Table 4. *Selected geometric parameters (Å, °) for Cs_3NiCl_5*

Cs1—Cl1^{i}	3.638 (2)	Cs2—Cl1^{iv}	3.4386 (8)
Cs1—Cl2^{ii}	3.8231 (14)	Cs2—Cl2^{v}	3.627 (2)
Cs2—Cl2^{iii}	3.431 (2)	Ni—Cl2^{vi}	2.245 (2)
Cl2^{vi}—Ni—Cl2^{vii}	111.23 (6)	Cl2^{vii}—Ni—Cl2^{viii}	106.01 (11)

Symmetry codes: (i) $-x, y, \frac{1}{2}-z$; (ii) $1-y, x, 1-z$; (iii) $\frac{1}{2}-x, \frac{3}{2}-y, z-\frac{1}{2}$; (iv) $x, 1+y, z$; (v) $\frac{1}{2}-y, \frac{1}{2}+x, \frac{1}{2}-z$; (vi) $x, y, 1-z$; (vii) $y-\frac{1}{2}, \frac{1}{2}-x, z-\frac{1}{2}$; (viii) $\frac{1}{2}-y, \frac{1}{2}+x, z-\frac{1}{2}$.

For Cs_3NiCl_5, residual electron density greater than 1 e Å^{-3} was observed. The largest positive peak in the final difference Fourier map was 0.70 Å from Cs2 and the largest negative peak was 0.69 Å from Cs2.

For both compounds, data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *LSUCR* (Evans *et al.*, 1963); data reduction: *NRCVAX* (Gabe *et al.*, 1989); program(s) used to solve structures: *SHELXS*86 (Sheldrick, 1985); program(s) used to refine structures: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *ATOMS* (Dowty, 1995); software used to prepare material for publication: *SHELXL*93.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1253). Services for accessing these data are described at the back of the journal.

References

Dowty, E. (1995). *ATOMS. A Computer Program for Displaying Atomic Structures.* Version 3.1 for Windows. 521 Hidden Valley Road, Kingsport, TN 37663, USA.

Dunitz, J. D. & Orgel, L. E. (1960). *Adv. Inorg. Chem. Radiochem.* **2**, 1–60.

Enraf–Nonius (1989). *CAD-4 Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.

Evans, H. T., Appleman, D. E. & Handwerker, D. S. (1963). *Am. Crystallogr. Assoc. Ann. Meet. Prog.* 42. Cambridge, Massachusetts, USA.

Gabe, E. J., Le Page, Y., Charland, J.-P., Lee, F. L. & White, P. S. (1989). *J. Appl. Cryst.* **22**, 384–387.

Gaebell, H.-Ch. & Meyer, G. (1984). *Z. Anorg. Allg. Chem.* **515**, 133–140.

Gill, N. S. & Nyholm, R. S. (1959). *J. Chem. Soc.* pp. 3997–4007.

Iberson, E., Gut, R. & Gruen, D. M. (1962). *J. Phys. Chem.* **66**, 65–69.

Lutz, H. D., Partik, M., Schneider, M. & Wickel, Ch. (1997). *Z. Kristallogr.* **212**, 418–422.

Minkiewicz, V. J., Cox, D. E. & Shirane, G. (1970). *Solid State Commun.* **8**, 1001–1005.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

Reynolds, P. A., Figgis, B. N. & White, A. H. (1981). *Acta Cryst.* B**37**, 508–513.

Sassmannshausen, M. (1998). PhD thesis, University of Siegen, Germany. In preparation.

Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures.* University of Göttingen, Germany.

Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.

Tishchenko, G. N. (1955). *Tr. Inst. Kristallogr. Akad. Nauk SSSR.* **11**, 93–96.

Trudeau, Y., Plumer, M. L., Poirier, M. & Caillé, A. (1993). *Phys. Rev. B*, **48**, 12805–12812.

Venanzi, L. M. (1958). *J. Chem. Soc.* pp. 719–724.

Acta Cryst. (1998). C**54**, 706–708

New Compounds Containing the Complex Anion $[Ta_2S_{11}]^{4-}$; $A_4Ta_2S_{11}$ (A = Rb, Cs)

PETER DÜRICHEN AND WOLFGANG BENSCH

Institut für Anorganische Chemie der Universität Kiel,
Olshausener Straße 40, 24098 Kiel, Germany. E-mail:
wbensch@ac.uni-kiel.de

(*Received 18 July 1997; accepted 1 December 1997*)

Abstract

The new tetra(alkali metal) ditantalum undecasulfides $A_4Ta_2S_{11}$ (A = Rb, Cs) were prepared at low temperature *via* the molten-flux method. The crystal structures consist of well separated A^+ and $[Ta_2S_{11}]^{4-}$ ions. Within the anions, the Ta atoms display a sevenfold coordination by S_2^{2-} units and S^{2-} anions; the coordination polyhedra can be described as distorted pentagonal bipyramids. Two such bipyramids share common faces, thus forming the $[Ta_2S_{11}]^{4-}$ anion.

Comment

Reactions in molten alkali–polychalcogenide melts (Sunshine *et al.*, 1987) have led to a wide variety of new compounds with interesting new structures (Kanatzidis & Sutorik, 1995). During our investigations into the reaction of group V metals with such melts, we were able to prepare a number of new ternary chalcogenometallates, *e.g.* $K_4Nb_2S_{11}$ (Bensch & Dürichen, 1996*a*), $K_6Nb_4S_{25}$ (Bensch & Dürichen, 1996*b*), $K_4Nb_2S_{14}$ (Bensch & Dürichen, 1997), $A_6Nb_4S_{22}$ (A = Rb, Cs; Bensch & Dürichen, 1996*c*) and $NaNbS_6$ (Bensch *et al.*, 1998). Most of these contain an Nb_2S_{11} unit of two face-sharing pentagonal bipyramids as a main structural 'building block'. The tendency to form this unit is also documented for the lighter homologue vanadium, for example, $[V_2S_{20}O_4]^{6-}$ (Simonnet-Jegat *et al.*, 1996), and for group VI chalcogenometallates as in the complex anions $[Mo_2S_9O_2]^{2-}$ (Coucouvanis & Hadjikyriacou, 1987) and $[W_2S_{11}]^{2-}$ (Manoli *et al.*, 1987).

The title compounds $Rb_4Ta_2S_{11}$ and $Cs_4Ta_2S_{11}$ are isotypic with the previously reported sulfides $K_4Ta_2S_{11}$ (Schreiner *et al.*, 1989) and $K_4Nb_2S_{11}$ (Bensch & Dürichen, 1996*a*). Their structures consist of complex $[Ta_2S_{11}]^{4-}$ anions that are well separated from the alkali cations. The complex anion $[Ta_2S_{11}]^{4-}$ is best described as two face-sharing distorted pentagonal TaS_7 bipyramids. In both bipyramids, one apical position is occupied by a terminal monosulfide S^{2-} anion and the second by one S atom of a neighbouring S_2^{2-} dumbbell. Within the pentagonal plane, two η^2-bound S_2^{2-} units and one μ_2-S^{2-} unit bridging the two Ta^{5+} centres are found. Hence, the anion may be described as $[Ta_2(\mu\text{-}S)(\mu\text{-}\eta^2,\eta^1\text{-}S_2)_2(\eta^2\text{-}S_2)_2(S)_2]^{4-}$. Fitting the $[Ta_2S_{11}]^{4-}$ anion of $Rb_4Ta_2S_{11}$ onto the $[Ta_2S_{11}]^{4-}$ anion of the caesium compound shows that the two anions are essentially identical, as the mean deviation of the atomic positions is only 0.02 Å. Therefore, except for the A—S distances, only the bond distances for the rubidium compound will be discussed. The Ta—S bonds within one bipyramid can be divided into three groups: one short bond of 2.23 (1) Å, five with medium bonds between 2.44 (1) and 2.49 (1) Å [$<x>$ = 2.47 (2) Å], and one long separation of 2.83 (1) Å, which must be regarded as a weak interaction. The S—S distances in the S_2^{2-} dumbbells are 2.08 (1) Å, which is in the range expected for an S—S single bond. Using a cutoff of 3.95 Å, the mean Rb· · ·S distances in $Rb_4Ta_2S_{11}$ are 3.55 (19) Å for Rb1 [coordination number (CN) 9], 3.57 (21) Å for Rb2 (CN 9), 3.47 (14) Å for Rb3 (CN 8) and 3.40 (18) Å for Rb4 (CN 8). For $Cs_4Ta_2S_{11}$, the values for the Cs· · ·S separations are 3.67 (18) Å for Cs1 (CN 10), 3.70 (18) Å for Cs2 (CN 9), 3.61 (14) Å for Cs3 (CN 8) and 3.52 (13) Å for Cs4 (CN 8), with a cutoff at 4.0 Å. These values are in agreement with the sum of the ionic radii [1.84 Å for S, 1.63 Å for Rb (CN 9) and 1.78 Å for Cs (CN 9); Shannon, 1976].

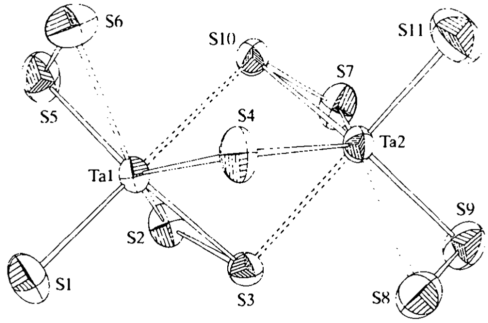

Fig. 1. View of the $[Ta_2S_{11}]^{4-}$ anion in $Rb_4Ta_2S_{11}$ with ellipsoids drawn at the 70% probability level. The broken lines between the Ta and S atoms indicate the long Ta—S interatomic distances.

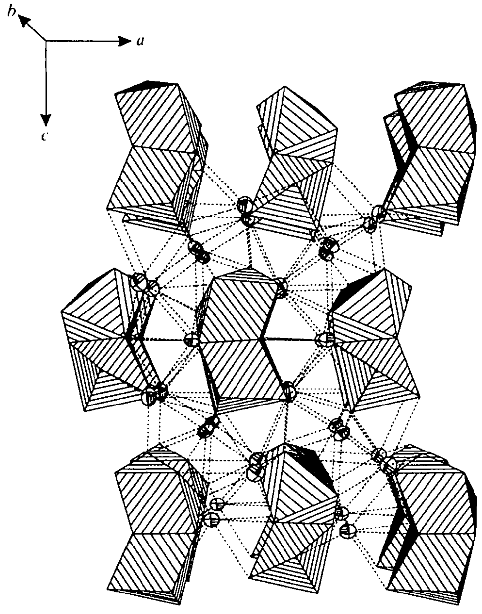

Fig. 2. Packing diagram of $Rb_4Ta_2S_{11}$ (view along the b axis). The displacement ellipsoids of the rubidium cations are drawn at the 70% probability level. The $[Ta_2S_{11}]^{4-}$ anions are drawn as polyhedra for clarity.

Experimental

Both compounds $A_4Ta_2S_{11}$ (A = Rb, Cs) were prepared in the same way by combining A_2S_3 with tantalum and additional sulfur in the ratio 2:1:4. A_2S_3 was prepared by the reaction of stoichiometric amounts of A and S in liquid ammonia under an argon atmosphere. The starting materials were thoroughly mixed in a dry box and then loaded into Pyrex-glass ampoules, which were subsequently evacuated (4×10^{-3} mbar; 1 mbar = 100 Pa) and sealed. The ampoules were heated to 773 K, held at that temperature for 6 d and then cooled to room temperature at a rate of 2 K h^{-1}. The resulting melts were washed with DMF and ether. The products consisted of orange crystals of $A_4Ta_2S_{11}$. The powder patterns could be successfully indexed on the basis of the orthorhombic unit cells. The compounds are stable in dry air for a long period.

$Rb_4Ta_2S_{11}$

Crystal data

$Rb_4Ta_2S_{11}$
M_r = 1056.44
Orthorhombic
$Pca2_1$
a = 13.4806 (13) Å
b = 7.6909 (6) Å
c = 18.1758 (15) Å
V = 1884.4 (3) Å^3
Z = 4
D_x = 3.724 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 102 reflections
θ = 18.3–25.0°
μ = 23.063 mm^{-1}
T = 293 (2) K
Rectangular block
0.16 × 0.15 × 0.14 mm
Orange

Data collection

Stoe AED-II diffractometer
ω–2θ scans
Absorption correction: face-indexed numerical (*SHELXTL/PC*; Siemens, 1990)
T_{min} = 0.047, T_{max} = 0.136
5651 measured reflections
4958 independent reflections (includes Friedel pairs)

3928 reflections with $I > 2\sigma(I)$
R_{int} = 0.024
θ_{max} = 32.50°
$h = -2 \rightarrow 20$
$k = 0 \rightarrow 11$
$l = -8 \rightarrow 27$
4 standard reflections frequency: 120 min intensity decay: negligible

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.035
$wR(F^2)$ = 0.092
S = 1.027
4958 reflections

Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.00111 (8)

154 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0558P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} \leq 0.001$
$\Delta\rho_{max} = 3.63$ e Å^{-3}
$\Delta\rho_{min} = -1.99$ e Å^{-3}

Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = −0.036 (11)

Table 1. *Selected bond lengths (Å) for $Rb_4Ta_2S_{11}$*

Ta1—S1	2.232 (3)	Ta2—S8	2.461 (3)
Ta1—S6	2.442 (3)	Ta2—S9	2.477 (3)
Ta1—S2	2.448 (3)	Ta2—S4	2.491 (3)
Ta1—S4	2.488 (3)	Ta2—S10	2.492 (3)
Ta1—S5	2.491 (3)	Ta2—S3	2.833 (3)
Ta1—S3	2.496 (3)	S2—S3	2.076 (4)
Ta1—S10	2.829 (3)	S5—S6	2.077 (5)
Ta2—S11	2.228 (3)	S7—S10	2.086 (4)
Ta2—S7	2.449 (3)	S8—S9	2.074 (4)

$Cs_4Ta_2S_{11}$

Crystal data

$Cs_4Ta_2S_{11}$
$M_r = 1246.20$
Orthorhombic
$Pca2_1$
$a = 13.913$ (4) Å
$b = 7.989$ (2) Å
$c = 18.327$ (5) Å
$V = 2037.1$ (10) Å^3
$Z = 4$
$D_x = 4.063$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 94 reflections
$\theta = 16.1–26.7°$
$\mu = 18.884$ mm^{-1}
$T = 293$ (2) K
Rectangular block
0.46 × 0.44 × 0.25 mm
Orange

Data collection

Stoe AED-II diffractometer
$\omega–2\theta$ scans
Absorption correction: face-indexed numerical (*SHELXTL/PC*; Siemens, 1990)
$T_{min} = 0.011$, $T_{max} = 0.068$
5388 measured reflections
4736 independent reflections (includes Friedel pairs)

4352 reflections with $I > 2\sigma(I)$
$R_{int} = 0.028$
$\theta_{max} = 32.45°$
$h = -2 \rightarrow 20$
$k = 0 \rightarrow 12$
$l = -5 \rightarrow 27$
4 standard reflections
frequency: 120 min
intensity decay: negligible

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.104$
$S = 1.070$
4736 reflections
155 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0807P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} \leq 0.001$
$\Delta\rho_{max} = 4.08$ e Å^{-3}
$\Delta\rho_{min} = -4.22$ e Å^{-3}

Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.00168 (11)
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = 0.000 (10)

Table 2. *Selected bond lengths (Å) for $Cs_4Ta_2S_{11}$*

Ta1—S1	2.234 (3)	Ta2—S8	2.461 (3)
Ta1—S2	2.442 (3)	Ta2—S9	2.465 (3)
Ta1—S6	2.449 (3)	Ta2—S4	2.493 (3)
Ta1—S5	2.485 (3)	Ta2—S10	2.496 (3)
Ta1—S4	2.488 (3)	Ta2—S3	2.853 (3)
Ta1—S3	2.496 (3)	S2—S3	2.076 (4)
Ta1—S10	2.826 (3)	S5—S6	2.071 (5)
Ta2—S11	2.223 (3)	S7—S10	2.081 (4)
Ta2—S7	2.446 (3)	S8—S9	2.069 (4)

The origin was fixed by floating-origin restraints (Flack & Schwarzenbach, 1988). The Flack (1983) parameter was determined using 1446 Friedel pairs in the case of the rubidium compound and 968 pairs for the caesium compound. The highest residual electron-density peak in both cases was located near the Ta2 atom (at 0.92 Å in $Cs_4Ta_2S_{11}$ and 0.72 Å in $Rb_4Ta_2S_{11}$).

For both compounds, data collection: *DIF*4 (Stoe & Cie, 1992*a*); cell refinement: *DIF*4; data reduction: *REDU*4 (Stoe & Cie, 1992*b*); program(s) used to solve structures: *SHELXS*86 (Sheldrick, 1985); program(s) used to refine structures: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *XP* in *SHELXTL/PC* (Siemens, 1990); software used to prepare material for publication: *CIFTAB* in *SHELXL*93.

Financial support by the Deutsche Forschungsgemeinschaft (DFG) is gratefully acknowledged.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1249). Services for accessing these data are described at the back of the journal.

References

Bensch, W. & Dürichen, P. (1996*a*). *Eur. J. Solid State Inorg. Chem.* **33**, 527–536.

Bensch, W. & Dürichen, P. (1996*b*). *Eur. J. Solid State Inorg. Chem.* **33**, 1233–1240.

Bensch, W. & Dürichen, P. (1996*c*). *Z. Anorg. Allg. Chem.* **622**, 1963–1967.

Bensch, W. & Dürichen, P. (1997). *Inorg. Chim. Acta*, **261**, 103–107.

Bensch, W., Näther, C. & Dürichen, P. (1998). *Angew. Chem.* **110**, 140–142.

Coucouvanis, D. & Hadjikyriacou, A. (1987). *Inorg. Chem.* **26**, 1–2.

Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.

Flack, H. D. & Schwarzenbach, D. (1988). *Acta Cryst.* A**44**, 499–506.

Kanatzidis, M. G. & Sutorik, A. C. (1995). *Prog. Inorg. Chem.* **43**, 151–265.

Manoli, J. M., Potvin, C. & Secheresse, F. (1987). *Inorg. Chem.* **26**, 340–342.

Schreiner, S., Aleandri, L. E., Kang, D. & Ibers, J. A. (1989). *Inorg. Chem.* **28**, 392–393.

Shannon, R. D. (1976). *Acta Cryst.* A**32**, 751–767.

Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures.* University of Göttingen, Germany.

Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.

Siemens (1990). *SHELXTL/PC. Program Package for the Solution, Refinement and Graphical Presentation of Crystal Structures.* Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Simonnet-Jegat, C., Delalande, S., Halut, S., Marg, B. & Secheresse, F. (1996). *J. Chem. Soc. Chem. Commun.* pp. 423–424.

Stoe & Cie (1992*a*). *DIF4. Diffractometer Control Program.* Version 7.09X/DOS. Stoe & Cie, Darmstadt, Germany.

Stoe & Cie (1992*b*). *REDU4. Data Reduction Program.* Version 7.03. Stoe & Cie, Darmstadt, Germany.

Sunshine, S. A., Kang, D. & Ibers, J. A. (1987). *J. Am. Chem. Soc.* **109**, 6202–6203.