

Preparation and Structure of Ditantalum Iodide Octaselenide, Ta<sub>2</sub>ISe<sub>8</sub>

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**Abstract.** Ta<sub>2</sub>ISe<sub>8</sub>,  $M_r = 1120.48$ , tetragonal,  $I422$ ,  $a = 9.531(1)$ ,  $c = 12.824(6)$  Å,  $V = 1164.9$  Å<sup>3</sup>,  $Z = 4$ ,  $D_m = 6.34$ ,  $D_x = 6.39$  Mg m<sup>-3</sup>,  $\mu(\text{Mo } K\alpha) = 49.3$  mm<sup>-1</sup>. The structure was solved by means of Patterson and Fourier syntheses and refined to  $R = 0.057$ ,  $R_w = 0.044$ , for 730 independent reflections [ $I \geq 1.5\sigma(I)$ ]. The structure consists of infinite [TaSe<sub>4</sub>] chains which develop in a direction parallel to the  $c$  axis. I atoms are located between these chains. From a geometrical point of view, this compound presents a marked one-dimensional character.

**Introduction.** Very recently, great interest has developed in transition-metal trichalcogenides in relation to their more or less one-dimensional character. Indeed, their physical properties are strongly anisotropic and are well explained by the structural arrangement. These low-dimensional materials are of interest because they exhibit some of the best examples of such phenomena as 'Peierls transitions', charge-density waves, etc.

From a structural consideration, Ta<sub>2</sub>ISe<sub>8</sub> appears to be a very promising candidate in this field of research. The infinite [TaSe<sub>4</sub>] chains which develop in a direction parallel to the  $c$  axis are well separated from each other and give a pseudo one-dimensional character to this compound. This structure is closely related to that of Nb<sub>3</sub>ISe<sub>12</sub> which we were able to synthesize and characterize before (Meerschaut, Palvadeau & Rouxel, 1977).

**Experimental.** Ta<sub>2</sub>ISe<sub>8</sub> was prepared by direct combination of the elements in sealed silica tubes at temperatures ranging from 850 to 900 K. Black shiny needle-shaped crystals grow from the powder. Chemical analyses by an electron microprobe analyser of the grown crystals proved the correct formulation (% experimental: Ta = 33.4, I = 11.0, Se = 54.5; % theoretical: Ta = 32.30, I = 11.32, Se = 56.37). The space group and cell dimensions were determined from rotation, Weissenberg and precession photographs (Laue symmetry  $4/mmm$ ).

The intensity data were collected on a CAD-4 Nonius diffractometer from a specimen of dimensions  $0.021 \times 0.025 \times 0.50$  mm, the longest along the  $c$  axis,

using graphite-monochromated Mo  $K\alpha$  radiation. 2240 reflections ( $+h, +k, +l$ ) were measured in the range  $1^\circ < \theta < 40^\circ$  using an  $\omega$ -scan mode. As a check on the mechanical and intensity stabilities, three reflexions for each control were selected (at every X-ray exposure hour for intensity control). The data were corrected for Lorentz and polarization factors and also for absorption: program *ABSCOR* in the SDP utility written by Frenz (1980); see Table 1.

The structure was solved from Patterson and Fourier maps and refined by full-matrix least squares minimizing the quantity  $\sum w(|F_o| - |F_c|)^2$ . The structure was further refined with anisotropic temperature factors assigned to all atoms. Refinement converged with  $R = 0.057$ ,  $R_w = 0.044$ . The 'goodness of fit' [ $\sum w(\Delta F)^2 / (NO - NV)$ ]<sup>1/2</sup> for the last cycle was 2.459 with  $NO = 730$  and  $NV = 29$  ( $NO$  and  $NV$  are respectively the number of observations and variables). A final difference Fourier map showed no significant features.

The scattering factors and corrections for the real and imaginary anomalous dispersion for neutral atoms

Table 1. Details of the intensity data collection and the least-squares refinement

Crystal faces	{ $\bar{1}\bar{1}0$ }, { $1\bar{1}0$ }, {100}, {110}, { $\bar{1}10$ }, {001}, {001}
Minimum and maximum transmission	28.38 and 41.21%
Systematic absence	$h + k + l \neq 2n$
Number of reflections used in final refinements, $I \geq 1.5\sigma(I)$	730
$R (= \sum  F_o  -  F_c  / \sum  F_o )$	0.057
$R_w (= [\sum w( F_o  -  F_c )^2 / \sum wF_o^2]^{1/2})$	0.044
Weighting scheme according to the pivot point	$A_2 = 135$ $F_o(\text{max.}) = 460$
$F(000)$	1884

Table 2. Positional parameters and  $B_{eq}$  (Å<sup>2</sup>)

E.s.d.'s are given in parentheses.

$$B_{eq} = \frac{4}{3} \sum_i \sum_j \beta_{ij} \mathbf{a}_i \cdot \mathbf{a}_j$$

		$x$	$y$	$z$	$B_{eq}$
Ta(1)	4(c)	0	$\frac{1}{2}$	0	1.0 (1)
Ta(2)	4(d)	0	$\frac{1}{2}$	$\frac{1}{4}$	1.2 (1)
I(1)	4(e)	0	0	0.1553 (3)	3.1 (3)
Se(1)	16(k)	0.1212 (2)	0.3120 (2)	0.8809 (2)	1.4 (1)
Se(2)	16(k)	0.2160 (2)	0.5449 (2)	0.8693 (2)	1.4 (1)

were taken from *International Tables for X-ray Crystallography* (1974). An extinction parameter  $g = 6.04 \times 10^{-7}$  was also refined.

All calculations were performed with SDP Enraf-Nonius programs written by Frenz (1980). The fractional atomic coordinates and isotropic thermal parameters, with their standard deviations, are given in Table 2.\*

**Discussion.** Fig. 1 shows the projection of the structure on the  $xyO$  plane, partly illustrating the channels in the structure. There is an obvious analogy with  $Nb_3ISe_{12}$  although the unit cell of  $Ta_2ISe_8$  is two thirds that of  $Nb_3ISe_{12}$ . The Ta atoms (4Ta) form linear chains along the  $c$  axis (Fig. 2). In these chains metallic distances are all identical (3.206 Å) as Ta atoms occupy the 4(c) and 4(d) positions, respectively  $0\frac{1}{2}0$ ,  $0\frac{1}{2}\frac{1}{2}$  and  $0\frac{1}{4}\frac{1}{4}$ ,  $0\frac{3}{4}\frac{3}{4}$ . Interatomic distances and correlated e.s.d.'s are given in Table 3.

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SU2 36966 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

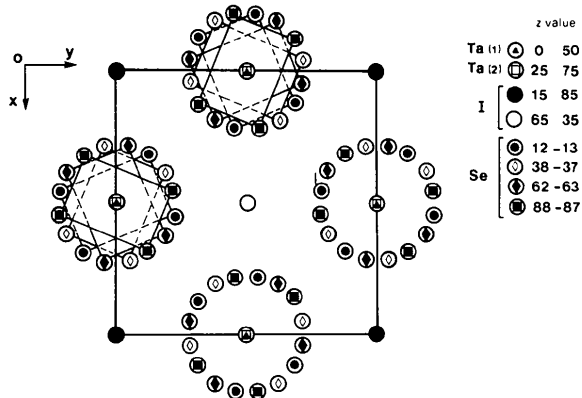


Fig. 1. Structure projection on the  $xyO$  plane.

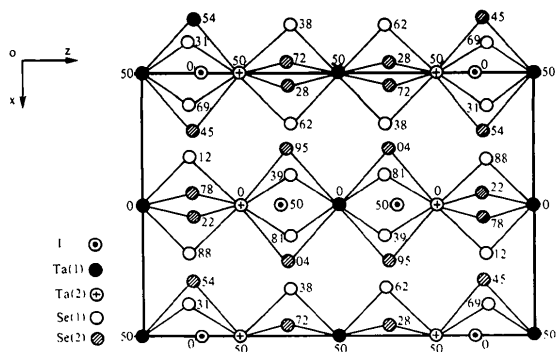


Fig. 2. Structure projection on the  $xOz$  plane. The atomic elevations ( $\times 10^2$ ) are indicated.

Table 3. Interatomic distances (Å) in  $[TaSe_8]$

E.s.d.'s are given in parentheses.

$\left. \begin{array}{l} Ta(1)-Ta(2) \\ Ta(1)-Se(1^I) \\ -Se(1^{II}) \\ -Se(1^{III}) \\ -Se(1^{IV}) \end{array} \right\} \begin{array}{l} 3.206 (1) \\ 2.623 (1) \end{array}$	$\left. \begin{array}{l} Ta(2)-Se(2^{III}) \\ -Se(2^{IV}) \\ -Se(2^V) \\ -Se(2^{VI}) \end{array} \right\} \begin{array}{l} 2.600 (1) \end{array}$
$\left. \begin{array}{l} Ta(1)-Se(2^I) \\ -Se(2^{II}) \\ -Se(2^{III}) \\ -Se(2^{IV}) \end{array} \right\} \begin{array}{l} 2.689 (1) \end{array}$	$\left. \begin{array}{l} Ta(2)-Se(1^{III}) \\ -Se(1^{IV}) \\ -Se(1^V) \\ -Se(1^{VI}) \end{array} \right\} \begin{array}{l} 2.713 (1) \end{array}$

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

The Ta-Ta distances between neighbouring chains are equal to the  $a\sqrt{2}$  value i.e. 6.74 Å. Ta is coordinated to eight Se atoms in a slightly distorted rectangular antiprismatic arrangement. The Se atoms lie in planes approximately perpendicular to the  $c$  axis as is shown in Fig. 3. These planes (separated by the  $c/4$  value) develop in a helicoidal way along the  $c$  axis. In the rectangular bases, the Se atoms are attributed to  $(Se_2)^{2-}$  groups. Indeed, the corresponding Se-Se bonds are characteristic of such a pairing [for example  $Se(1)-Se(2) = 2.401$  Å]. The structure can be described as built up with  $[TaSe_4]$  chains, the I atoms being incorporated between these chains. These I atoms lead to some slight modifications of the Ta-Se bond lengths. The nearest neighbouring Se atoms to the I atom are attracted by it and, as a consequence, the Ta-Se distances become more elongated (Ta-Se = 2.713 Å). This agrees with the fact that I is more electronegative than Se; thus the formal charge over Se perturbed atoms is less than  $-1$  (as is represented by the  $[Se_2]^{2-}$  pairs), which induces a weakening of the Ta-Se bond. Considering the I-I distance along the  $c$  axis (3.964 Å), we can envision isolated I atoms. This was suggested before with the  $Nb_3ISe_{12}$  compound; it was assumed that this compound could be formulated

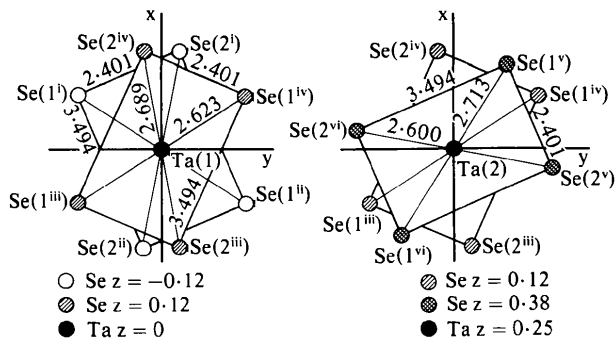


Fig. 3. Antiprism  $[TaSe_8]$  projections.

as  $2\text{Nb}^{4+}\text{Nb}^{5+}\text{I}^{-6}(\text{Se}_2)^{2-}$ . Thus, the tantalum derivative may be formulated as  $\text{Ta}^{4+}\text{Ta}^{5+}\text{I}^{-4}(\text{Se}_2)^{2-}$ . The only difference between the two compounds is the metal-metal bond sequence.  $\text{Nb}_3\text{ISe}_{12}$  exhibits one short (3.061 Å) and two long (3.252 Å) intermetallic distances, whereas no difference is observed with  $\text{Ta}_2\text{ISe}_8$ . The sequence of long and short bonds in the metal-metal chain plays an essential role concerning the semi-conducting properties of these materials (Gressier, Meerschaut, Guemas, Rouxel & Monceau, 1982). More structural investigations are needed in this series of  $\text{MY}_x\text{X}_4$  compounds ( $M = \text{Nb, Ta; } Y = \text{Cl, Br, I; } X = \text{S, Se}$ ). These derivatives may provide a complete

set of compounds to support a critical discussion in the scope of a bond-density wave theory (Whangbo, 1982).

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### Di- $\mu$ -hydroxo-bis[aquasulfatobismuth(III)]

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**Abstract.**  $[\text{Bi}_2(\text{H}_2\text{O})_2(\text{SO}_4)_2(\text{OH})_2]$ , monoclinic,  $P2_1/n$ ,  $a = 6.021$  (1),  $b = 13.363$  (2),  $c = 6.495$  (1) Å,  $\beta = 112.94$  (1)°,  $D_m = 4.62$ ,  $D_x = 4.69$  Mg m<sup>-3</sup>,  $Z = 2$ ;  $R = 0.063$  for 853 observed diffractometer data. The structure consists of molecules in which an O atom of an  $\text{SO}_4^{2-}$  anion and a water molecule are bonded at relatively short distances to each Bi atom of a planar  $\text{Bi}_2(\text{OH})_2^{4+}$  unit. The coordination sphere around the Bi atom is completed by two more O atoms of two different  $\text{SO}_4^{2-}$  anions at longer distances. The coordination polyhedron is a distorted octahedron with the stereochemically active electron lone pair. The molecules form a three-dimensional network.

**Introduction.** The systematic investigation of the hydrolysis of bismuth(III) nitrate (Lazarini, 1981) has been extended to study the chemical behavior and structure of bismuth basic sulfates. There are two compounds important in the scheme of the hydrolysis of bismuth(III) sulfate. The title compound seems to be the first solid product of the hydrolysis at pH below 1.1. Its formula is usually quoted in the literature as  $(\text{BiOH})\text{SO}_4 \cdot \text{H}_2\text{O}$ . The crystal structure of an isomorphous selenium compound has been determined by Aurivillius (1964). The title compound reconverts in the suspension at pH above 1.1 after a few hours into the second product of the hydrolysis,  $[\text{Bi}_2\text{O}(\text{OH})_2]\text{SO}_4$ .

The crystal structure of this compound has also been published by Aurivillius (1964). We decided to reinvestigate the crystal structures of both compounds to enable a precise comparison between the structures of bismuth basic nitrates and sulfates to be made. This paper concerns the crystal-structure analysis of the first product of hydrolysis,  $[\text{Bi}_2(\text{H}_2\text{O})_2(\text{SO}_4)_2(\text{OH})_2]$ , while the results of the crystal-structure analysis of the second product of the hydrolysis are given in the following paper (Golič, Graunar & Lazarini, 1982).

The crystals of the title compound were obtained by slow diffusion of water into an acid-saturated solution of bismuth(III) sulfate using a method described by Ozols (1950). A well developed crystal, selected for the diffraction measurements, was characterized by the following planes (in parentheses are the distances from the crystal faces to an arbitrary origin inside the crystal):  $\pm(110)$  (0.045 mm),  $\pm(1\bar{1}0)$  (0.050 mm),  $(120)$  (0.068 mm),  $(1\bar{2}\bar{1})$  (0.205 mm),  $(121)$  (0.180 mm) and  $\pm(001)$  (0.240 mm).

The intensity data were collected at 293 (1) K with an Enraf-Nonius CAD-4 diffractometer. Experimental conditions were: graphite-monochromatized Mo  $K\alpha$  radiation ( $\lambda = 0.71069$  Å),  $\omega$ - $2\theta$  scan,  $\theta_{\min} = 1^\circ$ ,  $\theta_{\max} = 25^\circ$ ,  $2\theta$  scan width =  $(1.0 + 0.6 \tan \theta)^\circ$ , aperture =  $(2.5 + 0.9 \tan \theta)$  mm, maximum scan time 40 s, background =  $\frac{1}{4}$  of the scan time at each of the