Haddad, S. F., Al-Far, R. H. & Ahmed, F. R. (1987). *Acta Cryst.* C**43**, 453–456.
Karbowiak, M., Drozdzynski, J. & Janczak, J. (1996). *Polyhedron*, **15**, 241–244.
Larson, A. C. (1970). *Crystallographic Computing*, edited by F. R. Ahmed, S. R. Hall & C. P. Huber, pp. 291–294. Copenhagen: Munksgaard.
Molecular Structure Corporation (1993*a*). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Molecular Structure Corporation (1993*b*). *TEXSAN. TEXRAY Structure Analysis Package*. Version 1.6b. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Rabinovich, D., Haswell, C. M., Scott, B. L., Miller, R. L., Nielsen, J. B. & Abney, K. D. (1996). *Inorg. Chem.* **35**, 1425–1426.
Rebizant, J., van den Bossche, G., Spirlet, M. R. & Goffart, J. (1987). *Acta Cryst.* C**43**, 1298–1300.
Rogers, R. D. (1989). *Lanth. Actin. Res.* **3**, 71–81.
Rogers, R. D. & Kurihara, L. K. (1986). *Inorg. Chim. Acta*, **116**, 171–177.
Rogers, R. D. & Kurihara, L. K. (1987). *Inorg. Chim. Acta*, **130**, 131–137.
Sheldrick, G. M. (1985). *SHELXS86. Crystallographic Computing* 3, edited by G. M. Sheldrick, C. Krüger & R. Goddard, pp. 175–189. Oxford University Press.
Sheldrick, G. M. (1990). *SHELXTL-Plus*. Version 4.0. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Spirlet, M. R., Rebizant, J., Apostolidis, C., Andreetti, G. D. & Kanellakopulos, B. (1989). *Acta Cryst.* C**45**, 739–741.
Spirlet, M. R., Rebizant, J., Kanellakopulos, B. & Dornberger, E. (1987). *Acta Cryst.* C**43**, 19–21.
Wet, J. F. de & Caira, M. R. (1986). *J. Chem. Soc. Dalton Trans.* pp. 2043–2048.
Zych, E., Starynowicz, P., Lis, T. & Drozdzynski, J. (1993). *Polyhedron*, **12**, 1661–1667.

Acta Cryst. (1998). C**54**, 1742–1744

K_3TaS_4

Sabine Herzog, Christian Näther and Wolfgang Bensch

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

(*Received 9 March 1998; accepted 29 May 1998*)

Abstract

The reaction of K_2S_3, Ta and S yields single crystals of tripotassium tetrathiotantalate, K_3TaS_4. The compound crystallizes with the K_3VS_4-type structure [van den Berg & de Vries (1964). *Proc. K. Ned. Akad. Wet. Ser. B*, **67**, 178–180]. The structure is based on discrete tetrahedral TaS_4^{3-} anions, which are connected *via* K^+ cations.

Comment

We obtained new ternary alkali niobium chalcogenides with structures that contain the $Nb_2S_{11}^{4-}$ anion as a subunit, *e.g.* $K_4Nb_2S_{11}$, *via* the reaction of niobium in alkali-polychalcogenide fluxes (Bensch & Dürichen, 1996). Attempts to prepare the analogous tantalum chalcogenides yielded single crystals of the title compound, for which lattice parameters only have been reported (Latroche & Ibers, 1990). K_3TaS_4 is isotypic with K_3NbS_4, K_3NbSe_4 and K_3TaSe_4 (Latroche & Ibers, 1990), as well as with Cs_3NbSe_4 and Cs_3TaSe_4 (Yun *et al.*, 1988).

The crystal structure of K_3TaS_4 is based on discrete tetrahedral TaS_4^{3-} anions which are connected by K^+ cations. The Ta—S distances range from 2.264 (3) to 2.269 (2) Å [average 2.266 (3) Å] and the S—Ta—S angles are between 108.48 (9) and 111.43 (12)°.

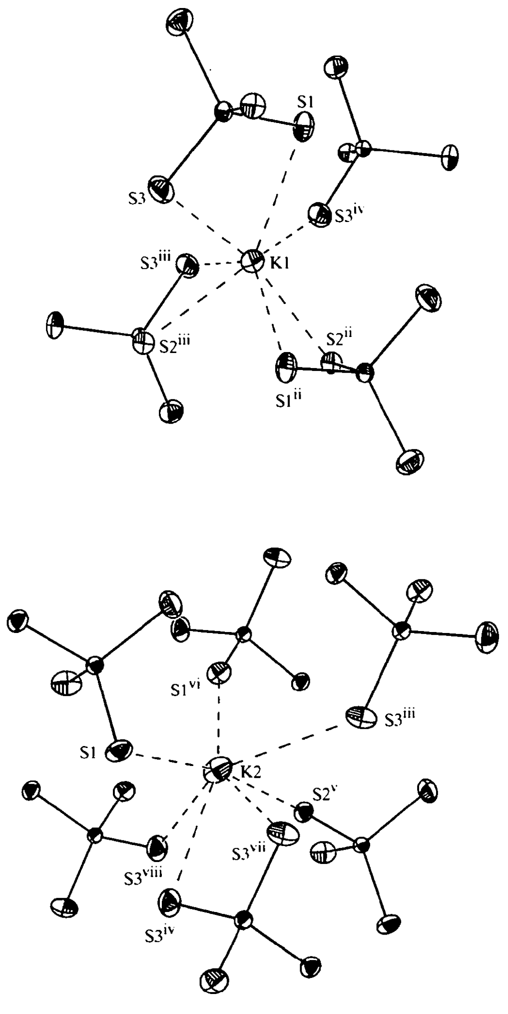

Fig. 1. The coordination spheres of the K^+ cations with the coordinating S atoms labelled; displacement ellipsoids are drawn at the 50% probability level.

Acta Crystallographica Section C
ISSN 0108-2701 © 1998

The two crystallographically independent K^+ cations are coordinated by seven S atoms within an irregular polyhedron. K1 connects four symmetry-related TaS_4^{3-} anions, whereas K2 is surrounded by six symmetry-related TaS_4^{3-} anions. The K1—S distances range from 3.222 (3) to 3.569 (3) Å [average 3.357 (3) Å]. K2 exhibits two short K—S distances of 3.139 (3) and 3.285 (4) Å, three medium K—S bonds of 3.414 (3), 3.414 (3) and 3.425 (4) Å, and two long K···S contacts of 3.783 (3) Å [average 3.463 (4) Å].

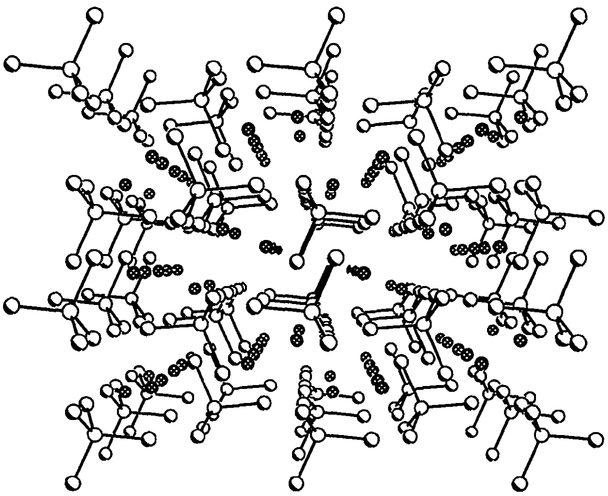

Fig. 2. The crystal structure viewed along the *b* axis.

Experimental

K_3TaS_4 was prepared by the reaction of K_2S_3, Ta and S in the ratio 2:1:4. K_2S_3 was prepared from stoichiometric amounts of K and S in liquid ammonia under an argon atmosphere. The starting materials were thoroughly mixed in a dry-box and sealed in a Pyrex-glass ampoule, which was evacuated at 2.7×10^{-13} Pa. The ampoule was heated at 753 K for 6 d, then cooled first to 473 K at 2 K h^{-1} and afterwards to 333 K at 3 K h^{-1}. The resulting melt was washed with DMF and the residue was dried in vacuum. Further cleaning was performed by ultrasonic treatment in ethanol.

Crystal data

K_3TaS_4
$M_r = 426.49$
Orthorhombic
Pnma
$a = 9.315$ (2) Å
$b = 10.849$ (2) Å
$c = 9.407$ (2) Å
$V = 950.7$ (3) Å^3
$Z = 4$
$D_x = 2.980$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 78 reflections
$\theta = 15.5$–$19.0°$
$\mu = 13.666$ mm^{-1}
$T = 293$ (2) K
Prism
$0.10 \times 0.10 \times 0.05$ mm
Yellow

Data collection

Stoe AED-II four-circle diffractometer
ω–θ scan
Absorption correction: ψ scan (*XEMP* in *SHELXTL/PC*; Siemens, 1990)
$T_{min} = 0.280$, $T_{max} = 0.505$
1227 measured reflections
1092 independent reflections

1024 reflections with $I > 2\sigma(I)$
$R_{int} = 0.027$
$\theta_{max} = 27.03°$
$h = 0 \rightarrow 11$
$k = 0 \rightarrow 13$
$l = -12 \rightarrow 1$
4 standard reflections
frequency: 120 min
intensity decay: 10%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.030$
$wR(F^2) = 0.078$
$S = 1.103$
1091 reflections
44 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0353P)^2 + 11.2664P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$

$\Delta\rho_{max} = 2.761$ e Å^{-3}
$\Delta\rho_{min} = -0.949$ e Å^{-3}
Extinction correction: *SHELXL93* (Sheldrick, 1993)
Extinction coefficient: 0.0114 (6)
Scattering factors from *International Tables for Crystallography* (Vol. C)

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	0.71401 (4)	1/4	0.51297 (4)	0.0176 (2)
K1	0.5564 (2)	0.5465 (2)	0.2895 (2)	0.0326 (4)
K2	0.6388 (3)	1/4	0.0827 (3)	0.0435 (7)
S1	0.4915 (3)	1/4	0.4162 (3)	0.0322 (6)
S2	0.6918 (3)	1/4	0.7532 (3)	0.0247 (5)
S3	0.8338 (2)	0.4226 (2)	0.4471 (2)	0.0396 (5)

Table 2. *Selected geometric parameters (Å, °)*

Ta1—S1	2.264 (3)	K1—S1	3.483 (2)
Ta1—S3^{i}	2.266 (2)	K1—S1^{ii}	3.569 (3)
Ta1—S3	2.266 (2)	K2—S2^{v}	3.139 (3)
Ta1—S2	2.269 (2)	K2—S1^{vi}	3.285 (4)
K1—S2^{ii}	3.222 (3)	K2—S3^{vii}	3.414 (3)
K1—S2^{iii}	3.239 (3)	K2—S3^{iv}	3.414 (3)
K1—S3	3.268 (3)	K2—S1	3.425 (4)
K1—S3^{iv}	3.325 (3)	K2···S3^{viii}	3.783 (3)
K1—S3^{iii}	3.396 (3)	K2···S3^{iii}	3.783 (3)
S1—Ta1—S3^{i}	109.93 (7)	S1—Ta1—S2	108.48 (9)
S1—Ta1—S3	109.93 (6)	S3^{i}—Ta1—S2	108.49 (7)
S3^{i}—Ta1—S3	111.43 (12)	S3—Ta1—S2	108.49 (7)

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

Data were corrected for Lorentz and polarization effects. All K, Ta and S atoms were refined with anisotropic displacement parameters. The highest peak in the electron-density map was located 1.11 Å from S3, which cannot be traced back to a disorder of the TaS_4^{3-} anion. In addition, the reciprocal space was thoroughly but unsuccessfully scanned for reflections that might give a hint of the formation of a superstructure.

Data collection: *DIF4* (Stoe & Cie, 1992*a*). Cell refinement: *DIF4*. Data reduction: *REDU4* (Stoe & Cie, 1992*b*). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *XP* in *SHELXTL/PC* (Siemens, 1990). Software used to prepare material for publication: *CIFTAB* in *SHELXL*93.

This work is supported by the state of Schleswig-Holstein.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1197). Services for accessing these data are described at the back of the journal.

References

Bensch, W. & Dürichen, P. (1996). *Eur. J. Solid State Inorg. Chem.* **33**, 527–536.
Berg, J. M. van den & de Vries, R. (1964). *Proc. K. Ned. Akad. Wet. Ser. B*, **67**, 178–180.
Latroche, M. & Ibers, J. A. (1990). *Inorg. Chem.* **29**, 1503–1505.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
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.
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.
Yun, H., Randall, C. R. & Ibers, J. A. (1988). *J. Solid State Chem.* **76**, 109–114.

Acta Cryst. (1998). C**54**, 1744-1745

$(NH_4)_8[Ce_2(SO_4)_8].4H_2O$

YONGKUI SHAN AND SONGPING D. HUANG*

Department of Chemistry, University of Puerto Rico,
PO Box 23346, San Juan, PR 00931, Puerto Rico. E-mail:
huang@zintl.chem.uprr.pr

(*Received 26 February 1998; accepted 18 May 1998*)

Abstract

Crystals of the title compound, octaammonium dicerium octasulfate tetrahydrate, suitable for X-ray work, were prepared by a hydrothermal reaction. The structure is made up of $[Ce_2(SO_4)_8]^{8-}$ anions, interacting with the crystallization waters and the NH_4^+ cations through hydrogen bonds. The Ce^{IV} atom in the $[Ce_2(SO_4)_8]^{8-}$ anion is ninefold coordinated by O atoms belonging to sulfate groups. The coordination polyhedron is a somewhat distorted tricapped trigonal prism. The Ce—O distances range from 2.325 (2) to 2.478 (2) Å.

Comment

Sulfates containing cerium(IV) are widely used as oxidants in quantitative analysis and organic chemical synthesis (Toshima & Yan, 1995). Several structures of cerium(IV) sulfates have been investigated by Lindgren (1976, 1977*a*,*b*) in the seventies. Barnes (Barnes, 1995; Barnes *et al.*, 1993) reported the structures of an acid terbium(III) cerium(IV) sulfate hydrate and an acid neodymium(III) cerium(IV) sulfate hydrate. These structures extend through sulfate bridges to form infinite strings, layers and three-dimensional networks. They contain Ce^{IV} ions coordinated by eight or nine O atoms. The coordination polyhedra are of different kinds, *e.g.* square antiprism, dodecahedron or tricapped trigonal prismatic coordination. In this paper, we report the structure of a new dimeric ammonium cerium(IV) sulfate hydrate. Because cerium(IV) sulfates strongly hydrolyze in aqueous solution, it is difficult to obtain crystals of such compounds under normal conditions. The hydrothermal method was employed to grow single crystals of the title compound.

The dimeric anion, $[Ce_2(SO_4)_8]^{8-}$, is a distinct chemical unit in the structure. The structure of this anion is shown in Fig. 1. First of all, two sulfate anions act as the bridging groups between the two Ce^{IV} ions. The other sulfate anions all act as bidentate terminal ligands. Each Ce^{IV} is nine-coordinated, with six O atoms forming a trigonal prism (top face: O13, O8 and O5; bottom face: O11, O4 and O15). The three rectangular faces are each capped by an O atom [$O9^{i}$, O10 and O3; symmetry code: (i) $1-x$, $-y$, $-z$]. All O atoms coordinated to the Ce^{IV} centers are from the sulfate groups. The nine Ce—O bond lengths range from 2.325 (2) to 2.478 (2) Å. The O—Ce—O angles, ranging from 56.86 (8) to 156.44 (9)°, are in agreement with those found in similar compounds (Barnes *et al.*, 1993;

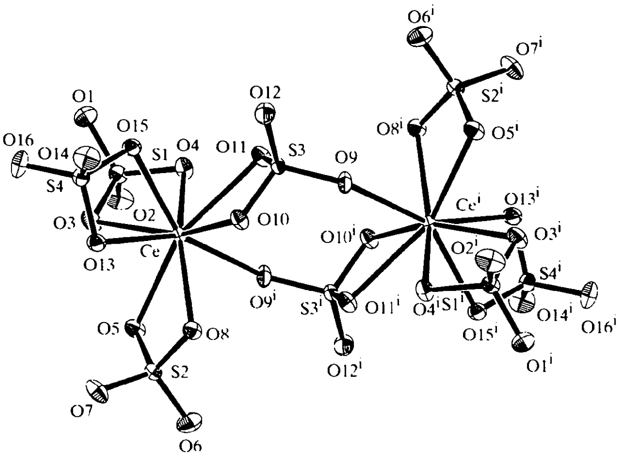

Fig. 1. An *ORTEP* (Johnson, 1965) representation of the title anion, showing 35% probability displacement ellipsoids and the atom-numbering scheme. The symmetry code is as given in Table 1.

Acta Crystallographica Section C
ISSN 0108-2701 © 1998