

Ca[Ag<sub>2</sub>(SCN)<sub>4</sub>]<sub>2</sub>·2H<sub>2</sub>O

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Calcium tetrathiocyanatodiargentate(I) dihydrate, Ca[Ag<sub>2</sub>(SCN)<sub>4</sub>]<sub>2</sub>·2H<sub>2</sub>O, contains eight-membered Ag<sub>4</sub>S<sub>4</sub> rings bonded together through shared atoms to form layers parallel to (100). The thiocyanate groups link the layers to Ca–O chains running parallel to the *c* axis. The Ca atom is located on a twofold rotation axis parallel to *b* and is surrounded by four water molecules of crystallization and four thiocyanate N atoms in a distorted square antiprism.

## Comment

A large synthetic study concerning thiocyanates was published at the beginning of the last century (Wells, 1902), and the title compound, Ca[Ag<sub>2</sub>(SCN)<sub>4</sub>]<sub>2</sub>·2H<sub>2</sub>O, was then synthesized for the first time. Subsequently, the formation of the title compound has been studied concisely (McKerrow *et al.*, 1946), but no other information about the title compound can be found in the literature. Both calcium and silver form simple thiocyanates. Ca(SCN)<sub>2</sub> crystallizes in the space group *C2/c* (Wickerled & Larsen, 2002), and AgSCN crystallizes in two polymorphic forms in the space groups *Pmnn* (Smith *et al.*, 1982) and *C2/c* (Lindqvist, 1957; Zhu *et al.*, 2003). Moreover, Ca(SCN)<sub>2</sub>·2H<sub>2</sub>O (Wickerled & Larsen, 2002) and Ca(SCN)<sub>2</sub>·4H<sub>2</sub>O (Held & Bohaty, 2001) crystallize in the space groups *Pnma* and *P3<sub>2</sub>21*, respectively. We have synthesized some compounds similar to the title compound, such as the potassium silver thiocyanates AgK(SCN)<sub>2</sub> (Valkonen & Güneş, 2001; Güneş, Lahtinen & Valkonen, 2002) and AgK<sub>2</sub>(SCN)<sub>3</sub> (Güneş, Lahtinen & Valkonen, 2002), and the triple thiocyanates Cs[AgZn(NCS)<sub>4</sub>] (Güneş & Valkonen, 2002*c*), Cs<sub>2</sub>[AgZn(SCN)<sub>5</sub>] (Güneş & Valkonen, 2002*a*), Cs[Ag<sub>4</sub>Zn<sub>2</sub>(SCN)<sub>9</sub>] (Güneş & Valkonen, 2002*b*) and CaCs<sub>2</sub>[Ag<sub>2</sub>(SCN)<sub>6</sub>]<sub>2</sub>·2H<sub>2</sub>O (Güneş, Nättinen & Valkonen, 2002), and have investigated their structural properties. Several compounds similar to the title compound are also known in the literature. The crystal structures of K[Ag(SCN)<sub>2</sub>] (Krautscheid & Gerber, 2001; Valkonen & Güneş, 2001), K<sub>3</sub>[Ag(SCN)<sub>4</sub>] and K<sub>4</sub>[Ag(SCN)<sub>6</sub>] (Krautscheid & Gerber, 2001) have been published recently, whereas the structures of NH<sub>4</sub>Ag(SCN)<sub>2</sub> (Lindqvist & Strandberg, 1957; Hall *et al.*,

1983), Rb<sub>2</sub>Ag(SCN)<sub>3</sub> and Cs<sub>2</sub>Ag(SCN)<sub>3</sub> (Thiele & Kehr, 1984) have been known for decades.

Our interest in silver and other thiocyanates arises from the fact that some of these complexes, such as Cs<sub>3</sub>Sr[Ag<sub>2</sub>(SCN)<sub>7</sub>] and Cs<sub>3</sub>Ba[Ag<sub>2</sub>(SCN)<sub>7</sub>] (Bohaty & Fröhlich, 1992), along with other thiocyanates like ZnCd(SCN)<sub>4</sub>, ZnHg(SCN)<sub>4</sub>, CdHg(SCN)<sub>4</sub> and MnHg(SCN)<sub>4</sub> (Wang *et al.*, 2001), have a non-centrosymmetric crystal structure, which can furthermore possess some very interesting optical, electro-optical and electrostrictive properties. These properties could be utilized, for example, in telecommunications, optical computing, optical information processing, optical disk data storage, laser remote sensing, laser-driven fusion, color 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). Another factor that makes thiocyanates such tempting materials for research is their chemical nature. Because thiocyanates are neither purely organic nor purely inorganic compounds, but a kind of semi-organic compounds instead, they might possess advantages over both organic and inorganic materials. We hope to synthesize more of these compounds in the future, as they may also possess the above-mentioned properties.

In the present compound, the Ca atom is located on a twofold rotation axis at ( $\frac{1}{2}$ , 0.58417,  $\frac{1}{4}$ ), and is coordinated to four thiocyanate N atoms and four O atoms of the water molecules of crystallization (Table 1). The coordination polyhedron of the Ca atom is a distorted square antiprism. The Ag atom is surrounded by four S atoms and its coordination polyhedron is a distorted tetrahedron. There are two crystal-

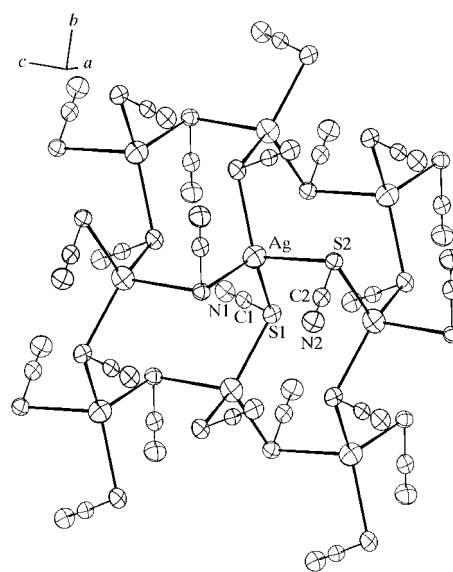
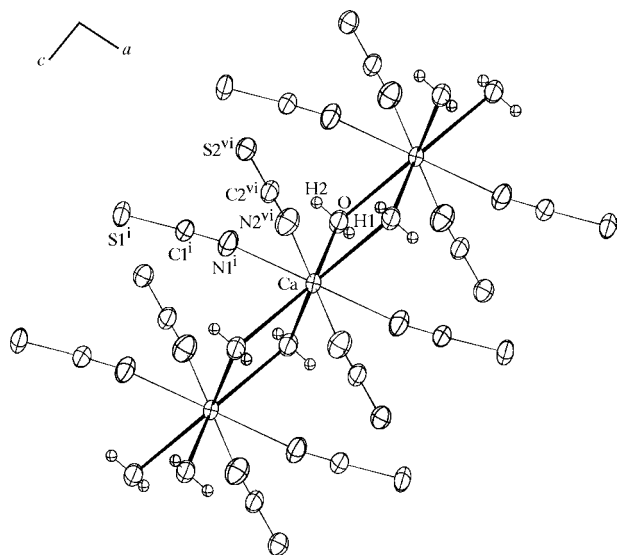


Figure 1

A view of the layer formed by eight-membered Ag<sub>4</sub>S<sub>4</sub> rings, sharing two common Ag atoms and one common S atom with every adjacent Ag<sub>4</sub>S<sub>4</sub> ring. Displacement ellipsoids are shown at the 50% probability level.



**Figure 2**  
A view of the Ca–O chain, showing 50% probability displacement ellipsoids. See Table 1 for symmetry codes.

lographically independent thiocyanate groups. Each group is bonded to two Ag atoms through the S atom at one end and to one Ca atom through the N atom at the other end. The average S–C bond length of the thiocyanate group is 1.67 (4) Å and the average C–N bond length is 1.15 (5) Å. The S–C–N angles of the thiocyanate groups are both close to 180°.

The title compound contains eight-membered Ag<sub>4</sub>S<sub>4</sub> rings in chair conformations. These rings are bonded together through two shared Ag atoms and one shared S atom to form layers parallel to (100) (Fig. 1). On the other hand, two Ca atoms and two O atoms form a Ca<sub>2</sub>O<sub>2</sub> rhombus. The rhombuses are further linked together at the shared Ca atoms to form chains parallel to the *c* axis (Fig. 2). The chains are linked to the Ag<sub>4</sub>S<sub>4</sub> layer *via* the thiocyanate groups.

**Experimental**

Silver thiocyanate was obtained from the Aldrich Chemical Company Inc. and calcium thiocyanate dihydrate was synthesized as described by Güneş, Nättinen & Valkonen (2002). All of the chemicals used were of analytical reagent grade. Ca[Ag<sub>2</sub>(SCN)<sub>4</sub>]<sub>2</sub>·2H<sub>2</sub>O was synthesized by dissolving Ca(SCN)<sub>2</sub>·2H<sub>2</sub>O (4.35 g) in deionized water (3 ml) and dissolving AgSCN (1.30 g) in this solution. The resulting solution was filtered through a dense sinter glass (No. 4). Within 2 d, colorless blocks of Ca[Ag<sub>2</sub>(SCN)<sub>4</sub>]<sub>2</sub>·2H<sub>2</sub>O crystallized from the filtrate.

*Crystal data*

Ca[Ag <sub>2</sub> (SCN) <sub>4</sub> ] <sub>2</sub> ·2H <sub>2</sub> O	<i>D</i> <sub>x</sub> = 2.575 Mg m <sup>-3</sup>
<i>M</i> <sub>r</sub> = 524.17	Mo Kα radiation
Monoclinic, <i>C</i> 2/ <i>c</i>	Cell parameters from 5864 reflections
<i>a</i> = 23.0272 (5) Å	<i>θ</i> = 1.0–30.0°
<i>b</i> = 7.5684 (2) Å	<i>μ</i> = 3.89 mm <sup>-1</sup>
<i>c</i> = 7.8595 (2) Å	<i>T</i> = 293 (2) K
<i>β</i> = 99.266 (2)°	Block, colorless
<i>V</i> = 1351.87 (6) Å <sup>3</sup>	0.15 × 0.10 × 0.10 mm
<i>Z</i> = 4	

*Data collection*

Nonius KappaCCD diffractometer	<i>θ</i> <sub>max</sub> = 30.0°
<i>φ</i> scans	<i>h</i> = -32 → 29
6337 measured reflections	<i>k</i> = -9 → 10
1958 independent reflections	<i>l</i> = -11 → 9
1552 reflections with <i>I</i> > 2σ( <i>I</i> )	
<i>R</i> <sub>int</sub> = 0.054	

*Refinement*

Refinement on <i>F</i> <sup>2</sup>	<i>w</i> = 1/[σ <sup>2</sup> ( <i>F</i> <sub>o</sub> <sup>2</sup> ) + (0.0591 <i>P</i> ) <sup>2</sup> ]
<i>R</i> ( <i>F</i> ) = 0.035	where <i>P</i> = ( <i>F</i> <sub>o</sub> <sup>2</sup> + 2 <i>F</i> <sub>c</sub> <sup>2</sup> )/3
<i>wR</i> ( <i>F</i> <sup>2</sup> ) = 0.112	(Δ/σ) <sub>max</sub> < 0.001
<i>S</i> = 1.17	Δ <i>ρ</i> <sub>max</sub> = 1.39 e Å <sup>-3</sup>
1958 reflections	Δ <i>ρ</i> <sub>min</sub> = -0.96 e Å <sup>-3</sup>
87 parameters	Extinction correction: <i>SHELXL97</i>
All H-atom parameters refined	Extinction coefficient: 0.0168 (8)

**Table 1**

Selected geometric parameters (Å, °).

Ag–S1	2.5119 (9)	Ca–N1 <sup>iii</sup>	2.469 (3)
Ag–S1 <sup>i</sup>	2.5560 (10)	Ca–N2 <sup>iv</sup>	2.493 (3)
Ag–S2 <sup>ii</sup>	2.6595 (9)	Ca–O	2.520 (3)
Ag–S2	2.7197 (9)	Ca–O <sup>v</sup>	2.561 (2)
S1–Ag1–S1 <sup>i</sup>	135.87 (2)	N1 <sup>i</sup> –Ca–O	75.38 (10)
S1–Ag1–S2 <sup>ii</sup>	112.01 (3)	N2 <sup>iv</sup> –Ca–O	150.20 (10)
S1 <sup>i</sup> –Ag1–S2 <sup>ii</sup>	102.47 (3)	N2 <sup>vi</sup> –Ca–O	109.65 (10)
S1–Ag1–S2	95.42 (3)	O–Ca–O <sup>viii</sup>	77.59 (13)
S1 <sup>i</sup> –Ag–S2	102.88 (3)	N1 <sup>iii</sup> –Ca–O <sup>v</sup>	70.06 (10)
S2 <sup>ii</sup> –Ag–S2	103.12 (3)	N1 <sup>i</sup> –Ca–O <sup>v</sup>	120.94 (9)
N1 <sup>iii</sup> –Ca–N1 <sup>i</sup>	142.52 (17)	N2 <sup>iv</sup> –Ca–O <sup>v</sup>	86.41 (10)
N1 <sup>iii</sup> –Ca–N2 <sup>iv</sup>	78.42 (12)	N2 <sup>vi</sup> –Ca–O <sup>v</sup>	69.30 (10)
N1 <sup>i</sup> –Ca–N2 <sup>iv</sup>	134.20 (11)	O–Ca–O <sup>v</sup>	71.21 (10)
N2 <sup>iv</sup> –Ca–N2 <sup>vi</sup>	78.85 (17)	O <sup>vii</sup> –Ca–O <sup>v</sup>	137.90 (9)
N1 <sup>iii</sup> –Ca–O	75.61 (11)	O <sup>v</sup> –Ca–O1 <sup>viii</sup>	148.75 (14)

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

A multi-scan absorption correction (Blessing, 1995) was performed 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 DENZO* (Otwinowski & Minor, 1997); data reduction: *HKL DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997); 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).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: IZ1044). Services for accessing these data are described at the back of the journal.

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