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Crystal structures of the silver iodide sulfates Ag_3ISO_4 and $Ag_4I_2SO_4$

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The crystal structures of two phases in the AgI–Ag_2SO_4 system, Ag_3ISO_4 (AgI:Ag_2SO_4 = 1:1; systematic name: trisilver iodide sulfate), and $Ag_4I_2SO_4$ (AgI:Ag_2SO_4 = 2:1; systematic name: tetrasilver diiodide sulfate), were determined by single-crystal X-ray diffraction. The crystal structure model of Ag_3ISO_4 contains triangularly arranged Ag atoms in zigzag ladder chains extending parallel to the *a* axis. The Ag zigzag ladder chains alternate with rows of SO_4 groups, while iodine atoms are accommodated within the concavities of the zigzag ladders. The crystal structure of $Ag_4I_2SO_4$ was refined using a split-atom model for two of the four Ag sites. The disordered Ag sites are situated between the layers containing SO_4 groups parallel to the *ac* plane, whereas the Ag sites within the SO_4 layers are fully occupied and exhibit no disorder. The positional disorder of some of the Ag sites is considered to be associated with the moderate ionic conductivity of $Ag_4I_2SO_4$, approximately 10^{-3} S cm^{-1} at room temperature. This is the first report describing the crystal structures of compounds containing Ag^+, SO_4^{2-} and I^-.

1. Chemical context

α-Silver iodide (α-AgI) has been known as an Ag^+ superionic conductor. The superionic conductive phase of AgI arises above the phase transition temperature of 420 K, and the ionic conductivity reaches a few S cm^{-1} (Tubandt & Lorenz, 1914; Boyce & Huberman, 1979). α-AgI undergoes a phase transition to the β phase when the temperature is decreased, and the superionic conductivity is lost on the phase transition. The superionic conductivity of Ag^+ at room temperature (RT) has been reported in ternary phases of AgI and alkali halides such as Ag_4RbI_5 (Owens & Argue, 1970, 1967; Geller, 1967; Bradley & Greene, 1967*a*,*b*), Ag_4KI_5 (Owens & Argue, 1967; Bradley & Greene, 1966, 1967*a*,*b*), and Ag_3KI_4 (Takahashi *et al.*, 1970), and AgI and silver oxyacid salts in the glass states such as 0.8AgI–0.2(Ag_2O–B_2O_3) (Chiodelli *et al.*, 1983), 0.58AgI–0.19Ag_2O–0.23WO_3 (Kuwano, 1990), 0.85AgI–0.15$Ag_4P_2O_7$ (Minami *et al.*, 1977, 1980) and 0.75AgI–0.25Ag_2MoO_4 (Minami & Tanaka, 1980*a*,*b*), and in the crystalline state such as $Ag_{19}I_{15}P_2O_7$, $Ag_7I_4PO_4$ (Takahashi *et al.*, 1972*a*) and $Ag_{26}I_{18}(WO_4)_4$ (Chan & Geller, 1977). We have recently reported two crystalline compounds $Ag_{17}(CO_3)_3I_{11}$ (Watanabe *et al.*, 2021) and $Ag_{10}(CO_3)_3I_4$ (Suzuki *et al.*, 2021) in the AgI–Ag_2CO_3 system and found that the former, $Ag_{17}(CO_3)_3I_{11}$, is a superionic conductor with a conductivity of about 0.1 S/cm at RT.

According to the phase diagram of the AgI–Ag_2SO_4 system proposed by Takahashi *et al.* (1972*b*), there is no stable crystalline phase with a specific composition. They reported an

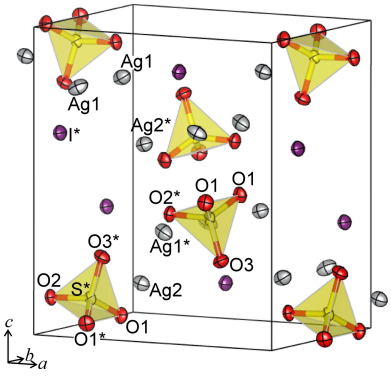

Table 1
Selected bond lengths (Å) for Ag_3ISO_4.

Ag1—O1^{i}	2.384 (3)	Ag2—O1^{i}	2.436 (3)
Ag1—O3	2.413 (3)	Ag2—O2	2.467 (4)
Ag1—O2	2.473 (3)	Ag2—I1^{vi}	2.8066 (7)
Ag1—I1^{ii}	2.7838 (5)	Ag2—I1	3.1714 (7)
Ag1—Ag2^{ii}	2.9973 (6)	S1—O1^{vii}	1.474 (3)
Ag1—Ag1^{iii}	3.0604 (8)	S1—O1	1.474 (3)
Ag1—Ag2^{iv}	3.2744 (6)	S1—O3	1.475 (4)
Ag2—O1^{v}	2.436 (3)	S1—O2^{viii}	1.488 (4)

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

ionic conductivity of 5.0×10^{-2} S cm^{-1} in the glass phase with composition $(1-x)$ AgI–$x(Ag_2SO_4)$ at x = 0.18–0.25. We synthesized new crystalline compounds at x = 0.5 (Ag_3ISO_4) and 0.33 ($Ag_4I_2SO_4$). Polycrystalline bulk samples of Ag_3ISO_4 and $Ag_4I_2SO_4$ prepared at 443 and 417 K had ionic conductivities of 9.5×10^{-6} and 9.2×10^{-4} S cm^{-1} at RT, respectively. These values are higher or comparable with those of $Ag_{13}(AsO_4)_3I_4$ (6.4×10^{-6} S cm^{-1} at 303 K; Pitzschke *et al.*, 2009*a*) and $Ag_{10}(CO_3)_3I_4$ (4.4×10^{-6} S cm^{-1} at RT; Suzuki *et al.*, 2021). The ionic conductivities of Ag_3ISO_4 and $Ag_4I_2SO_4$ are not necessarily high compared to the Ag^+ superionic conductors, but these compounds are important as precursors of superionic conductors in the $(1-x)$ AgI–$x(Ag_2SO_4)$ system.

2. Structural commentary

Ag_3ISO_4 and $Ag_4I_2SO_4$ crystallize with orthorhombic symmetry in the space groups *Pnma* and *Pna*2$_1$, respectively. Figs. 1 and 2 show perspective views of the crystal structures of

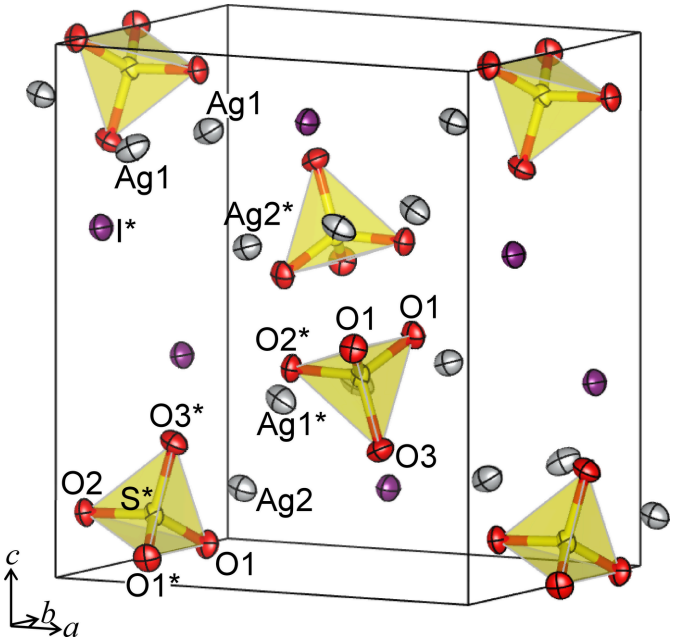

Figure 1
Perspective view of the crystal structure of Ag_3ISO_4. The probability of the anisotropic displacement ellipsoids is 50%. The asterisk denotes atoms located within the asymmetric unit.

Table 2
Selected bond lengths (Å) for $Ag_4I_2SO_4$.

Ag1*A*—O3	2.462 (5)	Ag3*A*—I1^{v}	2.838 (3)
Ag1*A*—O1^{i}	2.468 (7)	Ag3*A*—Ag4	3.184 (2)
Ag1*A*—I2	2.863 (2)	Ag3*B*—O2	2.375 (18)
Ag1*A*—I2^{ii}	3.038 (2)	Ag3*B*—I2	2.608 (17)
Ag1*A*—I1^{iii}	3.039 (5)	Ag3*B*—I1	2.686 (15)
Ag1*A*—Ag3*B*	3.256 (18)	Ag3*C*—O2	2.385 (19)
Ag1*B*—O3	2.412 (8)	Ag3*C*—I1^{v}	2.620 (17)
Ag1*B*—O4^{ii}	2.541 (10)	Ag3*C*—I1	2.694 (16)
Ag1*B*—Ag3*B*	2.805 (19)	Ag3*C*—I2	3.263 (17)
Ag1*B*—I2	2.889 (7)	Ag3*C*—Ag4	3.290 (16)
Ag1*B*—I2^{ii}	3.039 (7)	Ag4—O3^{v}	2.421 (6)
Ag1*B*—Ag3*A*	3.194 (10)	Ag4—O3^{vi}	2.469 (7)
Ag2—O1	2.347 (6)	Ag4—I1^{v}	3.0237 (13)
Ag2—O4^{iv}	2.386 (7)	Ag4—I2	3.0879 (13)
Ag2—O2^{i}	2.423 (5)	Ag4—I1^{iv}	3.1247 (12)
Ag2—I2	2.8799 (9)	Ag4—I2^{vii}	3.1741 (13)
Ag2—Ag3*C*^{iv}	3.283 (18)	S1—O1^{viii}	1.466 (6)
Ag3*A*—O2	2.522 (6)	S1—O2^{viii}	1.468 (5)
Ag3*A*—I2	2.798 (3)	S1—O4	1.469 (7)
Ag3*A*—I1	2.8113 (19)	S1—O3	1.505 (5)

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

Ag_3ISO_4 and $Ag_4I_2SO_4$, and selected interatomic distances are collated in Tables 1 and 2.

Ag_3ISO_4 contains two Ag sites, one I site, one S site, and three O sites in the asymmetric unit; $Ag_4I_2SO_4$ contains four Ag sites, two I sites, one S site, and four O sites. Among the four Ag sites in $Ag_4I_2SO_4$, Ag1 and Ag3 are split into two and three sites, respectively, with occupancies of 0.74 (1) and 0.26 (1) for Ag1*A* and Ag1*B*, and 0.803 (4), 0.098 (4), and 0.099 (4) for Ag3*A*, Ag3*B*, and Ag3*C*. S atoms in both compounds form tetrahedral SO_4 groups, and their S—O distances are 1.474 (3) Å for two O1, 1.488 (4) Å for O2, and 1.475 (4) Å for O3 in Ag_3ISO_4 and 1.466 (6) Å for O1, 1.468 (5) Å for O2, 1.505 (5) Å for O3, and 1.469 (7) Å for O4 in $Ag_4I_2SO_4$. These values are comparable to the bond lengths between S and O in the SO_4 groups found in inorganic crystals, including minerals and compounds such as barite, $BaSO_4$

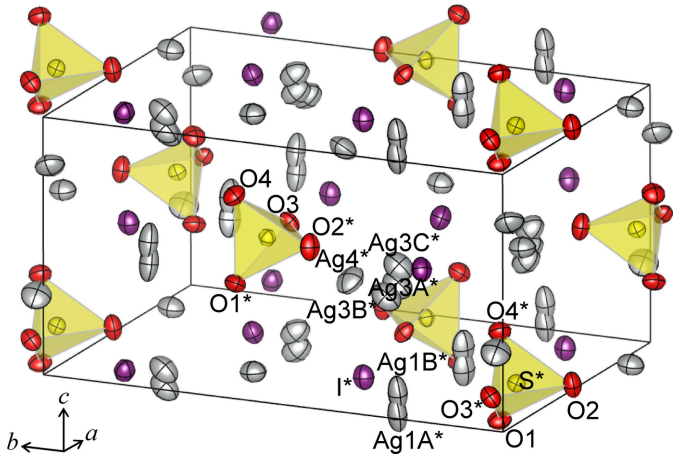

Figure 2
Perspective view of the crystal structure of $Ag_4I_2SO_4$. The probability of the anisotropic displacement ellipsoids is 50%.. The asterisk denotes atoms located within the asymmetric unit.

Table 3
Comparison of interatomic distances (Å) between Ag atoms and anions in several silver compounds.

Compound	Shortest Ag—O	Average Ag—O	Shortest Ag—I	Average Ag—I	Reference
Ag_3ISO_4	2.384	2.431	2.784	2.791	This work
$Ag_4I_2SO_4$	2.346	2.564	2.607	3.034	This work
Ag_2SO_4	2.405	2.511	–	–	Mehrotra *et al.* (1978)
Ag_2CO_3	2.245	2.421	–	–	Norby *et al.* (2002)
$Ag_{10}(CO_3)_3I_4$[i]	2.252	2.437	2.714	3.004	Suzuki *et al.* (2021)
γ-AgI	–	–	2.814	2.814	Hull & Keen (1999)
$Ag_{13}(AsO_4)_3I_4$	2.293	2.375	2.708	3.071	Pitzschke *et al.* (2009*a*)
$Ag_{26}I_{18}(WO_4)_4$	2.195	2.478	2.312	2.916	Chan & Geller (1977)
Ag_4IPO_4[ii]	2.278	2.368	2.706	3.034	Oleneva *et al.* (2008)
$Ag_{16}I_{12}P_2O_7$	1.886	2.340	2.680	2.835	Garrett *et al.* (1982)
$Ag_5IP_2O_7$	2.274	2.466	2.765	2.948	Adams & Preusser (1999)
$Ag_3I(NO_3)_2$	2.250	2.594	2.841	2.942	Birnstock & Britton (1970)
$Ag_8(CrO_4)_3I_2$[iii]	2.384	2.446	2.809	3.053	Pitzschke *et al.* (2009*b*)
$Ag_9I_3(IO_3)_2(SeO_4)_2$	2.306	2.508	2.719	2.886	Pitzschke *et al.* (2008*b*)
Ag_3ITeO_4	2.238	2.455	2.775	2.928	Pitzschke *et al.* (2008*a*)
$Ag_4I_2SeO_4$	2.322	2.508	2.822	3.069	Pitzschke *et al.* (2008*a*)
$Ag_8I_4V_2O_7$	2.182	2.364	1.927	3.128	Adams (1996)
$Ag_9(GeO_4)_2I$	2.106	2.222	3.364	3.431	Pitzschke *et al.* (2009*c*)

Measurement temperatures: (i) 90 K, (ii) 173 K, (iii) 273 K.

(1.464–1.483 Å; Sawada & Takeuchi, 1990), Ag_2SO_4 (1.473 Å; Mehrotra *et al.*, 1978), Na_2SO_4 (1.479 Å; Hawthorne & Ferguson, 1975), and gypsum, $CaSO_4{\cdot}2H_2O$ (1.457–1.461 Å; Cole & Lancucki, 1974).

In Ag_3ISO_4, Ag1 and O1 occupy the Wykoff position 8*d* with site symmetry 1. Ag2, S, O2, O3, and I reside at the 4*c* position with site symmetry *m* perpendicular to the *b* axis. In $Ag_4I_2SO_4$, all the atoms lie on a general position 4*a*.

The silver atoms in Ag_3ISO_4 and $Ag_4I_2SO_4$ are surrounded by oxygen and iodine atoms, and the coordination environments are different between the two structures. All silver atoms in Ag_3ISO_4 are coordinated by three O atoms and one I atom. On the other hand, in $Ag_4I_2SO_4$, Ag1 (split into Ag1*A* and Ag1*B*) is surrounded by three O atoms belonging to two SO_4 groups and nearly coplanar by four I atoms; Ag2 is surrounded by three O atoms of three different SO_4 groups and three I atoms; Ag3 (split into Ag3*A*, Ag3*B*, and Ag3*C*) is coordinated by two O atoms and three I atoms; Ag4 is coordinated in form of a distorted octahedron with four I atoms at the equatorial and two O atoms at the axial positions. Table 3 compares the shortest and average distances of Ag—O and Ag—I in Ag_3ISO_4 and $Ag_4I_2SO_4$ with several silver compounds. Here, the averages were calculated for Ag—O distances shorter than ∼2.8 Å and for Ag—I shorter than ∼3.7 Å. These boundaries are based on the ionic radii of Ag^+, O^{2-}, and I^- (Shannon, 1976). In averaging, a weight was taken into account, and the weight corresponds to the number of bonds present in the unit cell, which is calculated by multiplying the site multiplicity and the occupancy. The shortest Ag—O distances range from 1.886 Å in $Ag_{16}I_{12}P_2O_7$ to 2.405 Å in Ag_2SO_4. The shortest Ag—I distances in Ag_3ISO_4 and $Ag_4I_2SO_4$ are between the shortest Ag—I distance of 2.312 Å in $Ag_{26}I_{18}(WO_4)_4$ and 2.841 Å in $Ag_3I(NO_3)_2$. The average values of Ag—O and Ag—I distances in the title compounds are comparable to those observed for the other silver compounds listed in Table 3; the average Ag—I distance in Ag_3ISO_4, 2.791 Å, is slightly shorter than those in the other compounds, such as 2.814 Å in γ-AgI and 2.835 Å in $Ag_{16}I_{12}P_2O_7$.

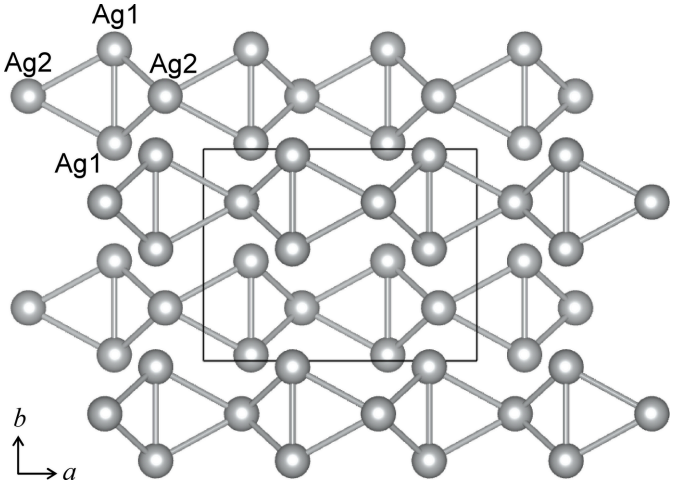

Figure 3
Arrangement of Ag atoms in Ag_3ISO_4. The linkers connect the Ag atoms within 3.3 Å for ease of visibility.

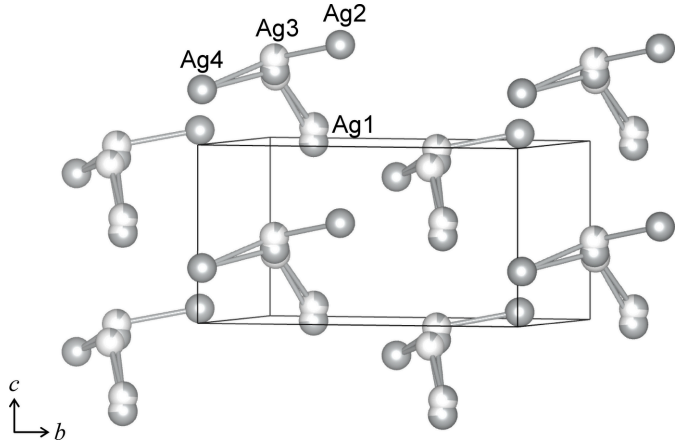

Figure 4
Arrangement of Ag atoms in $Ag_4I_2SO_4$ (sliced view in the range x = 0.5–1.0). The linkers connect the Ag atoms within 3.3 Å for ease of visibility.

The shortest Ag—Ag distance of 2.9973 (6) Å is observed in Ag_3ISO_4 between Ag1 and Ag2 generated by the symmetry operation $-x+\frac{1}{2}, -y+1, z-\frac{1}{2}$. The second shortest Ag—Ag distance is 3.0604 (8) Å between the adjacent Ag1 sites. $Ag_4I_2SO_4$ shows the shortest Ag—Ag distance between Ag1*B* and Ag3*B* of 2.805 (19) Å. These values are comparable to 2.873 Å in Ag_2CO_3 (Norby *et al.*, 2002), 2.880 Å in $Ag_8(CrO_4)_3I_2$ (Pitzschke *et al.*, 2009*b*), and 2.942 Å in $Ag_3I(NO_3)_2$ (Birnstock & Britton, 1970). These rather short Ag—Ag distances are considered to be due to the argentophilic interaction between Ag^+ ions in the d^{10} configuration, which often leads to characteristic arrangements of Ag in several inorganic crystals (Schmidbaur & Schier, 2015; Jansen, 1987). The arrangements of the silver atoms in the crystal structure of Ag_3ISO_4 and $Ag_4I_2SO_4$, excluding the other atoms, are illustrated in Figs. 3 and 4, respectively. In Ag_3ISO_4, the silver atoms form triangles, which are connected to each other by sharing the Ag1—Ag1 edges and the Ag2 corners, comprising zigzag ladder chains extending parallel to the *a* axis (Fig. 3). Fig. S1 (electronic supplementary information) shows the projected views of the crystal structure of Ag_3ISO_4 along the *a* axis (*a*) and *b* axis (*b*). It shows that the rows of SO_4 and the zigzag ladders of Ag are arranged alternately (*a*), and the iodine atoms are held in the concavities of the zigzag ladder chains (*b*). In $Ag_4I_2SO_4$, the Ag atoms form Ag_4 clusters, the arrangement of which in the crystal structure is shown in Fig. 4. The shortest and the second shortest I···I distances in $Ag_4I_2SO_4$ are 4.2135 (10) nd 4.3301 (8) Å. By connecting I1 and I2, helical chains of iodine atoms along the *c* axis are recognized in $Ag_4I_2SO_4$ (Fig. S2). The Ag_4 clusters and the SO_4 groups in $Ag_4I_2SO_4$ fill the space between the helical chains of I atoms.

3. Database survey

The Inorganic Crystal Structure Database (ICSD; Zagorac *et al.*, 2019) contains the crystal structure data for quaternary solid-state inorganic compounds comprising silver and iodide ions and oxyacid groups, such as $Ag_3I(NO_3)_2$ (Birnstock & Britton, 1970), $Ag_{16}I_{12}P_2O_7$ (Garrett *et al.*, 1982), $Ag_5IP_2O_7$ (Adams & Preusser, 1999), Ag_4IPO_4 (Oleneva *et al.*, 2008), $Ag_8(CrO_4)_3I_2$ (Pitzschke *et al.*, 2009*b*), $Ag_9(GeO_4)_2I$ (Pitzschke *et al.*, 2009*c*), $Ag_8I_4V_2O_7$ (Adams, 1996), $Ag_{13}(AsO_4)_3I_4$ (Pitzschke *et al.*, 2009*a*), $Ag_4I_2SeO_4$ (Pitzschke *et al.*, 2008*a*), Ag_3ITeO_4 (Pitzschke *et al.*, 2008*a*), $Ag_9I_3(IO_3)_2(SeO_4)_2$ (Pitzschke *et al.*, 2008*b*) and $Ag_{26}I_{18}(WO_4)_4$ (Chan & Geller, 1977). We have recently reported the crystal structures of two silver carbonate iodides with compositions of $Ag_{17}(CO_3)_3I_{11}$ (Watanabe *et al.*, 2021) and $Ag_{10}(CO_3)_3I_4$ (Suzuki *et al.*, 2021).

There are no data in the ICSD of a phase containing Ag^+, I^-, and SO_4^{2-}. Compounds containing I^- and SO_4^{2-} in the crystal structure included in ICSD are $(Pt(NH_3)_4)_2I_2(HSO_4)_3$-$OH{\cdot}H_2O$ (Clark *et al.*, 1982), $(Pt(NH_3)_4)(PtI_2(NH_3)_4)$-$(HSO_4)_4{\cdot}2H_2O$ (Tanaka *et al.*, 1986) and $H(I(SO_4)_2)$ (Jansen & Müller, 1998).

4. Synthesis and crystallization

The starting material AgI was precipitated at 323 K in aqueous solutions of $AgNO_3$ (99.8%, Kanto Chemical, Japan) and KI (99.5%, Kanto Chemical, Japan); Ag_2SO_4 was precipitated at RT in an aqueous solution of $AgNO_3$ and 5-times diluted sulfuric acid (Kanto Chemical, Japan). The resulting AgI and Ag_2SO_4 powders were thoroughly mixed in an agate mortar at a molar ratio of 1:1 using a small amount of water as a mixing medium. The mixed powder was placed in a glass tube with one end open, heated in air at 433 K for 1 h, and cooled slowly to 408 K at a rate of 0.5 K/h. These conditions were determined after thermogravimetric-differential thermal analysis (TG-DTA) under constant flow of synthetic dry air (Fig. S3). Fig. S3 shows the TG-DTA curves of a mixture of AgI and Ag_2SO_4 powders in a 1:1 ratio. A sharp endothermic effect was observed at 431 K, corresponding to the melting point of this composition. The TG curve showed no substantial mass loss, indicating thermal stability in air up to 520 K. Upon cooling to RT, translucent pale brown lumps were obtained. Like other silver compounds, the silver iodide sulfates are moderately photosensitive, so the samples were treated in the dark under red light through the color filter from an LED lamp. Each fragment of the two types of crystals found in the lumps was fixed on glass fibers with an epoxy resin and mounted on a goniometer. The XRD data were collected at RT in the dark.

Powder samples of Ag_3ISO_4 and $Ag_4I_2SO_4$ were prepared from AgI and Ag_2SO_4 to verify the validity of the crystal structure models determined by single crystal XRD, and the powder data were analyzed using the Rietveld method. Ag_2SO_4 was prepared from an aqueous solution of $AgNO_3$ and sulfuric acid for the synthesis of Ag_3ISO_4, and from aqueous solutions of $AgNO_3$ and Na_2SO_4 for the synthesis of $Ag_4I_2SO_4$. AgI and Ag_2SO_4 were then mixed in molar ratios of 1:1 and 1:2, and heated in air at 414 K for 1 h to obtain Ag_3ISO_4, and at 411 K for 3 h to obtain $Ag_4I_2SO_4$. For $Ag_4I_2SO_4$, in order to reduce unreacted AgI and the by-product Ag_3ISO_4 phase, the heated mixture was slowly cooled to 373 K in the heater, followed by the repeated heat treatment after thorough grinding.

5. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 4.

In the refined model of Ag_3ISO_4, the highest difference electron density peak of 1.18 e Å^{-3} is at a position 0.8646 (5) Å distant from I1. Two difference peaks of 1.10 and 1.03 e Å^{-3} remained at positions 0.7562 (5) and 0.7659 (4) Å distant from Ag1, and two peaks of 0.94 and 0.90 e Å^{-3} at positions 0.7782 (6) and 0.9591 (6) Å distant from Ag2. Difference peaks lower than 0.8 e Å^{-3} were detected near I1 (0.76 e Å^{-3}), O3 (0.60 e Å^{-3}), and Ag2 (0.55 e Å^{-3}).

The crystal structure of $Ag_4I_2SO_4$ was refined using a split-atom model for the Ag1 and Ag3 sites. For Ag1, 74.2% of the silver atoms occupy the Ag1*A* site, while the remaining 25.8%

Table 4
Experimental details.

	Ag_3ISO_4	$Ag_4I_2SO_4$
Crystal data		
Chemical formula	Ag_3ISO_4	$Ag_4I_2SO_4$
M_r	546.57	781.34
Crystal system, space group	Orthorhombic, *Pnma*	Orthorhombic, $Pna2_1$
Temperature (K)	300	301
a, b, c (Å)	8.9418 (6), 6.9182 (5), 10.2660 (7)	9.2072 (3), 13.1007 (4), 6.9528 (2)
V (Å^3)	635.07 (8)	838.65 (4)
Z	4	4
Radiation type	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	14.28	16.77
Crystal size (mm)	0.05 × 0.04 × 0.04	0.10 × 0.03 × 0.01
Data collection		
Diffractometer	Bruker APEXII CCD	Bruker APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Krause *et al.*, 2015)	Multi-scan (*SADABS*; Krause *et al.*, 2015)
T_{min}, T_{max}	0.615, 0.746	0.53, 0.75
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	16851, 790, 770	6220, 1806, 1768
R_{int}	0.039	0.035
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.650	0.649
Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.020, 0.047, 1.15	0.022, 0.051, 1.08
No. of reflections	790	1806
No. of parameters	49	115
No. of restraints	0	2
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.18, −0.87	0.93, −0.79
Absolute structure	–	Refined as an inversion twin
Absolute structure parameter	–	0.35 (4)

Computer programs: *APEX3* and *SAINT* (Bruker, 2017), *SHELXT* (Sheldrick, 2015*a*), *SHELXL* (Sheldrick, 2015*b*), *VESTA* (Momma & Izumi, 2011) and *publCIF* (Westrip, 2010).

are distributed over the Ag1*B* site, located 0.595 (13) Å distant from Ag1*A*. For the Ag3 site, 80.3% of the silver atoms reside on the Ag3*A* site, with approximately 10% each distributed on the Ag3*B* and Ag3*C* sites, located 0.508 (17) and 0.49 (3) Å distant from Ag3*A*, respectively. Figure S4 presents a projection of the crystal structure of $Ag_4I_2SO_4$ along the *a* axis. The disordered Ag1 and Ag3 sites are located between SO_4 layers parallel to the *ac* plane, whereas the Ag2 and Ag4 sites within the SO_4 layers are fully occupied. As described in section 1, $Ag_4I_2SO_4$ exhibits a moderate ionic conductivity of 9.2×10^{-4} S cm^{-1} at RT, and the positional disorder of the Ag sites is considered to be associated with this conductivity. Furthermore, the disorder observed at the Ag1 and Ag3 sites suggests site-dependent contributions to Ag^+ conduction. Specifically, Ag^+ diffusion occurs preferentially within the interlayer spaces between the SO_4 layers via the Ag1 and Ag3 sites, whereas silver atoms at the Ag2 and Ag4 sites provide a minor contribution to Ag^+ conduction. In the refined model of $Ag_4I_2SO_4$, the highest difference electron density peak of 0.93 e Å^{-3} is near the Ag3 site, with distances between 0.800 (3) Å from Ag3*A* and 1.16 (2) Å from Ag3*C*. The second and fourth highest difference peaks (0.79 and 0.57 e Å^{-3}) are at positions 0.8720 (7) and 0.7644 (7) Å distant from I1. The third-highest difference peak of 0.64 e Å^{-3} is found at (0.2880, 0.2611, 0.7269), corresponding to an interstitial position surrounded by two Ag atoms (Ag2 and Ag3), three I atoms, and O1. The distances are 1.86 (3) Å from Ag3*C*, 2.7660 (9) Å from Ag2, 2.6543 (7) and 2.6599 (7) Å from I1, 2.7182 (7) Å from I2, and 2.235 (7) Å from O1.

The structure models refined on basis of single crystal XRD data were verified by powder X-ray data using a Rietveld analysis (PDXL; Rigaku, 2018). The powder XRD data were collected using a Rigaku MiniFlex 600 powder X-ray diffractometer with Cu $K\alpha$ radiation (λ = 1.54183 Å) equipped with a 1D detector (Rigaku D/teX Ultra 250). The refinements were carried out with the atomic coordinates (x, y, z) and the atomic displacement parameters (B) fixed to those determined by the single crystal XRD study, and converged with $R_{wp}/R_p/S$ = 5.31%/3.53%/3.98 for Ag_3ISO_4 and 3.06%/2.40%/1.33 for $Ag_4I_2SO_4$ (Figure S5). The lattice parameters refined by the Rietveld analysis are a = 8.9437 (2), b = 6.9241 (2), and c = 10.2516 (2) Å for Ag_3ISO_4, and a = 9.2026 (4), b = 13.1072 (5), and c = 6.9545 (3) Å for $Ag_4I_2SO_4$. These values are in good agreement with those obtained by the single crystal XRD analysis (Table 4).

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Crystal structures of the silver iodide sulfates Ag_3ISO_4 and $Ag_4I_2SO_4$

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Computing details

Trisilver iodide sulfate (Ag3ISO4)

Crystal data

Ag_3ISO_4
M_r = 546.57
Orthorhombic, *Pnma*
a = 8.9418 (6) Å
b = 6.9182 (5) Å
c = 10.2660 (7) Å
V = 635.07 (8) Å^3
Z = 4
$F(000)$ = 968
D_x = 5.717 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 9985 reflections
θ = 3.0–27.5°
μ = 14.28 mm^{-1}
T = 300 K
Block, translucent colourless-brown
0.05 × 0.04 × 0.04 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: micro focus sealed tube
Detector resolution: 7.3910 pixels mm^{-1}
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Krause *et al.*, 2015)
T_{min} = 0.615, T_{max} = 0.746
16851 measured reflections
790 independent reflections
770 reflections with $I > 2\sigma(I)$
R_{int} = 0.039
θ_{max} = 27.5°, θ_{min} = 3.0°
h = −11→11
k = −8→8
l = −13→13

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.020
$wR(F^2)$ = 0.047
S = 1.15
790 reflections
49 parameters
0 restraints
$w = 1/[\sigma^2(F_o^2) + (0.0157P)^2 + 3.707P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 1.18 e Å^{-3}
$\Delta\rho_{min}$ = −0.87 e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Ag1	0.32585 (4)	0.52882 (5)	0.31134 (4)	0.03257 (12)
Ag2	0.36026 (6)	0.250000	0.61963 (5)	0.02763 (13)
S1	0.13364 (15)	0.250000	0.10724 (13)	0.0164 (3)
O1	0.1902 (3)	0.0758 (4)	0.0410 (3)	0.0241 (6)
O2	0.4673 (4)	0.250000	0.3981 (4)	0.0228 (9)
O3	0.1830 (5)	0.250000	0.2443 (4)	0.0261 (9)
I1	0.00623 (4)	0.250000	0.63835 (4)	0.02701 (12)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ag1	0.0456 (2)	0.0224 (2)	0.0297 (2)	−0.00483 (15)	−0.00981 (15)	0.00358 (13)
Ag2	0.0364 (3)	0.0214 (2)	0.0251 (2)	0.000000	0.00360 (19)	0.000000
S1	0.0173 (6)	0.0124 (6)	0.0196 (6)	0.000000	−0.0023 (5)	0.000000
O1	0.0279 (15)	0.0149 (14)	0.0296 (16)	0.0039 (12)	0.0007 (12)	−0.0033 (12)
O2	0.0167 (19)	0.022 (2)	0.029 (2)	0.000000	0.0022 (17)	0.000000
O3	0.032 (2)	0.025 (2)	0.021 (2)	0.000000	−0.0065 (18)	0.000000
I1	0.0207 (2)	0.0343 (2)	0.0260 (2)	0.000000	−0.00100 (15)	0.000000

Geometric parameters (Å, º)

Ag1—O1^{i}	2.384 (3)	Ag2—O1^{i}	2.436 (3)
Ag1—O3	2.413 (3)	Ag2—O2	2.467 (4)
Ag1—O2	2.473 (3)	Ag2—I1^{vi}	2.8066 (7)
Ag1—I1^{ii}	2.7838 (5)	Ag2—I1	3.1714 (7)
Ag1—Ag2^{ii}	2.9973 (6)	S1—O1^{vii}	1.474 (3)
Ag1—Ag1^{iii}	3.0604 (8)	S1—O1	1.474 (3)
Ag1—Ag2^{iv}	3.2744 (6)	S1—O3	1.475 (4)
Ag2—O1^{v}	2.436 (3)	S1—O2^{viii}	1.488 (4)
O1^{i}—Ag1—O3	111.03 (13)	Ag1^{x}—Ag2—I1	53.562 (13)
O1^{i}—Ag1—O2	77.35 (12)	O1^{v}—Ag2—Ag1^{iv}	131.52 (7)
O3—Ag1—O2	75.51 (11)	O1^{i}—Ag2—Ag1^{iv}	78.36 (7)
O1^{i}—Ag1—I1^{ii}	126.05 (7)	O2—Ag2—Ag1^{iv}	82.36 (9)
O3—Ag1—I1^{ii}	122.87 (11)	I1^{vi}—Ag2—Ag1^{iv}	53.825 (13)
O2—Ag1—I1^{ii}	112.50 (9)	Ag1^{ix}—Ag2—Ag1^{iv}	95.464 (13)
O1^{i}—Ag1—Ag2^{ii}	123.11 (7)	Ag1^{x}—Ag2—Ag1^{iv}	124.916 (17)
O3—Ag1—Ag2^{ii}	85.82 (8)	I1—Ag2—Ag1^{iv}	147.406 (12)
O2—Ag1—Ag2^{ii}	156.75 (9)	O1^{v}—Ag2—Ag1^{xi}	78.36 (7)
I1^{ii}—Ag1—Ag2^{ii}	66.419 (15)	O1^{i}—Ag2—Ag1^{xi}	131.52 (7)
O1^{i}—Ag1—Ag1^{iii}	82.17 (7)	O2—Ag2—Ag1^{xi}	82.36 (9)
O3—Ag1—Ag1^{iii}	143.06 (8)	I1^{vi}—Ag2—Ag1^{xi}	53.825 (13)
O2—Ag1—Ag1^{iii}	141.27 (8)	Ag1^{ix}—Ag2—Ag1^{xi}	124.916 (17)
I1^{ii}—Ag1—Ag1^{iii}	56.657 (9)	Ag1^{x}—Ag2—Ag1^{xi}	95.464 (13)
Ag2^{ii}—Ag1—Ag1^{iii}	59.302 (9)	I1—Ag2—Ag1^{xi}	147.406 (12)

O1^{i}—Ag1—Ag2^{iv}	76.94 (7)	Ag1^{iv}—Ag2—Ag1^{xi}	55.720 (16)
O3—Ag1—Ag2^{iv}	152.71 (9)	O1^{vii}—S1—O1	109.7 (3)
O2—Ag1—Ag2^{iv}	81.26 (8)	O1^{vii}—S1—O3	109.73 (16)
I1^{ii}—Ag1—Ag2^{iv}	54.469 (13)	O1—S1—O3	109.73 (16)
Ag2^{ii}—Ag1—Ag2^{iv}	112.299 (13)	O1^{vii}—S1—O2^{viii}	109.04 (16)
Ag1^{iii}—Ag1—Ag2^{iv}	62.141 (8)	O1—S1—O2^{viii}	109.04 (16)
O1^{v}—Ag2—O1^{i}	135.36 (14)	O3—S1—O2^{viii}	109.5 (3)
O1^{v}—Ag2—O2	76.49 (8)	S1—O1—Ag1^{xii}	123.18 (18)
O1^{i}—Ag2—O2	76.49 (8)	S1—O1—Ag2^{xiii}	122.67 (17)
O1^{v}—Ag2—I1^{vi}	112.31 (7)	Ag1^{xii}—O1—Ag2^{xiii}	100.99 (11)
O1^{i}—Ag2—I1^{vi}	112.31 (7)	S1^{xiv}—O2—Ag2	114.9 (2)
O2—Ag2—I1^{vi}	129.46 (10)	S1^{xiv}—O2—Ag1^{vii}	119.86 (13)
O1^{v}—Ag2—Ag1^{ix}	125.95 (7)	Ag2—O2—Ag1^{vii}	97.68 (11)
O1^{i}—Ag2—Ag1^{ix}	69.06 (7)	S1^{xiv}—O2—Ag1	119.86 (13)
O2—Ag2—Ag1^{ix}	145.14 (4)	Ag2—O2—Ag1	97.68 (11)
I1^{vi}—Ag2—Ag1^{ix}	71.152 (15)	Ag1^{vii}—O2—Ag1	102.54 (15)
O1^{v}—Ag2—Ag1^{x}	69.06 (7)	S1—O3—Ag1^{vii}	115.50 (15)
O1^{i}—Ag2—Ag1^{x}	125.95 (7)	S1—O3—Ag1	115.50 (15)
O2—Ag2—Ag1^{x}	145.14 (4)	Ag1^{vii}—O3—Ag1	106.12 (16)
I1^{vi}—Ag2—Ag1^{x}	71.152 (15)	Ag1^{ix}—I1—Ag1^{x}	66.688 (19)
Ag1^{ix}—Ag2—Ag1^{x}	61.397 (17)	Ag1^{ix}—I1—Ag2^{xv}	71.707 (15)
O1^{v}—Ag2—I1	80.51 (7)	Ag1^{x}—I1—Ag2^{xv}	71.707 (15)
O1^{i}—Ag2—I1	80.51 (7)	Ag1^{ix}—I1—Ag2	60.018 (13)
O2—Ag2—I1	116.30 (10)	Ag1^{x}—I1—Ag2	60.018 (13)
I1^{vi}—Ag2—I1	114.243 (18)	Ag2^{xv}—I1—Ag2	121.190 (18)
Ag1^{ix}—Ag2—I1	53.563 (13)		

Symmetry codes: (i) −*x*+1/2, *y*+1/2, *z*+1/2; (ii) −*x*+1/2, −*y*+1, *z*−1/2; (iii) *x*, −*y*+3/2, *z*; (iv) −*x*+1, −*y*+1, −*z*+1; (v) −*x*+1/2, −*y*, *z*+1/2; (vi) *x*+1/2, *y*, −*z*+3/2; (vii) *x*, −*y*+1/2, *z*; (viii) *x*−1/2, *y*, −*z*+1/2; (ix) −*x*+1/2, −*y*+1, *z*+1/2; (x) −*x*+1/2, *y*−1/2, *z*+1/2; (xi) −*x*+1, *y*−1/2, −*z*+1; (xii) −*x*+1/2, *y*−1/2, *z*−1/2; (xiii) −*x*+1/2, −*y*, *z*−1/2; (xiv) *x*+1/2, *y*, −*z*+1/2; (xv) *x*−1/2, *y*, −*z*+3/2.

Tetrasilver diiodide sulfate (Ag4I2SO4)

Crystal data

$Ag_4I_2SO_4$
M_r = 781.34
Orthorhombic, *Pna*2$_1$
a = 9.2072 (3) Å
b = 13.1007 (4) Å
c = 6.9528 (2) Å
V = 838.65 (4) Å^3
Z = 4
F(000) = 1368

D_x = 6.188 Mg m^{-3}
Mo *Kα* radiation, *λ* = 0.71073 Å
Cell parameters from 6005 reflections
θ = 2.7–27.5°
μ = 16.77 mm^{-1}
T = 301 K
Platelet, translucent light colourless-brown
0.10 × 0.03 × 0.01 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: micro focus sealed tube
Detector resolution: 7.3910 pixels mm^{-1}
φ and *ω* scans

Absorption correction: multi-scan (*SADABS*; Krause *et al.*, 2015)
T_{min} = 0.53, T_{max} = 0.75
6220 measured reflections
1806 independent reflections
1768 reflections with $I > 2\sigma(I)$

R_{int} = 0.035
θ_{max} = 27.5°, θ_{min} = 2.7°
h = −11→11
k = −14→17
l = −8→9

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.022
$wR(F^2)$ = 0.051
S = 1.08
1806 reflections
115 parameters
2 restraints

$w = 1/[\sigma^2(F_o^2) + (0.017P)^2 + 1.4488P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.93 e Å^{-3}
$\Delta\rho_{min}$ = −0.79 e Å^{-3}
Extinction correction: SHELXL-2017/1 (Sheldrick 2015b)
Extinction coefficient: 0.00063 (15)
Absolute structure: Refined as an inversion twin
Absolute structure parameter: 0.35 (4)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.
Refinement. Refined as a 2-component inversion twin.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
Ag1A	0.0380 (2)	0.24220 (17)	0.0000 (8)	0.0529 (8)	0.742 (10)
Ag1B	0.0376 (7)	0.2412 (6)	0.0855 (16)	0.0529 (8)	0.258 (10)
Ag2	0.11553 (8)	0.58050 (6)	0.06521 (13)	0.04291 (19)	
Ag3A	0.2608 (2)	0.31320 (14)	0.4098 (4)	0.0525 (4)	0.803 (4)
Ag3B	0.2122 (16)	0.3217 (11)	0.379 (3)	0.0525 (4)	0.098 (4)
Ag3C	0.2674 (19)	0.3129 (13)	0.480 (3)	0.0525 (4)	0.099 (4)
Ag4	0.48770 (11)	0.48881 (8)	0.31016 (16)	0.0547 (3)	
S1	0.31461 (18)	0.07193 (12)	0.0636 (3)	0.0208 (3)	
O1	0.1337 (7)	0.6252 (5)	0.3912 (9)	0.0317 (14)	
O2	0.1397 (6)	0.4646 (4)	0.5663 (12)	0.0350 (13)	
O3	0.1513 (5)	0.0756 (4)	0.0660 (10)	0.0263 (11)	
O4	0.3705 (7)	0.1259 (5)	0.2334 (10)	0.0337 (15)	
I1	0.04299 (6)	0.19055 (4)	0.57387 (12)	0.03413 (16)	
I2	0.26710 (6)	0.38893 (4)	0.03359 (10)	0.03490 (16)	

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ag1A	0.0359 (4)	0.0306 (4)	0.092 (2)	0.0056 (3)	−0.0114 (10)	0.0028 (11)
Ag1B	0.0359 (4)	0.0306 (4)	0.092 (2)	0.0056 (3)	−0.0114 (10)	0.0028 (11)
Ag2	0.0453 (4)	0.0525 (4)	0.0309 (4)	0.0006 (3)	−0.0006 (3)	−0.0021 (4)
Ag3A	0.0425 (8)	0.0608 (7)	0.0541 (11)	−0.0027 (6)	0.0023 (10)	0.0136 (8)
Ag3B	0.0425 (8)	0.0608 (7)	0.0541 (11)	−0.0027 (6)	0.0023 (10)	0.0136 (8)
Ag3C	0.0425 (8)	0.0608 (7)	0.0541 (11)	−0.0027 (6)	0.0023 (10)	0.0136 (8)

Ag4	0.0615 (5)	0.0574 (5)	0.0452 (5)	0.0062 (4)	0.0188 (4)	−0.0102 (4)
S1	0.0196 (8)	0.0210 (7)	0.0218 (8)	−0.0008 (6)	0.0004 (7)	−0.0001 (9)
O1	0.036 (3)	0.036 (4)	0.023 (3)	0.005 (3)	−0.006 (2)	0.001 (3)
O2	0.029 (3)	0.025 (2)	0.051 (4)	−0.004 (2)	0.004 (3)	0.003 (4)
O3	0.019 (2)	0.030 (2)	0.030 (3)	0.0000 (19)	0.004 (3)	0.008 (3)
O4	0.036 (3)	0.036 (4)	0.029 (3)	−0.001 (3)	−0.005 (3)	−0.005 (3)
I1	0.0326 (3)	0.0300 (3)	0.0397 (3)	−0.00035 (19)	0.0040 (3)	0.0033 (3)
I2	0.0268 (3)	0.0339 (3)	0.0440 (4)	0.00010 (18)	0.0011 (3)	0.0008 (3)

Geometric parameters (Å, º)

Ag1A—Ag1B	0.595 (7)	Ag3A—I1^{v}	2.838 (3)
Ag1A—O3	2.462 (5)	Ag3A—Ag4	3.184 (2)
Ag1A—O1^{i}	2.468 (7)	Ag3B—Ag3C	0.88 (3)
Ag1A—I2	2.863 (2)	Ag3B—O2	2.375 (18)
Ag1A—I2^{ii}	3.038 (2)	Ag3B—I2	2.608 (17)
Ag1A—I1^{iii}	3.039 (5)	Ag3B—I1	2.686 (15)
Ag1A—Ag3B	3.256 (18)	Ag3C—O2	2.385 (19)
Ag1B—O3	2.412 (8)	Ag3C—I1^{v}	2.620 (17)
Ag1B—O4^{ii}	2.541 (10)	Ag3C—I1	2.694 (16)
Ag1B—Ag3B	2.805 (19)	Ag3C—I2	3.263 (17)
Ag1B—I2	2.889 (7)	Ag3C—Ag4	3.290 (16)
Ag1B—I2^{ii}	3.039 (7)	Ag4—O3^{v}	2.421 (6)
Ag1B—Ag3A	3.194 (10)	Ag4—O3^{vi}	2.469 (7)
Ag2—O1	2.347 (6)	Ag4—I1^{v}	3.0237 (13)
Ag2—O4^{iv}	2.386 (7)	Ag4—I2	3.0879 (13)
Ag2—O2^{i}	2.423 (5)	Ag4—I1^{iv}	3.1247 (12)
Ag2—I2	2.8799 (9)	Ag4—I2^{vii}	3.1741 (13)
Ag2—Ag3C^{iv}	3.283 (18)	S1—O1^{viii}	1.466 (6)
Ag3A—Ag3B	0.508 (14)	S1—O2^{viii}	1.468 (5)
Ag3A—O2	2.522 (6)	S1—O4	1.469 (7)
Ag3A—I2	2.798 (3)	S1—O3	1.505 (5)
Ag3A—I1	2.8113 (19)		

Ag1B—Ag1A—O3	78.3 (9)	I2—Ag4—I1^{iv}	88.37 (3)
Ag1B—Ag1A—O1^{i}	108.5 (9)	O3^{v}—Ag4—I2^{vii}	94.40 (13)
O3—Ag1A—O1^{i}	162.3 (2)	O3^{vi}—Ag4—I2^{vii}	77.50 (12)
Ag1B—Ag1A—I2	86.5 (9)	I1^{v}—Ag4—I2^{vii}	88.60 (3)
O3—Ag1A—I2	105.54 (14)	I2—Ag4—I2^{vii}	170.55 (4)
O1^{i}—Ag1A—I2	91.39 (17)	I1^{iv}—Ag4—I2^{vii}	83.97 (3)
Ag1B—Ag1A—I2^{ii}	84.5 (9)	O3^{v}—Ag4—Ag3A	107.99 (13)
O3—Ag1A—I2^{ii}	80.34 (13)	O3^{vi}—Ag4—Ag3A	80.56 (12)
O1^{i}—Ag1A—I2^{ii}	84.01 (16)	I1^{v}—Ag4—Ag3A	54.34 (5)
I2—Ag1A—I2^{ii}	168.03 (17)	I2—Ag4—Ag3A	52.97 (5)
Ag1B—Ag1A—I1^{iii}	165.8 (9)	I1^{iv}—Ag4—Ag3A	131.78 (6)
O3—Ag1A—I1^{iii}	88.7 (2)	I2^{vii}—Ag4—Ag3A	136.45 (6)
O1^{i}—Ag1A—I1^{iii}	82.4 (2)	O3^{v}—Ag4—Ag3C	113.0 (3)
I2—Ag1A—I1^{iii}	102.59 (13)	O3^{vi}—Ag4—Ag3C	75.2 (3)

I2^{ii}—Ag1A—I1^{iii}	87.79 (10)	I1^{v}—Ag4—Ag3C	48.8 (3)
Ag1B—Ag1A—Ag3B	37.0 (9)	I2—Ag4—Ag3C	61.4 (3)
O3—Ag1A—Ag3B	85.6 (3)	I1^{iv}—Ag4—Ag3C	136.5 (3)
O1^{i}—Ag1A—Ag3B	109.8 (3)	I2^{vii}—Ag4—Ag3C	128.0 (3)
I2—Ag1A—Ag3B	49.9 (3)	Ag3A—Ag4—Ag3C	8.6 (3)
I2^{ii}—Ag1A—Ag3B	121.5 (3)	O1^{viii}—S1—O2^{viii}	111.9 (4)
I1^{iii}—Ag1A—Ag3B	148.5 (3)	O1^{viii}—S1—O4	108.3 (3)
Ag1A—Ag1B—O3	87.8 (9)	O2^{viii}—S1—O4	110.5 (4)
Ag1A—Ag1B—O4^{ii}	113.2 (9)	O1^{viii}—S1—O3	108.6 (4)
O3—Ag1B—O4^{ii}	154.4 (5)	O2^{viii}—S1—O3	108.5 (3)
Ag1A—Ag1B—Ag3B	135.6 (10)	O4—S1—O3	109.0 (4)
O3—Ag1B—Ag3B	97.5 (4)	S1^{vi}—O1—Ag2	134.0 (4)
O4^{ii}—Ag1B—Ag3B	78.2 (4)	S1^{vi}—O1—Ag1A^{x}	107.0 (4)
Ag1A—Ag1B—I2	81.6 (9)	Ag2—O1—Ag1A^{x}	115.2 (3)
O3—Ag1B—I2	106.1 (3)	S1^{vi}—O2—Ag3B	131.9 (5)
O4^{ii}—Ag1B—I2	92.0 (3)	S1^{vi}—O2—Ag3C	130.8 (5)
Ag3B—Ag1B—I2	54.5 (3)	Ag3B—O2—Ag3C	21.2 (6)
Ag1A—Ag1B—I2^{ii}	84.3 (9)	S1^{vi}—O2—Ag2^{x}	120.8 (3)
O3—Ag1B—I2^{ii}	81.1 (2)	Ag3B—O2—Ag2^{x}	94.5 (4)
O4^{ii}—Ag1B—I2^{ii}	86.4 (2)	Ag3C—O2—Ag2^{x}	105.9 (5)
Ag3B—Ag1B—I2^{ii}	140.1 (5)	S1^{vi}—O2—Ag3A	128.4 (4)
I2—Ag1B—I2^{ii}	163.8 (4)	Ag3B—O2—Ag3A	11.4 (4)
Ag1A—Ag1B—Ag3A	134.0 (10)	Ag3C—O2—Ag3A	11.1 (4)
O3—Ag1B—Ag3A	91.5 (3)	Ag2^{x}—O2—Ag3A	103.6 (2)
O4^{ii}—Ag1B—Ag3A	84.3 (3)	S1—O3—Ag1B	117.6 (3)
Ag3B—Ag1B—Ag3A	6.3 (3)	S1—O3—Ag4^{ii}	128.2 (4)
I2—Ag1B—Ag3A	54.51 (14)	Ag1B—O3—Ag4^{ii}	90.2 (3)
I2^{ii}—Ag1B—Ag3A	141.0 (4)	S1—O3—Ag1A	116.7 (3)
O1—Ag2—O4^{iv}	150.21 (19)	Ag1B—O3—Ag1A	13.97 (18)
O1—Ag2—O2^{i}	97.3 (3)	Ag4^{ii}—O3—Ag1A	100.2 (2)
O4^{iv}—Ag2—O2^{i}	96.7 (3)	S1—O3—Ag4^{viii}	119.7 (4)
O1—Ag2—I2	104.87 (16)	Ag1B—O3—Ag4^{viii}	103.3 (3)
O4^{iv}—Ag2—I2	96.73 (16)	Ag4^{ii}—O3—Ag4^{viii}	91.27 (16)
O2^{i}—Ag2—I2	104.94 (13)	Ag1A—O3—Ag4^{viii}	93.1 (2)
O1—Ag2—Ag3C^{iv}	85.3 (4)	S1—O4—Ag2^{ix}	132.5 (4)
O4^{iv}—Ag2—Ag3C^{iv}	65.0 (3)	S1—O4—Ag1B^{v}	102.5 (4)
O2^{i}—Ag2—Ag3C^{iv}	123.0 (3)	Ag2^{ix}—O4—Ag1B^{v}	122.0 (4)
I2—Ag2—Ag3C^{iv}	129.4 (3)	Ag3C^{ii}—I1—Ag3B	116.6 (6)
Ag3B—Ag3A—O2	68 (2)	Ag3C^{ii}—I1—Ag3C	133.9 (5)
Ag3B—Ag3A—I2	63 (2)	Ag3B—I1—Ag3C	18.7 (5)
O2—Ag3A—I2	97.68 (19)	Ag3C^{ii}—I1—Ag3A	126.9 (4)
Ag3B—Ag3A—I1	70.6 (18)	Ag3B—I1—Ag3A	10.3 (3)
O2—Ag3A—I1	87.66 (14)	Ag3C—I1—Ag3A	10.0 (4)
I2—Ag3A—I1	126.63 (9)	Ag3C^{ii}—I1—Ag3A^{ii}	9.3 (4)
Ag3B—Ag3A—I1^{v}	168.1 (17)	Ag3B—I1—Ag3A^{ii}	109.8 (3)
O2—Ag3A—I1^{v}	104.18 (17)	Ag3C—I1—Ag3A^{ii}	128.0 (4)
I2—Ag3A—I1^{v}	111.27 (7)	Ag3A—I1—Ag3A^{ii}	119.99 (8)
I1—Ag3A—I1^{v}	118.69 (9)	Ag3C^{ii}—I1—Ag4^{ii}	70.9 (4)

Ag3B—Ag3A—Ag4	109.1 (17)	Ag3B—I1—Ag4^{ii}	106.8 (4)
O2—Ag3A—Ag4	79.38 (13)	Ag3C—I1—Ag4^{ii}	116.4 (4)
I2—Ag3A—Ag4	61.75 (5)	Ag3A—I1—Ag4^{ii}	108.56 (5)
I1—Ag3A—Ag4	165.76 (9)	Ag3A^{ii}—I1—Ag4^{ii}	65.71 (4)
I1^{v}—Ag3A—Ag4	59.95 (5)	Ag3C^{ii}—I1—Ag1A^{xi}	103.4 (4)
Ag3B—Ag3A—Ag1B	37 (2)	Ag3B—I1—Ag1A^{xi}	111.0 (4)
O2—Ag3A—Ag1B	104.6 (2)	Ag3C—I1—Ag1A^{xi}	96.5 (4)
I2—Ag3A—Ag1B	57.19 (18)	Ag3A—I1—Ag1A^{xi}	106.20 (7)
I1—Ag3A—Ag1B	70.03 (18)	Ag3A^{ii}—I1—Ag1A^{xi}	112.45 (6)
I1^{v}—Ag3A—Ag1B	150.21 (16)	Ag4^{ii}—I1—Ag1A^{xi}	139.61 (5)
Ag4—Ag3A—Ag1B	118.82 (19)	Ag3C^{ii}—I1—Ag4^{ix}	91.6 (4)
Ag3A—Ag3B—Ag3C	29 (2)	Ag3B—I1—Ag4^{ix}	149.2 (3)
Ag3A—Ag3B—O2	101 (2)	Ag3C—I1—Ag4^{ix}	134.4 (4)
Ag3C—Ag3B—O2	80.0 (16)	Ag3A—I1—Ag4^{ix}	139.57 (5)
Ag3A—Ag3B—I2	107 (2)	Ag3A^{ii}—I1—Ag4^{ix}	96.54 (5)
Ag3C—Ag3B—I2	132.3 (15)	Ag4^{ii}—I1—Ag4^{ix}	69.285 (12)
O2—Ag3B—I2	107.1 (6)	Ag1A^{xi}—I1—Ag4^{ix}	71.00 (5)
Ag3A—Ag3B—I1	99.1 (19)	Ag3B—I2—Ag3A	10.0 (3)
Ag3C—Ag3B—I1	81.2 (14)	Ag3B—I2—Ag1A	72.9 (4)
O2—Ag3B—I1	93.7 (6)	Ag3A—I2—Ag1A	79.80 (12)
I2—Ag3B—I1	142.4 (7)	Ag3B—I2—Ag2	97.5 (3)
Ag3A—Ag3B—Ag1B	137 (2)	Ag3A—I2—Ag2	103.15 (5)
Ag3C—Ag3B—Ag1B	150.2 (19)	Ag1A—I2—Ag2	103.55 (5)
O2—Ag3B—Ag1B	122.3 (6)	Ag3B—I2—Ag1B	61.1 (4)
I2—Ag3B—Ag1B	64.4 (4)	Ag3A—I2—Ag1B	68.3 (2)
I1—Ag3B—Ag1B	78.1 (4)	Ag1A—I2—Ag1B	11.86 (15)
Ag3A—Ag3B—Ag1A	135 (2)	Ag2—I2—Ag1B	102.70 (14)
Ag3C—Ag3B—Ag1A	153.4 (19)	Ag3B—I2—Ag1A^{v}	92.2 (3)
O2—Ag3B—Ag1A	123.9 (6)	Ag3A—I2—Ag1A^{v}	83.59 (11)
I2—Ag3B—Ag1A	57.2 (4)	Ag1A—I2—Ag1A^{v}	102.64 (3)
I1—Ag3B—Ag1A	85.3 (4)	Ag2—I2—Ag1A^{v}	153.71 (5)
Ag1B—Ag3B—Ag1A	7.34 (19)	Ag1B—I2—Ag1A^{v}	103.38 (17)
Ag3B—Ag3C—O2	78.8 (15)	Ag3B—I2—Ag1B^{v}	82.0 (4)
Ag3B—Ag3C—I1^{v}	139.8 (16)	Ag3A—I2—Ag1B^{v}	73.0 (2)
O2—Ag3C—I1^{v}	115.5 (7)	Ag1A—I2—Ag1B^{v}	103.69 (16)
Ag3B—Ag3C—I1	80.1 (14)	Ag2—I2—Ag1B^{v}	151.25 (14)
O2—Ag3C—I1	93.3 (6)	Ag1B—I2—Ag1B^{v}	102.05 (7)
I1^{v}—Ag3C—I1	132.3 (7)	Ag1A^{v}—I2—Ag1B^{v}	11.23 (14)
Ag3B—Ag3C—I2	36.3 (13)	Ag3B—I2—Ag4	72.4 (3)
O2—Ag3C—I2	89.1 (5)	Ag3A—I2—Ag4	65.28 (5)
I1^{v}—Ag3C—I2	104.0 (5)	Ag1A—I2—Ag4	145.07 (11)
I1—Ag3C—I2	114.2 (6)	Ag2—I2—Ag4	84.37 (3)
Ag3B—Ag3C—Ag2^{ix}	117.2 (18)	Ag1B—I2—Ag4	133.4 (2)
O2—Ag3C—Ag2^{ix}	152.8 (7)	Ag1A^{v}—I2—Ag4	75.37 (8)
I1^{v}—Ag3C—Ag2^{ix}	67.8 (4)	Ag1B^{v}—I2—Ag4	67.96 (17)
I1—Ag3C—Ag2^{ix}	69.9 (4)	Ag3B—I2—Ag4^{xii}	139.4 (3)
I2—Ag3C—Ag2^{ix}	117.0 (5)	Ag3A—I2—Ag4^{xii}	130.63 (5)
Ag3B—Ag3C—Ag4	88.6 (15)	Ag1A—I2—Ag4^{xii}	145.36 (11)

O2—Ag3C—Ag4	79.1 (5)	Ag2—I2—Ag4^{xii}	86.69 (3)
I1^{v}—Ag3C—Ag4	60.3 (3)	Ag1B—I2—Ag4^{xii}	156.9 (2)
I1—Ag3C—Ag4	167.4 (7)	Ag1A^{v}—I2—Ag4^{xii}	70.35 (7)
I2—Ag3C—Ag4	56.2 (3)	Ag1B^{v}—I2—Ag4^{xii}	76.02 (16)
Ag2^{ix}—Ag3C—Ag4	120.8 (5)	Ag4—I2—Ag4^{xii}	67.860 (11)
O3^{v}—Ag4—O3^{vi}	171.17 (7)	Ag3B—I2—Ag3C	11.5 (5)
O3^{v}—Ag4—I1^{v}	92.83 (15)	Ag3A—I2—Ag3C	3.2 (3)
O3^{vi}—Ag4—I1^{v}	90.48 (13)	Ag1A—I2—Ag3C	82.7 (3)
O3^{v}—Ag4—I2	79.91 (14)	Ag2—I2—Ag3C	101.2 (3)
O3^{vi}—Ag4—I2	107.64 (13)	Ag1B—I2—Ag3C	71.2 (4)
I1^{v}—Ag4—I2	99.15 (3)	Ag1A^{v}—I2—Ag3C	84.3 (3)
O3^{v}—Ag4—I1^{iv}	89.01 (14)	Ag1B^{v}—I2—Ag3C	73.4 (4)
O3^{vi}—Ag4—I1^{iv}	86.69 (13)	Ag4—I2—Ag3C	62.3 (3)
I1^{v}—Ag4—I1^{iv}	172.46 (4)	Ag4^{xii}—I2—Ag3C	128.3 (3)

Symmetry codes: (i) −*x*, −*y*+1, *z*−1/2; (ii) *x*−1/2, −*y*+1/2, *z*; (iii) *x*, *y*, *z*−1; (iv) −*x*+1/2, *y*+1/2, *z*−1/2; (v) *x*+1/2, −*y*+1/2, *z*; (vi) −*x*+1/2, *y*+1/2, *z*+1/2; (vii) −*x*+1, −*y*+1, *z*+1/2; (viii) −*x*+1/2, *y*−1/2, *z*−1/2; (ix) −*x*+1/2, *y*−1/2, *z*+1/2; (x) −*x*, −*y*+1, *z*+1/2; (xi) *x*, *y*, *z*+1; (xii) −*x*+1, −*y*+1, *z*−1/2.