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Structure Refinement of Three Caesium Mercury Iodides, $Cs_2Hg_3I_8.H_2O$, Cs_2HgI_4 and Cs_3HgI_5

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Abstract. The crystal structures of three double iodides commonly formed from water solutions of caesium iodide and mercury diiodide have been redetermined at room temperature, Mo $K\alpha$ radiation, $\lambda = 0·71093$ Å. In order of increasing caesium iodide content they are: (I) $Cs_2Hg_3I_8.H_2O$, $M_r = 1900·83$, monoclinic, *Cm*, $a = 7·451\,(1)$, $b = 21·721\,(3)$, $c = 7·685\,(1)$ Å, $\beta = 108·03\,(1)°$, $V = 1182·7\,(3)$ Å^3, $Z = 2$, $D_x = 5·338\,(1)$ g cm^{-3}, $\mu = 327·4$ cm^{-1}, $R = 0·032$ for 1956 observed reflections; (II) Cs_2HgI_4, $M_r = 974·02$, monoclinic, $P2_1/m$, $a = 7·734\,(1)$, $b = 8·386\,(1)$, $c = 11·019\,(1)$ Å, $\beta = 110·06\,(1)°$, $V = 671·2\,(1)$ Å^3, $Z = 2$, $D_x = 4·820\,(1)$ g cm^{-3}, $\mu = 258·2$ cm^{-1}, $R = 0·032$ for 2009 observed reflections; (III) Cs_3HgI_5, $M_r = 1233·83$, orthorhombic, *Pbca*, $a = 18·789\,(3)$, $b = 18·433\,(3)$, $c = 10·106\,(2)$ Å, $V = 3500\,(1)$ Å^3, $Z = 8$, $D_x = 4·683\,(2)$ g cm^{-3}, $\mu = 236·4$ cm^{-1}, $R = 0·024$ for 1988 observed reflections. In each of the compounds, Hg is bonded tetrahedrally to four I atoms, with vertex sharing of the coordination polyhedra in (I), and isolated HgI_4^{2-} ions in (II) and (III). The Hg—I bond distances are in the range 2·68 to 2·95 Å for (I) and between 2·73 and 2·82 Å in (II) and (III). The Cs ions have irregular coordination based on capped trigonal prisms. In (I) there is a tricapped trigonal prism of one water O atom at 3·19 Å and eight I atoms at 3·93–4·17 Å. Compound (II) has one each of 6+2- and 7+2-coordinated Cs^+ with Cs—I distances 3·88–4·27 and 3·77–4·37 Å, respectively. The three independent Cs^+ ions of (III) have 9, 7+2 and 7+1 I neighbours at 3·89–4·16, 3·80–4·69 and 3·76–4·28 Å.

Introduction. As part of a study of double iodides of caesium we have investigated the crystal structures formed from mixtures of CsI and HgI_2 in water solution and from the melt. Wells (1892) described five caesium mercury iodides, in order of increasing CsI content: $CsHg_2I_5$, $Cs_2Hg_3I_8$, $CsHgI_3$ (possibly a hydrate), Cs_2HgI_4 and Cs_3HgI_5. Later, Pernot (1936, 1938) investigated the CsI–HgI_2–H_2O system between 273 and 351 K and found the same five compounds. Two of them, $CsHg_2I_5$ and $CsHgI_3$, were formed within very limited ranges of concentration and temperature. Of the other three, Cs_2HgI_4 crystallizes within the widest concentration/temperature limits, and it is often formed together with the others from an evaporating solution.

The CsI–HgI_2 phase diagram has since been studied by Pakhomov, Fedorov, Polyakov & Kirilenko (1977); Podorozhnyi, Safonov & Korshunov (1982); Podorozhnyi, Safonov & Sharipov (1984). The results show that there exist only two stable intermediate compounds, *viz* Cs_2HgI_4 with a solid phase transition at 518 K and $CsHg_2I_5$, which decomposes in air.

The three crystal structures commonly formed from water solution have been determined earlier on the basis of film data and with *R* factors of 0·12–0·15: (I) $Cs_2Hg_3I_8$ (Fedorov & Pakhomov, 1975), (II) the room-temperature phase of Cs_2HgI_4 [Pakhomov & Fedorov (1973); see also Zandbergen, Verschoor & IJdo (1979) for isomorphous compounds], and (III) Cs_3HgI_5 (Fedorov, Pakhomov & Ivanova-Korfini, 1975). In this report we re-examine these structures using diffractometer data, arriving at considerably refined structural models. One of the compounds, (I), is shown to be a hydrate, $Cs_2Hg_3I_8.H_2O$. This could easily have been overlooked in earlier studies because the water molecule represents only 0·9% of the formula weight. A preliminary report on the refinement of Cs_2HgI_4 has been published elsewhere (Sjövall & Svensson, 1986).

Experimental. The crystals used for X-ray data collection were grown at room temperature by slow evaporation from water solutions of CsI and HgI_2. The crystals were transparent with increasingly yellow tints for higher HgI_2 content. They were washed in *n*-hexane [(I) and (II)] or toluene [(III)] and then dried in air. Crystals of $Cs_2Hg_3I_8.H_2O$ appeared both short prismatic along **c** and as triangular plates. The crystals of Cs_2HgI_4 were thick tabular (001). Cs_3HgI_5 crystals were tabular (010) with hexagonal appearance or equant with several faces.

Unit-cell parameters were obtained from powder photographs taken with a Guinier–Hägg focusing camera and silicon as internal standard [λ(Cu $K\alpha_1$) = 1·540598 Å, *a*(Si) = 5·430975 Å at 292 K]. Least-squares refinements of the cell parameters were based on 27 (I), 37 (II) and 31 (III) single indexed lines.*

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* See deposition footnote. The JCPDS Diffraction File Nos. are 38-1387, 38-1386 and 38-1385 for (I), (II) and (III), respectively.

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Table 1. *Experimental parameters*

Compound	(I)	(II)	(III)
Formula	$Cs_2Hg_3I_8.H_2O$	Cs_2HgI_4	Cs_3HgI_5
Transmission	0·088–0·170	0·068–0·173	0·014–0·029
$n[I > 3\sigma_c(I)]$: unique	1956: 1157	2009: 1357	1988
h, k, l range	0–9, ±25, ±8	0–9, ±9, ±13	0–22, 0–21, 0–11
m	69	41	83
R	0·032	0·032	0·024
wR	0·041	0·043	0·033
S	1·02	1·11	1·01
g	2·0 (1) × 10^3	1·33 (4) × 10^4	3·5 (1) × 10^3
Δ/σ_{max}	0·02	0·03	0·02
$\Delta\rho_{max}$ (e Å^{-3})	1·8	1·5	1·0
c_1	0·028	0·025	0·010
c_2	5·0	1·0	20·0
Crystal dimensions(mm)	0·08 × 0·07 × 0·10	0·16 × 0·08 × 0·13	0·323 (sphere)

Table 2. *Final fractional coordinates and equivalent isotropic temperature factors with e.s.d.'s in parentheses*

$$U_{eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}(Å^2)
(I) $Cs_2Hg_3I_8.H_2O$				
Hg(1)	−0·11368 (20)	0·19433 (3)	−0·07508 (17)	0·0527 (3)
Hg(2)	0·0	0·0	0·0	0·0559 (4)
I(1)	0·35352 (25)	0·0	0·23006 (27)	0·0469 (5)
I(2)	−0·12005 (30)	0·0	−0·36760 (26)	0·0504 (6)
I(3)	0·28682 (22)	0·19263 (4)	0·06708 (20)	0·0432 (4)
I(4)	−0·26275 (25)	0·19482 (5)	−0·44084 (20)	0·0508 (4)
I(5)	−0·21132 (23)	0·09808 (4)	0·11746 (20)	0·0442 (4)
Cs	0·24381 (28)	0·12435 (6)	0·55965 (25)	0·0698 (5)
O	0·4258 (35)	0·0	0·7571 (31)	0·096 (10)
(II) Cs_2HgI_4				
Hg	0·09387 (6)	0·25	0·27397 (4)	0·0511 (2)
I(1)	0·18988 (12)	0·25	0·54496 (8)	0·0721 (4)
I(2)	0·26151 (8)	0·51474 (6)	0·21163 (5)	0·0558 (2)
I(3)	−0·27762 (12)	0·25	0·14263 (8)	0·0765 (4)
Cs(1)	0·66050 (10)	0·25	0·46777 (7)	0·0565 (3)
Cs(2)	0·21824 (14)	0·25	0·90527 (7)	0·0719 (3)
(III) Cs_3HgI_5				
Hg	0·34347 (3)	0·43378 (3)	0·30835 (6)	0·0410 (2)
I(1)	0·23091 (5)	0·52777 (6)	0·36354 (11)	0·0521 (3)
I(2)	0·28833 (6)	0·30722 (6)	0·20088 (11)	0·0548 (4)
I(3)	0·40279 (5)	0·38500 (5)	0·54694 (9)	0·0454 (3)
I(4)	0·45168 (5)	0·49677 (6)	0·16961 (11)	0·0545 (4)
I(5)	0·07078 (5)	0·25173 (6)	0·32969 (9)	0·0453 (3)
Cs(1)	0·42805 (5)	0·17955 (5)	0·41582 (10)	0·0493 (3)
Cs(2)	0·10168 (6)	0·40534 (5)	0·08608 (11)	0·0527 (3)
Cs(3)	0·18916 (5)	0·14445 (5)	0·07212 (10)	0·0449 (3)

Three-dimensional intensity data were collected with the ω–2θ scan technique on an Enraf–Nonius CAD-4 diffractometer with graphite-monochromated Mo $K\alpha$ radiation to a maximum $\theta = 25°$. Crystals of (I) and (II) were used as grown while (III) could be ground to a sphere. Scan ranges were $\Delta\omega = 0{\cdot}8° + 0{\cdot}5°\tan\theta$ with maximum counting times of 180 (I), 240 (II) and 240 (III) s. Three standard reflections were checked every two hours. No significant intensity changes were detected during the total exposure times of 80 (I), 104 (II) and 136 (III) h. Intensities were corrected for Lorentz, polarization and absorption (numerical integration) effects. No averaging of equivalent reflections. Structure solution by *MULTAN*80 for (I). Refinements (on F) of (II) and (III) were started from the models by Pakhomov & Fedorov (1973) and Fedorov *et al.* (1975). Scattering factors and anomalous-dispersion corrections for Cs^+ and neutral Hg, I and O atoms were taken from *International Tables for X-ray Crystallography* (1974). All atoms were assumed to vibrate anisotropically. Weights were calculated from $w^{-1} = \sigma_c^2(F_o) + (c_1|F_o|)^2 + c_2$; c_1, c_2 given in Table 1. Corrections for isotropic secondary extinction according to Becker & Coppens (1975) were included. Space groups were determined from systematic extinctions and by the results of refinements. The model of (I) in Cm is incompatible with $C2$ or $C2/m$. Refinement of (II) in the non-centrosymmetric $P2_1$ as proposed by Pakhomov & Fedorov (1973) did not significantly improve the fit with either polar axis sense. Space group $Pbca$ for (III) is unique. The refinements are summarized in Table 1. Final atomic coordinates and temperature factor coefficients are given in Table 2.* All calculations were performed with programs described by Lundgren (1982).

During the refinement of the structure of (I) a peak was found in a difference electron density map that could be identified as a water O atom. Samples of all three compounds, about 2 mg each, were then investigated by differential scanning calorimetry in a Perkin–Elmer DSC-2C with a flowing-nitrogen atmosphere and a heating rate of 5 K min^{-1}. The only effects observed between room temperature and the melting points were (*a*) an endothermic peak for (I) starting at 387 K and (*b*) an endothermic peak for (II) starting at 523 K. The latter corresponds to the solid phase transition of Cs_2HgI_4 (Pakhomov *et al.*, 1977). The first peak was assigned to the release of water of crystallization from

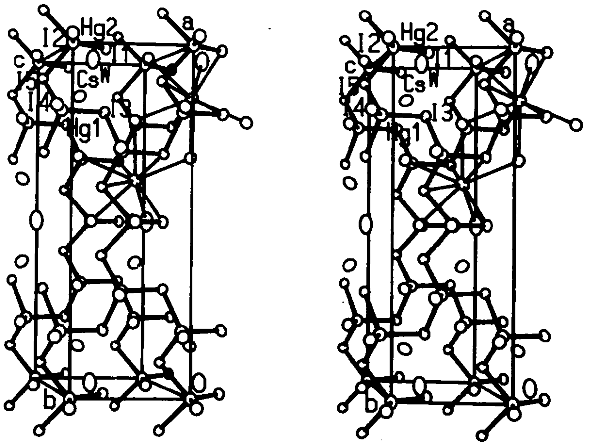

Fig. 1. Stereoview of the $Cs_2Hg_3I_8.H_2O$ (I) structure projected on (001). The atoms coordinated to Cs^+ are shown by thinner lines.

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* Lists of structure factors, anisotropic thermal parameters and powder data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44415 (64 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

(I). After reaction these crystals retained their habit but they were no longer transparent and had acquired an orange tint. The H atoms were not located.

Table 3. *Selected interatomic distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

(I) $Cs_2Hg_3I_8.H_2O$			
Hg(1)–I(4)	2·684 (1)	I(4)–Hg(1)–I(5)	117·90 (5)
Hg(1)–I(5)	2·785 (1)	I(4)–Hg(1)–I(3)	116·58 (5)
Hg(1)–I(3)	2·843 (1)	I(4)–Hg(1)–I(3)	108·82 (4)
Hg(1)–I(3)	2·876 (1)	I(5)–Hg(1)–I(3)	101·65 (4)
		I(5)–Hg(1)–I(3)	107·37 (4)
		I(3)–Hg(1)–I(3)	103·20 (4)
Hg(2)–I(1)	2·680 (2)	I(1)–Hg(2)–I(2)	129·28 (7)
Hg(2)–I(2)	2·686 (2)	I(1)–Hg(2)–I(5)	2 × 107·86 (4)
Hg(2)–I(5)	2 × 2·952 (1)	I(2)–Hg(2)–I(5)	2 × 106·62 (4)
		I(5)–Hg(2)–I(5)	92·40 (5)
Cs–O	3·19 (1)	Capping atoms	
Cs–I(4)	3·928 (2)	O–Cs–I(4)	148·3 (3)
Cs–I(1)	3·957 (2)	O–Cs–I(5)	113·9 (3)
Cs–I(4)	3·984 (2)	I(4)–Cs–I(5)	97·69 (4)
Cs–I(2)	3·987 (2)		
Cs–I(5)	4·030 (2)		
Cs–I(4)	4·072 (2)		
Cs–I(3)	4·091 (2)		
Cs–I(3)	4·169 (2)		
(II) Cs_2HgI_4			
Hg–I(3)	2·738 (1)	I(3)–Hg–I(2)	2 × 111·35 (2)
Hg–I(2)	2 × 2·774 (1)	I(3)–Hg–I(1)	114·03 (3)
Hg–I(1)	2·819 (1)	I(2)–Hg–I(2)	106·35 (3)
		I(2)–Hg–I(1)	2 × 106·66 (2)
Cs(1)–I(3)	3·774 (1)	Capping atoms	
Cs(1)–I(1)	3·886 (1)	I(1)–Cs(1)–I(1)	2 × 106·06 (2)
Cs(1)–I(2)	2 × 3·908 (1)	I(1)–Cs(1)–I(1)	147·75 (3)
Cs(1)–I(1)	4·012 (1)		
Cs(1)–I(2)	2 × 4·055 (1)		
Cs(1)–I(1)	2 × 4·365 (1)		
Cs(2)–I(3)	3·879 (1)	Capping atoms	
Cs(2)–I(1)	3·900 (1)	I(3)–Cs(2)–I(3)	158·14 (4)
Cs(2)–I(2)	2 × 3·958 (1)		
Cs(2)–I(2)	2 × 4·005 (1)		
Cs(2)–I(3)	2 × 4·271 (1)		
(III) Cs_3HgI_5			
Hg–I(4)	2·729 (1)	I(4)–Hg–I(2)	115·78 (4)
Hg–I(2)	2·774 (1)	I(4)–Hg–I(1)	113·78 (4)
Hg–I(1)	2·790 (1)	I(4)–Hg–I(3)	106·38 (4)
Hg–I(3)	2·804 (1)	I(2)–Hg–I(1)	108·50 (4)
		I(2)–Hg–I(3)	102·44 (4)
		I(1)–Hg–I(3)	109·18 (4)
Cs(1)–I(5)	3·888 (2)	Capping atoms	
Cs(1)–I(2)	3·905 (2)	I(3)–Cs(1)–I(3)	125·38 (3)
Cs(1)–I(5)	3·926 (2)	I(3)–Cs(1)–I(4)	111·08 (3)
Cs(1)–I(3)	3·942 (2)	I(3)–Cs(1)–I(4)	122·83 (3)
Cs(1)–I(3)	4·040 (2)		
Cs(1)–I(1)	4·126 (2)		
Cs(1)–I(2)	4·141 (2)		
Cs(1)–I(4)	4·148 (2)		
Cs(1)–I(4)	4·164 (2)		
Cs(2)–I(5)	3·797 (2)	Capping atoms	
Cs(2)–I(3)	3·886 (2)	I(4)–Cs(2)–I(2)	126·57 (4)
Cs(2)–I(5)	3·929 (2)	I(4)–Cs(2)–I(4)	103·59 (3)
Cs(2)–I(3)	3·989 (2)	I(2)–Cs(2)–I(4)	127·22 (3)
Cs(2)–I(1)	4·058 (2)		
Cs(2)–I(4)	4·108 (2)		
Cs(2)–I(2)	4·113 (2)		
Cs(2)–I(1)	4·342 (2)		
Cs(2)–I(4)	4·688 (2)		
Cs(3)–I(2)	3·764 (2)	Capping atoms	
Cs(3)–I(5)	3·823 (2)	I(4)–Cs(3)–I(2)	131·14 (3)
Cs(3)–I(1)	3·891 (2)		
Cs(3)–I(4)	3·922 (2)		
Cs(3)–I(1)	3·944 (2)		
Cs(3)–I(5)	3·954 (2)		
Cs(3)–I(3)	4·058 (2)		
Cs(3)–I(2)	4·283 (2)		

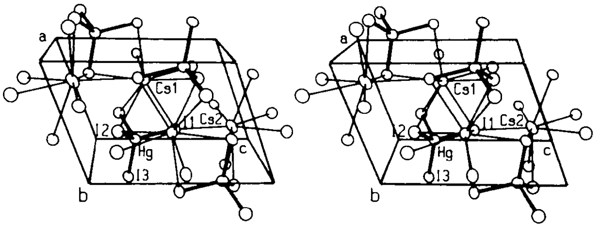

Fig. 2. Stereoview of the Cs_2HgI_4 (II) structure. The direction of projection is 15° off [010]. I atoms of HgI_4 groups from neighbouring unit cells have been added to show the coordination around the Cs^+ ions.

Discussion. The structure of $Cs_2Hg_3I_8.H_2O$ consists of layers parallel to (001) of vertex-sharing HgI_4 tetrahedra with overall composition $Hg_3I_8^{2-}$ (Fig. 1). All tetrahedra are oriented approximately the same, with the mirror plane perpendicular to the layers. The stacking vector is the **c** lattice translation. Cs^+ and H_2O are located between the layers. The two independent HgI_4 groups have slightly different geometry, both with considerably longer Hg–I distances to the vertex-shared I atoms, *cf.* Table 3. The caesium coordination polyhedron of (I) is a tricapped trigonal prism with a water O atom, at 3·19 (1) Å, as one of the capping atoms. The Cs–I distances range from 3·928 (2) to 4·169 (2) Å. The thermal vibration component of the O atom perpendicular to the mirror plane is fairly high, which might indicate a disordering of the water molecule.

Application of the transformation matrix $(\bar{1}00/0\bar{1}0/101)$ to the unit cell of Cs_2HgI_4 gives an almost identical cell with $a' = a$, $b' = b$, $c' = 11{\cdot}080\ (1)$ Å and $\beta' = 110{\cdot}91\ (1)^\circ$. This cell corresponds to the atomic coordinates used by Zandbergen *et al.* (1979) for isomorphous Rb_2FeI_4 and by Philippot, Ribes & Maurin (1971), with the axes in reverse order, for isomorphous Sr_2GeS_4. However, we have preferred the reduced cell and the coordinates originally used by Pakhomov & Fedorov (1973) for (II). There has been some uncertainty whether this structure belongs to space group $P2_1$ or $P2_1/m$. Both Zandbergen *et al.* (1979) and Pakhomov & Fedorov (1973) assumed $P2_1$ to be correct. We have, however, found no evidence in this study for the absence of the mirror plane in the structure of Cs_2HgI_4.

The structure of Cs_2HgI_4 has isolated tetrahedral HgI_4^{2-} ions with *m* symmetry (Fig. 2). The Hg–I distances are between 2·738 (1) and 2·819 (1) Å, *cf.*

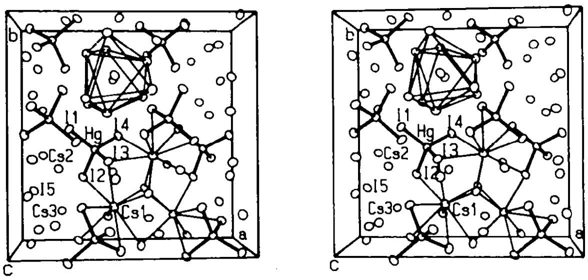

Fig. 3. Stereoview of the Cs_3HgI_5 (III) structure down [001]. In the upper half a column of distorted face-sharing Cs^+ octahedra centred by I(5) is shown. The coordination around three independent Cs^+ ions is shown in the lower half.

Table 3. The directions and amplitudes of thermal vibration of the I atoms indicate considerable librations of the entire HgI_4^{2-} ion. The two independent Cs^+ ions have 6+2 and 7+2 coordination, respectively, in capped trigonal prisms. The prism axes coincide with the mirror planes of the structure. In both cases there is a jump in the Cs—I distances of about 0·3 Å between the nearest neighbours and the two capping atoms further away. In isomorphous Sr_2GeS_4 both Sr^+ ions have 6+2 coordination in bicapped trigonal prisms.

Compound (III), Cs_3HgI_5, is built from Cs^+, HgI_4^{2-} and I^- ions (Fig. 3). The Hg—I bond distances, 2·729 (1) to 2·804 (1) Å, are comparable with those of (II). The Cs^+ ions are arranged so that an octahedron is formed around the I^- ion; the six Cs—I(5) distances are 3·797 (2) to 3·954 (2) Å. These octahedra share faces and form columns along **c**. The three Cs^+ ions have 9, 7+2 and 7+1 coordination. The three coordination polyhedra, which can be described as capped trigonal prisms, share a common edge I(5)–I(5). The Cs—I distances are 3·888 (2)–4·164 (2), 3·797 (2)–4·688 (2) and 3·764 (2)–4·283 (2) Å, respectively.

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Trichlorosulfonium(IV) Tetrachloroaurate(III)

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Abstract. $[SCl_3][AuCl_4]$, $M_r = 477{\cdot}2$, monoclinic, $P2_1/c$, $a = 8{\cdot}637$ (3), $b = 10{\cdot}240$ (4), $c = 11{\cdot}618$ (4) Å, $\beta = 107{\cdot}88$ (3)°, $V = 977{\cdot}9$ Å^3, $Z = 4$, $D_x = 3{\cdot}24$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 169$ cm^{-1}, $F(000) = 856$, $T = 293$ K, $R = 0{\cdot}043$ for 1303 unique observed reflections. The structure consists of pyramidal SCl_3^+ cations and square-planar $AuCl_4^-$ anions that are linked by secondary S···Cl interactions of average length 3·08 Å to form centrosymmetric dimers; the coordination geometry at sulfur is distorted octahedral. The compound is isostructural with its selenium analogue.

Introduction. We have investigated secondary $M \cdots X$ interactions in several $MX_3^+.AuX_4^-$ species (M = Te, X = Cl: Jones, Jentsch & Schwarzmann, 1986; M = Se, X = Cl; Jones, Schelbach & Schwarzmann, 1987; M = Te, X = Br; Freire Erdbrügger, Jentsch, Jones & Schwarzmann, 1987). These compounds, and also those of other halo-anions (Christian, Collins, Gillespie

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