

Dirubidium fluorotrioxophosphate, $\text{Rb}_2\text{PO}_3\text{F}$, at 290 and 130 K, and dicaesium fluorotrioxophosphate, $\text{Cs}_2\text{PO}_3\text{F}$, at 240 and 100 K

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The structure of $\text{Rb}_2\text{PO}_3\text{F}$ was determined at 290 and 130 K, while that of $\text{Cs}_2\text{PO}_3\text{F}$ was determined at 240 and 100 K. Both compounds belong to the $\beta\text{-K}_2\text{SO}_4$ family. The structure analysis did not reveal signs of a phase transition in either compound. Crystal chemical considerations do not favour the presence of a phase transition in either $\text{Rb}_2\text{PO}_3\text{F}$ or $\text{Cs}_2\text{PO}_3\text{F}$. However, glass-like phase transitions were observed by differential scanning calorimetry in slightly humid samples at 175 and 177 K for $\text{Rb}_2\text{PO}_3\text{F}$ and $\text{Cs}_2\text{PO}_3\text{F}$, respectively, but were not observed in well dried samples. The bond distances are normal and $\text{Cs}_2\text{PO}_3\text{F}$ is twinned.

Comment

Interest in the title compounds was generated by a previous analysis of the members of the $\beta\text{-K}_2\text{SO}_4$ family with simple (non-complex) cations (Fábry & Pérez-Mato, 1993) [see also Beznosikov (1993) and da Silva *et al.* (2005)]. This analysis resulted in the setting of criteria that enable qualitative distinction of the simple-cation members of the $\beta\text{-K}_2\text{SO}_4$ family that undergo low-temperature phase transitions from the stable compounds.

There are two symmetry-independent cations in the structures belonging to the $\beta\text{-K}_2\text{SO}_4$ family. The cation that is surrounded by eleven (or ten) anionic ligands (*i.e.* O atoms in the prototypic compound $\beta\text{-K}_2\text{SO}_4$) is less firmly bound than that with nine closest neighbours. The former cation will hereafter be called *M11*. Low-temperature phase transitions occur in those structures where the cation *M11* is significantly underbonded (Brown, 1992). Typically, the underbonding of this cation is accompanied by the presence of a very short cation–anion ligand interaction. Hereafter, this short interaction will be denoted *C1*. *C1* is often the shortest cation–anion interaction in $\beta\text{-K}_2\text{SO}_4$ structures. Its contribution to the

overall bond-valence sum tends to be high in the compounds where the low-temperature phase transitions occur. The shortening of *C1* is significant with regard to the sum of the ionic radii (Shannon, 1976).

C1 is approximately parallel to the unit-cell parameter *a* in the *Pnma* setting (Fig. 1). Therefore, the unit-cell ratios *a/b* and *a/c* also correlate with occurrences of the low-temperature phase transitions in this compound. This fact is illustrated in Fig. 2, in which the *a/b* and *a/c* unit-cell ratios for the title and related compounds are plotted. K_2SeO_4 (Yamada *et al.*, 1984) and Ti_2SeO_4 (Friese *et al.*, 2004) are representatives of the $\beta\text{-K}_2\text{SO}_4$ structures with confirmed low-temperature phase transitions. One of these compounds is situated towards the lower-left corner of the plot and the other lies well below the dashed line. This line depicts the loci that conform to the orthohexagonal metric of the unit cell, *i.e.* the loci for which the condition $c = b^{1/2}$ is fulfilled; the shorter the ratio, the more probable the low-temperature phase transitions. It can also be seen that the majority of the compounds are situated below the dashed line. The plot shows a certain regularity in the positions of the compounds with either corresponding cations or corresponding anions. For example, it can be seen that *Tl* compounds tend to be situated below the respective *Cs* compounds with the same anion, and that there is a similar tendency for the positions of the *K*, *Rb* and *Cs* compounds with the same anion. (A hypothetical structure of $\text{Ti}_2\text{PO}_3\text{F}$ would be in the vicinity of $a/b \simeq 1.31$ and $a/c \simeq 0.736$, *i.e.* in the region where a low-temperature phase transition can be expected.) Tables 1 and 2 list the numerical values of the criteria given above.

It follows from Fig. 2 that the fluorotrioxophosphates are unusual in their positions, especially $\text{K}_2\text{PO}_3\text{F}$, for which two opposite criteria are present; it is situated on the left side, but it is also situated above the dashed line. By analogy to the selenates, it can be assumed that a low-temperature phase transition would be more likely in $\text{K}_2\text{PO}_3\text{F}$ than in $\text{Rb}_2\text{PO}_3\text{F}$ and even in $\text{Cs}_2\text{PO}_3\text{F}$. [In $\text{K}_2\text{PO}_3\text{F}$, no phase transition was

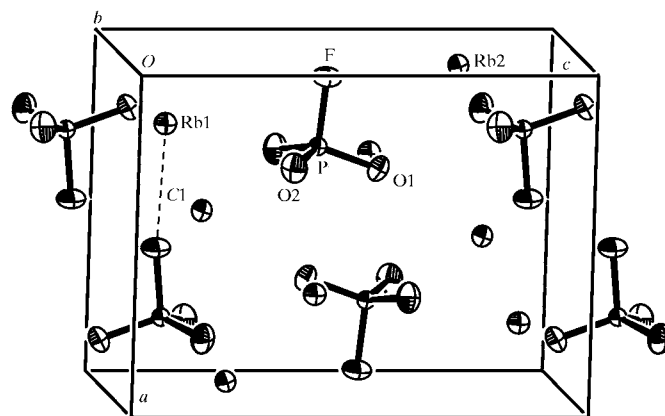


Figure 1

A view of the unit cell of $\text{Rb}_2\text{PO}_3\text{F}$ at 290 K. Displacement parameters are shown at the 50% probability level. The *C1* interaction (see *Comment*) is shown. (The structures of $\text{Cs}_2\text{PO}_3\text{F}$ are virtually the same.)

detected by a differential scanning calorimetry experiment (Vaněk, 2004) in the temperature region 96–483 K.]

The reason for the unusual positions of the fluorotrioxophosphates is plausibly related to the size and symmetry of the PO_3F^{2-} anion. The P–F bond distance is longer than the P–O bond lengths. It is of interest that in $\text{K}_2\text{PO}_3\text{F}$ (Payen *et al.*, 1979), as well as in the title structures, the C1 interaction involves the F atom. On the other hand, the longer P–F bond is accommodated in the structure by a significantly larger deviation of C1 from being parallel with the *a* axis (*cf.* Fig. 1 and Table 2.)

We were interested in confirming the hypothesis that $\text{Rb}_2\text{PO}_3\text{F}$ and $\text{Cs}_2\text{PO}_3\text{F}$ belong to the $\beta\text{-K}_2\text{SO}_4$ family and that fluorine is involved in the C1 interaction. It has also been of interest to find the deviation of C1 from being parallel to the *a* axis. Although low-temperature phase transitions were not expected, we still carried out differential-scanning calorimetry experiments.

In carefully dried samples of each compound, no phase transitions were observed by differential scanning calorimetry. However, in even slightly humid samples (the title compounds are hygroscopic), phase transitions were observed at 175 and 177 K for $\text{Rb}_2\text{PO}_3\text{F}$ and $\text{Cs}_2\text{PO}_3\text{F}$, respectively. The measured enthalpies were not reproducible. The structure determinations did not reveal signs of phase transitions in either compound.

The influence of humidity can perhaps be related to contradictory reports on the phase transition in K_2SO_4 . Gesi *et al.* (1982) observed a phase transition in K_2SO_4 at 56 K by dielectric measurements; Ahmed (1996) confirmed the presence of the phase transition at this temperature by powder diffraction. The low-temperature phase is monoclinic ($P2_1/n11$). It should be noted that the latter author had recrystallized the sample and had dried it before the

preparation of the powder for the diffraction experiment. On the other hand, Ojima *et al.* (1995) did not observe any phase transition down to 15 K by single-crystal diffractometry.

The interatomic distances are normal in the title structures. As expected, the C1 interaction involves fluorine in both compounds.

The twinning in $\text{Cs}_2\text{PO}_3\text{F}$ is remarkable. It is related to the lattice parameters *b* and *c*. The ratio *c/b* is $\sim 3^{1/2}$ and mimics orthohexagonal lattice parameters. The approximation of the lattice parameters *b* and *c* to the orthohexagonal metric in $\text{Cs}_2\text{PO}_3\text{F}$ could be predicted taking into account the positions of the related compounds in Fig. 2. The lattice parameters and their ratios in the $\beta\text{-K}_2\text{SO}_4$ family are dependent on the constituent ions, thus confirming the ionic character of these compounds (Aleksavska *et al.*, 1998). It is also of interest that only two and not three domain states were observed. Details regarding the twinning are given in the supplementary CIF for both determinations of $\text{Cs}_2\text{PO}_3\text{F}$.

We have also synthesized $\text{Tl}_2\text{PO}_3\text{F}$ and determined its structure. It was found that it belongs to an unprecedented new structural type with space group $R\bar{3}$ or $R3$. The structure determination will be published in the near future.

Experimental

The compounds were prepared by neutralization of stoichiometric amounts of Rb_2CO_3 (3.0375 g, 0.013153 mol) or Cs_2CO_3 (4.2855 g, 0.013153 mol) and $\text{H}_2\text{PO}_3\text{F}$. $\text{H}_2\text{PO}_3\text{F}$ was obtained from a solution of $(\text{NH}_4)_2\text{PO}_3\text{F}\cdot\text{H}_2\text{O}$ (2 g, 0.013153 mol) that was passed through a cation column. $(\text{NH}_4)_2\text{PO}_3\text{F}\cdot\text{H}_2\text{O}$ was prepared according to the method described by Schülke & Kayser (1991), and the raw material of $(\text{NH}_4)_2\text{PO}_3\text{F}\cdot\text{H}_2\text{O}$ prepared by this method was recrystallized in order to remove $\text{NH}_4\text{H}_2\text{PO}_4$. The volume of the eluted solution of $\text{H}_2\text{PO}_3\text{F}$ was about 120 ml in both cases. The solutions were placed in an evacuated desiccator over P_4O_{10} . Crystals appeared within a week. Technical details of the calorimetric experiments are provided in the supplementary CIF. For $\text{K}_2\text{PO}_3\text{F}$, no anomaly was found in the temperature region 96–483 K. 20 measurements of $\text{Rb}_2\text{PO}_3\text{F}$ and 24 measurements of $\text{Cs}_2\text{PO}_3\text{F}$ were carried out in the temperature region 96–433 K for six different samples of each compound. A reproducible and reversible glass-like phase transition took place at 175 K for $\text{Rb}_2\text{PO}_3\text{F}$ and at 177 K for $\text{Cs}_2\text{PO}_3\text{F}$, with a varying value of ΔC_p , unless the sample was carefully dried and placed in an aluminium pan in a dry-box.

$\text{Rb}_2\text{PO}_3\text{F}$ at 290 K

Crystal data

$\text{Rb}_2\text{PO}_3\text{F}$	$Z = 4$
$M_r = 268.9$	$D_x = 3.514 (1) \text{ Mg m}^{-3}$
Orthorhombic, $Pnma$	Mo $K\alpha$ radiation
$a = 7.8714 (2) \text{ \AA}$	$\mu = 19.49 \text{ mm}^{-1}$
$b = 6.1236 (2) \text{ \AA}$	$T = 290 (1) \text{ K}$
$c = 10.5424 (3) \text{ \AA}$	Prism, colourless
$V = 508.16 (3) \text{ \AA}^3$	$0.18 \times 0.15 \times 0.12 \text{ mm}$

Data collection

Nonius KappaCCD diffractometer	7793 measured reflections
ω scans	630 independent reflections
Absorption correction: Gaussian (Coppens, 1970)	570 reflections with $I > 3\sigma(I)$
$T_{\text{min}} = 0.073, T_{\text{max}} = 0.173$	$R_{\text{int}} = 0.079$
	$\theta_{\text{max}} = 27.5^\circ$

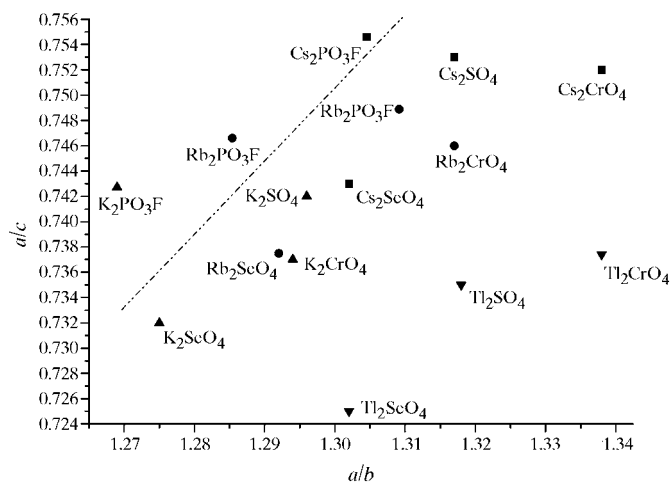


Figure 2 Lattice parameter ratios *ab* versus *a/c* for selected $\beta\text{-K}_2\text{SO}_4$ compounds ($Pnma$ setting). The dashed line depicts the loci of the unit cells with orthohexagonal metric. The same symbols are applied for compounds with the same cations. K_2Se_4 and $\text{Tl}_2\text{Se}_4\text{O}_4$ undergo confirmed low-temperature phase transitions (*Origin6.1*; OriginLab Corporation, 2000).

Refinement

Refinement on F
 $R[F^2 > 2\sigma(F^2)] = 0.018$
 $wR(F^2) = 0.030$
 $S = 1.21$
 630 reflections
 41 parameters
 Weighting scheme based on measured s.u.'s
 $w = 1/[\sigma^2(F) + 0.0004F^2]$

Rb₂PO₃F at 130 K

Crystal data

Rb₂PO₃F
 $M_r = 268.9$
 Orthorhombic, $Pnma$
 $a = 7.8403$ (2) Å
 $b = 6.1034$ (2) Å
 $c = 10.4813$ (3) Å
 $V = 501.56$ (3) Å³

Data collection

Nonius KappaCCD diffractometer
 ω scans
 Absorption correction: Gaussian (Coppens, 1970)
 $T_{\min} = 0.067$, $T_{\max} = 0.179$

Refinement

Refinement on F
 $R[F^2 > 2\sigma(F^2)] = 0.021$
 $wR(F^2) = 0.033$
 $S = 1.39$
 623 reflections
 41 parameters
 Weighting scheme based on measured s.u.'s
 $w = 1/[\sigma^2(F) + 0.0004F^2]$

Cs₂PO₃F at 240 K

Crystal data

Cs₂PO₃F
 $M_r = 363.8$
 Orthorhombic, $Pnma$
 $a = 8.308$ (2) Å
 $b = 6.3812$ (9) Å
 $c = 11.036$ (2) Å
 $V = 585.07$ (19) Å³

Data collection

Oxford Diffraction XCalibur-2 CCD diffractometer
 ω scans
 Absorption correction: analytical (CrysAlis RED; Oxford Diffraction, 2005); analytical numeric absorption correction using a multifaceted crystal model based

Refinement

Refinement on F
 $R[F^2 > 2\sigma(F^2)] = 0.022$
 $wR(F^2) = 0.037$
 $S = 1.48$
 974 reflections
 42 parameters
 Weighting scheme based on measured s.u.'s
 $w = 1/[\sigma^2(F) + 0.0004F^2]$

$(\Delta/\sigma)_{\max} = 0.008$
 $\Delta\rho_{\max} = 0.65$ e Å⁻³
 $\Delta\rho_{\min} = -0.46$ e Å⁻³
 Extinction correction: B–C type 1 Lorentzian isotropic (Becker & Coppens, 1974)
 Extinction coefficient: 0.132 (12)

$Z = 4$
 $D_x = 3.560$ (1) Mg m⁻³
 Mo $K\alpha$ radiation
 $\mu = 19.75$ mm⁻¹
 $T = 130$ (1) K
 Prism, colourless
 $0.18 \times 0.15 \times 0.12$ mm

7775 measured reflections
 623 independent reflections
 581 reflections with $I > 3\sigma(I)$
 $R_{\text{int}} = 0.084$
 $\theta_{\max} = 27.5^\circ$

$(\Delta/\sigma)_{\max} = 0.010$
 $\Delta\rho_{\max} = 0.83$ e Å⁻³
 $\Delta\rho_{\min} = -0.71$ e Å⁻³
 Extinction correction: B–C type 1 Lorentzian isotropic (Becker & Coppens, 1974)
 Extinction coefficient: 0.111 (12)

$Z = 4$
 $D_x = 4.129$ Mg m⁻³
 Mo $K\alpha$ radiation
 $\mu = 12.66$ mm⁻¹
 $T = 240$ (1) K
 Prism elongated along a , colourless
 $0.25 \times 0.10 \times 0.03$ mm

on expressions derived by Clark & Reid (1995)
 $T_{\min} = 0.168$, $T_{\max} = 0.460$
 6666 measured reflections
 974 independent reflections
 832 reflections with $I > 3\sigma(I)$
 $R_{\text{int}} = 0.041$
 $\theta_{\max} = 26.9^\circ$

$(\Delta/\sigma)_{\max} = 0.007$
 $\Delta\rho_{\max} = 0.58$ e Å⁻³
 $\Delta\rho_{\min} = -0.71$ e Å⁻³
 Extinction correction: B–C type 1 Lorentzian isotropic (Becker & Coppens, 1974)
 Extinction coefficient: 0.061 (6)

Cs₂PO₃F at 100 K

Crystal data

Cs₂PO₃F
 $M_r = 363.8$
 Orthorhombic, $Pnma$
 $a = 8.2821$ (8) Å
 $b = 6.3577$ (6) Å
 $c = 10.9827$ (8) Å
 $V = 578.30$ (9) Å³

$Z = 4$
 $D_x = 4.177$ Mg m⁻³
 Mo $K\alpha$ radiation
 $\mu = 12.81$ mm⁻¹
 $T = 100$ (1) K
 Prism elongated along a , colourless
 $0.25 \times 0.09 \times 0.03$ mm

Data collection

Oxford Diffraction XCalibur-2 CCD diffractometer
 ω scans
 Absorption correction: analytical (CrysAlis RED; Oxford Diffraction, 2005); analytical numeric absorption correction using a multifaceted crystal model based

on expressions derived by Clark & Reid (1995)
 $T_{\min} = 0.161$, $T_{\max} = 0.434$
 6856 measured reflections
 939 independent reflections
 849 reflections with $I > 3\sigma(I)$
 $R_{\text{int}} = 0.038$
 $\theta_{\max} = 26.6^\circ$

Refinement

Refinement on F
 $R[F^2 > 2\sigma(F^2)] = 0.017$
 $wR(F^2) = 0.036$
 $S = 1.52$
 939 reflections
 42 parameters
 Weighting scheme based on measured s.u.'s
 $w = 1/[\sigma^2(F) + 0.0004F^2]$

$(\Delta/\sigma)_{\max} = 0.014$
 $\Delta\rho_{\max} = 0.37$ e Å⁻³
 $\Delta\rho_{\min} = -0.41$ e Å⁻³
 Extinction correction: B–C type 1 Lorentzian isotropic (Becker & Coppens, 1974)
 Extinction coefficient: 0.040 (5)

Table 1

Some stereochemical parameters regarding selected compounds of the β -K₂SO₄ family.

$C1$ is the length (Å) of the $C1$ interaction; $C1/CR$ is the ratio of $C1$ to the sum of crystal radii (Shannon, 1976); $M11(bv)$ is the bond valence of $C1$ (Bresle & O'Keefe, 1991); Sum is the bond valence sum of the cation $M11$.

Compound	$C1$	$C1/CR$	$M11(bv)$	Sum	$M11(bv)/\text{Sum}$
K ₂ SO ₄ ^a	2.714 (2)	0.902	0.2065 (13)	1.0795 (18)	0.191 (2)
K ₂ CrO ₄ ^b	2.681 (1)	0.891	0.2256 (9)	0.9358 (12)	0.241 (1)
K ₂ SeO ₄ ^c	2.610 (6)	0.867	0.273 (4)	0.943 (5)	0.290 (6)
K ₂ PO ₃ F ^d	2.671 (6)	0.908	0.159 (3)	0.893 (5)	0.178 (4)
Rb ₂ SO ₄ ^e	2.921 (2)	0.945	0.1676 (11)	1.0759 (17)	0.156 (1)
Rb ₂ CrO ₄ ^f	2.876 (15)	0.931	0.189 (8)	0.984 (10)	0.192 (8)
Rb ₂ SeO ₄ ^g	2.810 (6)	0.909	0.228 (3)	0.943 (4)	0.242 (4)
Rb ₂ PO ₃ F ^h	2.865 (3)	0.949	0.149 (1)	0.913 (2)	0.163 (1)
Cs ₂ SO ₄ ^e	3.177 (2)	0.978	0.1293 (14)	1.061 (3)	0.122 (2)
Cs ₂ CrO ₄ ⁱ	3.136 (2)	0.965	0.1445 (9)	0.968 (2)	0.149 (10)
Cs ₂ SeO ₄ ^j	3.038 (4)	0.935	0.187 (2)	0.916 (3)	0.204 (3)
Cs ₂ PO ₃ F ^h	3.141 (4)	0.988	0.1118 (13)	0.901 (3)	0.124 (2)
Tl ₂ SO ₄ ^k	2.844 (11)	0.926	0.163 (5)	0.838 (6)	0.195 (7)
Tl ₂ CrO ₄ ^l	2.70 (9)	0.879	0.24 (6)	0.90 (6)	0.27 (8)
Tl ₂ SeO ₄ ^m	2.660 (18)	0.866	0.268 (13)	0.801 (15)	0.334 (2)

Notes: (a) Ojima *et al.* (1995); (b) Toriumi & Saito (1978); (c) González-Silgo *et al.* (1996); (d) Payen *et al.* (1979); (e) Weber *et al.* (1989); (f) Aleksovska *et al.* (1998); (g) Takahashi *et al.* (1987); (h) this study; (i) Morris *et al.* (1981); (j) Zúñiga *et al.* (1991); (k) Wallez *et al.* (2004); (l) Carter & Margulis (1972); (m) Fábry & Brezcewski (1993).

For Rb₂PO₃F, data collection: COLLECT (Hoof, 1998); cell refinement: SCALEPACK (Otwinowski & Minor, 1997); data reduction: DENZO (Otwinowski & Minor, 1997) and SCALEPACK. For Cs₂PO₃F, data collection: CrysAlis CCD (Oxford Diffraction, 2005); cell refinement: CrysAlis RED (Oxford Diffraction, 2005); data reduction: CrysAlis RED. For both compounds, program(s) used to solve structure: SIR97 (Altomare *et al.*, 1999); program(s) used to refine structure: JANA2000 (Petříček *et al.*, 2000); molecular graphics: ORTEP-3 for Windows (Farrugia, 1997); software used to prepare material for publication: JANA2000.

Table 2

Some stereochemical parameters regarding selected compounds of the β - K_2SO_4 family.

a/b , a/c and b/c are the unit-cell ratios, and $M11-\text{O}/\text{F}-X$ is the angle ($^\circ$) contained by the atoms involved in the C1 interaction.

Compound	a/b	a/c	b/c	$M11-\text{O}/\text{F}-X$
K_2SO_4^a	1.2959 (3)	0.74247 (6)	0.5730 (1)	179.7 (2)
K_2CrO_4^b	1.2945 (6)	0.7374 (2)	0.5696 (1)	178.96 (15)
K_2SeO_4^c	1.276 (3)	0.732 (2)	0.573 (1)	176.4 (3)
$\text{K}_2\text{PO}_3\text{F}^d$	1.269 (2)	0.7427 (8)	0.5854 (8)	166.0 (5)
Rb_2SO_4^e	1.3079 (6)	0.7490 (2)	0.5726 (2)	179.2 (2)
$\text{Rb}_2\text{CrO}_4^f$	1.317 (1)	0.7460 (4)	0.5665 (2)	178.3 (8)
$\text{Rb}_2\text{SeO}_4^g$	1.292 (1)	0.7375 (2)	0.5708 (3)	179.5 (4)
$\text{Rb}_2\text{PO}_3\text{F}^h$	1.28542 (8)	0.74664 (4)	0.58085 (4)	171.6 (2)
Cs_2SO_4^e	1.3170 (7)	0.7533 (3)	0.5720 (2)	178.7 (3)
$\text{Cs}_2\text{CrO}_4^i$	1.338 (1)	0.7524 (8)	0.5625 (5)	177.70 (11)
$\text{Cs}_2\text{SeO}_4^j$	1.3021 (5)	0.7430 (2)	0.5706 (3)	178.7 (3)
$\text{Cs}_2\text{PO}_3\text{F}^h$	1.3020 (5)	0.7528 (3)	0.5782 (2)	175.4 (3)
Ti_2SO_4^k	1.3182 (3)	0.7352 (2)	0.5577 (2)	179 (7)
$\text{Ti}_2\text{CrO}_4^l$	1.338 (2)	0.7374 (8)	0.5509 (7)	178 (4)
$\text{Ti}_2\text{SeO}_4^m$	1.3025 (8)	0.7250 (4)	0.5566 (3)	178.1 (14)

Note: the references are the same as in Table 1.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ3009). Services for accessing these data are described at the back of the journal.

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