

The Crystal Structure of $K_7Nb(SO_4)_6$ and $K_7Ta(SO_4)_6$

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Colourless crystals of $K_7M(SO_4)_6$ ($M = Nb$ and Ta) were prepared by dissolving the pentoxides Nb_2O_5 or Ta_2O_5 in molten $K_2S_2O_7$ at $440^\circ C$ followed by a slow cooling to $420^\circ C$. The compounds are isostructural, crystallizing in the rhombohedral space group $R\bar{3}$ (no. 148) with the hexagonal dimensions $a = 15.106(7)$, $c = 9.254(8)$ Å, (Nb), and $a = 14.969(8)$, $c = 9.283(5)$ Å (Ta), $\gamma = 120^\circ$ and $Z = 3$. The structures were refined to R -values of 0.035 (Nb) and 0.027 (Ta). The structures consist of hexasulfatometallate(V) ions, with an unidentate oxygen coordination of SO_4^{2-} to the metal ions. The MO_6 units have $\bar{3}$ symmetry, and form almost ideal octahedra with $M-O$ bond lengths of 1.955(2) Å (Nb) and 1.957(2) Å (Ta). The sulfate groups are tilted, forming $M-O-S$ bond angles around $148-150^\circ$ and short potassium–oxygen contacts (2.648 and 2.525 Å).

It is known that the relatively inert niobium and tantalum pentoxides can be dissolved in warm disulfuric acid (oleum), in hydrogen fluoride acid and in fused salts, e.g. alkali hydroxides, carbonates and pyrosulfates. Although several studies have been performed on the chemistry of Nb and Ta oxides in the former systems (e.g. Ref. 1–7), few experiments 8–12 have been carried out with pyrosulfate as a solvent or reactant. The type of compounds formed by dissolution of niobium and tantalum oxides in pure pyrosulfate melts is unknown. $Nb(V)$ and $Ta(V)$ are capable of forming anionic sulfato complexes, and a few structures of this type of compounds have been determined.^{2,4,7–9} Much more information is available on the chemistry of vanadium pentoxide in the potassium pyrosulfate melts owing to their importance as sulfuric acid production catalyst.^{13,14}

The present work resulted from a study on niobium and tantalum ore extraction by a pyrosulfate melting process. We report here on the structure of colourless crystals, which have been prepared by dissolving pentoxides Nb_2O_5 or Ta_2O_5 in molten $K_2S_2O_7$ at $440^\circ C$ followed by a slow cooling to $420^\circ C$. The compounds, $K_7M(SO_4)_6$ ($M = Nb$ and Ta), crystallized in the rhombohedral space group $R\bar{3}$ and contained $\bar{3}$ -symmetry hexasulfato ions, with SO_4^{2-} coordinated unidentately to the metal ions. The MO_6 core units formed almost ideal octahedra. The sulfate groups were tilted, forming $M-O-S$ bond angles around $148-150^\circ$ and giving short potassium–oxygen contacts (2.648 and 2.525 Å).

Experimental

Chemicals were handled in a N_2 -filled drybox, and kept in vacuum-sealed Pyrex ampoules. Anhydrous $K_2S_2O_7$ was

synthesized by thermal decomposition¹³ of $K_2S_2O_8$ (Merck, p.a.). Nb_2O_5 and Ta_2O_5 (Cerac Pure Inc., 99.95%) were used. Various amounts of $K_2S_2O_7$ and Nb_2O_5 or Ta_2O_5 in ampoules were heated in a rocking furnace at $440^\circ C$. Amounts of Nb_2O_5 or Ta_2O_5 less than 0.10 and 0.01 g per g of $K_2S_2O_7$ dissolved in the melt; if more oxide was used not

Table 1. The indexed X-ray powder patterns of the title compounds. The relative peak heights, I/I_0 , have been converted to fixed slit values. Apart from the lines that coincide in trigonal space groups, a second set may be obtained by the transformation given in the text.

<i>h</i>	<i>k</i>	<i>l</i>	$K_7Nb(SO_4)_6$		$K_7Ta(SO_4)_6$	
			$d_{obs}/\text{Å}$	I/I_0	$d_{obs}/\text{Å}$	I/I_0
1	–1	1	7.535	19	7.483	25
2	–2	1	5.333	12	5.305	15
3	–1	1	4.357	13	4.334	23
2	–2	2	–	–	3.759	3
3	–2	2	3.376	100	3.363	100
4	0	1	3.083	3	–	–
5	–1	0	2.856	36	2.844	54
4	–4	2	–	–	2.662	2
–3	3	3	2.518	8	2.512	12
6	–4	1	2.390	3	2.382	8
6	–1	1	2.279	10	2.271	9
2	–6	2	2.183	7	2.175	12
–3	2	4	2.096	11	2.090	16
7	–4	2	1.952	4	1.946	6
2	–5	4	1.833	4	1.830	6
–2	2	5	1.782	1	1.778	1
7	–5	3	1.735	9	1.730	14
4	–6	4	1.690	3	1.687	4
6	–1	4	1.649	2	1.646	5
–8	0	1	1.613	2	1.608	4
7	–3	4	1.577	4	1.572	5

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all could be dissolved. Colourless clear crystals were grown from the solutions by decreasing the temperature to 420 °C in steps of 0.1 °C at a rate of 1 °C per day. The crystals were separated from the melt by decantation. Crystals proved to be stable in ambient air. The melting points are 540 °C (Nb) and higher than 615 °C (Ta, limited by equipment). Chemical analysis of K₇Nb(SO₄)₆ was performed by atomic absorption and flame emission spectrometry with Nb and K₂SO₄ as standards (found Nb: 8.26 %, K: 28.89 %; calc. Nb: 9.86 %, K 29.02 %). The amounts of sulfate in both compounds were checked by weighing BaSO₄ precipitated from the hydrolysed compounds.

Powder diffractograms were obtained by use of a Philips PW1710 diffractometer with monochromated Cu K α radiation ($\lambda = 1.54186 \text{ \AA}$). The indexed lines are listed in Table 1. Apart from the lines that coincide in trigonal space groups, a second set of lines with almost identical d -values may be obtained. This is due to the value of the rhombohedral angle (ca. 109.47°), which implies that $(c^*/a^*)^2$ is nearly 2. The second set of indices ($h'k'l'$) is obtained by the following transformation.

$$\begin{pmatrix} h' \\ k' \\ l' \end{pmatrix} = 1/3 \begin{pmatrix} 3 & 0 & 0 \\ -1 & 1 & 4 \\ 1 & 2 & -1 \end{pmatrix} \begin{pmatrix} h \\ k \\ l \end{pmatrix}$$

The possible space groups were established from Weissenberg photographs.

Intensity data were collected at 18 °C on a four-circle diffractometer (Enraf-Nonius CAD-4F) with monochro-

Table 2. Crystal data.

	K ₇ Nb(SO ₄) ₆	K ₇ Ta(SO ₄) ₆
Formula	K ₇ Nb(SO ₄) ₆	K ₇ Ta(SO ₄) ₆
M_r	942.99	1031.03
Crystal system	Trigonal	Trigonal
$V/\text{\AA}^3$	1828.8	1801.4
Space group	$R\bar{3}$ (no. 148)	$R\bar{3}$ (no. 148)
$a/\text{\AA}$, Hexagonal	15.106(7)	14.969(8)
$c/\text{\AA}$, Hexagonal	9.254(8)	9.283(5)
$a/\text{\AA}$, Rhombohedral	9.251(3)	9.179(4)
α° , Rhombohedral	109.46(5)	109.26(6)
$D_s/g \text{ cm}^{-3}$	2.568	2.850
$D_x/g \text{ cm}^{-3}$	2.553	2.836
Z	3	3
$\mu(\text{Mo } K\alpha)/\text{cm}^{-1}$	22.6	63.4
$\max(\sin\theta/\lambda)/\text{\AA}^{-1}$	0.83	0.83
Total no. of reflections	1796	1765
Reflections with $I > 2\sigma(I)$	1522	1731
No. of parameters	59	59
Crystal size/mm (ca.)	0.1 × 0.1 × 0.05	0.1 × 0.1 × 0.05
$R_1 = \sum F_o - F_c / \sum F_o $	0.035	0.027
$R_2 = [\sum w(F_o - F_c)^2 / \sum w F_o ^2]^{1/2}$	0.040	0.028

mated Mo K α radiation. The intensities were corrected for Lorentz and polarization effects but not for absorption. The cell dimensions were determined by least-squares refinements based on the settings of 25 high-order reflections. The two structures were solved and refined in space group $R\bar{3}$. The calculations included full-matrix least-squares refinements of positional and anisotropic thermal parameters. The atomic scattering factors and anomalous dispersion corrections used were those given by Cromer and Mann.¹⁵

Crystal data and R -values are given in Table 2. Positional and equivalent isotropic thermal parameters are listed in

Table 3. Fractional coordinates and equivalent isotropic thermal parameters (\AA^2) for the atoms in K₇Nb(SO₄)₆ and K₇Ta(SO₄)₆ structures in space group $R\bar{3}$, hexagonal setting.^a

Atom	Site (multiplicity, symmetry)	x/a	y/b	z/c	B_{eq}
Nb	a(3, $\bar{3}$)	0.0	0.0	0.0	1.03(1)
K(1)	f(18, 1)	0.06175(6)	0.28028(5)	-0.37942(7)	3.39(4)
K(2)	b(3, $\bar{3}$)	0.0	0.0	0.5	3.39(3)
S	f(18, 1)	-0.15833(3)	0.03353(3)	-0.22276(4)	1.53(1)
O(1)	f(18, 1)	-0.0051(2)	0.1530(2)	-0.6352(2)	2.35(5)
O(2)	f(18, 1)	0.0144(1)	-0.0981(1)	-0.1211(2)	3.65(7)
O(3)	f(18, 1)	-0.1910(2)	-0.4313(2)	-0.4516(3)	5.49(13)
O(4)	f(18, 1)	-0.3348(3)	-0.4086(2)	-0.4957(3)	5.67(13)
Ta	a(3, $\bar{3}$)	0.0	0.0	0.0	1.13(1)
K(1)	f(18, 1)	0.05789(6)	0.27459(6)	-0.37206(7)	3.73(7)
K(2)	b(3, $\bar{3}$)	0.0	0.0	0.5	3.39(3)
S	f(18, 1)	-0.15905(4)	0.03215(4)	-0.22481(5)	7.82(1)
O(1)	f(18, 1)	0.0022(2)	0.1482(2)	-0.6331(2)	2.42(6)
O(2)	f(18, 1)	0.0167(1)	-0.0978(1)	-0.1211(2)	4.06(10)
O(3)	f(18, 1)	-0.1922(2)	-0.4251(2)	-0.4614(3)	4.84(10)
O(4)	f(18, 1)	-0.3470(3)	-0.4151(2)	-0.4801(3)	5.65(14)

^a B_{eq} is defined as $8\pi^2/3 \sum_{i=1}^3 \sum_{j=1}^3 U_{ij} a_i^* a_j^* \bar{a}_i \bar{a}_j$. The anisotropic temperature parameters U_{ij} can be obtained from the authors.

Table 4. Bond lengths (Å) and angles (°).

$K_7Nb(SO_4)_6$			
Nb–O(2)	1.955(2)	Nb–O(2)–S	149.81(12)
S–O(2)	1.546(2)	O(2)–Nb–O(2)	89.57(8)
S–O(1)	1.439(2)		90.43(8)
S–O(3)	1.434(2)	O(2)–S–O(1)	105.90(13)
S–O(4)	1.427(2)	O(2)–S–O(3)	107.13(11)
K(1)–O(1)	2.805(3)	O(2)–S–O(4)	105.60(16)
	2.894(3)	O(1)–S–O(3)	111.74(15)
K(1)–O(3)	2.648(3)	O(1)–S–O(4)	112.06(12)
	2.693(3)	O(3)–S–O(4)	113.76(19)
K(1)–O(4)	2.713(3)		
	2.778(3)		
K(2)–O(1)	2.663(3)		
$K_7Ta(SO_4)_6$			
Ta–O(2)	1.957(2)	Ta–O(2)–S	148.64(14)
S–O(2)	1.548(2)	O(2)–Ta–O(2)	89.69(9)
S–O(1)	1.438(2)		90.31(9)
S–O(3)	1.425(2)	O(2)–S–O(1)	105.41(15)
S–O(4)	1.425(2)	O(2)–S–O(3)	107.29(12)
K(1)–O(1)	2.927(3)	O(2)–S–O(4)	104.99(17)
	2.852(3)	O(1)–S–O(3)	111.86(16)
K(1)–O(3)	2.642(3)	O(1)–S–O(4)	111.78(14)
	2.697(4)	O(3)–S–O(4)	114.73(21)
K(1)–O(4)	2.790(4)		
	2.726(3)		
K(2)–O(1)	2.525(3)		

Table 3, bond lengths and bond angles are given in Table 4, and the packing of the structure is shown in Fig. 1. Lists of observed and calculated structure factors as well as atomic anisotropic thermal parameters can be obtained from the authors.

Results and discussion

Description and discussion of the structure. The two compounds are isostructural, and consist of hexasulfatometalate(V) complex ions. The MO_6 ($M = Nb, Ta$) units have $\bar{3}$ symmetry.

The deviations of the O–M–O angles from 90° ($Nb: \pm 0.43^\circ$, $Ta \pm 0.31^\circ$) show that the distortion of the octa-

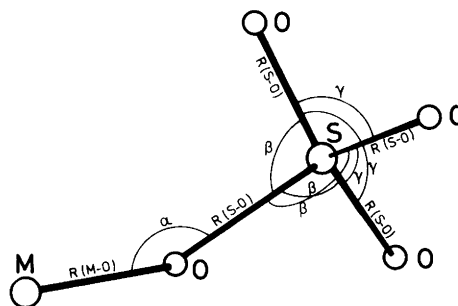


Fig. 2. Projection of the $M-O-SO_3$ fraction. Distances and angles are given in Table 4.

hedral symmetry (squeezing along the $\bar{3}$ -axis) is very small (Table 4). Furthermore, the distances and angles of the two MO_6 units are identical within experimental error.

The orientation of the sulfate group relative to the M–O coordinative bond is shown in Fig. 2. The M–O–S bond angles are $149.8(1)^\circ$ (Nb) and $148.6(1)^\circ$ (Ta).

In the sulfate groups, the S–O(2) distance, O(2) being the bridging oxygen atom, is ca. 0.11 \AA longer than the other S–O distances. Consequently, the O(2)–S–O angles are smaller (around $105\text{--}107^\circ$) and the remaining O–S–O angles larger (around $112\text{--}114^\circ$) than the ideal tetrahedral angle. This distance–angle relationship is in agreement with that observed in five different sulfate ions in the $K_4(VO)_3(SO_4)_5$ structure.¹⁴

Comparison to other related structures. Few other crystal structures of niobium and tantalum sulfates are known. The structure is known for $ANbO(SO_4)_2$ with $A = NH_4, Rb$ and Cs ^{16–20} and for $K_3Nb(SO_4)_4$,²¹ and unit cell parameters have been given for $A_3M(SO_4)_4$ with $A = K, Rb, Cs$, and $M = Nb, Ta$, respectively.^{20,22,23} The $ANbO(SO_4)_2$ crystals crystallize^{16–20} in the orthorhombic $Pnma$ space group and contain A^+ ions and undulating polymeric $NbO(SO_4)_2^-$ layers, in which each Nb atom is coordinated to one separate oxygen atom at a short distance and five oxygen atoms at much longer distances, all five belonging to different SO_4^{2-} groups, in such a way that a distorted NbO_6 octahedron is formed. The $A_3Nb(SO_4)_4$ compounds with $A = K$, and presumably also with $A = Rb$ and Cs , crystallize in the orthorhombic $Pnma$ space group and contain A^+ and

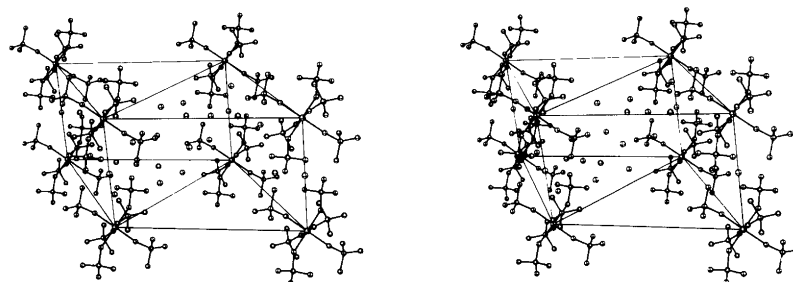


Fig. 1. Stereographic plot of the unit cell of $K_7Nb(SO_4)_6$, seen along the a axis.

Table 5. Comparison of Nb–O, Ta–O and S–O bond distances and shortest O–K contacts (Å) in different crystal structures.

Compound	M–O	S–O	O–K	Ref.
K ₇ Nb(SO ₄) ₆	1.955	1.427–1.546	2.648	This work
K ₇ Ta(SO ₄) ₆	1.957	1.425–1.548	2.525	This work
(NH ₄)NbO(SO ₄) ₂	1.64–2.26	1.44–1.54		19
RbNbO(SO ₄) ₂	1.71–2.28	1.37–1.55		16, 17, 19
CsNbO(SO ₄) ₂	1.56–2.35	1.41–1.56		18
K ₃ Nb(SO ₄) ₄	2.05–2.20 ^a	1.40–1.56	2.68	21
β-K ₂ SO ₄		1.459–1.473	2.723	24

^aDodecahedral eightfold oxygen coordination.

isolated Nb(SO₄)₄³⁻ complex ions, which have four cyclic bidentate sulfate ligands forming four-membered Nb–O–S–O rings and creating a dodecahedral oxygen environment.²¹

In Table 5 the bond lengths of the new structures are compared to other structures,^{16–19,21,24} and a close consistency is seen between the new and the previously found values; e.g. the S–O bond lengths found are close to the standard sulfate value of 1.47 Å.²⁵ Also, the Nb and Ta structures are apparently able to form very short oxygen–potassium contacts.

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References

- Bali, A. and Malhotra, K. C. *Aust. J. Chem.* 28 (1975) 481.
- Goroshchenko, Ya. G. and Andreeva, M. I. *Russ. J. Inorg. Chem. (Engl. Transl.)* 8 (1963) 505.
- Nabivanets, B. I. *Russ. J. Inorg. Chem. (Engl. Transl.)* 9 (1964) 590.
- Gridchina, G. I. *Russ. J. Inorg. Chem. (Engl. Transl.)* 11 (1966) 163.
- Belyaev, E. K., Annopol'skii, V. F., Panasenko, N. M. and Khomyakova, V. V. *Zh. Prikl. Khim.* 48 (1975) 2589.
- Doroshenko, A. K., Lopatin, S. S., Lupeiko, T. G. and Logvinova, S. V. *Izv. Akad. Nauk SSSR, Neorg. Mater.* 23 (1987) 1196.
- Land, J. E. and Sanchez-Caldas, J. R. *J. Less-Common Met.* 13 (1967) 233.
- Dartiguenave, M. *Bull. Soc. Chim. Fr.* (1967) 1233.
- Dartiguenave, M. and Dartiguenave, Y. *Bull. Soc. Chim. Fr.* (1968) 2783.
- Sears, G. W. *J. Am. Chem. Soc.* 48 (1926) 343.
- Sears, G. W. *J. Am. Chem. Soc.* 51 (1929) 122.
- Land, J. E. *J. Alabama Acad. Sci.* 31 (1959) 143.
- Hansen, N. H., Fehrmann, R. and Bjerrum, N. J. *Inorg. Chem.* 21 (1982) 744.
- Fehrmann, R., Boghosian, S., Papatheodorou, G. N., Nielsen, K., Berg, R. W. and Bjerrum, N. J. *Inorg. Chem.* 28 (1989) 1847.
- Cromer, D. T. and Mann, J. B. *Acta Crystallogr., Sect. A* 24 (1968) 321.
- Kuznetsov, V. Ya., Rogachev, D. L., Porai-Koshits, M. A. and Dikareva, L. M. *Izv. Akad. Nauk SSSR, Ser. Khim.* (1974) 2167.
- Kuznetsov, V. Ya., Porai-Koshits, M. A., Dikareva, L. M. and Rogachev, D. L. *Russ. J. Struct. Chem. (Engl. Transl.)* 15 (1974) 836.
- Kashaev, A. A. and Sokolova, G. V. *Sov. Phys. Crystallogr. (Engl. Transl.)* 18 (1973) 388.
- Kashaev, A. A., Postoenko, G. E. and Zel'bst, E. A. *Sov. Phys. Crystallogr. (Engl. Transl.)* 18 (1973–74) 802.
- Andreeva, M. I., Podozerskaya, E. A., Kuznetsov, V. Ya. and Popova, R. A. *Russ. J. Inorg. Chem. (Engl. Transl.)* 18 (1973) 641.
- Kuznetsov, V. Ya., Rogachev, D. L., Dikareva, L. M. and Porai-Koshits, M. A. *Russ. J. Struct. Chem. (Engl. Transl.)* 20 (1979) 569.
- Andreeva, M. I., Popova, R. A. and Kobychева, S. A. *Russ. J. Inorg. Chem. (Engl. Transl.)* 16 (1971) 551.
- Andreeva, M. I., Podozerskaya, E. A., Kobychева, T. A. and Kuznetsov, V. Ya. *Russ. J. Inorg. Chem. (Engl. Transl.)* 18 (1973) 288.
- McGinnety, J. A. *Acta Crystallogr., Sect. B* 28 (1972) 2845.
- Renner, B. and Lehmann, G. Z. *Kristallogr.* 175 (1986) 43.

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