Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

$K_4Ta_4P_4S_{24}$

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The quaternary tantalum thiophosphate $K_4Ta_4P_4S_{24}$ (tetrapotassium tetratantalum tetraphosphorus tetracosasulfide) was obtained by reacting elemental Ta with a melt formed *in situ* of K_2S_3, P_2S_5 and S. The crystal structure exhibits $[Ta_4P_4S_{24}]^{4-}$ anionic layers, which consist of dimeric Ta_2S_{11} units interconnected by PS_4 tetrahedra. The layers are stacked in an *ABAB* sequence in the direction of the crystallographic *a* axis and are separated by the K^+ ions. The title compound is isostructural with $A_4Ta_4P_4S_{24}$ (*A* = Rb and Cs).

Received 7 January 2005
Accepted 19 January 2005
Online 5 February 2005

Key indicators

Single-crystal X-ray study
$T = 293$ K
Mean σ(S–S) = 0.002 Å
R factor = 0.027
wR factor = 0.055
Data-to-parameter ratio = 26.4

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

In the past few years we have prepared several compounds of the *A*–*M*–P–S family (*A* is an alkali metal and *M* is a group V metal) and have shown that the use of the alkali metal polythiophosphate flux method is still a powerful synthetic tool for the preparation of new quaternary thiophosphates with interesting structural features. The dimensionality of the known quaternary alkali metal thiophosphates with group V metals varies from isolated anions to three-dimensional interconnected networks. The known compounds are $K_4VP_2S_9$ (Gutzmann *et al.*, 2004*a*), $K_2VP_2S_7$ (Tremel *et al.*, 1995), $NaV_{0.84}P_2S_6$ (Coste *et al.*, 2003), AVP_2S_7 (*A* = K and Rb; Kopnin *et al.*, 2000; Durand *et al.*, 1993), ANb_2PS_{10} (*A* = Na, K and Rb; Goh *et al.*, 2002; Do & Yun, 1996; Kim & Yun, 2002), $Rb_2Nb_2P_2S_{11}$ (Gutzmann & Bensch, 2002), $ANb_2P_2S_{12}$ (*A* = K, Rb and Cs; Gieck *et al.*, 2004), $CsTa_4P_3S_{19}$ (Derstroff & Tremel, 1998), $A_4Ta_4P_4S_{24}$ (*A* = Rb and Cs; Gutzmann & Bensch, 2003; Gutzmann *et al.*, 2004*b*), $Cs_2Ta_2P_2S_{12}$ (Gutzmann *et al.*, 2004*b*), and $K_{0.38}TaPS_6$ and $Rb_{0.46}TaPS_6$ (Gutzmann *et al.*, 2004*c*). Interestingly, analysing the structures of the ternary and quaternary tantalum thiophosphates, Ta_2S_{11} or Ta_2S_{12} units and tetrahedral PS_4 groups are found as the

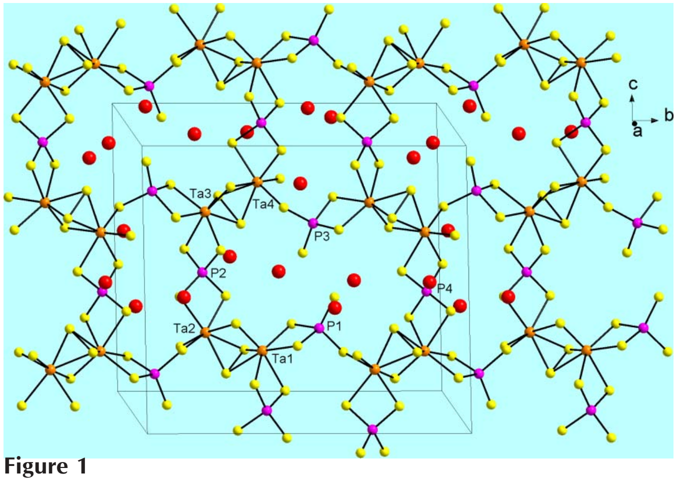

Figure 1
Crystal structure of $K_4Ta_4P_4S_{24}$, viewed approximately in the direction of the crystallographic *a* axis.

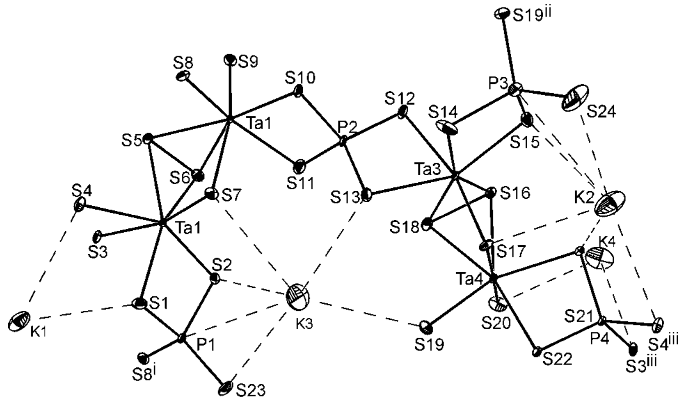

Figure 2

Crystal structure of $K_4Ta_4P_4S_{24}$, with the atom-labelling scheme and displacement ellipsoids drawn at the 70% probability level. The dashed lines represent K$\cdots$S contacts. [Symmetry codes: (i) $\frac{3}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; (ii) $\frac{3}{2} - x, -\frac{1}{2} + y, \frac{3}{2} - z$; (iii) $x, y, z + 1$.]

general structural motifs. Very recently, we reported the first quaternary tantalum thiophosphates composed of Ta_2S_{10} units (Gutzmann *et al.*, 2005). In our ongoing investigations in this field, we have synthesized $K_4Ta_4P_4S_{24}$, which is isostructural with $A_4Ta_4P_4S_{24}$ (A = Rb and Cs; Gutzmann & Bensch, 2003; Gutzmann *et al.*, 2004*b*).

The crystal structure of $K_4Ta_4P_4S_{24}$ consists of $[Ta_4P_4S_{24}]^{4-}$ layers and charge-compensating K^+ cations. The layers are formed by dimeric Ta_2S_{11} units which are interconnected by PS_4 tetrahedra (Fig. 1). Each of the four crystallographically independent Ta atoms is surrounded by one μ_2-η^2,η^2-S_2^{2-} anion, one μ_2-S^{2-} ion and four terminal S^{2-} anions in a distorted pentagonal–bipyramidal environment (Fig. 2). Two of these TaS_7 groups share a triangular face built up of mono- and disulfide anions to form the dimeric Ta_2S_{11} units. The Ta—S distances in the two distinct Ta_2S_{11} units range from 2.1847 (14) to 2.7592 (14) Å (average 2.513 Å). Each Ta atom has short bonds to S atoms (S19, S8, S22 and S5) of about 2.2 Å. The longest Ta—S bonds are observed in positions *trans* to the short Ta—S bonds. A similar observation was made in the structures of $Cs_2Ta_2P_2S_{12}$ (Gutzmann *et al.*, 2004*b*) and $A_4Ta_2S_{11}$ (A = K, Rb, Cs and Tl; Herzog *et al.*, 1999; Dürichen & Bensch, 1998; Teske & Bensch, 2001) containing the complex anion $[Ta_2S_{11}]^{4-}$. The Ta$\cdots$Ta separations in the Ta_2S_{11} units are 3.4725 (6) Å (Ta1$\cdots$Ta2) and 3.4417 (6) Å (Ta3$\cdots$Ta4), and they are slightly shorter than in $A_4Ta_4P_4S_{24}$ (A = Rb and Cs). The S—S bond lengths in the S_2^{2-} anions [2.0505 (18) and 2.0597 (18) Å] are typical for S—S single bonds.

An interesting feature of the structure is the connection mode of the Ta_2S_{11} units *via* the PS_4 tetrahedra. Each Ta_2S_{11} group shares a common corner as well as a common edge with two tridentate PS_4 tetrahedra, leading to infinite $[Ta_2S_4(PS_4)]_x$ chains running parallel to the crystallographic b axis. The tridentate $P1S_4$ tetrahedron joins the $Ta(1,2)S_{11}$ units, whereas the $P3S_4$ tetrahedron connects the $Ta(3,4)S_{11}$ groups. Within the individual chains the Ta_2S_{11} units alternate in their orientation. Neighbouring chains are interconnected into the final layered $[Ta_4P_4S_{24}]^{4-}$ anion within the (100) plane *via* the tetradentate $P2S_4$ and $P4S_4$ tetrahedra (Fig. 1). The layers are stacked in an *ABAB* fashion perpendicular to [100]. The connection scheme leads to two types of cavities within the layers (T1, T2), with approximate diameters of about 4 × 9.7 and 3.8 × 8.1 Å (Fig. 3). The P—S bond lengths in the four distinct PS_4 tetrahedra range between 1.963 (2) and 2.091 (2) Å, with the shortest bonds to the terminal S atoms of the tridentate PS_4 tetrahedra. The S—P—S angles exhibit a significant distortion. The four crystallographically independent potassium cations are located between the layers above and below the cavities. With a cutoff of 4.2 Å they are surrounded either by nine S atoms (average K4$\cdots$S distance 3.464 Å) or by ten S atoms (average K1$\cdots$S distance 3.473 Å, average K2$\cdots$S distance 3.649 Å, average K3$\cdots$S distance 3.653 Å). The charge balance of the compound may be formulated as $[K^+]_4[Ta^{5+}]_4[PS_4^{3-}]_4[S_2^{2-}]_2[S^{2-}]_4$. The comparison of the geometric parameters of the isostructural compounds $A_4Ta_4P_4S_{24}$ (A = Rb and Cs) reveals only a slight influence of the alkali metal cations on the geometric parameters of the layered anion.

Experimental

Single crystals of $K_4Ta_4P_4S_{24}$ were obtained by the reaction of K_2S_3 (0.25 mmol), Ta (0.25 mmol), P_2S_5 (0.25 mmol) and S (1.8 mmol). K_2S_3 was prepared from stoichiometric amounts of K and S in liquid ammonia under an argon atmosphere. The starting materials were loaded into a glass ampoule, which was evacuated (10^{-3} mbar) and flame-sealed. The ampoule was heated to 773 K within 18 h. After 4 d, the sample was cooled to 523 K at 2 K h^{-1} and then to room temperature within 10 h. To remove unreacted $K_xP_yS_z$, the resultant melt was washed with dry *N*,*N*-dimethylformamide and diethyl ether. The product was dried in a vacuum and consisted of orange crystals (yield about 80% based on Ta), which are stable in air and water. The IR spectrum of $K_4Ta_4P_4S_{24}$ displays absorptions at 638, 630, 591, 565, 551, 541, 519, 484, 434 and 424 cm^{-1}. These values are in good agreement with the observed IR data of $A_4Ta_4P_4S_{24}$ (A = Rb and Cs; Gutzmann & Bensch, 2003; Gutzmann *et al.*, 2004*b*). The absorptions at 591 and 541 cm^{-1} can be assigned to S—S stretching vibrations, whereas the remaining signals may be assigned to P—S stretching modes.

Crystal data

$K_4P_4S_{24}Ta_4$
$M_r = 1773.52$
Monoclinic, $P2_1/n$
$a = 13.6193$ (7) Å
$b = 17.7307$ (13) Å
$c = 15.8077$ (9) Å
$\beta = 108.356$ (6)°
$V = 3623.0$ (4) Å^3
$Z = 4$

$D_x = 3.251$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 8000 reflections
$\theta = 3$–28°
$\mu = 14.07$ mm^{-1}
$T = 293$ (2) K
Polyhedron, orange
0.11 × 0.08 × 0.08 mm

Data collection

Stoe IPDS diffractometer
φ scans
Absorption correction: numerical [*X-SHAPE* (Stoe & Cie, 1998) and *X-RED* (Stoe & Cie, 1998)]
$T_{min} = 0.261$, $T_{max} = 0.314$
34 379 measured reflections

8610 independent reflections
6878 reflections with $I > 2\sigma(I)$
$R_{int} = 0.049$
$\theta_{max} = 28.0°$
$h = -17 \rightarrow 17$
$k = -23 \rightarrow 23$
$l = -20 \rightarrow 20$

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Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.027$
$wR(F^2) = 0.055$
$S = 0.97$
8610 reflections
326 parameters
$w = 1/[\sigma^2(F_o^2) + (0.029P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 1.11$ e Å^{-3}
$\Delta\rho_{min} = -1.66$ e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.000392 (16)

Table 1
Selected interatomic distances (Å).

Ta1—S7	2.2610 (13)	Ta4—S21	2.5379 (13)
Ta1—S2	2.4885 (13)	Ta4—S19	2.5505 (13)
Ta1—S1	2.5057 (14)	Ta4—S16	2.5518 (14)
Ta1—S6	2.5153 (14)	Ta4—S22	2.5741 (14)
Ta1—S5	2.5556 (14)	Ta4—S17	2.6785 (14)
Ta1—S4	2.5981 (13)	S1—P1	2.0722 (19)
Ta1—S3	2.6653 (13)	S2—P1	2.079 (2)
Ta2—S9	2.1847 (14)	S3—P4^{iv}	2.0421 (18)
Ta2—S5	2.4922 (12)	S4—P4^{iv}	2.0438 (19)
Ta2—S11	2.5326 (13)	S5—S6	2.0505 (18)
Ta2—S10	2.5411 (13)	S8—P1^{v}	2.0769 (19)
Ta2—S6	2.5455 (14)	S10—P2	2.0477 (18)
Ta2—S8	2.5721 (13)	S11—P2	2.039 (2)
Ta2—S7	2.7592 (14)	S12—P2	2.0321 (18)
Ta3—S17	2.2479 (13)	S13—P2	2.049 (2)
Ta3—S14	2.4632 (15)	S14—P3	2.057 (2)
Ta3—S15	2.4892 (14)	S15—P3	2.091 (2)
Ta3—S16	2.5316 (14)	S16—S18	2.0597 (18)
Ta3—S13	2.5780 (13)	S19—P3^{vi}	2.065 (2)
Ta3—S18	2.5903 (14)	S21—P4	2.0644 (19)
Ta3—S12	2.6668 (14)	S22—P4	2.0326 (18)
Ta4—S20	2.1800 (14)	S23—P1	1.9736 (19)
Ta4—S18	2.4978 (13)	S24—P3	1.963 (2)

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

The highest peak in the difference map is located 0.91 Å from S17 and the deepest hole is located 0.87 Å from Ta4.

Data collection: *IPDS Program Package* (Stoe & Cie, 1998); cell refinement: *IPDS Program Package*; data reduction: *IPDS Program Package*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *CIFTAB* in *SHELXTL* (Bruker, 1998).

Financial support by the state of Schleswig-Holstein and the Deutsche Forschungsgemeinschaft (DFG) is gratefully acknowledged.

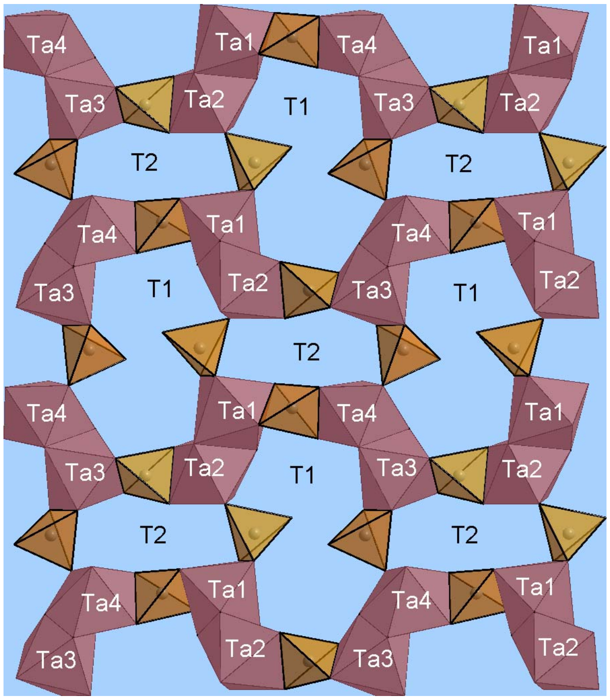

Figure 3
Crystal structure of $K_4Ta_4P_4S_{24}$ in a polyhedral representation, showing the two types of cavities.

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