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Dicaesium silver zinc thiocyanate, $Cs_2[AgZn(SCN)_5]$

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The title compound, dicaesium(I)-μ-thiocyanato-κ^2N:S-zinc(II)-tetra-μ-thiocyanato-κ^2S:N-argentate(I), crystallizes in the orthorhombic space group *Pmn*2$_1$ and contains units of composition $AgZn(SCN)_3$ lying on a mirror plane and bonded together through Cs^+ ions and thiocyanate groups. The crystal studied contained equal numbers of inversion twins.

Comment

The title compound has been known since the beginning of the last century (Wells, 1902, 1922). At that time, most studies were synthetic and analytical. Since those days, many crystal structures of thiocyanates have been solved. The crystal structure of the title compound has not been reported previously. Caesium, silver and zinc all form simple thiocyanates. CsSCN crystallizes in space group *Pnma*, AgSCN crystallizes in two polymorphic forms in space groups *Pmnn* and *C*2/*c*, and $Zn(NCS)_2$ crystallizes in space group $P\overline{1}$.

There are also other triple thiocyanates similar to the title compound, such as $Cs[AgZn(SCN)_4]\cdot H_2O$, $Cs[Ag_3Zn_2(SCN)_8]$ and $Cs[Ag_4Zn_2(SCN)_9]$ (Wells, 1902, 1922). We are especially interested in thiocyanates which include an odd number of thiocyanate groups. We presume that an odd number of thiocyanate groups could lead to a non-centrosymmetric crystal structure. Some very interesting optical, electro-optical and electrostrictive properties are related to non-centrosymmetric crystal structures. There are also other thiocyanate complexes of silver, such as $Cs_3Sr[Ag_2(SCN)_7]$ and $Cs_3Ba[Ag_2(SCN)_7]$ (Bohaty & Fröhlich, 1992), which have been found to have these same properties.

Caesium is 8+1-coordinated, with three S and five N atoms around it and, moreover, one C atom at a distance of 3.462 (6) Å. In thiocyanate structures, it is unusual to have a bond between a cation and the C atom of the thiocyanate group. The distance between the C and N atoms (about 1.15 Å) of the thiocyanate group indicates a triple bond between them, and the caesium is not actually bonded straight to the C4 atom (Fig. 1) but, by back coordination, forms a dihapto (η^2) π bond to the triple bond between the C4 and N4 atoms (see Fig. 1). The average S—C distance is 1.63 Å. The angles of the thiocyanate groups (at C) are all close to 180°. Zinc and silver are both tetrahedrally tetracoordinated, zinc being surrounded by four N atoms and silver being surrounded by four S atoms. The tetrahedra around silver and zinc are both slightly distorted. The coordination of the metal atoms in the title structure is shown in Fig. 1.

The structure of $Cs_2[AgZn(SCN)_5]$ is very interesting; the Flack parameter of 0.53 (3) indicates that the crystal studied contained equal numbers of inversion twins. One unit cell can be thought of as being composed of two basic units, indicated in Fig. 1 with thicker lines. The basic unit contains a mirror plane. Most of the atoms lie on this mirror plane, as can be deduced also from Fig. 1, with only Cs and one of the thiocyanate groups lying out of the mirror plane. In other words, the structure contains units of composition $AgZn(SCN)_3$ lying on a mirror plane and bonded together through the Cs^+ ions and thiocyanate groups. The structure can also be described with polyhedra around the metal atoms (Fig. 2). The basic unit described in Fig. 1 is shown in Fig. 2 with hatched polyhedra (bottom left). The thiocyanate groups of the basic unit are not shown fully in Fig. 2, with only the atoms in the coordination spheres being displayed. The vertices of the Cs polyhedra are composed of N and S atoms only, as the Cs—C bond indicated hatched in Fig. 1 has been omitted in Fig. 2. The polyhedra form continuous parallel chains in the direction of the *a* axis. The polyhedra between two Cs atoms share one common face, the polyhedra between Zn and two Cs atoms share two common edges, and the polyhedra between Ag and two Cs

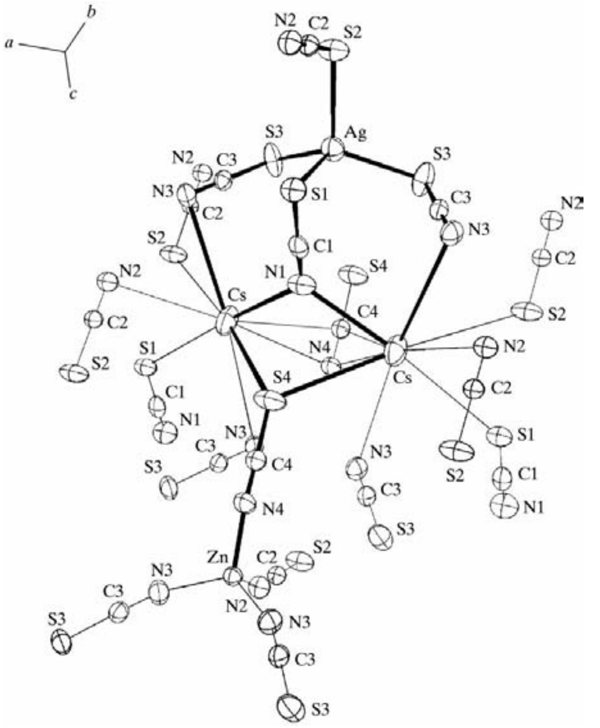

Figure 1
The coordination of the metal atoms in $Cs_2[AgZn(SCN)_5]$ (the basic structural unit is indicated with thicker lines), shown with displacement ellipsoids at the 50% probability level.

atoms share one common vertex. The chains passing through a unit cell are located at a distance of approximately $(0,0,\frac{1}{2})$ and are related by both the *n*-glide (*i.e.* are shifted $x = \frac{1}{2}$ and $z = \frac{1}{2}$) and the 2_1 axis. The parallel chains are bonded together with thiocyanate groups, forming a continuous network.

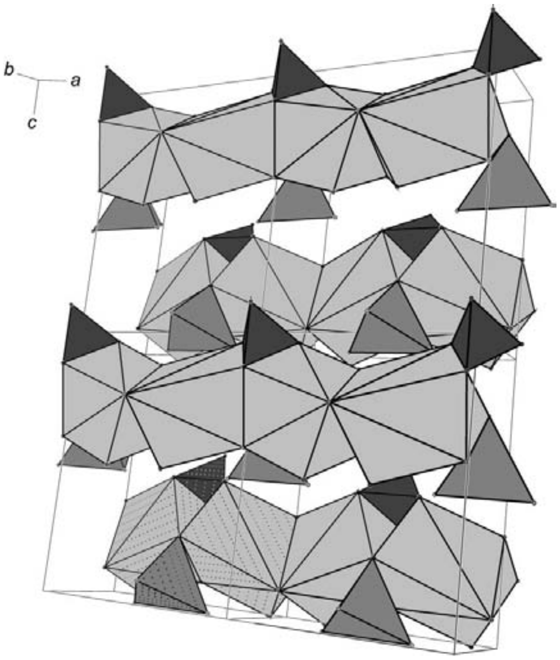

Figure 2
The layered structure of the title compound indicated as coordination polyhedra around the metal atoms. The basic unit shown in Fig. 1 is indicated by hatched polyhedra (bottom left). The 2 × 1 × 2 unit cell is viewed along [3,10,1]. Shading conventions used: Cs light grey, Ag medium grey and Zn dark grey.

Experimental

Silver thiocyanate was obtained from the Aldrich Chemical Company Inc. and zinc thiocyanate was obtained from the City Chemical LLC. Caesium thiocyanate was synthesized as follows: NH_4SCN (6.98 g) was dissolved in deionized water (20.0 g) and Cs_2CO_3 (15.0 g) was dissolved separately in deionized water (55.0 g). The solutions were mixed and the mixture heated with magnetic stirring until the smell of ammonia was no longer detected. The resulting solution was evaporated close to dryness on a water bath with continuous stirring. CsSCN was dried for two days using a vacuum pump and stored in a desiccator. $Cs_2[AgZn(SCN)_5]$ was synthesized at room temperature by dissolving CsSCN (2.30 g) in deionized water (3.00 g) and then dissolving AgSCN (0.125 g) in the resulting solution. An aqueous solution of zinc thiocyanate was prepared by dissolving $Zn(SCN)_2$ (0.270 g) in deionized water (3.25 g). When these two solutions were combined, white transparent crystals of $Cs_2[AgZn(SCN)_5]$ formed immediately.

Crystal data

$Cs_2[AgZn(SCN)_5]$	Mo $K\alpha$ radiation
$M_r = 729.46$	Cell parameters from 1721 reflections
Orthorhombic, $Pmn2_1$	$\theta = 1.0$–30.5°
$a = 10.8990$ (4) Å	$\mu = 7.33$ mm^{-1}
$b = 5.8759$ (2) Å	$T = 293$ (2) K
$c = 13.3784$ (5) Å	Prism, white
$V = 856.77$ (5) Å^3	0.1 × 0.1 × 0.1 mm
$Z = 2$	
$D_x = 2.828$ Mg m^{-3}	

Data collection

Nonius KappaCCD diffractometer	$R_{\rm int} = 0.060$
φ scans	$\theta_{\rm max} = 30.5°$
5859 measured reflections	$h = -15 \rightarrow 14$
2139 independent reflections	$k = -7 \rightarrow 8$
1809 reflections with $I > 2\sigma(I)$	$l = -14 \rightarrow 19$

Refinement

Refinement on F^2	$(\Delta/\sigma)_{\rm max} = 0.001$
$R(F) = 0.038$	$\Delta\rho_{\rm max} = 0.88$ e Å^{-3}
$wR(F^2) = 0.087$	$\Delta\rho_{\rm min} = -1.28$ e Å^{-3}
$S = 1.05$	Extinction correction: *SHELXL*97
2139 reflections	Extinction coefficient: 0.0039 (5)
105 parameters	Absolute structure: Flack (1983), 714 Friedel pairs
$w = 1/[\sigma^2(F_o^2) + (0.0318P)^2 + 0.9521P]$ where $P = (F_o^2 + 2F_c^2)/3$	Flack parameter = 0.53 (3)

Table 1
Selected geometric parameters (Å, °).

Ag—S1	2.582 (2)	Cs—N3	3.676 (6)
Ag—S3	2.5893 (19)	Cs—S4	3.691 (2)
Ag—S3$^{\rm i}$	2.5893 (19)	Cs—S2$^{\rm iv}$	3.7555 (14)
Ag—S2	2.668 (3)	Cs—N3$^{\rm iii}$	3.808 (6)
Cs—N1	3.081 (6)	Zn—N4	1.947 (7)
Cs—N4	3.388 (5)	Zn—N3$^{\rm v}$	1.962 (4)
Cs—C4$^{\rm ii}$	3.462 (6)	Zn—N3$^{\rm iii}$	1.962 (4)
Cs—N2$^{\rm iii}$	3.492 (4)	Zn—N2$^{\rm vi}$	1.984 (7)
Cs—S1$^{\rm iii}$	3.6184 (16)		
S1—Ag—S3	108.42 (4)	S1—Ag—S2	98.49 (8)
S1—Ag—S3$^{\rm i}$	108.42 (4)	S3—Ag—S2	108.99 (7)
S3—Ag—S3$^{\rm i}$	121.14 (12)	S3$^{\rm i}$—Ag—S2	108.99 (7)

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

The s.u.'s of the cell constants indicate the internal consistency of the measurements themselves, *i.e.* the precision of the measurements, not their accuracy. A multi-scan absorption correction (*XABS*2; Parkin *et al.*, 1995) was performed but not applied. The absorption correction was found to have no significant effect on the refinement results.

Data collection: *COLLECT* (Nonius, 2000); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *HKL DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 2000); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1342). Services for accessing these data are described at the back of the journal.

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