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Petra Stoll *et al.*

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Cs$_6$Ta$_4$S$_{22}$

Petra Stoll, Christian Näther, Inke Jeß and Wolfgang Bensch*

Institut für Anorganische Chemie, Christian-Albrechts-Universität Kiel, Olshausenstraße 40, D-24098 Kiel, Germany
Correspondence e-mail: wbensch@ac.uni-kiel.de

The reaction of Cs$_2$S$_3$, Ta and S yields single crystals of the new caesium tantalum chalcogenide hexacaesium tetratantalum docosasulfide, Cs$_6$Ta$_4$S$_{22}$, which is isotypic with Rb$_6$Ta$_4$S$_{22}$ and the niobium compounds A_6Nb$_4$S$_{22}$ (A = Rb, Cs). The structure consists of discrete [Ta$_4$S$_{22}$]$^{6-}$ anions and Cs$^+$ cations.

Comment

In recent years, we have successfully synthesized a large number of new polychalcogenide compounds in the $A/M/Q$ system (A = alkaline metal; M = Nb, Ta; Q = O, S, Se). All compounds exhibit the M_2Q_{11} unit as the general structural motif (Bensch *et al.*, 1999). We have synthesized compounds with isolated monomeric units or dimers, as well as polymers. The M_2Q_{11} units are connected either directly or *via* additional chalcogenide ligands. Most of the compounds contain niobium as the transition metal, whereas for tantalum, only a few examples have been reported (Bensch & Dürichen, 1996; Dürichen & Bensch, 1998; Herzog *et al.*, 1999; Schreiner *et al.*, 1989; Stoll *et al.*, 2000). Cs$_6$Ta$_4$S$_{22}$ was obtained as single crystals by reacting Cs$_2$S$_3$ with Ta and S. The crystal structure consists of Cs$^+$ cations and [Ta$_4$S$_{22}$]$^{6-}$ anions. Two Ta$_2$S$_{11}$ subunits are connected *via* terminal sulfur ligands thus forming the [Ta$_4$S$_{22}$]$^{6-}$ anion. Every Ta^{5+} ion is in a sevenfold coordination, forming a strongly distorted pentagonal bipyramid. The coordination mode within the [Ta$_4$S$_{22}$]$^{6-}$ anion can be described as [{Ta$_2$(μ_2-η^2,η^1-S$_2$)$_3$(η^2-S$_2$)(S)$_2$}$_2$(μ_2-η^1,η^1-S$_2$)]$^{6-}$.

Every Ta atom has a very short bond to the axial S^{2-} of about 2.2156 (13) Å for Ta1 and 2.2098 (11) Å for Ta2. In addition, for each Ta^{5+} cation, five Ta—S separations are found scattered around 2.4 Å [2.4324 (12), 2.4446 (13), 2.4499 (10), 2.4531 (12) and 2.5445 (11) Å for Ta1—S; 2.4422 (12), 2.4428 (10), 2.4784 (11) and 2.5007 (11) Å for Ta2—S]. Long interatomic Ta—S distances of 2.9306 (11) and 2.8706 (10) Å are observed to the S atom of a η^2-S$_2$$^{2-}$ anion attached to the neighbouring Ta atom. It is noteable that the long Ta—S distances are positioned *trans* to the short Ta—S bonds. The Ta—S distances agree well with those reported in

the literature (Herzog *et al.*, 1999; Schreiner *et al.*, 1989; Stoll *et al.*, 2000). The S—S distances in the S$_2$$^{2-}$ anions are in the range 2.081 (2)–2.093 (2) Å (average 2.088 Å) and are typical for S—S single bonds.

The three crystallographically independent Cs$^+$ cations are in an irregular environment of S atoms. Using a cutoff of 4 Å, the mean Cs—S distances in Cs$_6$Ta$_4$S$_{22}$ are 3.646 (2) Å for Cs1 (CN11), 3.656 (2) Å for Cs2 (CN10) and 3.617 (2) Å for Cs3 (CN9). These values are in good agreement with the sum of the ionic radii [1.84 Å for S^{2-} and 1.78 Å for Cs$^+$ (CN9); Shannon, 1976]. The two Ta atoms are displaced from the pentagonal planes composed of S atoms towards the terminal S atom by 0.5458 (6) (Ta1) and 0.5292 (5) Å (Ta2). The angle between the planes is 52.23 (3)°. These values are comparable with those reported for the isotypic compounds Rb$_6$Ta$_4$S$_{22}$ (0.550, 0.532 Å and 52.3 °, respectively; Stoll *et al.*, 2000) and Cs$_6$Nb$_4$S$_{22}$ (0.5593, 0.5417 Å and 52.4°, respectively; Bensch & Dürichen, 1996; Dürichen, 1998). The closest Ta—Ta distance amounts to 3.578 (2) Å and the shortest Cs—Cs distance to 4.849 (1) Å, which are too long for significant metal-to-metal interactions [0.69 Å for Ta^{5+} (CN7) and 1.78 Å for Cs^{1+} (CN9); Shannon, 1976]. Fitting the [Ta$_4$S$_{22}$]$^{6-}$ anion of the title compound onto the [Ta$_4$S$_{22}$]$^{6-}$ anion of the isotypic Rb$_6$Nb$_4$S$_{22}$ compound (Stoll *et al.*, 2000), a mean deviation of only 0.013 Å is obtained, demonstrating that the influence of the counterions on the geometry of the anions is small.

Experimental

Cs$_6$Ta$_4$S$_{22}$ was prepared by the reaction of Cs$_2$S$_3$, Ta and S in the ratio 1.3:1:5.6. Cs$_2$S$_3$ was prepared from stoichiometric amounts of Cs and S in liquid ammonia under an argon atmosphere. The tantalum powder was activated by treating it with ultrasonic radiation in dimethylformamide and was dried before use. The starting materials were mixed thoroughly in a dry box and sealed into a Pyrex-glass ampoule, which was evacuated to 10^{-5} Pa. The ampoule was heated at 673 K for 5 d, cooled to 373 K at 3 K h^{-1} and then to room temperature at 12 K h^{-1}. The resulting melt was washed with dry dimethylformamide and the residue was dried *in vacuo*. It consists of red–orange polyhedra (yield: about 50% based on Ta) which are stable in air for several weeks, and a yellow powder that has thus far not been identified.

Crystal data

Cs$_6$Ta$_4$S$_{22}$	D_x = 3.947 Mg m^{-3}
M_r = 2226.58	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 8000
a = 12.1251 (10) Å	reflections
b = 8.1320 (5) Å	θ = 6–60°
c = 19.5195 (15) Å	μ = 18.615 mm^{-1}
β = 103.230 (9)°	T = 293 (2) K
V = 1873.6 (2) Å^3	Polyhedra, red–orange
Z = 2	0.1 × 0.05 × 0.02 mm

Data collection

Stoe Imaging Plate Diffraction System	5393 independent reflections
	4878 reflections with $I > 2\sigma(I)$
φ scans	R_{int} = 0.044
Absorption correction: numerical (*X-SHAPE*; Stoe & Cie, 1997)	θ_{max} = 30.34°
	h = −17 → 17
T_{min} = 0.339, T_{max} = 0.689	k = −10 → 11
22 679 measured reflections	l = −27 → 27

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} = 0.002$
$R[F^2 > 2\sigma(F^2)] = 0.024$	$\Delta\rho_{max} = 1.13$ e Å^{-3}
$wR(F^2) = 0.059$	$\Delta\rho_{min} = -1.45$ e Å^{-3}
$S = 1.065$	Extinction correction: *SHELXL*97
5393 reflections	Extinction coefficient: 9.3 (10) $\times$
146 parameters	10^{-4}
$w = 1/[\sigma^2(F_o{}^2) + (0.0317P)^2$	
$+ 3.9178P]$	
where $P = (F_o{}^2 + 2F_c{}^2)/3$	

Table 1
Selected geometric parameters (Å).

Ta1—S1	2.2156 (13)	Ta2—S7	2.4784 (11)
Ta1—S4	2.4342 (12)	Ta2—S11	2.4869 (10)
Ta1—S2	2.4446 (13)	Ta2—S6	2.5007 (11)
Ta1—S5	2.4499 (10)	Ta2—S5	2.8706 (10)
Ta1—S3	2.4531 (12)	S2—S3	2.091 (2)
Ta1—S6	2.5445 (11)	S4—S5	2.0921 (16)
Ta1—S8	2.9306 (11)	S6—S7	2.0844 (15)
Ta2—S10	2.2098 (11)	S8—S9	2.0927 (17)
Ta2—S9	2.4422 (12)	S11—S11^i	2.081 (2)
Ta2—S8	2.4428 (10)		

Symmetry code: (i) $1 - x, 2 - y, 1 - z$.

Data collection: *IPDS* (Stoe & Cie, 1998); cell refinement: *IPDS*; data reduction: *IPDS*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); software used to prepare material for publication: *CIFTAB* in *SHELXL*97.

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