References

Bernardinelli, G. & Flack, H. D. (1985). *Acta Cryst.* A41, 500–511.

Blackburn, A. C. & Gerkin, R. E. (1994). *Acta Cryst.* C50, 835–838.

Cromer, D. T. & Waber, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, pp. 71, 148. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

Flack, H. D. (1983). *Acta Cryst.* A39, 876–881.

Hirshfeld, F. L. (1976). *Acta Cryst.* A32, 239–244.

Johnson, C. K. (1976). *ORTEPII.* Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Lindgren, O. (1977). *Acta Chem. Scand. Ser. A*, 31, 591–594.

Meulenaer, J. de & Tompa, H. (1965). *Acta Cryst.* 19, 1014–1018.

Molecular Structure Corporation (1988). *MSC/AFC Diffractometer Control Software.* MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Molecular Structure Corporation (1989). *TEXSAN. TEXRAY Structure Analysis Package.* Version 5.0. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Rosenfield, R. E., Trueblood, K. N. & Dunitz, J. D. (1978). *Acta Cryst.* A34, 828–829.

Schomaker, V. & Trueblood, K. N. (1968). *Acta Cryst.* B24, 63–76.

Sheldrick, G. M. (1993). *SHELXL93. Program for Crystal Structure Refinement.* Univ. of Göttingen, Germany.

Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* 42, 3174–3187.

Trueblood, K. N. (1986). *THMA11.* Univ. of California, Los Angeles, USA.

Ta$_3$S$_{2-x}$Se$_x$, Partial Substitution of Selenium for Sulfur into a Tantalum-Rich Sulfide

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Abstract

In the pentagonal antiprismatic columnar structure of Ta$_3$S$_2$, sulfur can be partially replaced by selenium. Selenium accumulates preferentially at one of two independent sites, which leads to unusually short Ch—Ch [2.973 (3) Å] contacts, where Ch denotes a chalcogen site.

Comment

The structural chemistries of tantalum-rich sulfides and selenides differ drastically. Whereas the structure of Ta$_2$S (Franzen & Smeggil, 1969) results from the interpenetration of centred Ta$_{13}$ icosahedra along a

pseudo fivefold axis of symmetry, Ta$_2$Se forms a unique layered-type structure which is symmetry related to b.c.c. Ta (Harbrecht, 1989). In order to gain information about the relative stability of the distinct structural arrangements, we systematically investigated the Ta-rich region of the ternary Ta–S–Se system.

Entropically stabilized high-temperature phases of Ta$_5$(S,Se)$_2$, the (Nb,Ta)$_5$S$_2$ structure type (Yao & Franzen, 1991) and Ta$_9$(S,Se)$_4$ are accessible above temperatures of approximately 1700 K. These b.c.c.-related phases have no pendants in the binary systems (Harbrecht & Degen, 1993). In contrast to earlier reports (Nanjundaswamy & Hughbanks, 1992), we found that a significant amount of selenium can be substituted for sulfur in the structures of the sulfides. Such a mixed chalcogenide of the Ta$_3$S$_2$ structure type (Wada & Onoda, 1989; Kim, Nanjundaswamy & Hughbanks, 1991) is the subject of this report.

The structure of Ta$_3$(S,Se)$_2$ consists of distorted Ta$_{13}$ icosahedra which interpenetrate along the c axis forming columns of face-shared pentagonal antiprismatic clusters, ∞^1[TaTa$_{10/2}$]. Very short Ta—Ta contacts exist [Ta4—Ta4 2.811 (2) Å, compared to 2.860 Å in b.c.c.-Ta] in the centre of the pentagonal antiprismatic TaTa$_{10}$ clusters. The columns of condensed clusters are linked to one another, parallel to a, by weaker Ta1—Ta3 [3.158 (1) Å] and Ta3—Ta3 [3.650 (1) Å] contacts and strong heteronuclear bonds Ch2—Ta [2.455 (2)–2.492 (2) Å], where Ch is S or Se.

As can be seen from Fig. 2, these complex layers are also covered by Ch1 over triangular faces [Ch1—Ta1 and 2 × Ch1—Ta2 2.472 (2)–2.529 (2) Å]. Heteronuclear interlayer contacts seem to be weaker [Ch1—Ta2 2.709 (2), Ch2—Ta1 2.547 (2) Å] than interactions within the two-dimensional arrays. The specific stacking of the layers along b results in empty channels running
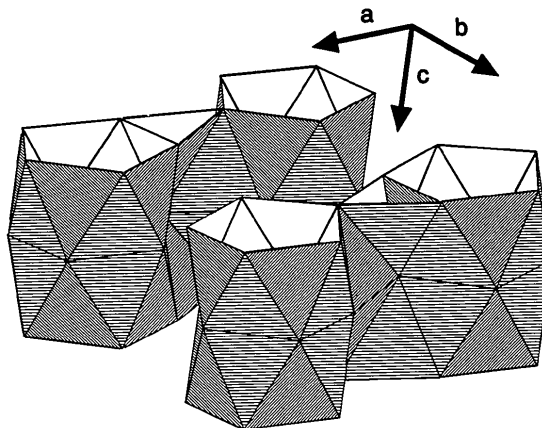

Fig. 1. Polyhedral representation of the tantalum partial structure of Ta$_3$(S,Se)$_2$ depicted as pentagonal antiprismatic columns connected *via* Ta$_4$ tetrahedra. Since the columns are centred by Ta4 (which are omitted for clarity) the layers are tetrahedrally close packed.
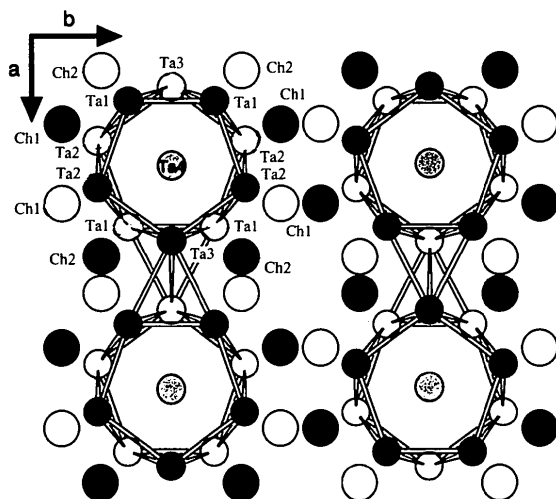
Fig. 2. Projection of the structure of $Ta_3(S,Se)_2$ along **c**. Distorted Ta_{13} icosahedra parallel to the **c** axis penetrate to form pentagonal antiprismatic cluster columns. Ta—Ch and Ta4—Ta bonds are omitted for clarity. Height of the atoms: black $z(Ta1,Ta2) = 1/2$, $z(Ch1,Ch2) \simeq 5/8$; grey $z(Ta4) \simeq 1/4$; white $z(Ta1,Ta2) = 0$, $z(Ch1,Ch2) \simeq 1/8$.

parallel to **c**. These void regions, which are enclosed by chalcogen atoms, are large enough to accommodate guest molecules. Distances to the peripheral square-antiprismatically arranged chalcogen atoms range from 2.46 to 2.94 Å. In spite of the presence of the empty channels there is some steric crowding among chalcogen atoms in the interlayer region. Short Ch—Ch contacts have values 2.973 (3) and 3.069 (3) Å. Nanjundaswamy & Hughbanks (1992) argued on the basis of their experimental observations that, due to spatial constraints, the structure type is unsuitable for accommodating selenium. The structure refinement, however, clearly proves that more than 15% of the Se atoms can be substituted for S atoms. Moreover, Se atoms accumulate preferentially at the Ch1 position [20.6 (9)%], the site with shorter Ch—Ch distances [2.973 (3) cf. 2.928 (6) Å in Ta_3S_2] and longer interlayer Ch—Ta contacts. The Ch2 position is 12.1 (9)% occupied by Se. The preference of Se atoms for one of the two distinct positions is also clearly indicated by a smaller increase in the difference of the mean Ch—Ta distance for Ch2 (0.023 Å) than for Ch1 (0.039 Å) compared with the respective mean values for Ta_3S_2.

Experimental

Crystals of $Ta_3(S,Se)_2$ near the Se-rich boundary were synthesized in a sealed molybdenum crucible (4 h, 1870–1270 K) from appropriate mixtures of tantalum disulfide, tantalum and selenium with the use of iodine as a transport agent. The selenium incorporation becomes apparent in an anisotropic expansion of the lattice parameters ($\Delta a = 0.022$, $\Delta b = 0.126$,

$\Delta c = 0.012$ Å) relative to those of the binary sulfide. Incorporation of molybdenum was below the detection limit of EDX analyses.

Crystal data

$S_{1.68}Se_{0.32}Ta_3$	Mo $K\alpha$ radiation
$M_r = 622.04$	$\lambda = 0.7107$ Å
Orthorhombic	Cell parameters from 25
$Abm2$	reflections
$a = 7.5018\,(10)$ Å	$\theta = 8–16.5°$
$b = 17.358\,(4)$ Å	$\mu = 93.372$ mm^{-1}
$c = 5.6204\,(4)$ Å	$T = 293\,(2)$ K
$V = 731.9\,(2)$ Å^3	Needle
$Z = 8$	$0.40 \times 0.10 \times 0.05$ mm
$D_x = 11.291$ Mg m^{-3}	Black

Data collection

Enraf–Nonius CAD-4 diffractometer	1292 observed reflections $[I > 2\sigma(I)]$
ω–2θ scans	$R_{int} = 0.0260$
Absorption correction:	$\theta_{max} = 34.91°$
ψ scan then refined from	$h = 0 \rightarrow 12$
ΔF (see below)	$k = -28 \rightarrow 28$
$T_{min} = 0.387$, $T_{max} = 0.997$	$l = -9 \rightarrow 9$
3403 measured reflections	1 standard reflection frequency: 43 min
1647 independent reflections	intensity decay: none

Refinement

Refinement on F^2	Extinction correction:
$R[F^2 > 2\sigma(F^2)] = 0.0222$	$F_c^* = 1/kF_c[1 + (0.001\chi$
$wR(F^2) = 0.0397$	$\times F_c^2\lambda^3/\sin2\theta)]^{1/4}$
$S = 0.970$	Extinction coefficient:
1647 reflections	$\chi = 0.000320\,(14)$
52 parameters	Atomic scattering factors
$w = 1/[\sigma^2(F_o^2) + (0.0123P)^2]$	from International Tables
where $P = (F_o^2 + 2F_c^2)/3$	for Crystallography (1992,
$(\Delta/\sigma)_{max} = 0.001$	Vol. C, Tables 4.2.6.8 and
$\Delta\rho_{max} = 2.542$ e Å^{-3}	6.1.1.4)
$\Delta\rho_{min} = -2.247$ e Å^{-3}	

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Ta1	0.71936 (4)	0.16727 (2)	0.0	0.00538 (7)
Ta2	0.10433 (4)	0.10867 (2)	0.9938 (2)	0.00544 (6)
Ta3	0.65524 (7)	1/4	0.4804 (2)	0.00560 (11)
Ta4	0.9956 (2)	1/4	0.7446 (3)	0.00468 (9)
Ch1†	0.8234 (3)	0.03888 (12)	0.8697 (4)	0.0087 (6)
Ch2‡	0.5822 (3)	0.1148 (2)	0.3698 (4)	0.0097 (6)

† Ch1 = 79.4 (9)% S + 20.6% Se.
‡ Ch2 = 87.9 (9)% S + 12.1% Se.

Table 2. Selected distances (Å)

Ta4—Ta1	2.901 (1) ×2	Ta4—Ta3	2.936 (2)	
Ta4—Ta1	2.920 (1) ×2	Ta4—Ta3	2.953 (2)	
Ta4—Ta2	2.927 (1) ×2	Ta4—Ta4	2.811 (2)	×2
Ta4—Ta2	2.940 (1) ×2			

Ta3—Ta1	3.290 (1) ×2	Ta2—Ta1	3.298 (1)	
Ta3—Ta1	3.096 (1) ×2	Ta2—Ta1	3.238 (1)	
Ta3—Ta1	3.158 (1) ×2	Ta2—Ta1	3.062 (1)	
Ta3—Ta2	3.046 (1) ×2	Ta2—Ta2	3.217 (1) ×2	
Ta1—Ta1	2.872 (1)			
Ch1—Ta1	2.472 (2)	Ch2—Ta1	2.492 (2)	
Ch1—Ta2	2.495 (2)	Ch2—Ta2	2.455 (2)	
Ch1—Ta2	2.529 (2)	Ch2—Ta3	2.489 (3)	
Ch1—Ta2	2.709 (2)	Ch2—Ta1	2.547 (2)	

Structure refinement on the basis of intensities that had been corrected for absorption using only ψ-scan data (SDP-Plus; B. A. Frenz & Associates Inc., 1984) led to $R[F^2 > 3\sigma(F^2)] = 0.039$; calculations on intensities corrected only by DIFABS (Walker & Stuart, 1983) led to $R[F^2 > 3\sigma(F^2)] = 0.025$. In order to obtain improved structural data, intensities were corrected via ψ scans before applying the correction based on ΔF. This refinement converged at $R[F^2 > 3\sigma(F^2)] = 0.024$. The same correction procedures were applied in the refinements using the program SHELXL93 (Sheldrick, 1993), which allowed twinning by inversion to be taken into account; this resulted in a decrease in the R values by about 0.003. Differences in the R values are due to the different $n\sigma(F^2)$ limits. The differences in the final positional parameters resulting from the different refinements were within the limits of the e.s.d.'s. The ratio T_{max}/T_{min} is in accord with a difference of 0.012 mm between the lengths of the two orthogonal edges perpendicular to the needle axis. Flack's absolute structure parameter (Flack, 1983) converged at 0.60 (3).

Data collection: Enraf–Nonius CAD-4 diffractometer software. Cell refinement: Enraf–Nonius CAD-4 diffractometer software. Data reduction: SDP-Plus. Program(s) used to refine structure: SHELXL93. Molecular graphics: SCHAKAL92 (Keller, 1992).

Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: SE1065). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

B. A. Frenz & Associates Inc. (1984). SDP-Plus Structure Determination Package. College Station, Texas, USA.
Flack, H. D. (1983). Acta Cryst. A39, 876–881.
Franzen, H. F. & Smeggil, J. G. (1969). Acta Cryst. B25, 1736–1741.
Harbrecht, B. (1989). Angew. Chem. 101, 1696–1698.
Harbrecht, B. & Degen, T. (1993). 7. Tagung Festkörperanalytik, Chemnitz, 22–25 June 1993, Book of Abstracts, p. 136.
Keller, E. (1992). SCHAKAL92. Fortran Program for the Graphical Representation of Molecular and Crystallographic Models. Univ. of Freiburg, Germany.
Kim, S.-J., Nanjundaswamy, K. S. & Hughbanks, T. (1991). Inorg. Chem. 30, 159–164.
Nanjundaswamy, K. S. & Hughbanks, T. (1992). J. Solid State Chem. 98, 278–290.
Sheldrick, G. M. (1993). SHELXL93. Program for the Refinement of Crystal Structures. Univ. of Göttingen, Germany.
Wada, H. & Onoda, M. (1989). Mater. Res. Bull. 24, 191–196.
Walker, N. & Stuart, D. (1983). Acta Cryst. A39, 158–166.
Yao, X. & Franzen, H. F. (1991). J. Am. Chem. Soc. 113, 1426–1427.

Synthetic Magnesium Sodium Hydrogen Monophosphate: MgNa3H(PO4)2

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Abstract

The structure belongs to the monophosphate group and contains one type of PO_4 tetrahedra connected to one type of MgO_6 octahedra by corner sharing. These PO_4–MgO_6 groups are connected along the two shorter a and b axes to form two-dimensional zigzag sheets. Two sheets are connected along the longer c axis by two types of Na–O polyhedra. Pairs of PO_4 tetrahedra in the sheets are connected by H atoms situated at the centres of symmetry, forming short hydrogen bonds.

Comment

This research was started with the purpose of contributing to the understanding of the structures of monophosphates. In previous structural studies of magnesium sodium monophosphates, Ghorbel, d'Yvoire & Dorémieux-Morin (1974) carried out the syntheses of three compounds: $MgNa_4(PO_4)_2.H_2O$ and α- and γ-$MgNa_4(PO_4)_2$. The structural relationships of these three compounds were investigated by means of X-ray powder diffractometry. Ben Amara, Vlasse, Olazcuaga, Le Flem & Hagenmuller (1983) have determined the structure of $Mg_4Na(PO_4)_3$. Approximate cell dimensions of $MgNa_3H(PO_4)_2$ have been determined by the National Bureau of Standards (Morris & MacMundy, 1984) and the space group was described as $P1$. A study on the same compound by X-ray powder method was reported by Ben Amor & Romdhane (1992). They assigned space group $C2/m$ to this compound. No further structural studies of this compound have been reported to date. The present study describes the synthesis and the structure determination of this compound.

The mean Mg—O distance is 2.095 Å [cf. 2.023, 2.076 and 2.080 Å reported by Ben Amara et al. (1983), and 2.102, 2.026 and 2.120 Å reported by Yamakawa, Yamada & Kawahara (1994)]. The mean P—O distance is 1.537 Å, which is compatible with the P—O distances found previously [1.526, 1.538 and 1.538 Å found by Ben Amara et al. (1983), 1.538 and 1.535 Å by Yamakawa et al. (1994) and 1.536 Å by Corbridge (1971)]. The interatomic distance of the short