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**Preparation and crystal structure of new one**dimensional Ta selenide: [Ta(Se<sub>2</sub>)<sub>2</sub>]<sub>2</sub>TaBr<sub>6</sub>

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Abstract—Compound [Ta(Se<sub>2</sub>)<sub>2</sub>]<sub>2</sub>TaBr<sub>6</sub> was prepared from elements by high temperature (450°C) stoichiometric reaction in high yield. The structure has been determined by single crystal X-ray diffraction. It contains infinite positively charged chains  $Ta(Se_2)_2$ ... separated by octahedral  $TaBr_6^-$  anions. The slightly alternating Ta-Ta distances within the chains [3.182(2)-3.234(2) Å] show a considerable degree of metal-metal interaction along the chain. © 1998 Elsevier Science Ltd. All rights reserved

Keywords: crystal structure; tantalum complexes; selenium complexes; bromides; one-dimensional materials.

## **INTRODUCTION**

Chemistry and solid state physics of low-dimensional materials is a well established field of research activity [1, 2]. Chalcogenides and chalcohalides of Group 5 transition elements have so far furnished dozens of one-dimensional materials, the prominent examples being TaSe<sub>3</sub> [3] and a remarkable family of "intercalated" selenides  $(NbSe_4)_{v}I(v = 2-4)[4]$ . The polymeric  $NbS_2Cl_2$  has a  $Nb_2(S_2)_2^{4+}$  core and was one of the first well-characterized transition metal chalcohalides [5]. It has recently been shown to be a convenient lead-in compound into the still largely unexplored area of molecular niobium chalcogen complexes [10, 11]. The corresponding Ta chemistry is far less developed. Well characterized products are Ta(Te<sub>2</sub>)<sub>2</sub>I [6],  $[Ta(Te_2)_2]_4I_2(TaI_6)$  [7],  $[Ta(Se_2)_2]_2I$ [12] and  $[Ta(Te_2)_2]_6I_4(TaI_6)$  [9]. Here we report synthesis and crystal structure of a novel one-dimensional Ta selenide bromide, [Ta(Se<sub>2</sub>)<sub>2</sub>]<sub>2</sub>TaBr<sub>6</sub> (1) as a result of our investigations in  $Ta/Se/X_2$  (X = Cl, Br) systems.

## **EXPERIMENTAL**

A mixture of Ta powder (1.00 g, 5.53 mmol), gray Se (1.16 g, 14.69 mmol) and Br<sub>2</sub> (0.28 ml, 5.43 mmol) was placed in a quartz tube which then was sealed under vacuum and heated at 450°C for 1 week. A temperature gradient was maintained. The tube was cooled at  $20^{\circ}$ C h<sup>-1</sup> rate to promote crystal growth. After cooling down, almost complete transport into the cooler end of the tube was observed. The compound crystallizes in the form of long (up to 1 cm), thin black needles. The yield was 90%. The elemental analysis agreed with the formula  $Ta_3Se_8Br_6$  (1). The compound can be handled in air for a limited period but must be stored under nitrogen to avoid degradation which releases HBr and H<sub>2</sub>Se in moist air.

Small amounts of bronze-colored TaSe<sub>2</sub> and red TaBr<sub>5</sub> (less than 5%) also form as byproducts but can be easily separated manually from the main product.

The electrical conductivity of crystals of 1 at room temperature was measured by a two-point contact method;  $\sigma = 10^{-4} \Omega^{-1} \text{ cm}^{-1}$ .

# Crystal structure determination of 1

The structure was determined by the single crystal X-ray crystallography. X-ray data were measured at 295K on a Rigaku AFC-5R diffractometer with

<sup>&</sup>lt;sup>1</sup>Further details of the crystal structure can be ordered from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen (e-mail: crysdata@fiz-karlsruhe.de) under the depository number CSD-408596.

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graphite-monochromated MoK<sub>x</sub> radiation ( $\lambda = 0.71069$  Å) with the  $\omega - 2\theta$  scan mode. The DIFABS program was used for absorption correction. A slight decay (5.42% in intensity) was detected during the data collection and the data were corrected accordingly. The structure was solved by direct methods (SHELX-86) [18]. The full-matrix refinements were performed with the teXsan programs [19]. Crystal data and refinement results are given in Table 1. Selected interatomic distances are given in Table 2.

## **RESULTS AND DISCUSSION**

Figure 1 shows the ORTEP drawing of the structure of 1. The Ta atoms form linear chains running along the c-axis with slightly alternating Ta-Ta distances 3.198(2), 3.234(2) and 3.182(2)Å. The sequence is Ta(1)-Ta(1)-Ta(2)-Ta(2)-Ta(1)-Ta(1)..., Ta(1)-Ta(2) being the largest distance. Se(1) and Se(2) are bridging Ta(1) atoms, two Ta(2) atoms are bridged by Se(3) and Se(4) whereas four non-equivalent Se atoms [Se(5), Se(6), Se(7) and Se(5)] connect Ta(1) with Ta(2). The closest analog to 1 is  $[Ta(Se_2)_2]_2I$ , where all the distances are equal at 3.206(1) Å [12]. Each Ta atom is coordinated to eight Se atoms of four diselenide bridges. The Se-Se distances in the Se<sub>2</sub> ligands vary between 2.35–2.38 Å which can be compared with 2.40 Å in [Ta(Se<sub>2</sub>)<sub>2</sub>]<sub>2</sub>I [12]. It has already been pointed that Se2 groups are rather flexible and use their  $\pi$ -antibonding orbitals to serve as an electronic pool for adjacent metal chains [1]. The significantly shorter Se-Se distance in 1 than in closely related [Te(Se<sub>2</sub>)<sub>2</sub>]<sub>2</sub>I can thus be explained by stronger

1a(1)-	I a(1)	3.198(2)	1a(1) - Se(5)	2./13(3)
Ta(1)-7	Γa(2)	3.234(2)	Ta(1)-Se(2)	2.626(2)
Ta(1)-5	Se(1)	2.653(3)	Ta(1)-Se(6)	2.593(3)
Ta(1)-5	Se(7)	2.690(3)	Ta(1)-Se(8)	2.593(2)
Ta(2)-7	Γa(2)	3.182(2)	Ta(2)-Se(3)	2.625(2)
Ta(2)-5	Se(4)	2.654(3)	Ta(2)-Se(7)	2.595(3)
Ta(2)-5	Se(5)	2.602(3)	Ta(3)–Br(1)	2.518(3)
Ta(2)-5	Se(8)	2.698(2)	Ta(3)–Br(2)	2.520(3)
Ta(2)-5	Se(6)	2.731(3)	Ta(3)–Br(5)	2.490(3)
Ta(3)-l	Br(3)	2.466(3)	Ta(3)–Br(6)	2.498(3)
Ta(3)-l	Br(4)	2.516(3)	Se(5)–Se(8)	2.364(4)
Se(1)-S	e(2)	2.345(4)	Se(6)–Se(7)	2.375(4)
Se(3)-S	e(4)	2.353(4)		
Ta(1)-Ta(1)-Ta(2)			179.35(6)	
Ta(1)-Ta(2)-Ta(2)			179.36(6)	
Ta–Se–Ta			61.21(8)-75.44(7)	
Se(7)–Ta(2)–Se(6)			52.89(8)	
Se(7)–Ta(2)–Se(8)			81.03(8)	
Se(5)-Ta(2)-Se(7)			107.71(8)	
Se(2)–Ta(1)–Se(5)			165.25(9) and 78.88(8)	
Se(1)-Ta(1)-Se(8)			93.30(8) and 130.67(9)	
Br–Ta–Br (cis)			87.9(1)-93.0(1)	
Br–Ta–Br (trans)			175.3(1)-178.1(1)	

Table 2. Bond lengths (Å) and some characteristic angles (°)

electronic demand of metal chains in the bromine compound. The four Se atoms of each bridging pair of the Se<sub>2</sub> ligands lie approximately in planes perpendicular to the chains of Ta atoms, thus forming a

Table 1. Crystal data and refinement results for 1

Formula	Ta <sub>3</sub> Se <sub>8</sub> Br <sub>6</sub>
a (Å)	11.239 (2)
b (Å)	12.847 (2)
<i>c</i> (Å)	7.201 (1)
$\alpha$ (°)	102.51 (1)
$\beta$ (°)	98.04 (1)
γ (°)	70.49(1)
$V(Å^3)$	954.2 (3)
Ζ	2
Formula weight	1653.95
Space group	P1 (No. 2)
$F_{000}$	1402.00
Calculated density (g cm <sup>-3</sup> )	5.756
$\mu ({\rm cm}^{-1})$	411.52
Reflections collected	5823
Unique	5561
Observed $[I > 2.00\sigma(I)]$	3970
Reflections/parameters ratio	25.78
$R^{\mathrm{a}}$	0.063
$R_{ m w}{}^{ m b}$	0.058

 $^{\mathrm{a}}R = \Sigma |F_{\mathrm{o}} - F_{\mathrm{c}}| / \Sigma F_{\mathrm{o}}. \label{eq:relation}$ 

$${}^{\rm b}R_{\rm w} = [\Sigma w (F_{\rm o} - F_{\rm c})^2 / \Sigma w F_{\rm o}^2]^{1/2}.$$



Fig. 1. ORTEP drawing of two repeating units of **1**. Thermal ellipsoids are drawn at the 50% probability level.



Fig. 2. Structure projection on the xyO plane.

rectangle with two short and two long sides. The dihedral angles between each pair of adjacent Se<sub>4</sub> units are close to  $45^{\circ}$  to minimize repulsion between Se atoms and to increase the overlap with 5d orbitals of Ta [6]. These restrictions still leave enough room for different modes of stacking of the Se<sub>4</sub> rectangles in the chain [6]. In 1 (Fig. 2) the stacking pattern is the same as found in the structure of [Nb(Te<sub>2</sub>)<sub>2</sub>]I [6] but differs from those observed for other Ta(Se<sub>2</sub>)<sub>2</sub> and Ta(Te<sub>2</sub>)<sub>2</sub> chains [6, 12]. The chains are separated by slightly distorted TaBr<sub>6</sub><sup>-</sup> anions (the Ta-Br distances are in the range 2.47–2.52 Å). In a relevant complex

[TaBr<sub>4</sub>(diars)<sub>2</sub>][TaBr<sub>6</sub>], this anion forms almost perfect octahedron (Ta–Br 2.49 Å) [14]. The distortions may be due to additional Se...Br contacts (the shortest one, between Se(5) and Br(5), is 3.162(4) Å), which may also favor the observed stacking pattern for the Se<sub>4</sub> rectangles. The contacts of this kind fall well shorter than the corresponding sum of van-der Waals radii and are a well established feature in the chemistry of heavier chalcogens [15].

Since the bond distances in the anion show the oxidation state of the Ta atom in the  $TaBr_6^-$  unit to be five, a positive charge +1 should he assigned to the  $[Ta(Se_2)_2]_2$  unit. It means that the Ta atoms have the oxidation state +4.5 which leaves 0.5e per one Ta-Ta bond (if we consider the diselenium bridges as  $Se_2^{2-}$ ). If we take into account the donation of an extra electron density from the bridging ligands it will give us less negative charge on the Se<sub>2</sub> unit and correspondingly stronger bonding interaction between tantalum atoms. This is in keeping with the observed distances of about 3.20 Å for 1 and  $[Ta(Se_2)_2]_2I$  with the same formal oxidation state. It is thus considerably shorter than that in  $[Ta(Te_2)_2]I$ (3.33-3.35 Å) where the oxidation state is +5 which implies zero bonding order. Accordingly, preliminary resistivity measurements on the single crystals of 1 gave value which may indicate semiconductive behavior.

The prepared material thus belongs to the by now extensive family of one-dimensional structures, hav-



Fig. 3. Unit cell drawing of 1.

ing positively charged metal-dichalcogen chains separated by counteranions (Fig. 3). As for the latter, both simple small anions (like I<sup>-</sup>) and large complex ones (PtI<sub>6</sub><sup>2-</sup> [8], TaI<sub>6</sub><sup>-</sup> [7, 9], TaBr<sub>6</sub><sup>-</sup>) are effective in the stabilization of this type of structure. It seems possible that other anions of various shape and size may be good candidates as well.

In conclusion it may be mentioned that the synthesis of **1** is one of the rare cases when Nb and Ta do not behave in a similar way. Thus, in the reaction conditions similar to those used in the present study, Nb forms NbSe<sub>2</sub>Br<sub>2</sub>, a coordination polymer where Nb<sub>2</sub>(Se<sub>2</sub>)<sub>2</sub> cluster units are linked by bromine atoms similar to NbS<sub>2</sub>Cl<sub>2</sub> [13]. On the other hand it was not possible to prepare the Ta analog of NbS<sub>2</sub>Cl<sub>2</sub>, only TaS<sub>3</sub> and TaCl<sub>5</sub> could be detected [13]. One of the reasons may be the greater reluctance of Ta to form low oxidation states, in keeping with the overall trend in the periodic table.

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