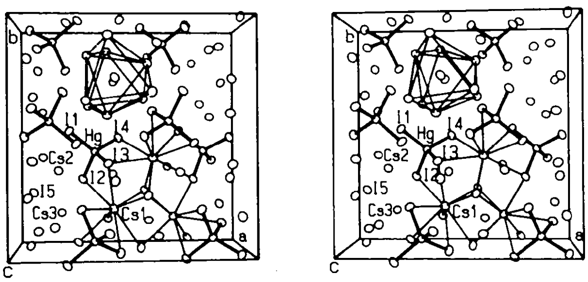

Fig. 3. Stereoview of the Cs_3HgI_5 (III) structure down [001]. In the upper half a column of distorted face-sharing Cs^+ octahedra centred by I(5) is shown. The coordination around three independent Cs^+ ions is shown in the lower half.

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. $[SCl_3][AuCl_4]$, $M_r = 477·2$, monoclinic, $P2_1/c$, $a = 8·637$ (3), $b = 10·240$ (4), $c = 11·618$ (4) Å, $\beta = 107·88$ (3)°, $V = 977·9$ Å^3, $Z = 4$, $D_x = 3·24$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 169$ cm^{-1}, $F(000) = 856$, $T = 293$ K, $R = 0·043$ 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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& Sawyer, 1986; Edwards, 1978), generally display an extended coordination geometry (including secondary interactions) at M that is octahedral or, in the case of $M = \mathrm{Te}$, $X = \mathrm{Cl}$, square pyramidal.

There is some confusion in the literature as to whether these compounds display isomorphism. On the basis of X-ray powder data, Novitskaya, Timoshchenko & Fokina (1979) found no such relationship for $M\mathrm{Cl}_3^+.\mathrm{AuCl}_4^-$ ($M = \mathrm{S}$, Se, Te); they indexed the powder pattern for $M = \mathrm{S}$ according to a tetragonal cell. Finch, Gates, Page & Dillon (1983) state that the S and Se analogues and also form (I) of $\mathrm{SCl}_3^+.\mathrm{ICl}_4^-$ are isomorphic, also based on powder data, but they quote neither the data directly nor a reference to them. Edwards (1978) subjected form (I) of $\mathrm{SCl}_3^+.\mathrm{ICl}_4^-$ to single-crystal X-ray structure analysis; although it crystallizes in the same space group as does $\mathrm{SeCl}_3^+.\mathrm{AuCl}_4^-$ and with very similar cell constants, the axes are in a different order and we can see no isomorphism [an additional complication here is that the b axis in the *Abstract* of Edwards (1978) is misprinted]. We were able to confirm that $\mathrm{SeCl}_3^+.\mathrm{AuCl}_4^-$ and its Te analogue are not isomorphic (see above references), and to show that the structural units of $\mathrm{SeCl}_3^+.\mathrm{AuCl}_4^-$ and $\mathrm{SCl}_3^+.\mathrm{ICl}_4^-$ are similar (centrosymmetric dimers linked by $M\cdots\mathrm{Cl}$ secondary interactions, with distorted octahedral coordination at M), although differing in detail.

NQR investigations of the AuCl_4^- salts (Finch *et al.*, 1983) suggested considerable distortion of the anion from the ideal $4/mmm$ symmetry for $M = \mathrm{S}$, Se (attributed to $M\cdots\mathrm{Cl}$ secondary interactions), and rather less distortion in the Te analogue.

Here we present the single-crystal X-ray structure analysis of $\mathrm{SCl}_3^+.\mathrm{AuCl}_4^-$.

Experimental. The title compound was prepared from metallic gold and SCl_2 in a sealed tube using the method of Lindet (1887). Single crystals separated on cooling the reaction mixture. The compound is extremely sensitive to moisture and appropriate precautions were taken.

A yellow prismatic crystal 0·12 × 0·1 × 0·07 mm was mounted in inert oil in a glass capillary and used to record 1767 profile-fitted intensities (Clegg, 1981) on a Stoe–Siemens four-circle diffractometer with monochromated Mo $K\alpha$ radiation: $2\theta_{\max}$ 50°, quadrant $\pm h+k+l$ and a few equivalents. Three check reflections showed decay of *ca* 5% and the intensities were corrected accordingly. An empirical absorption correction, based on ψ scans, gave transmission factors of 0·70–0·92. Of 1687 unique reflections (R_{int} 0·046), 1303 with $F > 4\sigma(F)$ were used for all calculations (program *SHELX*76, Sheldrick, 1976, locally modified). Index range: h $-10\to9$, k $0\to12$, l $0\to13$. Cell constants were refined from 2θ values of 38 reflections in the range 19–23°.

Table 1. *Atomic coordinates* (× 10^4) *and equivalent isotropic displacement parameters* (Å^2 × 10^3)

	x	y	z	U_{eq}*
Au	2171 (1)	5961 (1)	5355 (1)	31 (1)
Cl(1)	3849 (5)	4388 (3)	6458 (3)	53 (1)
Cl(2)	1399 (5)	4616 (3)	3695 (3)	46 (1)
Cl(3)	581 (4)	7584 (3)	4252 (3)	50 (1)
Cl(4)	2938 (4)	7301 (4)	6983 (3)	51 (1)
S	2438 (4)	1967 (3)	4918 (3)	33 (1)
Cl(5)	1018 (4)	964 (4)	3542 (3)	49 (1)
Cl(6)	3040 (5)	664 (4)	6234 (4)	60 (1)
Cl(7)	4451 (4)	2050 (4)	4428 (4)	55 (1)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 2. *Bond lengths* (Å) *and angles* (°)

Au–Cl(1)	2·279 (3)	Au–Cl(2)	2·296 (3)
Au–Cl(3)	2·282 (3)	Au–Cl(4)	2·265 (4)
S–Cl(5)	1·978 (5)	S–Cl(6)	1·974 (5)
S–Cl(7)	1·991 (6)		
Cl(2)–Au–Cl(1)	91·1 (1)	Cl(3)–Au–Cl(1)	177·7 (1)
Cl(3)–Au–Cl(2)	89·7 (1)	Cl(4)–Au–Cl(1)	89·2 (1)
Cl(4)–Au–Cl(2)	179·5 (1)	Cl(4)–Au–Cl(3)	89·9 (1)
Cl(6)–S–Cl(5)	103·0 (2)	Cl(7)–S–Cl(5)	99·8 (2)
Cl(7)–S–Cl(6)	101·8 (2)		

The atom coordinates of the Se analogue were assumed (see below) and their refinement proved successful. Anisotropic refinement on F proceeded to R 0·043, wR 0·043, $S = 1·35$. The weighting scheme was $w^{-1} = \sigma^2(F) + 0·0003F^2$. An extinction correction of the form $F_{\mathrm{corr}} = F_c/(1 + xF_c^2/\sin 2\theta)^{0·25}$ was applied, where x refined to 2·0 (2) × 10^{-6}. 83 parameters were refined; max. shift/e.s.d. 0·01, max. and min. residual electron density +1·2 and −1·4 e Å^{-3} (near Au). Atomic scattering factors as incorporated in *SHELX*76.

Discussion. Final atomic coordinates are presented in Table 1, with derived bond lengths and angles in Table 2.[*]

Isomorphism. The similarity of the cell constants of the title compound and its selenium analogue suggested strongly that the two compounds are isostructural, and the full structure analysis confirms this. The title compound is *not* isomorphous with $\mathrm{TeCl}_3^+.\mathrm{AuCl}_4^-$ or $\mathrm{SCl}_3^+.\mathrm{ICl}_4^-$ (I) and is clearly different, in structure if not in composition, from the compound described by Novitskaya *et al.* (1979) as tetragonal $\mathrm{SCl}_3^+.\mathrm{AuCl}_4^-$. We cannot of course rule out polymorphism of these compounds, with its attendant complications.

Primary structure. The title compound consists of pyramidal SCl_3^+ cations and planar AuCl_4^- anions (see

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[*] Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44403 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

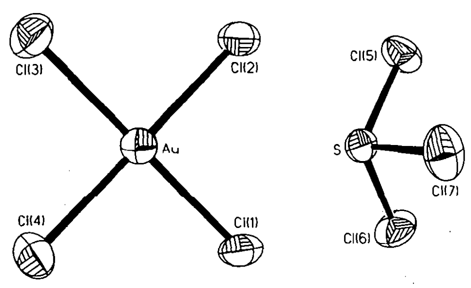

Fig. 1. Thermal-ellipsoid plot (50% level) of the asymmetric unit, showing the atom-numbering scheme.

Fig. 1). The average S—Cl bond length is 1·981 Å and the average Cl—S—Cl angle 101·5°, very similar to the values in $SCl_3^+.ICl_4^-$ (Edwards, 1978) of 1·988 Å, 101·3°. In the $SbCl_6^-$ salt (Christian *et al.*, 1986) the bonds are somewhat shorter (av. 1·956 Å) and the angles wider (av. 103·7°). The authors attribute these differences, and those between other SCl_3^+ salts in the literature, to secondary interactions (see below). The anions display considerable distortion from the ideal geometry, with a short Au—Cl(4) bond (2·265 Å, *cf.* 2·279, 2·282, 2·296 Å for the other Au—Cl bonds). This is also rationalized in terms of secondary interactions. The extent of the distortion is marginally less than in the Se analogue (Jones *et al.*, 1987).

Secondary interactions. Fig. 2 shows the formation of a centrosymmetric dimer by secondary S···Cl interactions of average length 3·08 Å (*cf.* 3·11 Å in $SCl_3^+.ICl_4^-$). These complete a distorted octahedral coordination at the S atom. The secondary interactions in the isostructural Se analogue are appreciably shorter (av. 2·94 Å). The one anionic chlorine that does not take part in secondary interactions, Cl(4), is the one with the shortest Au—Cl bond (see above).

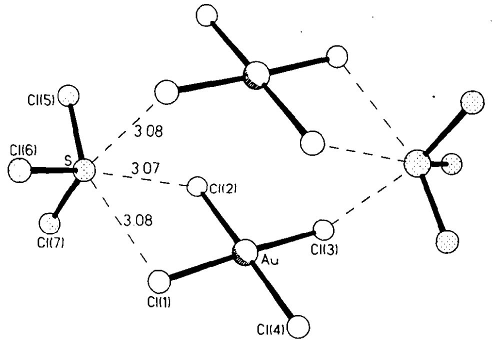

Fig. 2. The centrosymmetric dimer $[SCl_3.AuCl_4]_2$, showing the secondary interactions (dashed lines, distances in Å). The symmetry operator generating the second half of the dimer is $-x$, $1-y$, $1-z$.

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Crystal Structures of Two New Types of *cyclo*-Tetraphosphates: Tetracalcium Tetrapotassium Tris(*cyclo*-tetraphosphate) Octahydrate and Calcium Disodium *cyclo*-Tetraphosphate 5·5-Hydrate

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Abstract. $Ca_4K_4(P_4O_{12})_3.8H_2O$, $M_r = 1408·50$, monoclinic, $P2_1/a$, $a = 20·38\,(1)$, $b = 12·683\,(5)$, $c = 7·830\,(2)$ Å, $\beta = 89·31\,(5)°$, $V = 2024\,(5)$ Å^3, $Z = 2$, $D_x = 2·311$ Mg m^{-3}, $\lambda(\text{Mo }K\alpha) = 0·7107$ Å, $\mu = 1·520$ mm^{-1}, $F(000) = 1408$, $T = 295$ K, $R = 0·031$ for 2793 independent reflexions. $CaNa_2P_4O_{12}.5·5H_2O$, $M_r = 501·03$, orthorhombic, $Pma2$, $a = 27·88\,(10)$, $b = 7·536\,(5)$, $c = 7·378\,(5)$ Å, $V = 1550\,(3)$ Å^3, $\mu =$

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