

Polymorphism in Cs[AgZn(NCS)₄]

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Received 2 September 2002

Accepted 1 October 2002

Online 8 November 2002

The title compound, caesium silver zinc tetrathiocyanate, crystallizes in two polymorphic forms, in space groups $P2_1/n$ and $C2/c$. Both structures form a continuous three-dimensional network. The structure in $C2/c$ contains a delocalized Ag atom in a binuclear-like anion, where two [Ag(NCS)₄] units (delocalized Ag as an average) share two common NCS⁻ ligands.

Comment

Caesium silver zinc tetrathiocyanate monohydrate has been known for a century (Wells, 1902, 1922), but its anhydrous form, Cs[AgZn(NCS)₄], has not been mentioned in the literature until now. Our research indicates that Cs[AgZn(NCS)₄] crystallizes in two polymorphic forms, in space groups $P2_1/n$, (I), and $C2/c$, (II). There are a total of four different caesium silver zinc thiocyanates known in the literature, namely Cs[AgZn(NCS)₄·H₂O], Cs₂[AgZn(NCS)₅], Cs[Ag₃Zn₂(NCS)₈] and Cs[Ag₄Zn₂(NCS)₉] (Wells, 1902, 1922; Güneş & Valkonen, 2002*a,b*). Cs, Ag and Zn all form simple thiocyanates. CsNCS crystallizes in space group $Pnma$, AgNCS in two polymorphic forms in space groups $C2/c$ and $Pmnn$, and Zn(NCS)₂ in space group $P\bar{1}$. Also, Zn(NCS)₂·2H₂O is known in the literature and crystallizes in space group $P2_12_12_1$.

Our interest in triple thiocyanates of silver arises from the fact that some of them, such as Cs₃Sr[Ag₂(NCS)₇] and Cs₃Ba[Ag₂(NCS)₇], have been found to have a non-centrosymmetric crystal structure (Bohaty & Fröhlich, 1992). Such a structure can possess some very interesting optical, electro-optic and electrostrictive properties, which could be utilized in, for example, 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 ability 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).

The structure of Cs[AgZn(NCS)₄] is very interesting, as it seems to crystallize in two different polymorphic forms. In form (I), the structure forms a simple three-dimensional

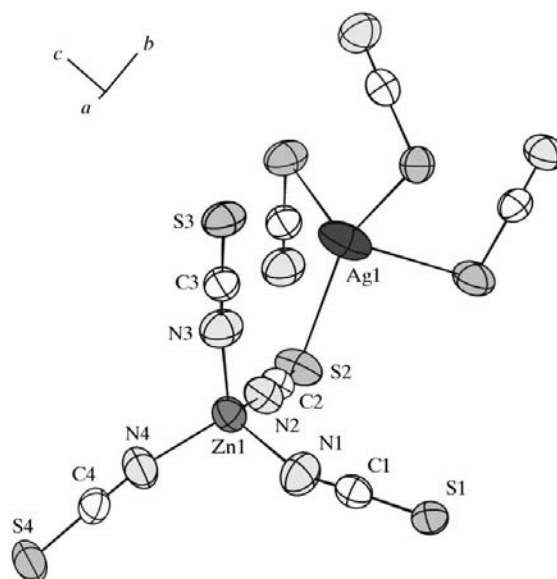


Figure 1

A view of the bonding of the Ag and Zn atoms in (I), shown with 50% probability displacement ellipsoids. Shading convention: from the heaviest atom (Ag) to the lightest (C), the shading gets lighter, *viz.* in the sequence Ag > Zn > S > N > C.

network. The Ag is bonded to four S atoms of four thiocyanate groups, which are then bonded from the other end to Zn atoms (Fig. 1). This simple bonding mode continues throughout the

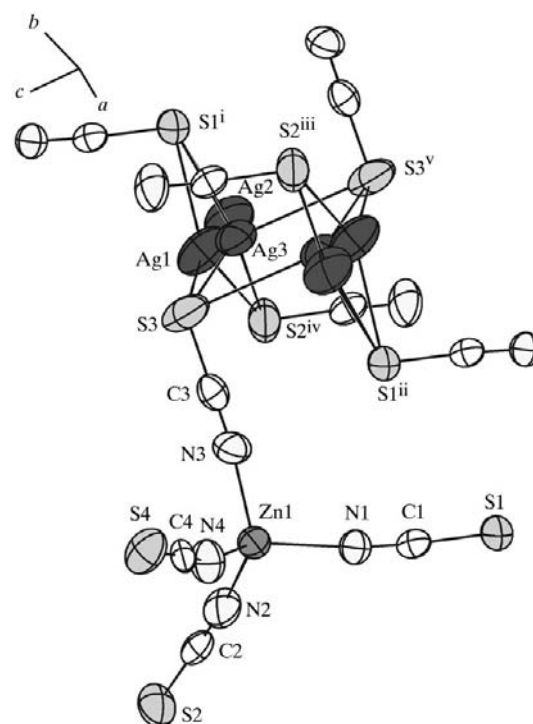


Figure 2

A view of the bonding of the Ag and Zn atoms in (II), shown with 50% probability displacement ellipsoids. Shading convention: from the heaviest atom (Ag) to the lightest (C), the shading gets lighter, *viz.* in the sequence Ag > Zn > S > N > C. [Symmetry codes: (i) $-\frac{1}{2} + x, \frac{1}{2} + y, z$; (ii) $\frac{1}{2} - x, \frac{1}{2} - y, -z$; (iii) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; (iv) $-\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z$; (v) $-x, 1 - y, -z$.]

structure, where the Cs atoms further connect the thiocyanate groups through S and N atoms.

The Ag and Zn atoms of (I) are both tetrahedrally coordinated, the Ag atom being surrounded by four S atoms and the Zn atom by four N atoms. The tetrahedron around the Ag atom is quite strongly distorted, but the tetrahedron around the Zn atom is nearly ideal. The Cs atom is ten-coordinated, being surrounded by five S, three C and two N atoms. The C atoms do not actually participate in bonding but Cs can, by back coordination, form a dihapto (η^2) π bond to the $C\equiv N$ triple bond of a thiocyanate group.

The structure of form (II) is slightly more complicated, as it includes a delocalized Ag atom disordered over three sites, Ag1, Ag2 and Ag3, with occupancies of 0.36 (2), 0.26 (2) and 0.38 (2), respectively. Only one of the three possible positions of the disordered Ag atom (Ag3) actually has clear four-coordination, which is common for an Ag atom, and the other two possible positions are clearly only three- (Ag1) and two-coordinated (Ag2). The separations between the three disordered Ag atoms are Ag1 \cdots Ag2 0.843 (12) Å, Ag2 \cdots Ag3 0.766 (11) Å and Ag1 \cdots Ag3 0.775 (9) Å. However, on average, the Ag atom is in a four-coordinate-like environment and the structure includes a binuclear-like anion (Fig. 2), which can be compared with the binuclear $[Ag_2(NCS)_6]^{4-}$ anions in $K_4[Ag_2(NCS)_6]$ (Krautscheid & Gerber, 2001), where there are two $[Ag(NCS)_4]$ units sharing two common NCS^- ligands.

The structure of form (II) also forms a three-dimensional network, where the thiocyanate groups of the binuclear-like anion bonded from S to the delocalized Ag atom are bonded from the other end to the four-coordinated Zn atom. One of the thiocyanate groups is not bonded to Ag at all, but is bonded from N to the Zn atom and from S only to the Cs atom. The tetrahedron around the Zn atom is very slightly distorted. The Cs atom, which connects the network in all dimensions, is a total of 13-coordinated.

Experimental

All reagents used were of analytical grade. Caesium thiocyanate was synthesized as follows: NH_4NCS (13.96 g; Aldrich Chemical Company Inc.) was dissolved in deionized water (40.0 g) and, in a separate beaker, Cs_2CO_3 (30.0 g; Aldrich Chemical Company Inc.) was also dissolved in deionized water (110.0 g). The solutions were mixed and the mixture was heated with stirring until ammonia was no longer sensed. The residue was evaporated close to dryness in a water bath with continuous stirring, and the $CsNCS$ was dried and stored in a desiccator. Polymorph (I) was synthesized at room temperature by dissolving NH_4NCS (2.05 g) in deionized water (20.0 g) and then dissolving $AgNCS$ (0.28 g; City Chemical LLC) in the resulting solution. Next, $Zn(NCS)_2$ (1.33 g; City Chemical LLC) and $CsNCS$ (1.75 g) were added. Not all of the $Zn(NCS)_2$ and $CsNCS$ dissolved. The solution was heated with hot tap water for a while, stirred with a glass rod and then filtered. Within 1 d, colourless crystals of (I) formed. Polymorph (II) was synthesized at room temperature by dissolving $Zn(NCS)_2$ (4.30 g) in deionized water (5.00 g). The solution was filtered to remove the turbidity. Another solution was made by dissolving $CsNCS$ (1.10 g) in deionized water (5.00 g) and adding $AgNCS$ (0.13 g) to the resulting solution. Not all of the $AgNCS$ dissolved, and the second solution was filtered to remove the excess

$AgNCS$. These two solutions were mixed and the precipitate, which formed immediately, was removed by filtration. Within a couple of days, colourless crystals of (II) formed.

Polymorph (I)

Crystal data

$Cs[AgZn(NCS)_4]$
 $M_r = 538.47$
 Monoclinic, $P2_1/n$
 $a = 9.0398$ (2) Å
 $b = 16.6679$ (4) Å
 $c = 9.0973$ (2) Å
 $\beta = 98.190$ (1)°
 $V = 1356.75$ (5) Å³
 $Z = 4$
 $D_x = 2.636$ Mg m⁻³

Mo $K\alpha$ radiation
 Cell parameters from 13 915 reflections
 $\theta = 1.0$ – 24.7°
 $\mu = 6.44$ mm⁻¹
 $T = 293$ (2) K
 Botryoidal (like a bunch of grapes), colourless
 0.15 × 0.15 × 0.15 mm

Data collection

Nonius KappaCCD area-detector diffractometer
 φ scans
 12 064 measured reflections
 2298 independent reflections
 1852 reflections with $I > 2\sigma(I)$

$R_{int} = 0.072$
 $\theta_{max} = 24.7^\circ$
 $h = -10 \rightarrow 10$
 $k = -19 \rightarrow 19$
 $l = -10 \rightarrow 10$

Refinement

Refinement on F^2
 $R(F) = 0.041$
 $wR(F^2) = 0.101$
 $S = 1.04$
 2298 reflections
 137 parameters
 $w = 1/[\sigma^2(F_o^2) + (0.0287P)^2 + 7.9708P]$
 where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
 $\Delta\rho_{max} = 1.86$ e Å⁻³
 $\Delta\rho_{min} = -1.76$ e Å⁻³
 Extinction correction: *SHELXL97* (Sheldrick, 1997)
 Extinction coefficient: 0.0017 (3)

Table 1

Selected geometric parameters (Å, °) for polymorph (I).

Ag1–S1 ⁱ	2.5600 (19)	S1–C1	1.633 (8)
Ag1–S2	2.573 (2)	S2–C2	1.634 (8)
Ag1–S3 ⁱⁱ	2.667 (2)	S3–C3	1.634 (8)
Ag1–S4 ⁱⁱⁱ	2.944 (2)	S4–C4	1.614 (8)
Zn1–N3	1.943 (7)	C1–N1	1.146 (9)
Zn1–N4	1.951 (7)	C2–N2	1.141 (9)
Zn1–N2	1.951 (7)	C3–N3	1.153 (10)
Zn1–N1	1.975 (7)	C4–N4	1.148 (9)
S1 ⁱ –Ag1–S2	142.15 (7)	N4–Zn1–N2	111.6 (3)
S1 ⁱ –Ag1–S3 ⁱⁱ	110.08 (6)	N3–Zn1–N1	105.4 (3)
S2–Ag1–S3 ⁱⁱ	107.38 (7)	N4–Zn1–N1	107.1 (3)
S1 ⁱ –Ag1–S4 ⁱⁱⁱ	91.83 (6)	N2–Zn1–N1	108.4 (3)
S2–Ag1–S4 ⁱⁱⁱ	88.83 (7)	N1–C1–S1	179.0 (7)
S3 ⁱⁱ –Ag1–S4 ⁱⁱⁱ	97.09 (7)	N2–C2–S2	179.0 (7)
N3–Zn1–N4	111.6 (3)	N3–C3–S3	178.1 (7)
N3–Zn1–N2	112.3 (3)	N4–C4–S4	176.7 (7)

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

Polymorph (II)

Crystal data

$Cs[AgZn(NCS)_4]$
 $M_r = 538.47$
 Monoclinic, $C2/c$
 $a = 13.964$ (2) Å
 $b = 14.851$ (2) Å
 $c = 13.389$ (2) Å
 $\beta = 113.35$ (1)°
 $V = 2549.2$ (7) Å³
 $Z = 8$

$D_x = 2.806$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 25 reflections
 $\theta = 4.4$ – 12.5°
 $\mu = 6.86$ mm⁻¹
 $T = 293$ (2) K
 Rod, colourless
 0.20 × 0.05 × 0.05 mm

Data collection

Nonius MACH3 diffractometer
 $\omega/2\theta$ scans
 Absorption correction: ψ scan
 (North *et al.*, 1968)
 $T_{\min} = 0.579$, $T_{\max} = 0.710$
 7410 measured reflections
 3705 independent reflections
 1447 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.084$
 $\theta_{\text{max}} = 30^\circ$
 $h = -19 \rightarrow 19$
 $k = -20 \rightarrow 20$
 $l = -18 \rightarrow 18$
 3 standard reflections
 frequency: 60 min
 intensity decay: 0.8%

Refinement

Refinement on F^2
 $R(F) = 0.060$
 $wR(F^2) = 0.119$
 $S = 0.94$
 3705 reflections
 155 parameters
 $w = 1/[\sigma^2(F_o^2) + (0.0374P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.67 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.78 \text{ e } \text{\AA}^{-3}$
 Extinction correction: *SHELXL97*
 (Sheldrick, 1997)
 Extinction coefficient: 0.00018 (4)

Table 2

Selected geometric parameters (\AA , $^\circ$) for polymorph (II).

Ag1—S2 ⁱ	2.430 (5)	Zn1—N1	1.958 (7)
Ag1—S3	2.573 (8)	Zn1—N3	1.961 (7)
Ag1—S1 ⁱⁱ	2.598 (6)	S1—C1	1.627 (9)
Ag2—S1 ⁱⁱ	2.381 (8)	S2—C2	1.640 (9)
Ag2—S2 ⁱ	2.457 (8)	S3—C3	1.628 (9)
Ag3—S1 ⁱⁱ	2.512 (5)	S4—C4	1.615 (9)
Ag3—S3	2.573 (7)	C1—N1	1.133 (9)
Ag3—S2 ⁱ	2.612 (6)	C2—N2	1.108 (9)
Ag3—S3 ⁱⁱⁱ	2.916 (8)	C3—N3	1.142 (9)
Zn1—N4	1.940 (7)	C4—N4	1.146 (9)
Zn1—N2	1.945 (8)		
S2 ⁱ —Ag1—S3	112.9 (3)	N4—Zn1—N2	109.1 (3)
S2 ⁱ —Ag1—S1 ⁱⁱ	146.3 (3)	N4—Zn1—N1	119.0 (3)
S3—Ag1—S1 ⁱⁱ	97.6 (2)	N2—Zn1—N1	105.3 (3)
S1 ⁱⁱ —Ag2—S2 ⁱ	168.4 (7)	N4—Zn1—N3	108.5 (3)
S1 ⁱⁱ —Ag3—S3	99.8 (2)	N2—Zn1—N3	110.3 (3)
S1 ⁱⁱ —Ag3—S2 ⁱ	139.8 (2)	N1—Zn1—N3	104.5 (3)
S3—Ag3—S2 ⁱ	107.1 (2)	N1—C1—S1	176.0 (7)
S1 ⁱⁱ —Ag3—S3 ⁱⁱⁱ	93.3 (2)	N2—C2—S2	177.2 (8)
S3—Ag3—S3 ⁱⁱⁱ	116.00 (19)	N3—C3—S3	176.7 (8)
S2 ⁱ —Ag3—S3 ⁱⁱⁱ	100.9 (2)	N4—C4—S4	177.8 (8)

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

The s.u. values of the cell constants of (I) indicate the internal consistency of the measurements themselves, *i.e.* the precision of the measurement, not their accuracy.

For (I), data collection: *COLLECT* (Nonius, 1997–2000); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *HKL DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*. For (II), data collection, cell refinement and data reduction: *CAD-4 Software* (Enraf–Nonius, 1989). For both compounds, program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 2000); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

The Alfred Kordelin Foundation and the Finnish Konkordia Association are acknowledged for their financial support of this work.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: IZ1027). Services for accessing these data are described at the back of the journal.

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