}H_{36}N)_4[(p\text{-NC-C}_6\text{H}_4\text{As})_4\text{Mo}_{12}\text{O}_{46}]$  or  $(C_{16}H_{36}N)_4[\{\text{As}(\text{C}_7\text{H}_4\text{N})\}_4\text{Mo}_{12}\text{O}_{46}]$ , were synthesized by the reaction of *p*-cyanophenylarsonic acid and sodium molybdate at low pH. With nitrile groups pointed in tetrahedral directions, these new organically modified polyoxometalate clusters are potential building blocks in coordination networks.

### Comment

During the course of our studies into extended network solids, a new type of building block was synthesized as the tetrabutylammonium (TBA) salt. This building block, a hybrid  $[(p\text{-NC-C}_6\text{H}_4\text{As})_4\text{Mo}_{12}\text{O}_{46}]^{4-}$  cluster, (I), is related to the organically modified polyoxometalate clusters synthesized by Barkigia *et al.* (1981). It has been shown that these types of polyoxometalate clusters can be synthesized with a variety of organic groups

(benzene, aniline, methyl, 2-hydroxyethyl) and differing molybdenum to arsenic ratios (Kwak *et al.*, 1976; Matsumoto, 1979). We have synthesized a new organic derivative with a molybdenum/arsenic ratio of 3:1 and benzonitrile groups. This derivative was developed as a potential tetrahedral linking unit for networks based on the well developed coordination chemistry of aryl nitriles (Hoskins & Robson, 1990; Liu & Tilley, 1997, 1998; Hirsch *et al.*, 1995, 1998). The organic precursors for these functionalized polyoxometalate clusters are arsonic acids. The literature contains a fair number of syntheses, and the synthesis of *p*- $\text{H}_3\text{O}_2\text{AsC}_6\text{H}_4\text{CN}$  by the Bart method is relatively straightforward (Bart, 1922).



The crystal structure of the title compound consists of  $[(p\text{-NC-C}_6\text{H}_4\text{As})_4\text{Mo}_{12}\text{O}_{46}]^{4-}$  anions (Fig. 1) that are packed in layers of staggered clusters. The inter-cluster space is filled by four charge-balancing tetrabutylammonium ions for each discrete cluster. Two of the butyl side chains are disordered over two positions. Some of the C—C bond distances are shorter than expected as a result of coupled translational and librational motions in this non-rigid molecule. Due to the large cation size, the crystal density is significantly lower than that of the related compound  $[(p\text{-H}_3\text{NC}_6\text{H}_4\text{As})_4\text{Mo}_{12}\text{O}_{46}] \cdot 10\text{CH}_3\text{CN} \cdot 6\text{H}_2\text{O}$  (Barkigia *et al.*, 1981) ( $1.86 \text{ g cm}^{-3}$  versus  $2.27 \text{ g cm}^{-3}$ ). No solvent molecules were found within the crystal. The structure of the anion is similar to that of  $[(p\text{-H}_3\text{NC}_6\text{H}_4\text{As})_4\text{Mo}_{12}\text{O}_{46}]$ . It can be described as an ‘inverse Keggin’ cluster, where four tetrahedral atoms bridge a metal–oxygen core, instead of a tetrahedral interior atom bridging the metal–oxygen exterior. The molybdenum–oxygen skeleton contains four corner-sharing groups of three edge-sharing Mo—O octahedra, which are bridged by tetrahedral As atoms. The Mo—O distances coincide with those found for the cluster substituted with protonated aminophenylarsonic acid groups, namely 1.690–1.705 Å for terminal O atoms, 1.876–1.900 Å for doubly bridging O atoms, 2.037–2.060 Å for triply bridging O atoms bound to three Mo atoms, and 2.282–2.347 Å for triply bridging O atoms