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Calcium dicaesium silver thiocyanate dihydrate

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The title compound, $CaCs_2[Ag_2(SCN)_6]\cdot 2H_2O$, forms a continuous structure where the Ag atoms form chains with S atoms in the *c*-axis direction. The chains are bonded together through Cs and Ca atoms. The crystal water of the structure is bonded to the Ca atoms, which lie on centers of symmetry.

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. Calcium, caesium and silver all form simple thiocyanates. CsSCN crystallizes in space group *Pnma* and AgSCN crystallizes in two polymorphic forms in space groups *Pmnn* and *C*2/*c*. The crystal structure of $Ca(SCN)_2\cdot 2H_2O$ is not available in the literature because while crystallizing it forms powder instead of large single crystals, and until recently it has not usually been possible to determine the crystal structure of a powder sample. However, a quite recently published crystal structure determination of $Ca(SCN)_2\cdot 4H_2O$ (Held & Bohaty, 2001) is now available in the literature.

The main reason for our interest in thiocyanates like the title compound is that some of the thiocyanates of silver have very interesting optical, electro-optic and electrostrictive properties (Bohaty & Fröhlich, 1992), which are interrelated with non-centrosymmetric crystal structures. Earlier, we reported the crystal structures of $KAg(SCN)_2$ (Valkonen & Güneş, 2001) and $Cs_2[AgZn(SCN)_5]$ (Güneş & Valkonen, 2001), of which the latter has a non-centrosymmetric crystal structure. We presume that an odd number of thiocyanate groups could lead to a non-centrosymmetric crystal structure, as there are 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 the same property. We look forward to synthesizing more of these compounds in the future as it might turn out that they will indeed have non-centrosymmetric crystal structures and as a consequence some chemically useful optical, electro-optic and electrostrictive properties.

In the present compound, Cs is nine-coordinated by four S, four N and one O atom. Ag is tetrahedrally four-coordinated by four S atoms; the tetrahedron is slightly distorted (see Table 1). Ca is octahedrally six-coordinated by two O and four N atoms; the octahedron is nearly regular (see Table 1). The average thiocyanate S—C distance is 1.65 Å and the average C—N distance approximately 1.15 Å. The bond angles of the thiocyanate groups are all close to 180°.

The title compound consists of a continuous structure where the Ag atoms form chains (Fig. 1) in the *c*-axis direction, bonded together through the S2 atoms of the bridging thiocyanate groups which bond through N to Ca atoms, thereby connecting the Ag–S–Ag chains in the *b*-axis direction. There are also two terminal thiocyanate groups attached through S to every Ag atom of the Ag–S–Ag chains. One of the terminal thiocyanate groups of every other Ag atom of the chain is bonded through N to Ca atoms, thereby also connecting the Ag–S–Ag chains. The bonding of the Ag–S–Ag chains is presented in Fig. 1. The Cs atoms connect the Ag–S–Ag chains in both the *b*- and *a*-axis directions. The crystal water of the structure is bonded to the Ca atoms. The water molecules are located in the capping positions of the coordination octahedron around Ca.

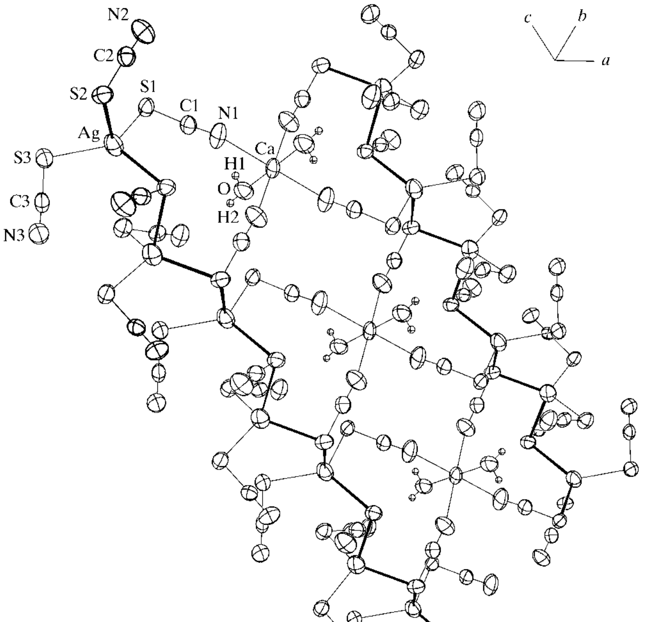

Figure 1
The Ag–S–Ag chains connected through Ca atoms. The Cs atom has been omitted for clarity. Displacement ellipsoids are represented at the 50% probability level.

Experimental

Silver thiocyanate was obtained from the Aldrich Chemical Company Inc. Calcium thiocyanate dihydrate and caesium thiocyanate were synthesized in our laboratory. $CaCs_2[Ag_2(SCN)_6]\cdot 2H_2O$ was synthesized at room temperature by separately dissolving $Ca(SCN)_2\cdot 2H_2O$

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(1.45 g) in deionized water (1.00 ml) and CsSCN (2.63 g) in deionized water (2.00 ml). The $Ca(SCN)_2{\cdot}2H_2O$ solution was added to the CsSCN solution and AgSCN (2.28 g) was dissolved in this solution. The dissolution of AgSCN was accelerated by heating the solution on a water bath. The final solution was filtered through a dense sinter glass (No. 4) while hot. The filtered solution was allowed to cool and evaporate at room temperature. Within 2 d, colorless crystals of $CaCs_2[Ag_2(SCN)_6]{\cdot}2H_2O$ had formed.

Calcium thiocyanate dihydrate was synthesized at room temperature by suspending $Ca(OH)_2$ (60.00 g) in deionized water (150 ml) and NH_4SCN (102.53 g) in deionized water (65.0 ml). The solutions were mixed and the resulting mixture heated under magnetic stirring until the smell of ammonia was no longer detected (about 2 h). The solution was filtered while hot. The filtered solution was evaporated to dryness at 350–360 K using a vacuum pump on a water bath. $Ca(SCN)_2{\cdot}2H_2O$ was stored in a desiccator because of its hygroscopicity.

Caesium thiocyanate was synthesized by separately dissolving NH_4SCN (6.98 g) in deionized water (20.0 ml) and Cs_2CO_3 (15.0 g) in deionized water (55.0 ml). The solutions were mixed at room temperature and the resulting mixture heated under magnetic stirring until the smell of ammonia was no longer detected (about 2.5 h). The residue was evaporated close to dryness at room temperature. CsSCN was dried using a vacuum pump and was stored in a desiccator because of its hygroscopicity.

Calcium hydroxide was supplied by the Merck KGaA and ammonium thiocyanate and caesium carbonate were supplied by the Aldrich Chemical Company Inc.

Crystal data

$CaCs_2[Ag_2(SCN)_6]{\cdot}2H_2O$
$M_r = 906.15$
Monoclinic, $P2_1/c$
$a = 7.8696$ (1) Å
$b = 19.0910$ (2) Å
$c = 7.7411$ (1) Å
$\beta = 93.338$ (1)°
$V = 1161.04$ (2) Å^3
$Z = 2$
$D_x = 2.592$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5696 reflections
$\theta = 1.0$–28.3°
$\mu = 5.55$ mm^{-1}
$T = 293$ (2) K
Prism, colorless
0.1 × 0.1 × 0.1 mm

Data collection

Nonius KappaCCD diffractometer
φ scans
11 177 measured reflections
2881 independent reflections
2588 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.024$
$\theta_{\rm max} = 28.3°$
$h = -10 \rightarrow 10$
$k = -25 \rightarrow 25$
$l = -10 \rightarrow 10$

Refinement

Refinement on F^2
$R(F) = 0.033$
$wR(F^2) = 0.059$
$S = 1.12$
2881 reflections
124 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + 3.4217P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 1.86$ e Å^{-3}
$\Delta\rho_{\rm min} = -1.41$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.00268 (16)

Table 1
Selected geometric parameters (Å, °).

Cs—N3$^{\rm i}$	3.401 (5)	Cs—S1$^{\rm iii}$	3.8599 (10)
Cs—N1$^{\rm ii}$	3.421 (5)	Ag—S3	2.5259 (11)
Cs—O	3.483 (4)	Ag—S1	2.5513 (10)
Cs—S1	3.6042 (12)	Ag—S2	2.5927 (11)
Cs—S2$^{\rm ii}$	3.6389 (11)	Ag—S2$^{\rm i}$	2.7461 (11)
Cs—S3	3.6970 (12)	Ca—O	2.365 (4)
Cs—N1$^{\rm iii}$	3.811 (5)	Ca—N2$^{\rm v}$	2.397 (4)
Cs—N2$^{\rm iv}$	3.848 (5)	Ca—N1$^{\rm vi}$	2.407 (4)
S3—Ag—S1	114.24 (4)	S2—Ag—S2$^{\rm i}$	93.03 (3)
S3—Ag—S2	129.99 (4)	O—Ca—N2$^{\rm v}$	96.13 (14)
S1—Ag—S2	108.10 (3)	N2$^{\rm v}$—Ca—N1$^{\rm vi}$	89.35 (15)
S3—Ag—S2$^{\rm i}$	98.98 (4)	O—Ca—N1$^{\rm ii}$	90.81 (15)
S1—Ag—S2$^{\rm i}$	106.71 (4)		

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

The s.u.'s of the cell constants indicate the internal consistency of the measurements themselves, *i.e.* the precision of the measurement, not their accuracy. During the crystal structure determination, an absorption correction for the measured intensities was calculated but not applied. The absorption correction was found to have no significant effect on the refinement results.

Data collection: *COLLECT* (Nonius, 1997–2000); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *HKL DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997); 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: BR1348). Services for accessing these data are described at the back of the journal.

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