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$Cs[Ag_4Zn_2(SCN)_9]$

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Caesium tetrasilver dizinc nonathiocyanate, $Cs[Ag_4Zn_2(SCN)_9]$, forms a continuous structure, where the Ag atoms and the S atoms of the thiocyanate groups form chains which run along [101]. These chains are bonded together through the Cs and Zn atoms. It is not possible to distinguish between space groups $P1$ and $P\overline{1}$, but, if the latter space group is correct, the structure contains a thiocyanate group disordered across a centre of inversion. The structure is described in space group $P\overline{1}$, in which the Cs atom also lies on a centre of inversion.

Comment

Caesium tetrasilver dizinc nonathiocyanate, (I), has been known for a century, but there has been practically no research concerning the compound since the initial studies (Wells, 1902, 1922). One reason for this might have been the difficulty of the synthesis of (I). There are a total of four different caesium silver zinc thiocyanates known in the literature, namely $Cs[AgZn(SCN)_4]\cdot H_2O$, $Cs_2[AgZn(SCN)_5]$, $Cs[Ag_3Zn_2(SCN)_8]$ and (I) (Wells, 1902, 1922; Güneş & Valkonen, 2002), and the synthesis may yield any of these four thiocyanates. Moreover, any of the reactants or several possible combinations of them may crystallize, or, what is worse and is often the case, the yield of the synthesis can be a mixture of different types of crystals. Caesium, silver and zinc all form simple thiocyanates. CsSCN crystallizes in space group *Pnma*, AgSCN in two polymorphic forms in space groups *C*2/*c* and *Pmnn*, and $Zn(NCS)_2$ in space group $P\overline{1}$. $Zn(NCS)_2\cdot 2H_2O$ is also known in the literature and crystallizes in space group $P2_12_12_1$.

Our interest in triple thiocyanates arises from the fact that some of the triple thiocyanates of silver, such as $Cs_3Sr[Ag_2(SCN)_7]$ and $Cs_3Ba[Ag_2(SCN)_7]$, have been found to have a non-centrosymmetric crystal structure (Bohaty & Fröhlich, 1992). Such structures can possess some very interesting optical, electro-optical and electrostrictive properties, which could be utilized, for example, in telecommunications, optical computing, optical information processing, optical-disk data storage, laser remote sensing, laser-driven fusion, colour displays, medical diagnostics and so on. The idea is based on the capability of these materials to convert IR laser radiation efficiently to visible and UV wavelengths, and especially their highly efficient second-harmonic generation of blue–violet light (Wang *et al.*, 2001).

During optimization of the synthesis of the thiocyanate complexes of silver, zinc and caesium, we managed to obtain some crystals of (I), but, as stated above, the synthesis of these compounds is not so straightforward. The crystals of (I) were obtained in low yield as a co-precipitate during the synthesis and, despite numerous trials, we have not yet been able to crystallize a pure crop of (I).

The structure of (I) is very interesting, as it cannot be clearly determined whether the space group in which it crystallizes is $P1$ or $P\overline{1}$. In this paper, we have defined the space group to be $P\overline{1}$, but we will also discuss the possibility of the space group being $P1$.

The assignment of the space group is uncertain. The structure refines well in both $P1$ and $P\overline{1}$, giving reasonable molecular geometries in both cases, with a slightly lower goodness-of-fit in $P1$ (1.031 *versus* 1.039). The Flack parameter (Flack, 1983) is 0.48 (6), which is consistent with either $P\overline{1}$ or with a $P1$ crystal containing equal volumes of inversion twins. We have chosen to describe the structure in $P\overline{1}$, in which two atoms lie on centres of inversion, namely the Cs atom, located at $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$, and the C2 atom, located at $(\frac{1}{2},0,\frac{1}{2})$. This means that one of the SCN groups is disordered and, locally, atom C2 is slightly displaced from the centre of inversion toward the N atom, as can be seen from the highly anisotropic atomic displacement ellipsoid shown in Fig. 1.

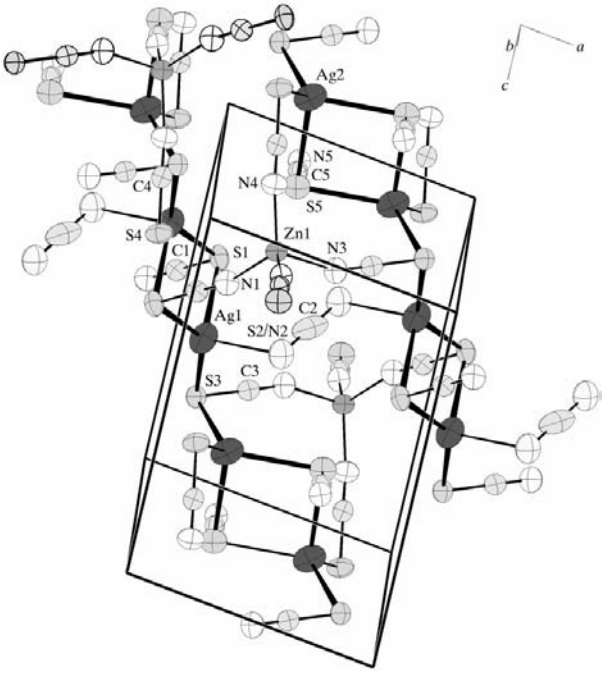

Figure 1
A view of the Ag—S—Ag chains in (I), connected together through Zn atoms. Displacement ellipsoids are drawn at the 50% probability level and the Cs atom has been omitted for clarity. The heaviest atoms (Ag) are shaded the darkest grey, and the shading is graduated through Zn, S and C, with the N atoms being white; the exception is atom S2/N2, which is nearly white.

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Because of the disordered thiocyanate group, Cs is ten-coordinated by 2S+8N atoms or 4S+6N atoms, each occurring in a quarter of the unit cells, and by 3S+7N atoms in the remaining half of the unit cells, although if the space group were $P1$, all the Cs atoms would be coordinated by 3S+7N atoms. When coordinated by 3S+7N, the Cs atom is displaced from the centre of inversion, which is reflected in the large value of U_{22} for this atom.

Zn and Ag are both tetrahedrally coordinated, Zn being surrounded by four N atoms, Ag2 by four S atoms, and Ag1 by four S atoms or by three S atoms and one N atom, because of the disordered thiocyanate group. The tetrahedra around Ag and Zn are both slightly distorted.

In (I), the Ag and S atoms form chains (Fig. 1) along [101]. These chains are then bonded through the N atoms of the thiocyanate groups to Zn atoms, thereby connecting the Ag—S—Ag chains in the *ac* plane and in the direction of *b* axis, thus forming a three-dimensional network. The chains in the *ac* plane are further connected through the disordered thiocyanate group. This group does not bond to Zn but lies between two Ag1 atoms of different chains. The Cs atoms connect the chains in all three dimensions.

Experimental

Compound (I) was synthesized at room temperature by dissolving NH_4SCN (2.05 g; Aldrich Chemical Company Inc.) in deionized water (20.0 g) and then dissolving AgSCN (1.49 g; City Chemical LLC) in the resulting solution. Not all of the AgSCN dissolved. Without filtering the solution, $Zn(NO_3)_2\cdot 4H_2O$ (1.92 g; Merck KGaA) and $CsNO_3$ (1.75 g; Fluka Chemie AG) were added. The solution was heated with hot tap water for a while and then filtered. Bulbous crystals of (I) were found in the deposit.

Crystal data

$Cs[Ag_4Zn_2(SCN)_9]$
$M_r = 1217.85$
Triclinic, $P\bar{1}$
$a = 7.5493$ (1) Å
$b = 8.9297$ (2) Å
$c = 10.5701$ (2) Å
$\alpha = 78.045$ (1)°
$\beta = 82.912$ (1)°
$\gamma = 82.828$ (1)°
$V = 688.15$ (2) Å^3
$Z = 1$

$D_x = 2.939$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 9151 reflections
$\theta = 1.0$–30.0°
$\mu = 6.51$ mm^{-1}
$T = 293$ (2) K
Botryoidal (like a bunch of grapes), colourless
0.1 × 0.1 × 0.1 mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ scans
9429 measured reflections
4007 independent reflections
2733 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.04$
$\theta_{\rm max} = 30°$
$h = -10 \rightarrow 10$
$k = -12 \rightarrow 12$
$l = -14 \rightarrow 14$

Refinement

Refinement on F^2
$R(F) = 0.049$
$wR(F^2) = 0.114$
$S = 1.04$
4007 reflections
158 parameters

$w = 1/[\sigma^2(F_o^2) + (0.0266P)^2 + 3.6770P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 2.33$ e Å^{-3}
$\Delta\rho_{\rm min} = -2.27$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0034 (4)

Table 1
Selected geometric parameters (Å, °).

Ag1—S1$^{\rm i}$	2.5399 (17)	Cs1—N5$^{\rm vi}$	3.748 (5)
Ag1—S2	2.541 (3)	Zn1—N4	1.931 (5)
Ag1—S3	2.5443 (16)	Zn1—N5$^{\rm vi}$	1.954 (5)
Ag1—S1	2.8505 (19)	Zn1—N1	1.956 (5)
Ag2—S4$^{\rm ii}$	2.5286 (17)	Zn1—N3	2.006 (5)
Ag2—S3$^{\rm iii}$	2.5752 (16)	S1—C1	1.649 (6)
Ag2—S5	2.7217 (19)	S2—C2	1.389 (3)
Ag2—S5$^{\rm iv}$	2.7938 (19)	S3—C3	1.646 (6)
Cs1—N2$^{\rm v}$	3.480 (3)	S4—C4	1.634 (6)
Cs1—S2	3.480 (3)	S5—C5	1.643 (6)
Cs1—N3$^{\rm v}$	3.512 (6)	C1—N1$^{\rm i}$	1.153 (8)
Cs1—N3	3.512 (6)	C2—N2$^{\rm vii}$	1.389 (3)
Cs1—S1$^{\rm vi}$	3.6262 (15)	C3—N3$^{\rm vii}$	1.150 (7)
Cs1—N1$^{\rm v}$	3.701 (6)	C4—N4$^{\rm ii}$	1.147 (8)
Cs1—N1	3.701 (6)	C5—N5	1.138 (7)
S1$^{\rm i}$—Ag1—S2	102.71 (8)	N4—Zn1—N5$^{\rm vi}$	115.2 (2)
S1$^{\rm i}$—Ag1—S3	139.45 (6)	N4—Zn1—N1	113.5 (2)
S2—Ag1—S3	107.20 (9)	N5$^{\rm vi}$—Zn1—N1	111.1 (2)
S1$^{\rm i}$—Ag1—S1	100.83 (5)	N4—Zn1—N3	105.4 (2)
S2—Ag1—S1	105.19 (8)	N5$^{\rm vi}$—Zn1—N3	106.0 (2)
S3—Ag1—S1	97.10 (5)	N1—Zn1—N3	104.5 (2)
S4$^{\rm ii}$—Ag2—S3$^{\rm iii}$	118.89 (5)	N1$^{\rm i}$—C1—S1	179.4 (6)
S4$^{\rm ii}$—Ag2—S5	110.14 (5)	S2—C2—N2$^{\rm vii}$	180.0 (2)
S3$^{\rm iii}$—Ag2—S5	107.07 (5)	N3$^{\rm vii}$—C3—S3	177.6 (5)
S4$^{\rm ii}$—Ag2—S5$^{\rm iv}$	114.33 (6)	N4$^{\rm ii}$—C4—S4	178.9 (6)
S3$^{\rm iii}$—Ag2—S5$^{\rm iv}$	114.09 (5)	N5—C5—S5	178.8 (6)
S5—Ag2—S5$^{\rm iv}$	87.35 (6)		

Symmetry codes: (i) $-x, -y, 1 - z$; (ii) $-x, 1 - y, -z$; (iii) $x, y, z - 1$; (iv) $1 - x, -y, -z$; (v) $1 - x, 1 - y, 1 - z$; (vi) $x, 1 + y, z$; (vii) $1 - x, -y, 1 - z$.

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.

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

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1385). Services for accessing these data are described at the back of the journal.

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