

Potassium thiocyanate argentates: $K_3[Ag(SCN)_4]$, $K_4[Ag_2(SCN)_6]$ and $K[Ag(SCN)_2]$

Harald Krautscheid* and Stefan Gerber

Institut für Anorganische Chemie, Universität Karlsruhe, Engesserstrasse 30.45,
D-76128 Karlsruhe, Germany

Correspondence e-mail: harald@achibm6.chemie.uni-karlsruhe.de

Received 6 February 2001

Accepted 2 April 2001

The anions of the title compounds contain $[Ag(SCN)_4]^{3-}$ units, with the S atoms coordinating to Ag^+ in a tetrahedral arrangement. Whereas in the isolated anions of tripotassium tetrathiocyanatoargentate(I), $K_3[Ag(SCN)_4]$, (I), all SCN^- groups are bonded as terminal ligands, in tetrapotassium di- μ -thiocyanato-*S:S*-bis[dithiocyanatoargentate(I)], $K_4[Ag_2(SCN)_6]$, (II), two AgS_4 tetrahedra share one common edge. In poly[potassium [argentate(I)-di- μ -thiocyanato-*S:S*]], $K[Ag(SCN)_2]$, (III), edge- and vertex-sharing of AgS_4 tetrahedra results in infinite $[Ag(SCN)_2]^-$ layers.

Comment

The compounds $K[Ag(SCN)_2]$ and $K_2[Ag(SCN)_3]$ are reported to form stable phases in the system $AgSCN/KSCN/H_2O$, whereas $K_3[Ag(SCN)_4]$ is metastable and decomposes in saturated solution into $K_2[Ag(SCN)_3]$ and $KSCN$ (Merriam, 1902; Foote, 1903*a,b*; Occleshaw, 1932). Although these compounds were known at the beginning of the last century, only the unit-cell parameters of $K[Ag(SCN)_2]$ have been reported to date (Chateau *et al.*, 1962). We isolated the title compounds, $K_3[Ag(SCN)_4]$, (I), $K_4[Ag_2(SCN)_6]$, (II), and $K[Ag(SCN)_2]$, (III), during the optimization of the synthesis of heteronuclear thiocyanate complexes (Krautscheid *et al.*, 1998; Krautscheid & Gerber, 1999) and we report their crystal structures here.

All three complexes contain Ag^+ in a distorted tetrahedral environment of four S atoms from the SCN^- ligands. Whereas the tetrathiocyanatoargentate anions in (I) are mononuclear, the binuclear anions in (II) can be regarded as two $[Ag(SCN)_4]^{3-}$ units sharing two common SCN^- ligands. The asymmetric unit of (II) contains a half of each of two crystallographically independent centrosymmetric $[Ag_2(SCN)_6]^{4-}$ anions, which differ in the orientation of two terminal SCN^- ligands.

In (III), such $[Ag_2(SCN)_6]$ units are linked by common SCN^- groups to form a two-dimensional polymeric network perpendicular to [100]. The existence of two different SCN^- ligands coordinating to Ag^+ through the S atoms, *i.e.* 1,1- μ_2

bridging in the $[Ag_2(SCN)_2]$ ring and between these rings, is in accordance with vibrational spectroscopic investigations, in which doublet splitting of the ν_1 band (2086 and 2099 cm^{-1}) was observed (Tramer, 1962).

In contrast with (III), the SCN^- anions in $(NH_4)[Ag(SCN)_2]$ can be described as terminal S-coordinating and 1,1,1- μ_3 -bridging, respectively, also leading to a two-dimensional polymeric structure and distorted tetrahedral coordination of the Ag^+ cations (Lindqvist & Strandberg, 1957; Hall *et al.*, 1983). In the crystal structure of $Cs_2[Ag(SCN)_3]$, dinuclear $[Ag_2(SCN)_6]^{4-}$ anions similar to

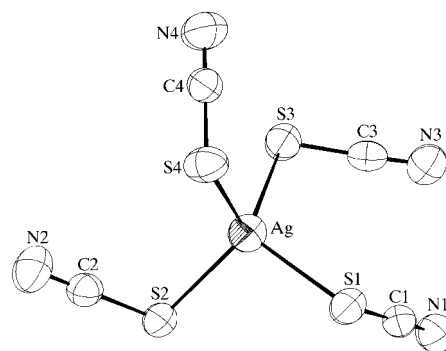


Figure 1
The structure of the $[Ag(SCN)_4]^{3-}$ anion in (I) shown with 70% probability displacement ellipsoids.

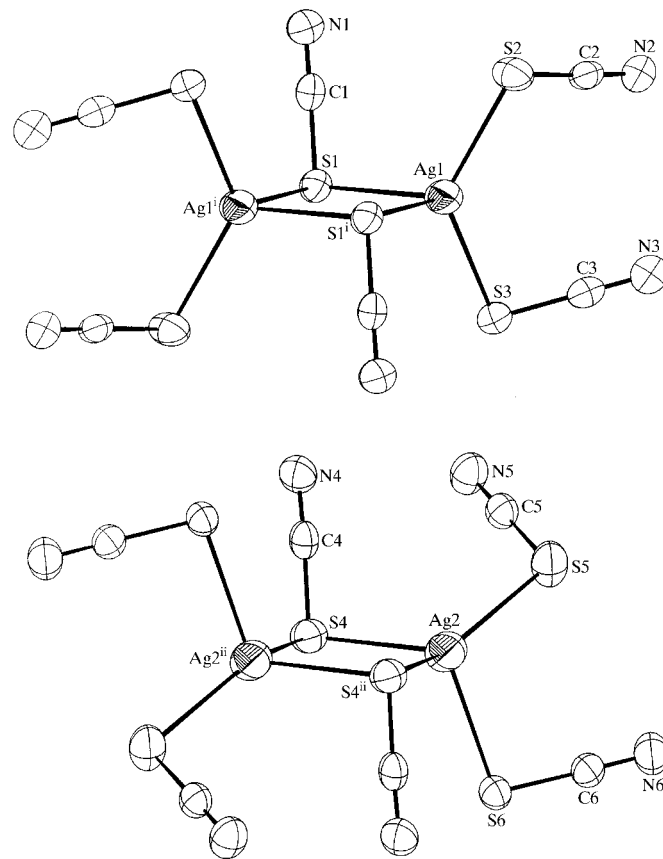


Figure 2
The structure of the two crystallographically independent $[Ag_2(SCN)_6]^{4-}$ anions in (II) with 70% probability displacement ellipsoids [symmetry codes: (i) $1-x, 1-y, 1-z$; (ii) $1-x, 1-y, -z$].

those in (II) are found, whereas $[\text{Ag}(\text{SCN})_4]$ tetrahedra are connected by common vertices to polymeric $[\text{Ag}(\text{SCN})_2(\mu_2\text{-SCN})_2]^{2-}$ anions in $\text{Rb}_2[\text{Ag}(\text{SCN})_3]$ (Thiele & Kehr, 1984).

As expected, the Ag–S bond lengths in compounds (I), (II) and (III) are longer for bridging SCN^- ligands than for terminal ligands and increase with the negative charge of the thiocyanatoargentate anions. The mean Ag–S bond lengths are 2.59 (1) Å in (I) and 2.56 (1) Å in (II) for terminal ligands, and 2.69 (3) Å in (II) and 2.62 (5) Å in (III) for 1,1- μ_2 -bridging SCN^- . The Ag–S–Ag angle for S1 in (III) connecting two Ag_2S_2 rings [111.30 (2)°] is significantly greater than the values for the bridging ligands in the Ag_2S_2 rings of (II) and (III) [83.69 (3)–87.30 (2)°].

In (I), (II) and (III), all K^+ ions are surrounded by seven N and S atoms, in distance ranges of 2.732 (4)–3.194 (2) Å ($\text{K}\cdots\text{N}$) and 3.230 (1)–3.663 (1) Å ($\text{K}\cdots\text{S}$), respectively. The only exception is K3 in compound (I), with two neighbouring N and six S atoms.

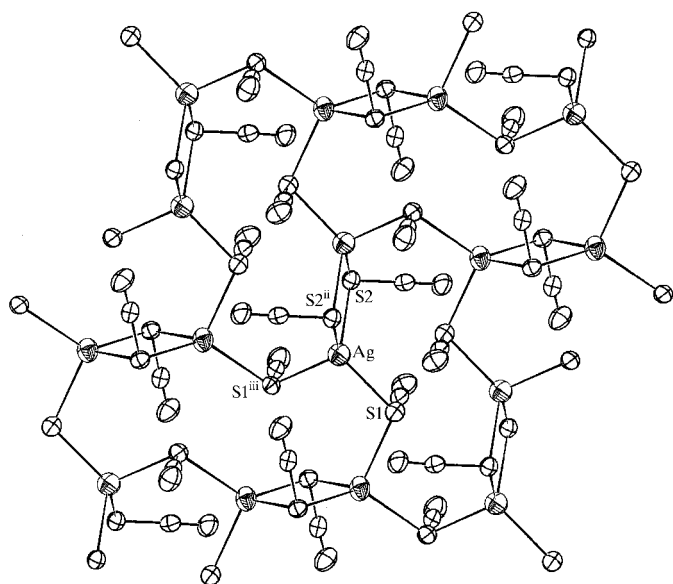


Figure 3
Fragment of the two-dimensional polymeric structure of the $[\text{Ag}(\text{SCN})_2]^{2-}$ anion in (III) with 70% probability displacement ellipsoids [symmetry codes: (ii) $1-x, 1-y, -z$; (iii) $x, \frac{1}{2}-y, z-\frac{1}{2}$].

Experimental

Crystals of (I) and (III) were grown by the condensation of methanol into concentrated aqueous solutions of AgSCN and KSCN in molar ratios of 1:4.5 and 1:2, respectively. Crystals of (II) were obtained in low yield as a side product during crystallization of (III).

Compound (I)

Crystal data

$\text{K}_3[\text{Ag}(\text{SCN})_4]$	$D_x = 2.180 \text{ Mg m}^{-3}$
$M_r = 457.49$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 27 reflections
$a = 14.343$ (2) Å	$\theta = 5\text{--}10^\circ$
$b = 12.778$ (3) Å	$\mu = 2.92 \text{ mm}^{-1}$
$c = 7.798$ (2) Å	$T = 293$ (2) K
$\beta = 102.772$ (18)°	Prism, colourless
$V = 1393.7$ (6) Å ³	$0.33 \times 0.15 \times 0.12 \text{ mm}$
$Z = 4$	

Data collection

Stoe Stadi-4 diffractometer	$R_{\text{int}} = 0.033$
ω scans	$\theta_{\text{max}} = 25^\circ$
Absorption correction: numerical (<i>X-RED</i> ; Stoe & Cie, 1997)	$h = -17 \rightarrow 17$
$T_{\text{min}} = 0.604, T_{\text{max}} = 0.688$	$k = -15 \rightarrow 15$
7208 measured reflections	$l = -9 \rightarrow 5$
2446 independent reflections	3 standard reflections
1944 reflections with $I > 2\sigma(I)$	frequency: 120 min
	intensity decay: 2%

Refinement

Refinement on F^2	$(\Delta/\sigma)_{\text{max}} < 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.027$	$\Delta\rho_{\text{max}} = 0.58 \text{ e \AA}^{-3}$
$wR(F^2) = 0.059$	$\Delta\rho_{\text{min}} = -0.50 \text{ e \AA}^{-3}$
$S = 1.10$	Extinction correction: <i>SHELXL97</i>
2446 reflections	(Sheldrick, 1997)
146 parameters	Extinction coefficient: 0.0073 (3)
$w = 1/[\sigma^2(F_o^2) + (0.0255P)^2 + 0.1891P]$	
where $P = (F_o^2 + 2F_c^2)/3$	

Table 1

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

Ag1–S1	2.5798 (11)	S1–C1	1.653 (4)
Ag1–S2	2.5953 (12)	C1–N1	1.154 (4)
S1–Ag1–S2	106.06 (4)	C2–S2–Ag1	100.95 (13)
C1–S1–Ag1	104.97 (13)	N1–C1–S1	178.2 (3)

Compound (II)

Crystal data

$\text{K}_4[\text{Ag}_2(\text{SCN})_6]$	$D_x = 2.358 \text{ Mg m}^{-3}$
$M_r = 720.62$	Ag $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 8000 reflections
$a = 9.8701$ (6) Å	$\theta = 1.8\text{--}22.4^\circ$
$b = 20.0893$ (8) Å	$\mu = 1.75 \text{ mm}^{-1}$
$c = 10.6229$ (7) Å	$T = 213$ (2) K
$\beta = 105.494$ (8)°	Block, colourless
$V = 2029.8$ (2) Å ³	$0.22 \times 0.18 \times 0.15 \text{ mm}$
$Z = 4$	

Data collection

Stoe IPDS diffractometer	4557 reflections with $I > 2\sigma(I)$
φ scans	$R_{\text{int}} = 0.036$
Absorption correction: numerical (<i>X-RED</i> ; Stoe & Cie, 1997)	$\theta_{\text{max}} = 22.4^\circ$
$T_{\text{min}} = 0.741, T_{\text{max}} = 0.803$	$h = -13 \rightarrow 13$
31 846 measured reflections	$k = -25 \rightarrow 25$
5096 independent reflections	$l = -14 \rightarrow 14$
	Intensity decay: none

Table 2

Selected geometric parameters (Å, °) for (II).

Ag1–S2	2.4914 (9)	Ag2–S5	2.5839 (9)
Ag1–S1	2.7083 (8)	Ag2–S4	2.6601 (9)
Ag1–S1 ⁱ	2.6538 (8)	Ag2–S4 ⁱⁱ	2.7400 (9)
S1–C1	1.660 (3)	S4–C4	1.660 (3)
C1–N1	1.158 (4)	C4–N4	1.153 (4)
S2–C2	1.650 (3)	S5–C5	1.653 (3)
S2–Ag1–S1	113.66 (3)	S5–Ag2–S4	110.08 (3)
S2–Ag1–S1 ⁱ	105.83 (3)	S5–Ag2–S4 ⁱⁱ	138.07 (3)
S1 ⁱ –Ag1–S1	92.70 (2)	S4–Ag2–S4 ⁱⁱ	96.31 (3)
C1–S1–Ag1	100.18 (10)	C4–S4–Ag2	102.26 (10)
C1–S1–Ag1 ⁱ	101.13 (10)	C4–S4–Ag2 ⁱⁱ	105.03 (10)
N1–C1–S1	178.7 (3)	N4–C4–S4	177.4 (3)
C2–S2–Ag1	106.95 (10)	C5–S5–Ag2	106.54 (11)
N2–C2–S2	177.7 (3)	N5–C5–S5	179.3 (3)

Symmetry codes: (i) $1-x, 1-y, 1-z$; (ii) $1-x, 1-y, -z$.

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.035$
 $wR(F^2) = 0.085$
 $S = 1.05$
 5096 reflections
 217 parameters

$w = 1/[\sigma^2(F_o^2) + (0.0448P)^2 + 4.099P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 2.23 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -2.08 \text{ e } \text{Å}^{-3}$

Compound (III)

Crystal data

$\text{K}[\text{Ag}(\text{SCN})_2]$
 $M_r = 263.13$
 Orthorhombic, $Pbca$
 $a = 17.9382 (14) \text{ Å}$
 $b = 10.7801 (8) \text{ Å}$
 $c = 6.6879 (6) \text{ Å}$
 $V = 1293.28 (18) \text{ Å}^3$
 $Z = 8$
 $D_x = 2.703 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation
 Cell parameters from 50 reflections
 $\theta = 10\text{--}12.5^\circ$
 $\mu = 4.29 \text{ mm}^{-1}$
 $T = 213 (2) \text{ K}$
 Triangular fragment of a plate, colourless
 $0.35 \times 0.25 \times 0.12 \text{ mm}$

Data collection

Stoe Stadi-4 diffractometer
 ω scans
 Absorption correction: numerical (*X-RED*; Stoe & Cie, 1997)
 $T_{\min} = 0.315$, $T_{\max} = 0.627$
 4667 measured reflections
 1561 independent reflections
 1458 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.022$
 $\theta_{\max} = 28^\circ$
 $h = 0 \rightarrow 23$
 $k = -14 \rightarrow 14$
 $l = -8 \rightarrow 8$
 2 standard reflections
 frequency: 120 min
 intensity decay: none

Table 3

Selected geometric parameters (Å , $^\circ$) for (III).

Ag—S1	2.5774 (6)	S1—C1	1.667 (2)
Ag—S2 ⁱⁱ	2.5794 (5)	C1—N1	1.157 (3)
Ag—S1 ⁱⁱⁱ	2.5984 (6)	S2—C2	1.668 (2)
Ag—S2	2.7262 (5)	C2—N2	1.158 (3)
S1—Ag—S2 ⁱⁱ	127.211 (17)	C1—S1—Ag ^{iv}	103.28 (7)
S1—Ag—S1 ⁱⁱⁱ	100.157 (14)	Ag—S1—Ag ^{iv}	111.30 (2)
S2 ⁱⁱ —Ag—S1 ⁱⁱⁱ	118.855 (17)	N1—C1—S1	177.5 (2)
S1—Ag—S2	111.142 (17)	C2—S2—Ag ⁱⁱ	101.47 (7)
S2 ⁱⁱ —Ag—S2	95.192 (17)	C2—S2—Ag	98.41 (7)
S1 ⁱⁱⁱ —Ag—S2	101.565 (17)	Ag ⁱⁱ —S2—Ag	84.808 (17)
C1—S1—Ag	96.76 (8)	N2—C2—S2	178.1 (2)

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

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.020$
 $wR(F^2) = 0.046$
 $S = 1.13$
 1561 reflections
 74 parameters
 $w = 1/[\sigma^2(F_o^2) + (0.0161P)^2 + 1.391P]$
 where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.003$
 $\Delta\rho_{\max} = 0.96 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.57 \text{ e } \text{Å}^{-3}$
 Extinction correction: *SHELXL97* (Sheldrick, 1997)
 Extinction coefficient: 0.0193 (4)

For compounds (I) and (III), data collection: *STADIA* (Stoe & Cie, 1997); cell refinement: *STADIA*; data reduction: *X-RED* (Stoe & Cie, 1997). For compound (II), data collection: *IPDS* (Stoe & Cie, 1999); cell refinement: *IPDS*; data reduction: *IPDS* and *X-RED*. For all three compounds, program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 1998).

We thank Professor Dr D. Fenske for his support.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: IZ1011). Services for accessing these data are described at the back of the journal.

References

- Brandenburg, K. (1998). *DIAMOND*. Release 2.0. Crystal Impact GbR, Bonn, Germany.
- Chateau, H., de Cugnac, A. & Cerisy, B. (1962). *C. R. Acad. Sci.* **255**, 1727–1728.
- Foote, H. W. (1903a). *J. Am. Chem. Soc.* **30**, 330–339.
- Foote, H. W. (1903b). *Z. Phys. Chem.* **46**, 79–86.
- Hall, S. R., Mills, N. K. & White, A. H. (1983). *Aust. J. Chem.* **36**, 1255–1258.
- Krautscheid, H., Emig, N., Klaassen, N. & Seringer, P. (1998). *J. Chem. Soc. Dalton Trans.* pp. 3071–3077.
- Krautscheid, H. & Gerber, S. (1999). *Z. Anorg. Allg. Chem.* **625**, 2041–2044.
- Lindqvist, I. & Strandberg, B. (1957). *Acta Cryst.* **10**, 173–177.
- Merriam, H. F. (1902). *J. Am. Chem. Soc.* **28**, 265–266.
- Occlshaw, V. J. (1932). *J. Chem. Soc.* pp. 2404–2410.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Stoe & Cie (1997). *STADIA* and *X-RED*. Stoe & Cie, Darmstadt, Germany.
- Stoe & Cie (1999). *IPDS*. Stoe & Cie, Darmstadt, Germany.
- Thiele, G. & Kehr, W. (1984). *Z. Anorg. Allg. Chem.* **515**, 199–206.
- Tramer, A. (1962). *J. Chim. Phys.* **59**, 232–240, 241–248, 637–654.