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KAg_5S_3

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Abstract

Potassium pentasilver trisulfide, KAg_5S_3, was synthesized in supercritical ethylenediamine using previously reported techniques [Wood *et al.* (1992). *J. Am. Chem. Soc.* **114**, 9233–9235]. Dark-red crystals of KAg_5S_3 crystallize in the hexagonal space group $P\bar{6}2c$. The compound has an open-channeled structure composed of Ag and S atoms, with K^+ cations sitting in the middle of these channels.

Comment

The anionic framework of KAg_5S_3 crystallizes as infinite columns composed of Ag and S atoms. The channels created by the silver sulfide network contain the K^+ cations. The unit-cell view of this compound is shown in Fig. 1. Ag and S atoms form planar 12-membered rings which reside on mirror planes. The unit cell contains two unique 12-membered rings, with a distance between them of approximately 4 Å. As a result of this, the unit-cell *c*-axis length is approximately 8 Å. As shown in Fig. 2, the Ag1 and Ag4 atoms are coordinated in a distorted trigonal-planar fashion by S atoms. The angles about these Ag atoms range from 142.8 (2) to 101.1 (2)°. The interconnected 12-membered Ag–S rings form layers which stack along the *c* axis. The layers are connected diagonally by Ag atoms between the sheets. These Ag2 and Ag3 atoms are linearly coordinated to S atoms in adjacent silver sulfide sheets. The linear Ag—S bond distances range from 2.397 (3) to 2.403 (3) Å. This is in agreement with the general trend of shorter bond distances with lower coordination number. All close Ag···Ag contacts range from 2.948 (2) to 3.001 (2) Å, but these are probably not indicative of formal single bonds (Jansen, 1987). In this compound, all of the Ag atoms are formally +1, and the S atoms have an oxidation state of −2. All the distances within the anionic framework are very close to those found in the Rb analog (Wood *et al.*, 1994). However, as expected, the average K—S distance of 3.187 (8) Å is shorter than the average Rb—S distance of 3.283 Å, due in large part to the decrease in the radius of the cation on going from Rb^+ to K^+. Each of the two unique K^+ cations sits along threefold rotation axes at the center of the channels created by the 12-membered Ag–S rings. Each K^+ cation is six-coordinate to S atoms, with a slightly distorted octahedral geometry. We wish to note that during the investigation of KAg_5S_3, it was determined that $RbAg_5S_3$ (Wood *et al.*, 1994) can also be successfully refined in $P\bar{6}2c$, not $P\bar{6}$ as reported. Thus, the K and Rb members are isostructural. Details of the heavier analog are available from the authors.

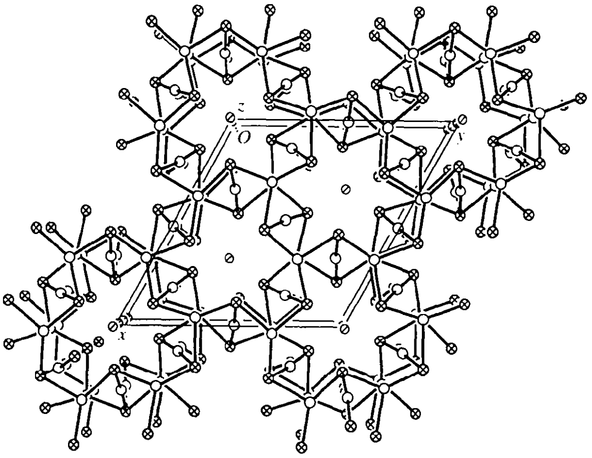

Fig. 1. Unit-cell view of KAg_5S_3. Ag atoms are open circles, S atoms are cross-hatched circles, and K atoms are lined circles.

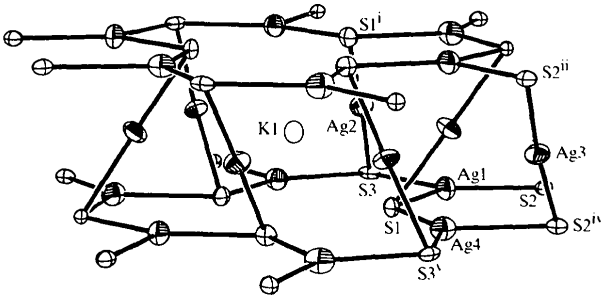

Fig. 2. View of the silver sulfide rings. Ag atoms are full displacement ellipsoids, S atoms are principal ellipsoids, and the K^+ cation is a boundary ellipsoid; all are at the 70% probability level.

The space group $P6_3/mmc$ (No. 194) was also considered. Given the atomic positions reported here in $P\bar{6}2c$, space group No. 194 would result in Ag1 and

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Ag4 being nearly related by mirror symmetry, implying that the unique atom would reside on the 12*j* Wyckoff site. Ag2, S1 and S2 are also nearly mirror-related partners of themselves, suggesting 12*i*, 6*h* and 6*h* sites, respectively, in space group No. 194. Also, Ag3 is near an inversion-related partner of itself, implying it would reside on a 2*a* site. All the above listed atoms are between 0.5 and 1.0 Å from their pseudosymmetry-related partners before refinement. Careful refinements in *P*6$_3$/*mmc*, taking into account occupancy and location, were unsuccessful, and lead us to conclude that at least the heavy (Ag) atoms have only pseudosymmetry and thus $P\bar{6}2c$ is the correct space group choice. This is not unexpected; for example, in $P\bar{6}2c$, Ag1 and Ag4 are both bonded to S1, S2 and S3, yet the individual bond distances (Ag—S1, Ag—S2 and Ag—S3) are quite different. This would not be symmetry-allowed in *P*6$_3$/*mmc*. Silver is a rather 'soft' cation, and these variations in bonding are not atypical (Wood *et al.*, 1992).

Experimental

Single crystals of KAg_5S_3 were obtained from a reaction mixture of K_2S (32 mg, 0.29 mmol), S (44 mg, 0.38 mmol) and Ag (30 mg 0.28 mmol). This mixture was loaded into a 10 cm quartz tube in a dry-box. Subsequently, 0.7 ml (40% fill) of ethylenediamine was added to the reagents. The contents were frozen and the tube was flame sealed. The tubes were placed inside an autoclave, which was counterpressured to 15 200 kPa to keep the tubes from bursting. The autoclave was heated for 60 h at 613 K and then taken out of the furnace and left to cool down to room temperature under flowing air. The dark-red crystals were found in a pale-yellow solution, which also had a light-brown oily phase on top.

Crystal data

KAg_5S_3
$M_r = 674.62$
Hexagonal
$P\bar{6}2c$
$a = 13.196$ (2) Å
$c = 7.943$ (3) Å
$V = 1197.8$ (5) Å^3
$Z = 6$
$D_x = 5.611$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 23.6$–$26.4°$
$\mu = 13.247$ mm^{-1}
$T = 183$ K
Needle
0.224 × 0.192 × 0.160 mm
Dark red

Data collection

Rigaku AFC-7 diffractometer
ω–2θ scans
Absorption correction: empirical *via* ψ scans (Sheldrick, 1991)
$T_{min} = 0.05$, $T_{max} = 0.12$
3393 measured reflections
1095 independent reflections

894 reflections with $F > 4\sigma(F)$
$R_{int} = 0.080$
$\theta_{max} = 28.47°$
$h = -17 \rightarrow 14$
$k = 0 \rightarrow 17$
$l = 0 \rightarrow 10$
3 standard reflections every 100 reflections intensity decay: −0.85%

Refinement

Refinement on *F*
$R = 0.062$
$wR = 0.040$
$S = 2.71$
894 reflections
51 parameters
$w = 1/[\sigma^2(F) + 0.0005F^2]$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 4.1$ e Å^{-3}
$\Delta\rho_{min} = -7.6$ e Å^{-3}

Extinction correction: Zachariasen (1963) type 2 Gaussian isotropic
Extinction coefficient: 4.6 (1) × 10^{-7}
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^i a^j \mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	U_{eq}
Ag1	0.6338 (1)	0.6312 (1)	3/4	0.023 (1)
Ag2	0.8159 (1)	0.6656 (1)	1.0014 (2)	0.021 (1)
Ag3	0.4651 (1)	0.4651 (1)	0	0.019 (1)
Ag4	−0.0041 (1)	0.7034 (1)	3/4	0.021 (1)
K1	1	1	0	0.016 (2)
K2	2/3	1/3	0.0018 (10)	0.016 (1)
S1	0.7838 (4)	0.8634 (4)	3/4	0.014 (2)
S2	0.4150 (4)	0.5329 (4)	3/4	0.012 (2)
S3	0.7783 (4)	0.5509 (3)	3/4	0.013 (2)

Table 2. *Selected geometric parameters (Å, °)*

Ag1—S1	2.691 (4)	Ag4—S1^{iii}	2.516 (4)
Ag1—S2	2.505 (5)	Ag4—S2^{iv}	2.747 (2)
Ag1—S3	2.604 (6)	Ag4—S3^{v}	2.552 (4)
Ag2—S1^{i}	2.397 (3)	K1—S1^{ii} × 6	3.192(3)
Ag2—S3	2.403 (3)	K2—S2^{vi} × 3	3.173(7)
Ag3—S2^{ii} × 2	2.402(3)	K2—S3^{ii} × 3	3.191(5)
S1—Ag1—S2	126.2 (2)	Ag1—S1—Ag4^{iv}	120.2 (2)
S1—Ag1—S3	101.1 (2)	Ag2^{vii}—S1—Ag4^{iv} × 2	75.2(2)
S2—Ag1—S3	132.7 (2)	Ag1—S2—Ag3^{viii} × 2	74.5(1)
S3—Ag2—S1^{i}	177.2 (2)	Ag3^{viii}—S2—Ag3^{ix}	111.5 (2)
S2^{ii}—Ag3—S2^{vi}	174.4 (2)	Ag1—S2—Ag4^{iii}	116.2 (2)
S1^{iii}—Ag4—S2^{iv}	109.8 (2)	Ag3^{ix}—S2—Ag4^{iii} × 2	70.9(1)
S1^{iii}—Ag4—S3^{v}	142.8 (2)	Ag1—S3—Ag2 × 2	72.9(1)
S2^{iv}—Ag4—S3^{v}	107.4 (2)	Ag2—S3—Ag2^{x}	112.4 (2)
Ag1—S1—Ag2^{i} × 2	72.0(1)	Ag1—S3—Ag4^{xi}	116.3 (2)
Ag2^{i}—S1—Ag2^{vii}	110.9 (2)	Ag2—S3—Ag4^{xi} × 2	72.9(1)

Symmetry codes: (i) $y, x, 2 - z$; (ii) $x, y, z - 1$; (iii) $1 - y, 1 + x - y, z$; (iv) $-x + y, 1 - x, z$; (v) $x - 1, y, z$; (vi) $y, x, 1 - z$; (vii) $y, x, z - \frac{1}{2}$; (viii) $x, y, 1 + z$; (ix) $x, y, \frac{1}{2} - z$; (x) $x, y, \frac{3}{2} - z$; (xi) $1 + x, y, z$.

The structure was solved by direct methods and refined by full-matrix least-squares techniques. All atoms were refined with anisotropic displacement parameters. The highest residual peak is located 0.61 Å from Ag1, and the lowest residual peak is located 0.07 Å from Ag4. This large residual electron density is not atypical for the ternary alkali metal–Ag^{I} sulfides or selenides. Displacement parameters on the Ag atoms are generally larger than those of any of the other atoms. An outcome of this observation may be the resultant placement of minimum and maximum difference Fourier peaks near the 'soft' Ag atoms. Another possibility for the large residual electron density may be a less than superior absorption correction. The structure was also refined as the other enantiomorph. The final residuals obtained were essentially the same as those of the reported structure.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software.* Data reduction: *TEXSAN* (Molecular Structure Corporation, 1993).

Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *SHELXTL-Plus* (Sheldrick, 1991).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1202). Services for accessing these data are described at the back of the journal.

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Pentaamminenitrocobalt(III) Dichloride at Pressures of 0.24, 0.52, 1.25, 1.91 and 3.38 GPa

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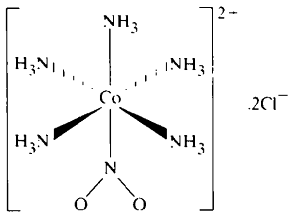
Abstract

The structure of $[Co(NO_2)(NH_3)_5]Cl_2$ has been refined anisotropically from data collected at 0.24, 0.52, 1.25, 1.91 and 3.38 GPa in a diamond anvil cell (DAC). For comparison, the structure of the same crystal in the same DAC was also refined at ambient pressure. The structures at high pressures are anisotropically distorted compared with that at ambient pressure determined in this work and by Börtin [*Acta Chem. Scand.* (1968), **22**, 2890–2898], Kubota & Ohba [*Acta Cryst.* (1992), B**48**, 627–632] and Boldyreva *et al.* [*Acta Cryst.* (1997*c*), C**53**, 523–526], but the space group and the general structural pattern remain the same.

Comment

A comparative study of the structures of the title compound at ambient pressure and at high pressures formed part of a project on the study of the anisotropy of structural distortion of Co^{III}–nitroammine complexes induced by various means, *i.e.* cooling (Boldyreva *et al.*, 1997*a*,*b*,*c*,*d*), increasing pressure (Boldyreva *et al.*, 1994, 1996; Boldyreva, Naumov & Ahsbahs, 1997, 1998*b*; Boldyreva, Kuz'mina & Ahsbahs, 1997), isomorphous substitution and homogeneous linkage isomerization (Boldyreva, 1994, 1996; Boldyreva *et al.*, 1993; Masciocchi *et al.*, 1994).

The present contribution reports on the structural data for the title compound, (I), at ambient pressure, 0.24, 0.52, 1.25, 1.91 and 3.38 GPa, as well as providing details of the data collection and data refinement procedures. A detailed comparison of the structures,



(I)

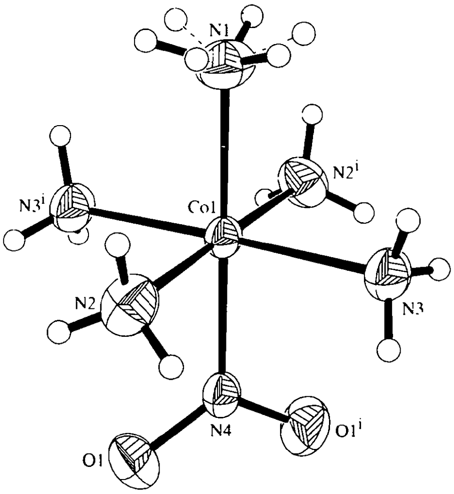


Fig. 1. View of the $[Co(NO_2)(NH_3)_5]^{2+}$ cation showing the labelling of the non-H atoms. Displacement ellipsoids are shown at 50% probability levels as at ambient pressure; H atoms are drawn as small circles of arbitrary radii.