

Acta Crystallographica Section E

## Structure Reports

Online

ISSN 1600-5368

The mixed-metal tris(disulfide) thiophosphate,  $\text{KNb}_{1.77}\text{Ta}_{0.23}\text{PS}_{10}$ 

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Received 6 January 2014; accepted 9 January 2014

Key indicators: single-crystal X-ray study;  $T = 290\text{ K}$ ; mean  $\sigma(\text{S}-\text{S}) = 0.001\text{ \AA}$ ; disorder in main residue;  $R$  factor = 0.019;  $wR$  factor = 0.040; data-to-parameter ratio = 22.9.

The title compound *catena*-poly[potassium [tri- $\mu$ -disulfido- $\mu$ -tetrathiophosphato-di[niobate(IV)/tantalate(IV)(0.885/0.115)]]], has been obtained through the reaction of the elements with KCl. The title compound is isostructural with  $\text{KNb}_2\text{PS}_{10}$ , with the Nb sites occupied by statistically disordered Nb (88.5%) and Ta (11.5%) atoms. The structure is composed of anionic  $[\infty[\text{M}_2\text{PS}_{10}]^-]$  chains along [100] ( $M = \text{Nb}/\text{Ta}$ ) and  $\text{K}^+$  ions. This chain is built up from distorted bicapped trigonal prisms  $[\text{MS}_8]$  and  $[\text{PS}_4]$  tetrahedra. There are no interchain bonding interactions, except for electrostatic and van der Waals forces. The  $\text{S}_2^{2-}$  and  $\text{S}^{2-}$  anionic species and the  $\text{M}^{4+}-\text{M}^{4+}$  pair [ $M-M = 2.8939(3)\text{ \AA}$ ] are observed. The classical charge balance is represented by  $[\text{K}^+][\text{M}^{4+}]_2[\text{PS}_4^{3-}]_2[\text{S}_2^{2-}]_3$ .

## Related literature

For the related mixed-metallic phase  $\text{KNb}_{1.75}\text{V}_{0.25}\text{PS}_{10}$ , see: Yu & Yun (2011). For related quaternary compounds, see: Goh *et al.* (2002); Do & Yun (1996, 2009); Kim & Yun (2002); Kwak *et al.* (2007); Bang *et al.* (2008) and for quinary compounds, see: Kwak & Yun (2008); Dong *et al.* (2005*a,b*). For  $\text{Cs}_{0.5}\text{Ag}_{0.5}\text{Nb}_2\text{PS}_{10}$ , see: Park & Yun (2010). For a typical  $\text{Nb}^{4+}-\text{Nb}^{4+}$  bond length, see: Angenault *et al.* (2000).

## Experimental

## Crystal data

 $\text{KNb}_{1.77}\text{Ta}_{0.23}\text{PS}_{10}$  $M_r = 596.52$ Orthorhombic,  $Pca2_1$  $a = 13.0049(3)\text{ \AA}$  $b = 7.5262(2)\text{ \AA}$  $c = 13.3616(3)\text{ \AA}$  $V = 1307.81(6)\text{ \AA}^3$  $Z = 4$ Mo  $K\alpha$  radiation $\mu = 5.45\text{ mm}^{-1}$  $T = 290\text{ K}$  $0.32 \times 0.06 \times 0.04\text{ mm}$ 

## Data collection

Rigaku R-AXIS RAPID S diffractometer

Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995) $T_{\text{min}} = 0.724$ ,  $T_{\text{max}} = 1.000$ 12074 measured reflections  
2974 independent reflections2842 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.031$ 

## Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.019$  $wR(F^2) = 0.040$  $S = 1.08$ 

2974 reflections

130 parameters

1 restraint

 $\Delta\rho_{\text{max}} = 0.40\text{ e \AA}^{-3}$  $\Delta\rho_{\text{min}} = -0.64\text{ e \AA}^{-3}$ 

Absolute structure: Flack (1983)

Absolute structure parameter:

0.102 (14)

Table 1

Selected bond lengths ( $\text{\AA}$ ).

Nb1/Ta1—S8 <sup>i</sup>	2.4753 (10)	Nb2/Ta2—S6 <sup>i</sup>	2.5568 (9)
Nb1/Ta1—S7 <sup>ii</sup>	2.4895 (9)	Nb2/Ta2—S10 <sup>iii</sup>	2.5597 (8)
Nb1/Ta1—S2 <sup>iii</sup>	2.5133 (10)	Nb2/Ta2—S5	2.5802 (8)
Nb1/Ta1—S9 <sup>i</sup>	2.5255 (9)	Nb2/Ta2—S4	2.6369 (8)
Nb1/Ta1—S6 <sup>i</sup>	2.5545 (9)	P—S3	1.9725 (14)
Nb1/Ta1—S10 <sup>iii</sup>	2.5653 (8)	P—S5	2.0470 (14)
Nb1/Ta1—S1	2.5831 (9)	P—S1	2.0568 (13)
Nb1/Ta1—S4	2.6438 (8)	P—S4	2.0888 (14)
Nb2/Ta2—S9 <sup>iv</sup>	2.4742 (9)	S2—S8 <sup>ii</sup>	2.0302 (16)
Nb2/Ta2—S2 <sup>i</sup>	2.4805 (9)	S6—S10 <sup>v</sup>	2.0568 (13)
Nb2/Ta2—S8 <sup>iv</sup>	2.5185 (10)	S7—S9 <sup>iv</sup>	2.0452 (15)
Nb2/Ta2—S7	2.5513 (9)		

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

Data collection: *RAPID-AUTO* (Rigaku, 2006); cell refinement: *RAPID-AUTO*; data reduction: *RAPID-AUTO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: locally modified version of *ORTEP* (Johnson, 1965); software used to prepare material for publication: *WinGX* (Farrugia, 2012).

This research was supported by the Basic Science Research Program through the National Research Foundation of Korea funded by the Ministry of Education, Science and Technology (grant No. 2011-0011309).

Supporting information for this paper is available from the IUCr electronic archives (Reference: RU2056).

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## supporting information

*Acta Cryst.* (2014). E70, i8 [doi:10.1107/S1600536814000592]

## The mixed-metal tris(disulfide) thiophosphate, $\text{KNb}_{1.77}\text{Ta}_{0.23}\text{PS}_{10}$

Yoonjeong Lee, Woojin Yoon and Hoseop Yun

### S1. Comment

A number of monovalent metal Nb thiophosphates have been investigated. Among them are  $\text{NaNb}_2\text{PS}_{10}$  (Goh *et al.*, 2002),  $\text{KNb}_2\text{PS}_{10}$  (Do & Yun, 1996),  $\text{RbNb}_2\text{PS}_{10}$  (Kim & Yun, 2002),  $\text{CsNb}_2\text{PS}_{10}$  (Kwak *et al.*, 2007),  $\text{TiNb}_2\text{PS}_{10}$  (Bang *et al.*, 2008),  $\text{Ag}_{0.88}\text{Nb}_2\text{PS}_{10}$  (Do & Yun, 2009),  $\text{K}_{0.34}\text{Cu}_{0.5}\text{Nb}_2\text{PS}_{10}$  (Kwak & Yun, 2008),  $\text{K}_{0.5}\text{Ag}_0\text{Nb}_2\text{PS}_{10}$  (Dong *et al.*, 2005a),  $\text{Rb}_{0.38}\text{Ag}_{0.5}\text{Nb}_2\text{PS}_{10}$  (Dong *et al.*, 2005b),  $\text{Cs}_{0.5}\text{Ag}_{0.5}\text{Nb}_2\text{PS}_{10}$  (Park & Yun, 2010), and  $\text{KNb}_{1.75}\text{V}_{0.25}\text{PS}_{10}$  (Yu & Yun, 2011). As a result of efforts to find new phases in this family, we have found a mixed-metallic phase,. In this paper we report the synthesis and structure of another mixed-metallic quinary thiophosphate,  $\text{KNb}_{1.77}\text{Ta}_{0.23}\text{PS}_{10}$ .

The structure of  $\text{KNb}_{1.77}\text{Ta}_{0.23}\text{PS}_{10}$  is isostructural with  $\text{KNb}_2\text{PS}_{10}$  and mixed-metallic  $\text{KNb}_{1.75}\text{V}_{0.25}\text{PS}_{10}$ . Detailed description of the structure is given previously (Do & Yun, 1996; Yu & Yun, 2011). The title compound is made up of the usual bicapped trigonal bipyramidal  $[\text{M}_2\text{S}_{12}]$  unit ( $M=\text{Nb}/\text{Ta}$ ) and the tetrahedral  $[\text{PS}_4]$  group. The  $M$  sites are occupied by the statistically disordered Nb(88.5%) and Ta(11.5%) atoms. The bicapped bipyramidal  $[\text{M}_2\text{S}_{12}]$  units and its neighboring tetrahedral  $[\text{PS}_4]$  groups are given in Figure 1. These  $[\text{M}_2\text{S}_{12}]$  units are linked together to form the one-dimensional chains,  $\infty^1[\text{M}_2\text{PS}_{10}^-]$  by sharing the  $\text{S}_2^{2-}$  prism edge.

The  $M$  atoms associate in pairs with  $M-M$  interactions alternating in the sequence of one short (2.8939 (3) Å) and one long (3.7670 (3) Å) distances. The short distance is typical of  $\text{Nb}^{4+}-\text{Nb}^{4+}$  bonding interactions (Angenault *et al.*, 2000). There are no interchain bonding interactions except the van der Waals forces and the  $\text{K}^+$  ions in this van der Waals gap stabilize the structure through the electrostatic interactions (Figure 2).

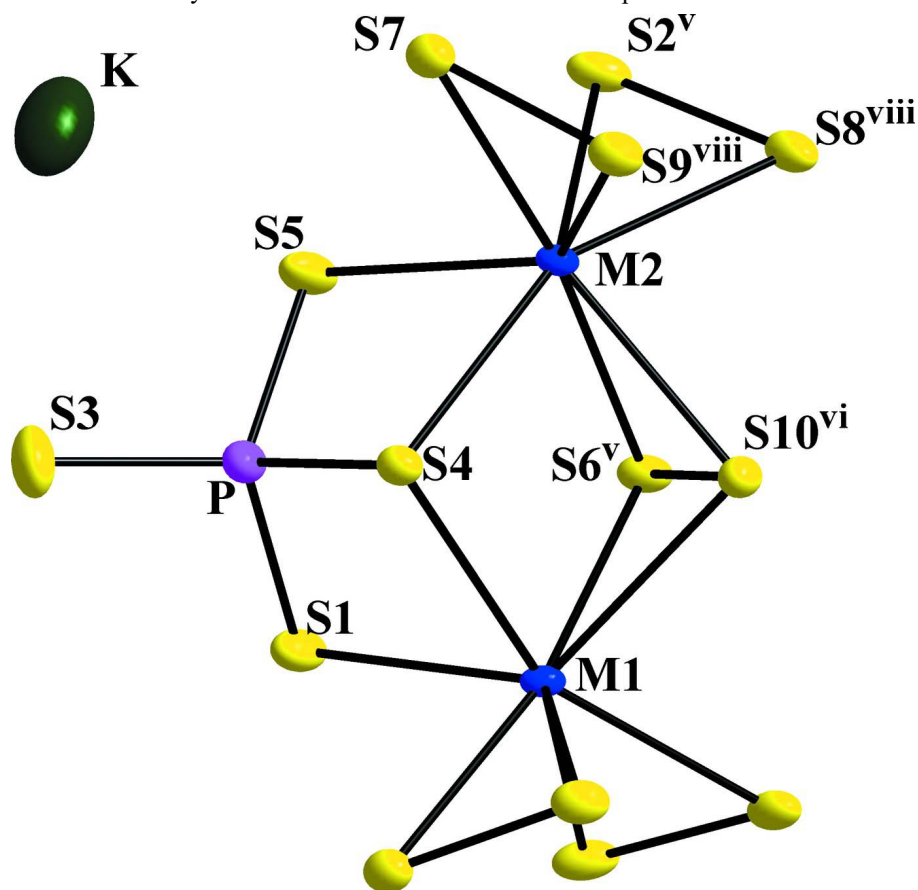
The structural studies of the three different crystals from the same reaction tube implied that the stoichiometry of each metal can vary,  $\text{KNb}_{2-x}\text{Ta}_x\text{PS}_{10}$ ,  $0.18 \leq x \leq 0.26$  and they seem to form a random substitutional solid solution. However Ta analogue of this phase,  $\text{ATa}_2\text{PS}_{10}$  has never been synthesized and thus the maximum  $x$  should be small. Finally, the classical charge balance of this phase can be represented by  $[\text{K}^+][\text{M}^{4+}]_2[\text{PS}_4^{3-}][\text{S}_2^{2-}]_3$ .

### S2. Experimental

The title compound,  $\text{KNb}_{1.77}\text{Ta}_{0.23}\text{PS}_{10}$  was prepared by the reaction of the elemental with the use of the reactive alkali metal halides-flux technique. A combination of the pure elements, Nb powder (CERAC 99.8%), Ta powder (CERAC 99.9%), P powder (Aldrich 99.9%), and S powder (Aldrich 99.999%) were mixed in a fused silica tube in a molar ratio of Nb: Ta: P: S = 1:1:1:10 with KCl (CERAC 99.9%). The mass ratio of the reactants and the alkali metal halides flux was 1:1. The tube was evacuated to 0.133 Pa, sealed and heated gradually (70 K/h) to 1073 K, where it was kept for 72 h. The tube was cooled to 473 K at 6 K/h and then was quenched to room temperature. The excess halides were removed with distilled water and black needle-shaped single crystals were obtained. The crystals are stable in air and water. Qualitative analysis of these crystals using XRF showed the presence of K, Nb, Ta, P, and S.

## S3. Refinement

The refinement of the model with occupational disorder on the *M* site caused significant decrease of the *R*-factor ( $wR2 = 0.042$ ) in comparison if the full occupation by either metal had been considered ( $wR2 > 0.077$ ). Also the displacement parameters in the disordered model became plausible. The disordered atoms were supposed to have the same displacement parameters. With the nonstoichiometric model, the parameter remained the same. The large anisotropic displacement parameters for alkali metals are also found in the related compounds such as  $\text{KNb}_2\text{PS}_{10}$  (Do & Yun, 1996). The highest residual electron density is  $0.40 \text{ \AA}^{-3}$  from the M2 site and the deepest hole is  $0.64 \text{ \AA}^{-3}$  from the M1 site.



**Figure 1**

A view of the bicapped trigonal bipyrametric  $[M_2S_{12}]$  unit ( $M=\text{Nb}/\text{Ta}$ ) and its neighboring tetrahedral  $[PS_4]$  groups. Yellow circles are S atoms, blue circles are Nb atoms, pink and dark green circles are P and K atoms, respectively. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry code: (v)  $0.5 - x, y, -0.5 + z$ ; (vi)  $-0.5 + x, -y, z$ ; (viii)  $1 - x, -y, -0.5 + z$ ]

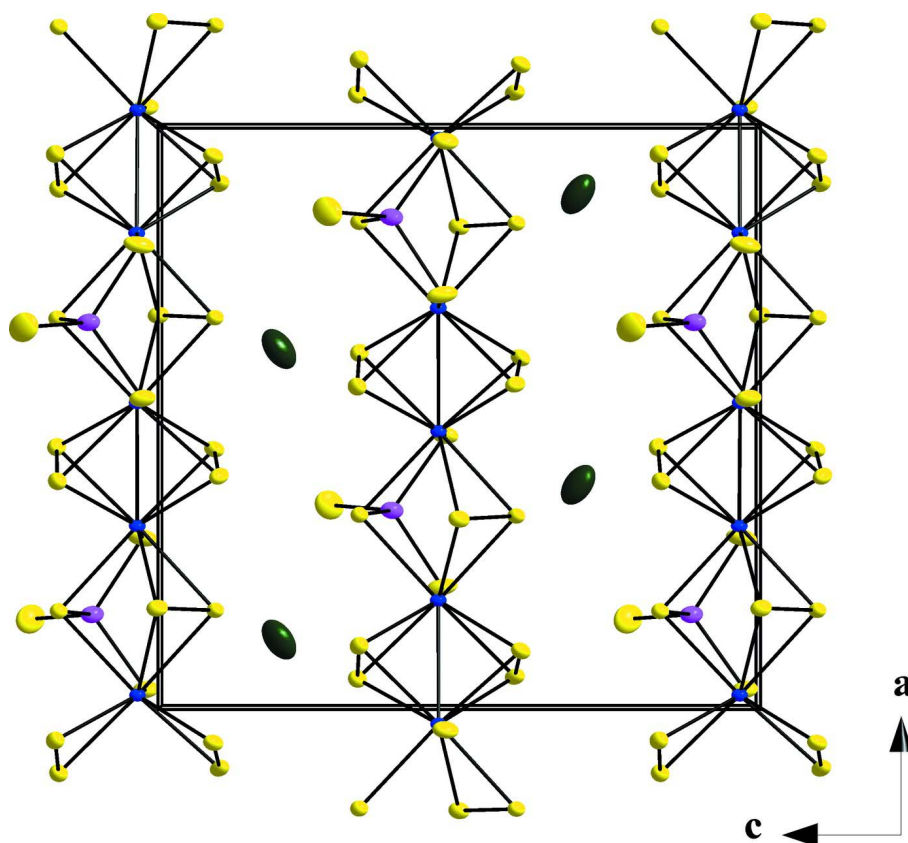


Figure 2

View of the  $\text{KNb}_{1.77}\text{Ta}_{0.23}\text{PS}_{10}$  down the  $b$  axis showing the one-dimensional nature of the compound. Atoms are as marked in Fig. 1.

*catena*-Poly[potassium [tri- $\mu$ -disulfido- $\mu$ -tetrathiophosphato-di[niobate(IV)/tantalate(IV)(0.885/0.115)]]]

#### Crystal data

$\text{KNb}_{1.77}\text{Ta}_{0.23}\text{PS}_{10}$

$M_r = 596.52$

Orthorhombic,  $Pca2_1$

Hall symbol: P 2c -2ac

$a = 13.0049(3) \text{ \AA}$

$b = 7.5262(2) \text{ \AA}$

$c = 13.3616(3) \text{ \AA}$

$V = 1307.81(6) \text{ \AA}^3$

$Z = 4$

$F(000) = 1133$

$D_x = 3.03 \text{ Mg m}^{-3}$

Mo  $K\alpha$  radiation,  $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 10926 reflections

$\theta = 3.1\text{--}27.4^\circ$

$\mu = 5.45 \text{ mm}^{-1}$

$T = 290 \text{ K}$

Needle, black

$0.32 \times 0.06 \times 0.04 \text{ mm}$

#### Data collection

Rigaku R-AXIS RAPID S  
diffractometer

Radiation source: sealed X-ray tube

Graphite monochromator

$\omega$  scans

Absorption correction: multi-scan

(*ABSCOR*; Higashi, 1995)

$T_{\min} = 0.724$ ,  $T_{\max} = 1.000$

12074 measured reflections

2974 independent reflections

2842 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.031$

$\theta_{\max} = 27.4^\circ$ ,  $\theta_{\min} = 3.1^\circ$

$h = -16 \rightarrow 16$

$k = -9 \rightarrow 9$

$l = -17 \rightarrow 17$

*Refinement*

Refinement on  $F^2$   
 Least-squares matrix: full  
 $R[F^2 > 2\sigma(F^2)] = 0.019$   
 $wR(F^2) = 0.040$   
 $S = 1.08$   
 2974 reflections  
 130 parameters  
 1 restraint

$w = 1/[\sigma^2(F_o^2) + (0.0132P)^2 + 0.4965P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.001$   
 $\Delta\rho_{\max} = 0.40 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -0.64 \text{ e } \text{\AA}^{-3}$   
 Absolute structure: Flack (1983)  
 Absolute structure parameter: 0.102 (14)

*Special details*

**Geometry.** All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'s involving l.s. planes.

**Refinement.** Refinement of  $F^2$  against ALL reflections. The weighted  $R$ -factor  $wR$  and goodness of fit  $S$  are based on  $F^2$ , conventional  $R$ -factors  $R$  are based on  $F$ , with  $F$  set to zero for negative  $F^2$ . The threshold expression of  $F^2 > 2\sigma(F^2)$  is used only for calculating  $R$ -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement.  $R$ -factors based on  $F^2$  are statistically about twice as large as those based on  $F$ , and  $R$ -factors based on ALL data will be even larger.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
K	0.38318 (10)	0.50405 (16)	0.30118 (10)	0.0643 (3)	
Nb1	0.024329 (14)	0.05323 (3)	0.03456 (2)	0.01373 (8)	0.8870 (16)
Ta1	0.024329 (14)	0.05323 (3)	0.03456 (2)	0.01373 (8)	0.1130 (16)
Nb2	0.313802 (14)	0.07133 (3)	0.03507 (2)	0.01349 (8)	0.8848 (16)
Ta2	0.313802 (14)	0.07133 (3)	0.03507 (2)	0.01349 (8)	0.1152 (16)
P	0.16059 (6)	0.40111 (13)	0.11222 (8)	0.02029 (19)	
S1	0.03152 (5)	0.39563 (11)	0.02331 (9)	0.0241 (2)	
S2	0.05537 (7)	0.15129 (15)	0.40771 (7)	0.0231 (2)	
S3	0.15181 (9)	0.58446 (14)	0.21735 (9)	0.0393 (3)	
S4	0.16755 (6)	0.14082 (12)	0.16603 (6)	0.01689 (19)	
S5	0.29233 (6)	0.41195 (10)	0.02861 (11)	0.0285 (2)	
S6	0.33066 (6)	0.05475 (12)	0.40561 (7)	0.0189 (2)	
S7	0.44837 (7)	0.13315 (14)	0.16957 (6)	0.0207 (2)	
S8	0.60107 (7)	0.10612 (14)	0.39842 (7)	0.0235 (2)	
S9	0.60965 (7)	0.11936 (13)	0.66622 (6)	0.0201 (2)	
S10	0.67408 (5)	0.16023 (11)	0.00053 (6)	0.01866 (18)	

*Atomic displacement parameters ( $\text{\AA}^2$ )*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
K	0.0846 (8)	0.0454 (7)	0.0629 (8)	0.0038 (6)	-0.0317 (7)	0.0034 (6)
Nb1	0.00877 (11)	0.01781 (13)	0.01460 (12)	-0.00086 (7)	0.00002 (16)	0.00118 (14)
Ta1	0.00877 (11)	0.01781 (13)	0.01460 (12)	-0.00086 (7)	0.00002 (16)	0.00118 (14)
Nb2	0.00838 (11)	0.01692 (13)	0.01516 (12)	0.00106 (7)	0.00005 (15)	-0.00009 (14)
Ta2	0.00838 (11)	0.01692 (13)	0.01516 (12)	0.00106 (7)	0.00005 (15)	-0.00009 (14)
P	0.0158 (4)	0.0172 (4)	0.0279 (5)	0.0018 (3)	-0.0010 (4)	-0.0027 (4)
S1	0.0156 (3)	0.0208 (4)	0.0359 (6)	0.0022 (3)	-0.0026 (5)	0.0045 (5)

S2	0.0139 (4)	0.0342 (6)	0.0213 (5)	-0.0031 (4)	-0.0019 (4)	0.0071 (4)
S3	0.0450 (6)	0.0281 (5)	0.0449 (7)	0.0070 (5)	-0.0044 (5)	-0.0179 (5)
S4	0.0138 (4)	0.0200 (5)	0.0169 (4)	0.0004 (3)	0.0002 (3)	-0.0011 (4)
S5	0.0160 (3)	0.0192 (4)	0.0503 (6)	-0.0005 (3)	0.0068 (6)	0.0056 (6)
S6	0.0125 (4)	0.0275 (5)	0.0166 (4)	0.0000 (3)	0.0002 (3)	0.0027 (4)
S7	0.0168 (4)	0.0267 (5)	0.0185 (5)	0.0007 (4)	-0.0008 (4)	-0.0050 (4)
S8	0.0150 (4)	0.0354 (6)	0.0202 (5)	0.0047 (4)	0.0029 (4)	0.0084 (5)
S9	0.0166 (4)	0.0253 (5)	0.0183 (5)	0.0017 (4)	-0.0009 (4)	-0.0033 (4)
S10	0.0152 (4)	0.0169 (4)	0.0239 (4)	-0.0001 (3)	-0.0012 (3)	0.0018 (3)

*Geometric parameters (Å, °)*

K—S3	3.2671 (16)	S2—S8 <sup>vi</sup>	2.0302 (16)
K—S1 <sup>i</sup>	3.2720 (16)	S2—Ta2 <sup>i</sup>	2.4805 (9)
K—S9 <sup>ii</sup>	3.3606 (15)	S2—Nb2 <sup>i</sup>	2.4805 (9)
K—S7	3.4064 (16)	S2—Nb1 <sup>x</sup>	2.5133 (10)
K—S2 <sup>iii</sup>	3.7107 (16)	S2—Ta1 <sup>x</sup>	2.5133 (10)
K—S6	3.7213 (15)	S2—K <sup>xi</sup>	3.7107 (16)
K—S3 <sup>iii</sup>	3.7288 (19)	S3—K <sup>xi</sup>	3.7288 (19)
K—S10 <sup>iv</sup>	3.7461 (16)	S6—S10 <sup>xii</sup>	2.0568 (13)
Nb1—S8 <sup>v</sup>	2.4753 (10)	S6—Ta1 <sup>i</sup>	2.5545 (9)
Nb1—S7 <sup>vi</sup>	2.4895 (9)	S6—Nb1 <sup>i</sup>	2.5545 (9)
Nb1—S2 <sup>vii</sup>	2.5133 (10)	S6—Ta2 <sup>i</sup>	2.5568 (9)
Nb1—S9 <sup>v</sup>	2.5255 (9)	S6—Nb2 <sup>i</sup>	2.5568 (9)
Nb1—S6 <sup>v</sup>	2.5545 (9)	S7—S9 <sup>viii</sup>	2.0452 (15)
Nb1—S10 <sup>vi</sup>	2.5653 (8)	S7—Ta1 <sup>ix</sup>	2.4895 (9)
Nb1—S1	2.5831 (9)	S7—Nb1 <sup>ix</sup>	2.4895 (9)
Nb1—S4	2.6438 (8)	S8—S2 <sup>ix</sup>	2.0302 (17)
Nb1—Nb2 <sup>vi</sup>	2.8939 (3)	S8—Nb1 <sup>i</sup>	2.4753 (10)
Nb1—Ta2 <sup>vi</sup>	2.8939 (3)	S8—Ta1 <sup>i</sup>	2.4753 (10)
Nb2—S9 <sup>viii</sup>	2.4742 (9)	S8—Nb2 <sup>xii</sup>	2.5185 (10)
Nb2—S2 <sup>v</sup>	2.4805 (9)	S8—Ta2 <sup>xii</sup>	2.5185 (10)
Nb2—S8 <sup>viii</sup>	2.5185 (10)	S9—S7 <sup>xii</sup>	2.0452 (15)
Nb2—S7	2.5513 (9)	S9—Ta2 <sup>xii</sup>	2.4742 (9)
Nb2—S6 <sup>v</sup>	2.5568 (9)	S9—Nb2 <sup>xii</sup>	2.4742 (9)
Nb2—S10 <sup>vi</sup>	2.5597 (8)	S9—Nb1 <sup>i</sup>	2.5255 (9)
Nb2—S5	2.5802 (8)	S9—Ta1 <sup>i</sup>	2.5255 (9)
Nb2—S4	2.6369 (8)	S9—K <sup>iv</sup>	3.3606 (15)
Nb2—Ta1 <sup>ix</sup>	2.8939 (3)	S10—S6 <sup>viii</sup>	2.0568 (13)
Nb2—Nb1 <sup>ix</sup>	2.8939 (3)	S10—Ta2 <sup>ix</sup>	2.5597 (8)
P—S3	1.9725 (14)	S10—Nb2 <sup>ix</sup>	2.5597 (8)
P—S5	2.0470 (14)	S10—Nb1 <sup>ix</sup>	2.5653 (8)
P—S1	2.0568 (13)	S10—Ta1 <sup>ix</sup>	2.5653 (8)
P—S4	2.0888 (14)	S10—K <sup>ii</sup>	3.7461 (16)
S1—K <sup>v</sup>	3.2720 (16)		
S3—K—S1 <sup>i</sup>	132.02 (6)	S5—Nb2—Ta1 <sup>ix</sup>	115.097 (18)
S3—K—S9 <sup>ii</sup>	71.66 (3)	S4—Nb2—Ta1 <sup>ix</sup>	138.44 (2)

S1 <sup>i</sup> —K—S9 <sup>ii</sup>	133.45 (4)	S9 <sup>viii</sup> —Nb2—Nb1 <sup>ix</sup>	55.46 (2)
S3—K—S7	101.77 (4)	S2 <sup>v</sup> —Nb2—Nb1 <sup>ix</sup>	55.12 (2)
S1 <sup>i</sup> —K—S7	100.34 (4)	S8 <sup>viii</sup> —Nb2—Nb1 <sup>ix</sup>	53.89 (2)
S9 <sup>ii</sup> —K—S7	114.03 (5)	S7—Nb2—Nb1 <sup>ix</sup>	53.97 (2)
S3—K—S2 <sup>iii</sup>	123.90 (4)	S6 <sup>v</sup> —Nb2—Nb1 <sup>ix</sup>	132.67 (2)
S1 <sup>i</sup> —K—S2 <sup>iii</sup>	67.78 (3)	S10 <sup>vi</sup> —Nb2—Nb1 <sup>ix</sup>	116.78 (2)
S9 <sup>ii</sup> —K—S2 <sup>iii</sup>	66.39 (3)	S5—Nb2—Nb1 <sup>ix</sup>	115.097 (18)
S7—K—S2 <sup>iii</sup>	128.37 (5)	S4—Nb2—Nb1 <sup>ix</sup>	138.44 (2)
S3—K—S6	97.35 (4)	Ta1 <sup>ix</sup> —Nb2—Nb1 <sup>ix</sup>	0.000 (14)
S1 <sup>i</sup> —K—S6	59.70 (3)	S3—P—S5	114.15 (6)
S9 <sup>ii</sup> —K—S6	166.57 (4)	S3—P—S1	112.22 (6)
S7—K—S6	59.64 (3)	S5—P—S1	111.63 (7)
S2 <sup>iii</sup> —K—S6	127.02 (4)	S3—P—S4	114.42 (7)
S3—K—S3 <sup>iii</sup>	142.46 (6)	S5—P—S4	100.89 (5)
S1 <sup>i</sup> —K—S3 <sup>iii</sup>	84.85 (3)	S1—P—S4	102.44 (5)
S9 <sup>ii</sup> —K—S3 <sup>iii</sup>	87.91 (4)	P—S1—Nb1	90.91 (4)
S7—K—S3 <sup>iii</sup>	57.68 (3)	P—S1—K <sup>v</sup>	104.02 (5)
S2 <sup>iii</sup> —K—S3 <sup>iii</sup>	71.02 (3)	Nb1—S1—K <sup>v</sup>	108.29 (4)
S6—K—S3 <sup>iii</sup>	97.02 (4)	S8 <sup>vi</sup> —S2—Ta2 <sup>i</sup>	67.02 (4)
S3—K—S10 <sup>iv</sup>	86.32 (4)	S8 <sup>vi</sup> —S2—Nb2 <sup>i</sup>	67.02 (4)
S1 <sup>i</sup> —K—S10 <sup>iv</sup>	65.83 (3)	Ta2 <sup>i</sup> —S2—Nb2 <sup>i</sup>	0.000 (15)
S9 <sup>ii</sup> —K—S10 <sup>iv</sup>	79.53 (3)	S8 <sup>vi</sup> —S2—Nb1 <sup>x</sup>	65.01 (4)
S7—K—S10 <sup>iv</sup>	165.76 (4)	Ta2 <sup>i</sup> —S2—Nb1 <sup>x</sup>	70.83 (3)
S2 <sup>iii</sup> —K—S10 <sup>iv</sup>	51.37 (3)	Nb2 <sup>i</sup> —S2—Nb1 <sup>x</sup>	70.83 (3)
S6—K—S10 <sup>iv</sup>	108.05 (4)	S8 <sup>vi</sup> —S2—Ta1 <sup>x</sup>	65.01 (4)
S3 <sup>iii</sup> —K—S10 <sup>iv</sup>	121.36 (4)	Ta2 <sup>i</sup> —S2—Ta1 <sup>x</sup>	70.83 (3)
S8 <sup>v</sup> —Nb1—S7 <sup>vi</sup>	111.20 (3)	Nb2 <sup>i</sup> —S2—Ta1 <sup>x</sup>	70.83 (3)
S8 <sup>v</sup> —Nb1—S2 <sup>vii</sup>	48.02 (4)	Nb1 <sup>x</sup> —S2—Ta1 <sup>x</sup>	0.000 (11)
S7 <sup>vi</sup> —Nb1—S2 <sup>vii</sup>	88.85 (3)	S8 <sup>vi</sup> —S2—K <sup>xi</sup>	145.11 (5)
S8 <sup>v</sup> —Nb1—S9 <sup>v</sup>	91.47 (3)	Ta2 <sup>i</sup> —S2—K <sup>xi</sup>	147.85 (4)
S7 <sup>vi</sup> —Nb1—S9 <sup>v</sup>	48.13 (3)	Nb2 <sup>i</sup> —S2—K <sup>xi</sup>	147.85 (4)
S2 <sup>vii</sup> —Nb1—S9 <sup>v</sup>	107.82 (3)	Nb1 <sup>x</sup> —S2—K <sup>xi</sup>	115.97 (4)
S8 <sup>v</sup> —Nb1—S6 <sup>v</sup>	89.43 (3)	Ta1 <sup>x</sup> —S2—K <sup>xi</sup>	115.97 (4)
S7 <sup>vi</sup> —Nb1—S6 <sup>v</sup>	141.65 (3)	P—S3—K	93.51 (5)
S2 <sup>vii</sup> —Nb1—S6 <sup>v</sup>	81.51 (3)	P—S3—K <sup>xi</sup>	98.23 (5)
S9 <sup>v</sup> —Nb1—S6 <sup>v</sup>	168.03 (3)	K—S3—K <sup>xi</sup>	136.62 (6)
S8 <sup>v</sup> —Nb1—S10 <sup>vi</sup>	118.08 (3)	P—S4—Nb2	89.36 (4)
S7 <sup>vi</sup> —Nb1—S10 <sup>vi</sup>	94.41 (3)	P—S4—Nb1	88.54 (4)
S2 <sup>vii</sup> —Nb1—S10 <sup>vi</sup>	79.05 (3)	Nb2—S4—Nb1	91.02 (3)
S9 <sup>v</sup> —Nb1—S10 <sup>vi</sup>	140.41 (3)	P—S5—Nb2	91.88 (4)
S6 <sup>v</sup> —Nb1—S10 <sup>vi</sup>	47.37 (3)	S10 <sup>xii</sup> —S6—Ta1 <sup>i</sup>	66.59 (3)
S8 <sup>v</sup> —Nb1—S1	79.67 (3)	S10 <sup>xii</sup> —S6—Nb1 <sup>i</sup>	66.59 (3)
S7 <sup>vi</sup> —Nb1—S1	128.22 (3)	Ta1 <sup>i</sup> —S6—Nb1 <sup>i</sup>	0.000 (13)
S2 <sup>vii</sup> —Nb1—S1	125.92 (3)	S10 <sup>xii</sup> —S6—Ta2 <sup>i</sup>	66.37 (3)
S9 <sup>v</sup> —Nb1—S1	82.47 (3)	Ta1 <sup>i</sup> —S6—Ta2 <sup>i</sup>	94.95 (3)
S6 <sup>v</sup> —Nb1—S1	85.96 (3)	Nb1 <sup>i</sup> —S6—Ta2 <sup>i</sup>	94.95 (3)
S10 <sup>vi</sup> —Nb1—S1	125.95 (3)	S10 <sup>xii</sup> —S6—Nb2 <sup>i</sup>	66.37 (3)
S8 <sup>v</sup> —Nb1—S4	155.83 (3)	Ta1 <sup>i</sup> —S6—Nb2 <sup>i</sup>	94.95 (3)

S7 <sup>vi</sup> —Nb1—S4	86.48 (3)	Nb1 <sup>i</sup> —S6—Nb2 <sup>i</sup>	94.95 (3)
S2 <sup>vii</sup> —Nb1—S4	153.05 (3)	Ta2 <sup>i</sup> —S6—Nb2 <sup>i</sup>	0.000 (6)
S9 <sup>v</sup> —Nb1—S4	88.51 (3)	S10 <sup>xii</sup> —S6—K	162.09 (5)
S6 <sup>v</sup> —Nb1—S4	85.81 (3)	Ta1 <sup>i</sup> —S6—K	96.98 (3)
S10 <sup>vi</sup> —Nb1—S4	74.88 (3)	Nb1 <sup>i</sup> —S6—K	96.98 (3)
S1—Nb1—S4	76.37 (3)	Ta2 <sup>i</sup> —S6—K	110.13 (4)
S8 <sup>v</sup> —Nb1—Nb2 <sup>vi</sup>	55.28 (2)	Nb2 <sup>i</sup> —S6—K	110.13 (4)
S7 <sup>vi</sup> —Nb1—Nb2 <sup>vi</sup>	55.97 (2)	S9 <sup>viii</sup> —S7—Ta1 <sup>ix</sup>	66.86 (4)
S2 <sup>vii</sup> —Nb1—Nb2 <sup>vi</sup>	54.06 (2)	S9 <sup>viii</sup> —S7—Nb1 <sup>ix</sup>	66.86 (4)
S9 <sup>v</sup> —Nb1—Nb2 <sup>vi</sup>	53.81 (2)	Ta1 <sup>ix</sup> —S7—Nb1 <sup>ix</sup>	0.000 (14)
S6 <sup>v</sup> —Nb1—Nb2 <sup>vi</sup>	134.55 (2)	S9 <sup>viii</sup> —S7—Nb2	64.03 (3)
S10 <sup>vi</sup> —Nb1—Nb2 <sup>vi</sup>	121.05 (2)	Ta1 <sup>ix</sup> —S7—Nb2	70.06 (2)
S1—Nb1—Nb2 <sup>vi</sup>	110.949 (17)	Nb1 <sup>ix</sup> —S7—Nb2	70.06 (2)
S4—Nb1—Nb2 <sup>vi</sup>	138.22 (2)	S9 <sup>viii</sup> —S7—K	132.92 (5)
S8 <sup>v</sup> —Nb1—Ta2 <sup>vi</sup>	55.28 (2)	Ta1 <sup>ix</sup> —S7—K	159.16 (5)
S7 <sup>vi</sup> —Nb1—Ta2 <sup>vi</sup>	55.97 (2)	Nb1 <sup>ix</sup> —S7—K	159.16 (5)
S2 <sup>vii</sup> —Nb1—Ta2 <sup>vi</sup>	54.06 (2)	Nb2—S7—K	110.02 (4)
S9 <sup>v</sup> —Nb1—Ta2 <sup>vi</sup>	53.81 (2)	S2 <sup>ix</sup> —S8—Nb1 <sup>i</sup>	66.97 (4)
S6 <sup>v</sup> —Nb1—Ta2 <sup>vi</sup>	134.55 (2)	S2 <sup>ix</sup> —S8—Ta1 <sup>i</sup>	66.97 (4)
S10 <sup>vi</sup> —Nb1—Ta2 <sup>vi</sup>	121.05 (2)	Nb1 <sup>i</sup> —S8—Ta1 <sup>i</sup>	0.000 (12)
S1—Nb1—Ta2 <sup>vi</sup>	110.949 (17)	S2 <sup>ix</sup> —S8—Nb2 <sup>xii</sup>	65.06 (4)
S4—Nb1—Ta2 <sup>vi</sup>	138.22 (2)	Nb1 <sup>i</sup> —S8—Nb2 <sup>xii</sup>	70.83 (3)
Nb2 <sup>vi</sup> —Nb1—Ta2 <sup>vi</sup>	0.000 (16)	Ta1 <sup>i</sup> —S8—Nb2 <sup>xii</sup>	70.83 (3)
S9 <sup>viii</sup> —Nb2—S2 <sup>v</sup>	110.53 (3)	S2 <sup>ix</sup> —S8—Ta2 <sup>xii</sup>	65.06 (4)
S9 <sup>viii</sup> —Nb2—S8 <sup>viii</sup>	91.66 (3)	Nb1 <sup>i</sup> —S8—Ta2 <sup>xii</sup>	70.83 (3)
S2 <sup>v</sup> —Nb2—S8 <sup>viii</sup>	47.92 (4)	Ta1 <sup>i</sup> —S8—Ta2 <sup>xii</sup>	70.83 (3)
S9 <sup>viii</sup> —Nb2—S7	48.00 (3)	Nb2 <sup>xii</sup> —S8—Ta2 <sup>xii</sup>	0.000 (13)
S2 <sup>v</sup> —Nb2—S7	88.20 (2)	S7 <sup>xii</sup> —S9—Ta2 <sup>xii</sup>	67.97 (4)
S8 <sup>viii</sup> —Nb2—S7	107.81 (3)	S7 <sup>xii</sup> —S9—Nb2 <sup>xii</sup>	67.97 (4)
S9 <sup>viii</sup> —Nb2—S6 <sup>v</sup>	138.29 (3)	Ta2 <sup>xii</sup> —S9—Nb2 <sup>xii</sup>	0.000 (13)
S2 <sup>v</sup> —Nb2—S6 <sup>v</sup>	92.96 (3)	S7 <sup>xii</sup> —S9—Nb1 <sup>i</sup>	65.01 (3)
S8 <sup>viii</sup> —Nb2—S6 <sup>v</sup>	78.85 (3)	Ta2 <sup>xii</sup> —S9—Nb1 <sup>i</sup>	70.73 (2)
S7—Nb2—S6 <sup>v</sup>	171.69 (3)	Nb2 <sup>xii</sup> —S9—Nb1 <sup>i</sup>	70.73 (2)
S9 <sup>viii</sup> —Nb2—S10 <sup>vi</sup>	91.05 (3)	S7 <sup>xii</sup> —S9—Ta1 <sup>i</sup>	65.01 (3)
S2 <sup>v</sup> —Nb2—S10 <sup>vi</sup>	121.90 (3)	Ta2 <sup>xii</sup> —S9—Ta1 <sup>i</sup>	70.73 (2)
S8 <sup>viii</sup> —Nb2—S10 <sup>vi</sup>	79.64 (3)	Nb2 <sup>xii</sup> —S9—Ta1 <sup>i</sup>	70.73 (2)
S7—Nb2—S10 <sup>vi</sup>	137.57 (3)	Nb1 <sup>i</sup> —S9—Ta1 <sup>i</sup>	0.000 (11)
S6 <sup>v</sup> —Nb2—S10 <sup>vi</sup>	47.41 (3)	S7 <sup>xii</sup> —S9—K <sup>iv</sup>	141.46 (5)
S9 <sup>viii</sup> —Nb2—S5	130.06 (4)	Ta2 <sup>xii</sup> —S9—K <sup>iv</sup>	149.10 (4)
S2 <sup>v</sup> —Nb2—S5	79.06 (4)	Nb2 <sup>xii</sup> —S9—K <sup>iv</sup>	149.10 (4)
S8 <sup>viii</sup> —Nb2—S5	123.38 (4)	Nb1 <sup>i</sup> —S9—K <sup>iv</sup>	124.00 (4)
S7—Nb2—S5	85.22 (4)	Ta1 <sup>i</sup> —S9—K <sup>iv</sup>	124.00 (4)
S6 <sup>v</sup> —Nb2—S5	86.92 (3)	S6 <sup>viii</sup> —S10—Ta2 <sup>ix</sup>	66.22 (3)
S10 <sup>vi</sup> —Nb2—S5	126.41 (3)	S6 <sup>viii</sup> —S10—Nb2 <sup>ix</sup>	66.22 (3)
S9 <sup>viii</sup> —Nb2—S4	86.29 (3)	Ta2 <sup>ix</sup> —S10—Nb2 <sup>ix</sup>	0.000 (17)
S2 <sup>v</sup> —Nb2—S4	154.41 (3)	S6 <sup>viii</sup> —S10—Nb1 <sup>ix</sup>	66.04 (3)
S8 <sup>viii</sup> —Nb2—S4	154.60 (3)	Ta2 <sup>ix</sup> —S10—Nb1 <sup>ix</sup>	94.62 (3)
S7—Nb2—S4	89.49 (3)	Nb2 <sup>ix</sup> —S10—Nb1 <sup>ix</sup>	94.62 (3)



S6 <sup>v</sup> —Nb2—S4	85.91 (3)	S6 <sup>viii</sup> —S10—Ta1 <sup>ix</sup>	66.04 (3)
S10 <sup>vi</sup> —Nb2—S4	75.09 (3)	Ta2 <sup>ix</sup> —S10—Ta1 <sup>ix</sup>	94.62 (3)
S5—Nb2—S4	75.35 (3)	Nb2 <sup>ix</sup> —S10—Ta1 <sup>ix</sup>	94.62 (3)
S9 <sup>viii</sup> —Nb2—Ta1 <sup>ix</sup>	55.46 (2)	Nb1 <sup>ix</sup> —S10—Ta1 <sup>ix</sup>	0.000 (16)
S2 <sup>v</sup> —Nb2—Ta1 <sup>ix</sup>	55.12 (2)	S6 <sup>viii</sup> —S10—K <sup>ii</sup>	94.94 (4)
S8 <sup>viii</sup> —Nb2—Ta1 <sup>ix</sup>	53.89 (2)	Ta2 <sup>ix</sup> —S10—K <sup>ii</sup>	136.76 (3)
S7—Nb2—Ta1 <sup>ix</sup>	53.97 (2)	Nb2 <sup>ix</sup> —S10—K <sup>ii</sup>	136.76 (3)
S6 <sup>v</sup> —Nb2—Ta1 <sup>ix</sup>	132.67 (2)	Nb1 <sup>ix</sup> —S10—K <sup>ii</sup>	113.42 (3)
S10 <sup>vi</sup> —Nb2—Ta1 <sup>ix</sup>	116.78 (2)	Ta1 <sup>ix</sup> —S10—K <sup>ii</sup>	113.42 (3)

Symmetry codes: (i)  $-x+1/2, y, z+1/2$ ; (ii)  $-x+1, -y+1, z-1/2$ ; (iii)  $x+1/2, -y+1, z$ ; (iv)  $-x+1, -y+1, z+1/2$ ; (v)  $-x+1/2, y, z-1/2$ ; (vi)  $x-1/2, -y, z$ ; (vii)  $-x, -y, z-1/2$ ; (viii)  $-x+1, -y, z-1/2$ ; (ix)  $x+1/2, -y, z$ ; (x)  $-x, -y, z+1/2$ ; (xi)  $x-1/2, -y+1, z$ ; (xii)  $-x+1, -y, z+1/2$ .