

## Synthesis and Crystal Structure of the Layer Compound $\text{Sb}_3\text{TeO}_6\text{Cl}$ †

José Antonio Alonso, Enrique Gutiérrez-Puebla, Antonio Jerez, Angeles Monge,\* and Caridad Ruiz-Valero

*Instituto de Química Inorgánica 'Elhúyar,' Serrano 113, 28006 Madrid, Spain and Departamento de Química Inorgánica, Facultad de Químicas, Universidad Complutense, 28040 Madrid, Spain*

The mixed oxohalide  $\text{Sb}_3\text{TeO}_6\text{Cl}$  has been obtained and characterized for the first time. The structure has been determined by single-crystal X-ray techniques, using diffractometer data. The compound crystallizes in the orthorhombic space group  $I_{mmm}$ , with  $a = 4.1283(8)$ ,  $b = 9.390(3)$ ,  $c = 12.968(8)$  Å, and  $Z = 2$ . Refinement led to a final  $R$  value of 0.037 using 278 observed reflections. The co-ordination of the heavy atom can be considered as a distorted trigonal bipyramid with the lone pair directed towards one of the equatorial positions. The crystal consists of parallel layers of  $(\text{Sb}_3\text{TeO}_6)_n^+$  perpendicular to the  $c$  axis, the isolated  $\text{Cl}^-$  anions being situated between these layers. Thus,  $\text{Sb}_3\text{TeO}_6\text{Cl}$  is an example of a positively-charged network structure.

Relatively little work has been done on mixed oxo-compounds of the semi-metallic  $p$  elements, of which we have studied<sup>1</sup> some mixed oxides of Se and Te.

For the simple oxohalides of Sb and Te, the structures of  $\text{Sb}_4\text{O}_5\text{Cl}_2$ ,<sup>2</sup>  $\text{SbOCl}$ ,<sup>3</sup> and  $\text{Te}_6\text{O}_{11}\text{Cl}_2$ <sup>4</sup> have been reported. In  $\text{Sb}_4\text{O}_5\text{Cl}_2$  the co-ordination polyhedra of Sb atoms share corners forming infinite layers parallel to the  $bc$  plane.  $\text{SbOCl}$  is formed by puckered sheets in which two-thirds of the Sb atoms are linked to  $2\text{O} + 1\text{Cl}$ , and the remainder to four O, the sheets  $(\text{Sb}_6\text{O}_6\text{Cl}_4)_n^{2n+}$  being held together by  $\text{Cl}^-$  ions.  $\text{Te}_6\text{O}_{11}\text{Cl}_2$  contains infinite cationic  $(\text{Te}_{12}\text{O}_{22})_\infty^{4+}$  chains with three different sites for Te, which are co-ordinated with three and four oxygen atoms.

The aim of this paper is two-fold: to report the existence of the mixed oxohalide  $\text{Sb}_3\text{TeO}_6\text{Cl}$  and to describe its crystal structure.

### Experimental

$\text{Sb}_3\text{TeO}_6\text{Cl}$  was obtained by dissolving a mixture of analytical grade  $\text{TeO}_2$  and  $\text{Sb}_2\text{O}_3$  (Te:Sb = 1:5, 1 g) in concentrated HCl (10 cm<sup>3</sup>), and subsequently dilution with water up to 80 cm<sup>3</sup>. After 3 d some colourless needle-shaped crystals appeared. Once filtered off and washed with water and ethanol, they were air dried at 60 °C.

The contents of Te, Sb, and Cl were determined by usual techniques of chemical analysis<sup>5-7</sup> [Found: Cl, 5.9; O (determined by difference), 15.9; Sb, 58.1; Te, 20.1.  $\text{ClO}_6\text{Sb}_3\text{Te}$  requires Cl, 5.70; O, 15.35; Sb, 58.5; Te, 20.45%]. The absence of OH groups was confirmed by n.m.r., using a Bruker SXP4-100 spectrometer for solids, and by i.r. spectroscopy, using a Perkin-Elmer 425 and KBr discs.

The crystal chosen for data collection was cut to a size of  $0.05 \times 0.05 \times 0.05$  mm and mounted in a Nonius CAD4-F diffractometer. All the dimensions were refined by least-squares fitting of the  $\theta$  values of 25 reflections.

**Crystal Data.**— $\text{Sb}_3\text{TeO}_6\text{Cl}$ ,  $M = 624.35$ , orthorhombic,  $a = 4.1283(8)$ ,  $b = 9.390(3)$ ,  $c = 12.968(8)$  Å,  $U = 502.7(4)$  Å<sup>3</sup>,  $Z = 2$ ,  $D_c = 4.12$  Mg m<sup>-3</sup>,  $F(000) = 540$ ,  $\mu(\text{Mo-K}\alpha) = 11.17$  mm<sup>-1</sup>, space group  $I_{mmm}$ ,  $T = 295$  K,  $R = 0.037$  for 278 observed reflections.

**Table 1.** Atomic co-ordinates for  $\text{Sb}_3\text{TeO}_6\text{Cl}$ , with estimated standard deviations (e.s.d.s) in parentheses

Atom	$X/a$	$Y/b$	$Z/c$
Sb or Te	0	0.311 4(1)	0.155 6(1)
Cl	0	0	0.5
O(1)	0	0.214 6(13)	0.293 9(10)
O(2)	0	0.5	0.219 2(17)

**Data Collection.**—The intensities of 429 unique reflections with  $1 < \theta < 30^\circ$  were measured at 295 K with monochromatic Mo-K $\alpha$  radiation ( $\lambda = 0.710 69$  Å) and a  $\omega/2\theta$  scan technique. There was no appreciable drop in intensity of three standard reflections, checked every hour.

The systematic absences were  $h,k,l$  for  $h + k + l = 2n + 1$ . The four possible space groups are  $I_{2,2,2}$ ,  $I_{222}$ ,  $I_{mm2}$ , and  $I_{mmm}$ . Intensities were corrected for Lorentz and polarization effects, and 278 of these were considered as observed by the criterion  $I > 2\sigma(I)$ .

Scattering factors for neutral atoms and anomalous dispersion corrections for Sb and Cl were taken from International Tables.<sup>8</sup> The centrosymmetric space group  $I_{mmm}$  was obtained during the course of the structure solution.

**Structure Determination.**—The heavy atom and Cl atom were located from a three-dimensional Patterson map. The positions of the O atoms were obtained from Fourier synthesis. An empirical absorption correction<sup>9</sup> was applied at the end of the isotropic refinement. Anisotropic full-matrix least-squares refinement with unit weights led to  $R = 0.037$  and  $R' = 0.047$ . No trend in  $\Delta F$  vs.  $F_0$  or  $\sin\theta/\lambda$  was observed. Maximum and average shift-to-error ratios were 0.01 and 0.004 respectively. A final difference synthesis shows an electron density of  $2 e \text{ \AA}^{-3}$  located in the heavy-atom position.

Most of the calculations were carried out with X-RAY 76.<sup>10</sup>

### Results and Discussion

Table 1 shows the final atomic parameters. All the atoms have been located in special positions: the heavy atom (Te or Sb) and one of the oxygen atoms [O(1)] in the 8(1) positions, and the other atoms [O(2) and Cl] in positions 4(j) and 2(c) respectively.

Table 2 shows bond lengths and angles. The heavy atom (Te or Sb) is bonded to four oxygen atoms (Figure 1).<sup>11</sup> The co-ordination polyhedron can be considered as a trigonal

† Supplementary data available (No. SUP 56227, 3 pp.): thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii–xix. Structure factors are available from the editorial office.

bipyramid with the lone pair directed towards one of the equatorial positions.

The formula obtained through the X-ray structure determination was  $E_4O_6Cl$  ( $E = Te$  or  $Sb$ ) with two formula weights per unit cell. The scattering factors of  $Sb$  or  $Te$  atoms are so similar that it was rather difficult to distinguish between them by X-ray diffraction, and thus all the heavy atoms were considered equivalent. Chemical analysis, however, determined that the proportion of  $Sb^{III}$  to  $Te^{IV}$  is 3:1, and that one  $Cl$  atom exists per formula. Hence in the unit cell, for every three  $Sb^{III}$  atoms there

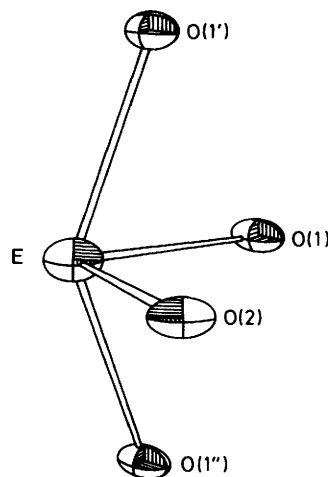
is one  $Te^{IV}$ . In this way, electric neutrality is maintained, and the crystallographic formula  $E_4O_6Cl$  agrees with the chemical one,  $Sb_3TeO_6Cl$ .

The crystal consists of parallel layers of composition  $(Sb_3TeO_6)_n^+$  perpendicular to the  $c$  axis (Figure 2).<sup>11</sup> The  $Cl^-$  ions are located between these layers. Each layer is formed by infinite zig-zag chains of bipyramids that share common edges, with the lone pairs directed out from the layers. These chains parallel to the  $a$  axis are linked by the apical corners of the bipyramids, in such a way that there are channels or tunnels

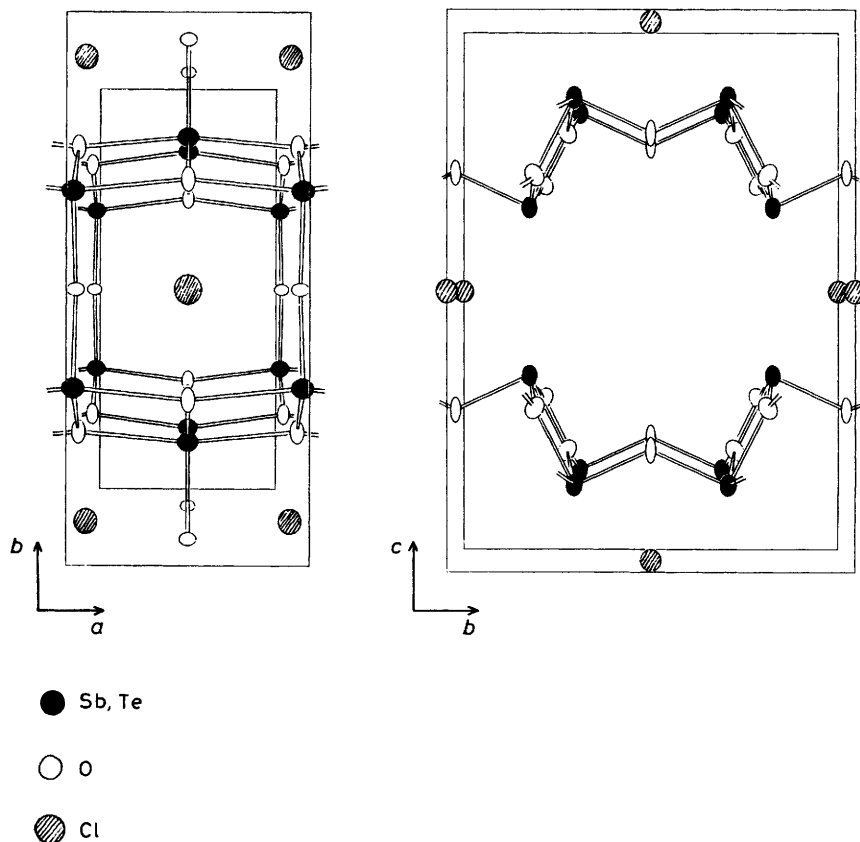
**Table 2.** Bond lengths (Å) and angles (°) and principal contact distances for  $Sb_3TeO_6Cl$  ( $E = Sb$  or  $Te$ )

E-O(1)	2.011(5)
E-O(2)	1.954(5)
E-O(1')	2.179(5)
E-Cl	3.387(5)
E-E	3.403(5) (in the same chain)
E-E	3.542(5) (between chains)
O(1)-E-O(2)	91.9(5)
O(1)-E-O(1')	71.4(5)
O(2)-E-O(1')	88.6(5)
O(1')-E-O(1'')	142.6(5)
E-O(1)-E'	108.6(5)
E'-O(1)-E''	142.6(5)
E-O(1)-E''	130.1(5)

Symmetry code: (')  $\frac{1}{2} - x, \frac{1}{2} - y, \frac{1}{2} - z$ ; (")  $-\frac{1}{2} - x, \frac{1}{2} - y, \frac{1}{2} - z$ ; (""')  $x, y, z$ .



**Figure 1.** Co-ordination polyhedron of the heavy atom ( $E = Te$  or  $Sb$ )



**Figure 2.** Two views of the unit cell of  $Sb_3TeO_6Cl$

along the  $c$  axes, where the  $\text{Cl}^-$  ions lie. The strong observed anisotropy for the O(2) atom could be explained by taking into account that this oxygen is only bonded to two heavy atoms and, on the other hand, that its motion is not hindered in the direction normal to the layers.

In  $\text{Sb}_4\text{O}_5\text{Cl}_2$ <sup>2</sup> and  $\text{SbOCl}$ <sup>3</sup> the atoms of Cl and those of Sb are located at distances equal to or less than 2.909 Å and can be thought as chemically bonded. For  $\text{Te}_6\text{O}_{11}\text{Cl}_2$ <sup>4</sup> all the Cl atoms lie at distances equal to or less than 3.01 Å from two Te atoms. In these three cases all the Cl atoms can be considered as forming part of the co-ordination polyhedra of either Sb or Te. On the contrary, all the Cl atoms in  $\text{Sb}_3\text{TeO}_6\text{Cl}$  are situated at 3.387(1) Å from the heavy atoms, and cannot be considered co-ordinated.

As Kostiner and co-workers<sup>12</sup> have recently indicated, it is unusual that no examples of positively-charged networks exist in the crystal chemistry of inorganic structures, considering the large number of known examples of negatively-charged networks.

With the exception of  $[\text{Te}_2\text{O}_4\text{H}]^+[\text{NO}_3]^-$ , in all the complex compounds of the heavier  $p$  elements of Groups 5—7, whose structures have been claimed to be formed by positively charged one- or two-dimensional networks, either<sup>12</sup> a discrete anion does not exist or the anion forms covalent bonds which complete the primary co-ordination polyhedra about the metal atoms in the network.

In two-dimensional  $\text{Sb}_3\text{TeO}_6\text{Cl}$ , parallel layers of composition  $(\text{Sb}_3\text{TeO}_6)_n^+$  are stacked in a direction perpendicular to the  $c$  axis and separated by rows of isolated chloride ions. Thus,  $\text{Sb}_3\text{TeO}_6\text{Cl}$  is another compound with discrete  $\text{Cl}^-$  anions, although other interactions besides the electrostatic forces are not to be excluded.

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### References

- 1 A. Castro, A. Jerez, C. Pico, and M. L. Veiga, *J. Chem. Soc., Dalton Trans.*, 1982, 733.
- 2 Ch. Särnstrand, *Acta Crystallogr., Sect. B*, 1978, **34**, 2402.
- 3 A. F. Wells, 'Structural Inorganic Chemistry,' 4th edn., Clarendon Press, Oxford, 1975, p. 716.
- 4 W. Abriel, *Z. Naturforsch., Teil B*, 1981, **36**, 405.
- 5 K. Kodama, 'Methods of Quantitative Inorganic Analysis,' Interscience, New York, 1963.
- 6 L. A. Wooton, *Ind. Eng. Chem. Anal. Ed.*, 1941, **13**, 771.
- 7 L. Erdey, 'Gravimetric Analysis,' Pergamon, Oxford, 1965.
- 8 'International Tables for X-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4, pp. 72—98.
- 9 N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 1983, **39**, 158.
- 10 J. M. Stewart, F. A. Kundell, and J. C. Baldwin, X-RAY 76 system, Computer Science Center, University of Maryland, College Park, Maryland, 1976.
- 11 C. K. Johnson, ORTEP, Report ORNL-3794, Oak Ridge National Laboratory, Tennessee, 1965.
- 12 J. B. Anderson, M. H. Raposch, C. P. Anderson, and E. Kostiner, *Monatsh. Chem.*, 1980, **11**, 798.

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