

Synthesis and characterization of new vanadates of antimony, ASbV_2O_8 (A = K, Rb, Tl or Cs)†

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Four new vanadates of antimony, KSbV_2O_8 **1**, RbSbV_2O_8 **2**, TlSbV_2O_8 **3** and CsSbV_2O_8 **4**, have been prepared by solid state synthesis and structurally characterized by single crystal X-ray diffraction. Compounds **1** to **3** have a three-dimensional $(\text{SbV}_2\text{O}_8^-)_\infty$ anionic framework with one dimensional channels occupied by counter cations. Compound **4** has two dimensional $(\text{SbV}_2\text{O}_8^-)_\infty$ layers interleaved with Cs^+ ions. Both types of anionic frameworks are built from corner connected SbO_6 octahedra and VO_4 tetrahedra. The spectroscopic data are briefly discussed.

Introduction

Solid compounds possessing structural frameworks with well defined tunnels and layers are extensively investigated because their unique and complex structural chemistry endows them with interesting chemical and physical properties. Phosphates in the A–M–P–O quaternary system form one such family of compounds showing rich structural chemistry with anionic frameworks built from MO_6 octahedra and PO_4 tetrahedra and A^{n+} ions as counter cations.^{1–13} Research on the synthetic and structural chemistry of these materials continues to be pursued with the idea of obtaining them with accessible redox catalytic activity, anisotropic electrical conductivity and ion exchange properties. For instance, a series of phosphates with general formula AMP_2O_8 (A = K, Rb, Cs or Tl; M = Nb, Ta or Sb)^{8–13} exhibit interesting properties like ion exchange and luminescence. These compounds have been shown to possess three types of structures, namely, layered α -ZrP type,¹⁴ with $[\text{M}(\text{PO}_4)_2]^-$ anionic framework, layered and three dimensional structures with $[\text{MO}(\text{P}_2\text{O}_7)]^-$ anionic framework containing pyrophosphates. One would expect similar structural diversity in isomorphous vanadates containing VO_4 tetrahedra, but surprisingly we have found that not many binary vanadates with extended structures have been reported. Such vanadates, when compared to phosphates, could be expected to show enhanced redox activity. We have, therefore, initiated a project on the synthetic and structural chemistry of new vanadates isomorphous with the phosphates. Here we report the synthesis and characterization of four new vanadates, ASbV_2O_8 (A = K, Rb, Tl or Cs), with two types of structures.

Results and discussion

The four ASbV_2O_8 compounds, M = K **1**, Rb **2**, Tl **3** or Cs **4**, could be prepared by solid state synthesis at temperatures as low as 600 °C. Our attempts to grow single crystals of **1**, which has a low melting point of 700 °C, by slow cooling of melt were not successful. Only the chemical vapour transport technique, using the transporting agent SbCl_5 , enabled the isolation of these compounds in the form of single crystals suitable for X-ray diffraction. The pertinent crystallographic data and the data collection parameters of these four compounds are summarized in Table 1. The powder X-ray diffraction (XRD) patterns (SUP 57412) of these compounds compare well

with those simulated based on the single crystal structure using the LAZY PULVERIX¹⁵ program and thus establish the monophasic nature of the polycrystalline samples. Our attempts to prepare NaSbV_2O_8 were not successful.

Crystal structure

Compounds **1**, **2** and **3** have a three-dimensional anionic framework $(\text{SbV}_2\text{O}_8^-)_\infty$ containing one-dimensional channels occupied by the counter cations K^+ , Rb^+ and Tl^+ . While **1** and **2** are isostructural, crystallizing in the space group $Pnma$, **3** crystallizes in the space group $P2_1/c$ with β angle very close to 90° (Table 1).

The three-dimensional $(\text{SbV}_2\text{O}_8^-)_\infty$ anionic framework of these three compounds is built from corner sharing of SbO_6 octahedra and VO_4 tetrahedra. Each SbO_6 octahedron is corner connected to six VO_4 tetrahedra. Each VO_4 tetrahedron, on the other hand, is corner connected to only three SbO_6 octahedra. The three-dimensional nature of the framework can be conceived as follows. First, each SbO_6 octahedron, with its two *trans* corners unshared, is corner connected to four VO_4 tetrahedra and each VO_4 tetrahedron connects two such octahedra to form a one-dimensional $\text{Sb}_2\text{V}_2\text{O}_{10}$ chain as shown in Fig. 1. It is noteworthy that the edge connecting the unshared oxygen atoms of each tetrahedron in one row is approximately perpendicular to that of the tetrahedron in the other row. In other words, one row of the tetrahedra in the chain is oriented perpendicular to the other row. Two such chains are laterally fused, whereby one row of tetrahedra of each chain is corner connected to octahedra of the other chain to form a one-dimensional ribbon of composition $\text{Sb}_2\text{V}_4\text{O}_{18}$ as shown in Fig. 1. Such ribbons are connected to one another by further sharing of corners of octahedra with tetrahedra to form a three-dimensional framework with one-dimensional channels as shown in the unit cell diagram (Fig. 2) of KSbV_2O_8 . It is evident from the figure that each tetrahedron points its unshared oxygen towards one-dimensional channels and these channels, parallel to the short (≈ 5.5 Å) *b* axis, are occupied by monovalent counter cations. In the case of compound **3** the channels are parallel to the short *a* axis. This type of three dimensional structure has been reported for molybdates of indium,^{16,17} KInMo_2O_8 , β - $\text{RbInMo}_2\text{O}_8$ and β - $\text{CsInMo}_2\text{O}_8$.

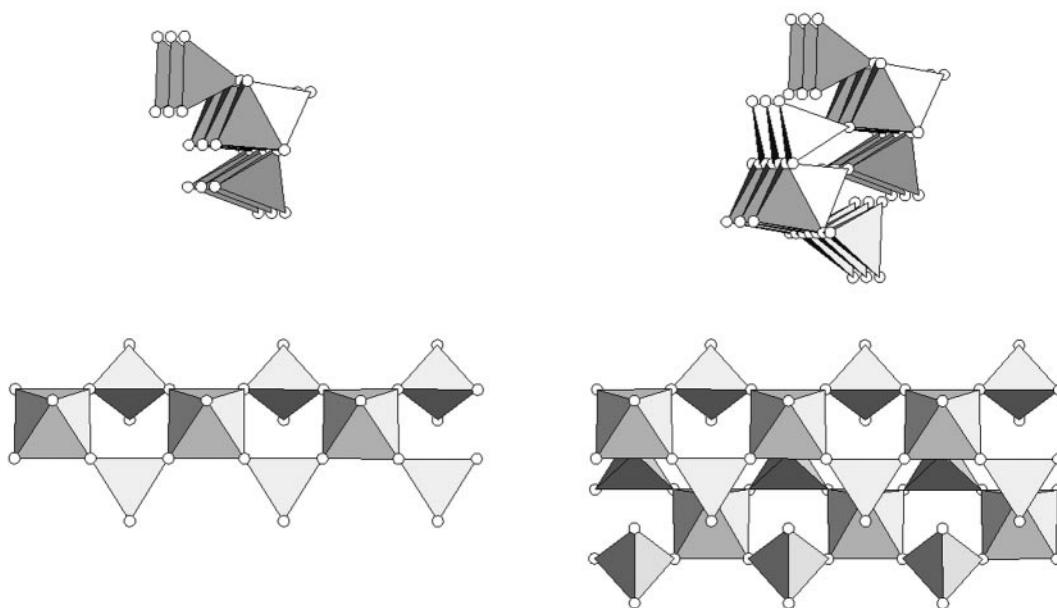
For compounds **1** and **2** there are one antimony atom, two crystallographically distinct vanadium atoms, V(1) and V(2), and six oxygen atoms in the asymmetric unit. The asymmetric unit of **3** and **4**, however, contains two more oxygen atoms. The oxygen co-ordinations of antimony and vanadium atoms for **1**, **3** and **4** are represented in Fig. 3 with the atom labelling scheme. The features of these polyhedra in **1**, **2** and **3** are the same and

† Supplementary data available: XRD powder data. For direct electronic access see <http://www.rsc.org/suppdata/dt/1998/3013/>, otherwise available from BLDSC (No. SUP 57412, 8 pp.) or the RSC Library. See Instructions for Authors, 1998, Issue 1 (<http://www.rsc.org/dalton>).

Table 1 Crystal data and data collection parameters for compounds **1–4**

Formula	KO ₈ SbV ₂ 1	O ₈ RbSbV ₂ 2	O ₈ SbTlV ₂ 3	CsO ₈ SbV ₂ 4
<i>M</i>	390.68	437.05	555.96	484.49
Crystal system	Orthorhombic	Orthorhombic	Monoclinic	Monoclinic
Space group	<i>Pnma</i>	<i>Pnma</i>	<i>P2₁/c</i>	<i>P2₁/n</i>
<i>a</i> /Å	14.6248(10)	14.722(2)	5.569(5)	5.627(2)
<i>b</i> /Å	5.5633(10)	5.5679(8)	8.670(4)	16.178(4)
<i>c</i> /Å	8.5168(10)	8.6697(13)	14.630(3)	8.400(5)
β /°			90.14(4)	90.30(5)
<i>U</i> /Å ³	692.9(2)	710.7(2)	706.4(7)	764.6(6)
Crystal dimensions/mm	0.09 × 0.15 × 0.3	0.08 × 0.12 × 0.2	0.07 × 0.1 × 0.25	0.08 × 0.12 × 0.3
<i>D_c</i> /Mg m ⁻³	3.745	4.085	5.228	4.209
<i>F</i> (000)	720	792	968	864
2 θ Range	5.54–49.94 (+ <i>h</i> , + <i>k</i> , + <i>l</i>)	5.46–49.92 (+ <i>h</i> , + <i>k</i> , + <i>l</i>)	5.46–49.94 (\pm <i>h</i> , + <i>k</i> , + <i>l</i>)	5.04–49.96 (\pm <i>h</i> , + <i>k</i> , + <i>l</i>)
μ (Mo-K α)/mm ⁻¹	7.078	12.918	28.215	10.563
Maximum, minimum transmission factors	0.92, 0.75	0.82, 0.50	0.82, 0.48	0.85, 0.48
Total no. reflections	676	700	1492	1550
No. independent reflections (<i>R</i> _{int})	676 (0.0000)	700 (0.0000)	1250 (0.0205)	1345 (0.0551)
No. parameters refined	67	68	105	109
<i>R</i>	0.0254	0.0310	0.0261	0.0491
<i>R</i> '	0.0744	0.0779	0.0580	0.1262
<i>x</i>	0.0248	0.0500	0.0375	0.0494
<i>y</i>	7.11	2.65	0.24	36.51
Goodness of fit	1.411	1.163	1.155	1.186
Largest shift/e.s.d.	0.00	0.00	0.049	0.00
Largest peak/e Å ⁻³	1.042	1.037	1.477	2.742

Details in common: graphite-monochromated Mo-K α radiation (λ 0.710 73 Å); 2 θ - ω scans; *Z* = 4; $R = \sum ||F_o| - |F_c|| / \sum |F_o|$; $R' = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]$; $w = 1/[\sigma^2(|F_o|)^2 + (xP)^2 + yP]$; $P = [\text{Max}(F_o^2, 0) + 2F_c^2]/3$.

**Fig. 1** End-on view (top) and side view (bottom) of the SbV₂O₁₀ chain (left) and Sb₂V₄O₁₈ ribbon (right).

we discuss these features by taking **1** as an example. The SbO₆ octahedron, corner connected to three V(1)O₄ and three V(2)O₄ tetrahedra, is nearly regular with antimony occupying the centre of the octahedron as evident from the values of the Sb–O bond lengths, O···O non-bonding edges and bond angles given in Tables 2 and 3. The V(1)O₄ tetrahedra are involved in the fusion of SbV₂O₁₀ chains to form Sb₂V₄O₁₈ ribbons whereas V(2)O₄ tetrahedra connect such ribbons to form the three dimensional network. These two types of tetrahedra are oriented perpendicular to each other. The vanadium atom forms a shorter bond with an unshared oxygen atom, namely O(3) in V(1)O₄ and O(6) in V(2)O₄ tetrahedra, than with the other three oxygen atoms (Fig. 3). For **3** the unshared oxygen atoms are O(4) and O(8). The three longer V–O bonds have more or less the same length in V(1)O₄ tetrahedra but not in V(2)O₄

(Tables 2 and 3). The vanadium atoms occupy the centres of the tetrahedra and the difference between the minimum and maximum values of O···O distances is more for V(2)O₄ tetrahedra (0.219 Å) than for V(1)O₄ tetrahedra (0.177 Å), indicating a greater distortion in the former. This difference in distortion is reflected in the values of their bond angles as well. Among the isostructural compounds **1** and **2**, the bigger Rb⁺ ion seems to lead to a decrease in the average Sb–O bond length with concomitant increase in the average V(1)–O bond length.

The compound **4**, CsSbV₂O₈, has a layer structure consisting of two dimensional (SbV₂O₈)_∞ layers interleaved with counter cations Cs⁺. The two-dimensional (SbV₂O₈)_∞ anionic framework is built, as in the three dimensional framework of **1** to **3**, from corner sharing of Sb₂V₄O₁₈ ribbons but the mode of connection is different. The connectivity between these ribbons

extends in only one direction, so as to give a two dimensional anionic layer. As in the other three compounds, each SbO_6 octahedron is corner connected to six VO_4 tetrahedra and each VO_4 tetrahedron is connected to three SbO_6 octahedra. The

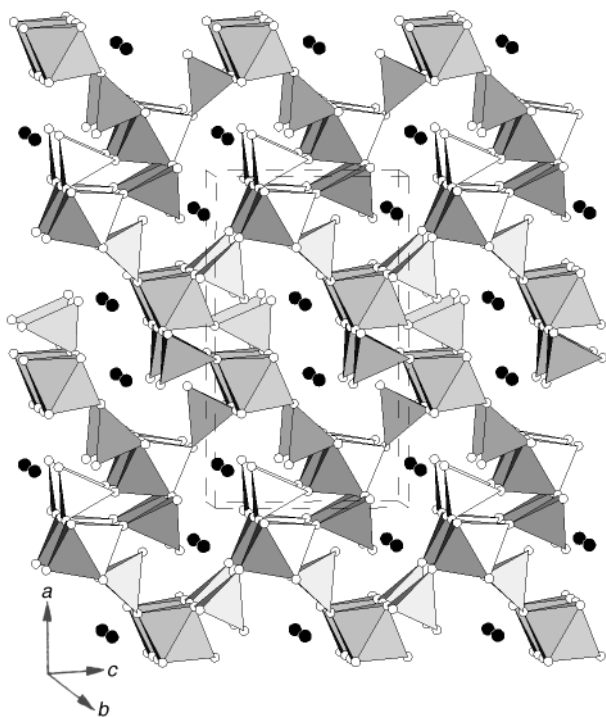


Fig. 2 Structure of $\text{K}_8\text{SbV}_2\text{O}_{18}$ with polyhedral representation of the $(\text{SbV}_2\text{O}_8)_\infty$ framework and potassium as filled circles. All atoms are represented by circles of arbitrary radii.

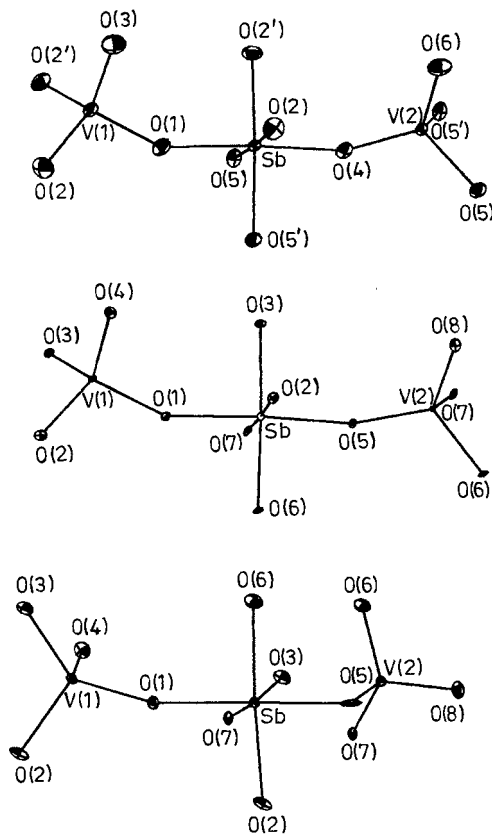


Fig. 3 The ORTEP¹⁸ plots of the $\text{SbV}_2\text{O}_{12}$ units in compounds **1** (top), **3** (middle) and **4** (bottom) showing the atom labelling scheme. Antimony in **3** is represented by a circle of arbitrary radius and all the other atoms with 50% probability.

Table 2 Bond lengths (Å) and selected angles (°) and $\text{O} \cdots \text{O}$ non-bonding distances in ASbV_2O_8 (A = K or Rb)

SbO₆ octahedra

A = K

Sb	O(4)	O(5)	O(1)	O(2)	O(5)	O(2)
O(4)	1.974(6)	2.778(7)	—	2.863(7)	2.778(7)	2.863(7)
O(5)	89.5(2)	1.971(4)	2.705(6)	2.848(6)	2.749(9)	—
O(1)	175.1(2)	87.0(2)	1.960(6)	2.786(7)	2.705(6)	2.786(7)
O(2)	93.2(2)	177.1(2)	90.4(2)	1.966(4)	—	2.683(9)
O(5)	89.5(2)	88.4(2)	87.0(2)	92.7(2)	1.971(4)	2.848(6)
O(2)	93.2(2)	92.7(2)	90.4(2)	86.0(3)	177.1(2)	1.966(4)

A = Rb

Sb	O(4)	O(5)	O(1)	O(2)	O(5)	O(2)
O(4)	1.964(6)	2.756(7)	—	2.844(6)	2.756(7)	2.844(6)
O(5)	89.1(2)	1.964(4)	2.706(6)	2.829(6)	2.750(8)	—
O(1)	175.0(2)	87.3(2)	1.956(5)	2.782(6)	2.706(6)	2.782(6)
O(2)	93.0(2)	92.4(2)	90.7(2)	1.957(4)	—	2.676(7)
O(5)	89.1(2)	88.9(2)	87.3(2)	92.4(2)	1.964(4)	2.829(6)
O(2)	93.0(2)	92.4(2)	90.7(2)	86.3(2)	177.57(15)	1.957(4)

VO₄ tetrahedra

A = K

V(1)	O(1)	O(3)	O(2)	O(2)
O(1)	1.750(6)	2.711(9)	2.889(7)	2.889(7)
O(3)	108.4(3)	1.591(7)	2.711(7)	2.711(7)
O(2)	111.0(2)	108.1(2)	1.756(4)	2.880(9)
O(2)	111.0(2)	108.1(2)	110.2(3)	1.756(4)
V(2)	O(4)	O(6)	O(5)	O(5)
O(4)	1.711(6)	2.724(9)	2.920(7)	2.920(7)
O(6)	111.1(3)	1.592(6)	2.701(6)	2.701(6)
O(5)	113.7(2)	106.5(2)	1.777(4)	2.814(9)
O(5)	113.0(2)	106.5(2)	104.7(3)	1.777(4)

A = Rb

O(1)	O(3)	O(2)	O(2)
O(1)	1.764(5)	2.726(8)	2.910(6)
O(3)	108.9(3)	1.585(6)	2.703(6)
O(2)	107.6(2)	111.2(2)	1.763(4)
O(2)	107.6(2)	111.2(2)	110.2(3)
O(4)	O(6)	O(5)	O(5)
O(4)	1.710(6)	2.725(9)	2.928(6)
O(6)	111.0(3)	1.596(6)	2.690(6)
O(5)	114.3(2)	105.7(2)	1.775(4)
O(5)	114.3(2)	105.7(2)	105.0(2)

	K	Rb	K	Rb
A—O(1) × 2	3.213(3)	3.278(3)	A—O(5) × 2	2.987(5)
A—O(2) × 2	2.953(5)	2.985(4)	A—O(5) × 2	3.042(5)
A—O(3)	2.712(7)	2.849(7)	A—O(6) × 2	3.062(3)
				3.055(3)

Table 3 Bond lengths (Å) and selected angles (°) and O···O non-bonding distances in ASbV₂O₈ (A = Tl or Cs)SbO₆ octahedra

A = Tl

Sb	O(3)	O(2)	O(5)	O(1)	O(6)	O(7)
O(3)	1.963(4)	2.682(5)	2.855(6)	2.792(6)	—	2.841(5)
O(2)	86.1(2)	1.966(4)	2.858(6)	2.795(6)	2.829(5)	—
O(5)	93.1(2)	93.2(2)	1.969(4)	—	2.746(6)	2.746(5)
O(1)	90.5(2)	90.5(2)	175.0(2)	1.969(4)	2.719(5)	2.722(5)
O(6)	177.6(2)	92.3(2)	88.8(2)	87.7(2)	1.956(4)	2.739(6)
O(7)	92.8(2)	177.9(2)	88.7(2)	87.7(2)	88.7(2)	1.961(4)

A = Cs

Sb	O(7)	O(6)	O(1)	O(3)	O(5)	O(2)
O(7)	1.946(10)	2.801(13)	2.729(14)	—	2.781(13)	2.889(15)
O(6)	90.5(4)	1.997(9)	2.847(13)	2.674(14)	2.752(13)	—
O(1)	88.6(4)	92.0(4)	1.962(8)	2.752(12)	—	2.785(12)
O(3)	175.9(4)	85.8(4)	89.9(4)	1.932(9)	2.752(12)	2.712(12)
O(5)	91.1(4)	88.5(4)	179.5(3)	90.4(4)	1.948(8)	2.740(12)
O(2)	95.4(4)	173.6(4)	90.5(4)	88.4(4)	89.1(4)	1.959(9)

VO₄ tetrahedra

A = Tl

V(1)	O(1)	O(4)	O(3)	O(2)
O(1)	1.741(4)	2.711(5)	2.883(6)	2.890(5)
O(4)	108.4(2)	1.598(4)	2.715(6)	2.711(6)
O(3)	110.8(2)	107.8(2)	1.760(4)	2.887(6)
O(2)	111.4(2)	107.8(2)	110.4(2)	1.756(4)

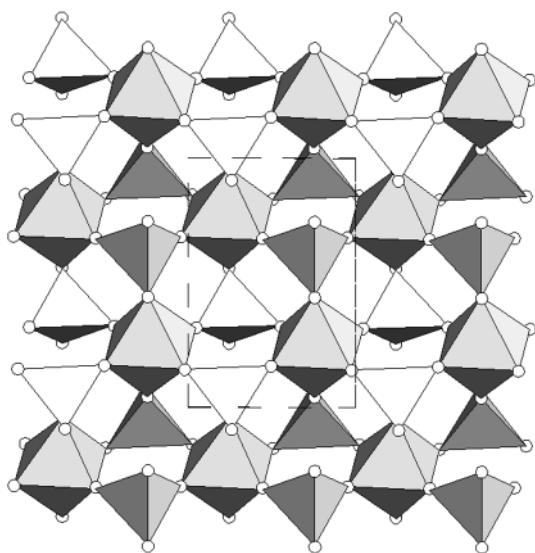
A = Cs

O(1)	O(4)	O(3)	O(2)
O(1)	1.736(9)	2.781(13)	2.914(13)
O(4)	1.608(9)	2.717(13)	2.709(13)
O(3)	111.4(4)	1.790(9)	2.927(12)
O(2)	108.4(4)	107.2(5)	1.757(9)

V(2)	O(5)	O(6)	O(8)	O(7)
O(5)	1.702(4)	2.899(6)	2.727(6)	2.904(6)
O(6)	113.4(2)	1.767(4)	2.696(5)	2.830(6)
O(8)	111.2(2)	106.2(2)	1.602(4)	2.696(5)
O(7)	113.4(2)	106.2(2)	106.0(2)	1.773(4)

	Tl	Cs
A-O(1)	3.304(4)	—
	3.305(4)	
A-O(2)	2.946(4)	3.295(10)
		3.558(9)
A-O(3)	2.944(4)	3.112(9)
		3.594(9)
A-O(4)	2.772(5)	3.279(10)
		3.433(9)
		3.481(10)

	Tl	Cs
A-O(5)	—	3.214(8)
		3.399(8)
A-O(6)	3.064(4)	—
	3.127(4)	
A-O(7)	3.051(4)	3.412(11)
	3.126(4)	
A-O(8)	3.021(5)	3.017(10)
	3.027(4)	3.503(10)

**Fig. 4** The (SbV₂O₈)_∞ layer in CsSbV₂O₈ viewed along the *b* axis.

polyhedral representation of the (SbV₂O₈)_∞ layer viewed along the *b* axis is given in Fig. 4. It is evident from the unit cell diagram (Fig. 5) that this anionic layer is corrugated and the

unshared corner of each tetrahedron points towards the inter-layer region which is occupied by Cs⁺ ions. A similar corrugated anionic layer has been reported for BaMoP₂O₈¹⁹ with the yavapaiite structure. However, this type of layer is perfectly planar in phosphates like ASbP₂O₈ (A = K or Tl)^{8,12} and other layered oxides such as CsVMo₂O₈²⁰, KAlMo₂O₈ and α modifications of AlInMo₂O₈ (A = Rb or Cs).^{17,21}

Even though the SbO₆ octahedron in compound **4** (Fig. 3) can be regarded as similar to those of **1** to **3**, there is a wide variation of ≈ 0.065 Å in Sb–O bond lengths from 1.932 to 1.997 Å and a deviation of $\approx 5^\circ$ in O–Sb–O bond angles from the ideal values (Table 3). Thus the distortion of the SbO₆ octahedron is more in **4** than in the other three. As in **1** to **3**, V(1)O₄ and V(2)O₄ tetrahedra interconnect the chains and ribbons with the vanadium atoms, V(1) and V(2), forming short bonds with the unshared oxygen atoms, O(4) and O(8) respectively (Table 3). Even though the distribution of the values of the longer V–O bond lengths among these two types of tetrahedra in this compound is not as distinct as in **1** to **3**, it is similarly more uniform in V(1)O₄ than in V(2)O₄. The vanadium atoms occupy the centres of both the tetrahedra.

We now refer to the oxygen co-ordinations of counter cations A, which are represented in Fig. 6. Potassium, rubidium and thallium present in the one dimensional channels of **1** to **3** are all eleven-co-ordinated and have the same type of co-ordination polyhedra. Cesium ions present in the interlayer

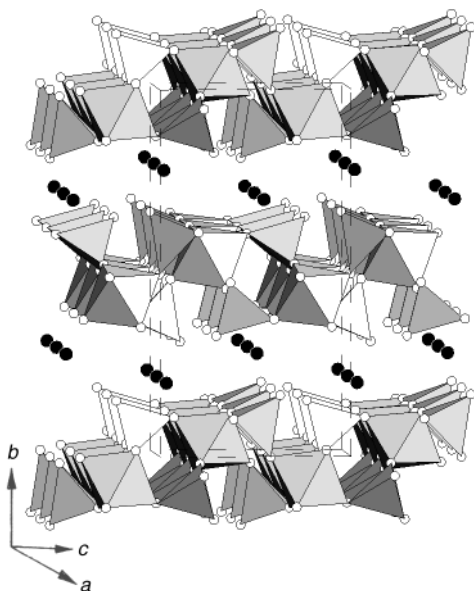


Fig. 5 Structure of CsSbV₂O₈. Isolated circles represent Cs atoms.

region of compound **4** can be considered as twelve-coordinated with one of the bonds namely, Cs–O(3), being very long (3.594 Å). It is to be noted that the co-ordination of Cs in other layered oxides, ^{10,17,20,22} such as CsVMO₂O₈ containing a planar (VMO₂O₈)_∞ anionic layer, is more symmetrical. The average A–O bond lengths for **1** to **4** are 3.020, 3.064, 3.062 and 3.358 Å respectively and these values are in accordance with the fact that the ionic radii of alkali metal ions increase from potassium to cesium and rubidium and thallium have almost the same ionic radii.

A comparison of the structural features of these four compounds and other AMX₂O₈ compounds (A = K, Rb, Cs or Tl; M with octahedral co-ordination; X with tetrahedral co-ordination) shows that Cs favours mostly layered structures whereas other monovalent A, smaller than Cs, adopt both layered and three dimensional structures. It is possible that the accommodation of larger Cs with higher co-ordination number is relatively easy in the layered structural frameworks. It is to be noted that the three dimensional structure of these vanadates has not been observed in the corresponding phosphates.^{8,12}

Vibrational spectroscopy

The infrared and Raman spectra of polycrystalline samples of compounds **1** to **4** show similar features (Fig. 7). A partial assignment of the modes is attempted here. The symmetric and antisymmetric stretching vibration modes of the PO₄³⁻ group are generally observed between 1200 to 1300 and 1060 to 1160 cm⁻¹ respectively.²³ It has been established from a series of IR and Raman studies²⁴ that the stretching frequencies of SO₄²⁻ tetrahedra lie in the range 1200 to 950 cm⁻¹. Accordingly, the range of vibrational stretching frequencies for VO₄³⁻ of the present compounds can be tentatively assigned to the region 1022 to 920 cm⁻¹. Similarly the bands from 300 to 200 cm⁻¹ can be assigned to V–O bending modes and those in the intermediate range of 500 to 400 cm⁻¹ to the Sb–O–V stretching modes. Vanadates in solution, on the other hand, are known²⁵ to show peaks around 827, 780 and 340 cm⁻¹ corresponding to ν₁, ν₃ and both ν₃ and ν₄ modes of tetrahedral VO₄³⁻, respectively. Generally the SbO₆ octahedra present typical bands at 900 to 800 cm⁻¹ for antimony oxides.²⁶ The ν₁, ν₂ and ν₃ of SbO₆ octahedra are reported to be present in the regions 830–680, 640–590 and 570–480 cm⁻¹ respectively.²⁷ The symmetric and antisymmetric stretchings in the case of the SbO₆ octahedra

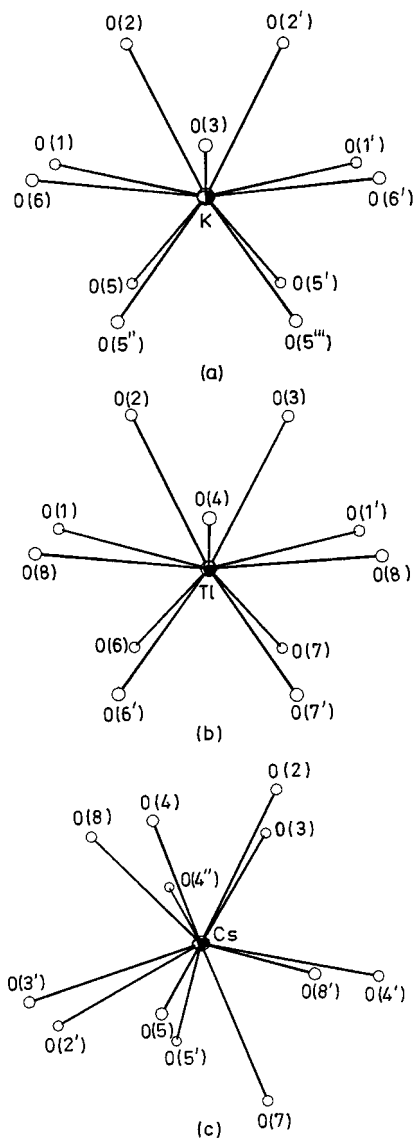


Fig. 6 The ORTEP plots of oxygen co-ordinations of (a) potassium in **1**, (b) thallium in **3** and (c) cesium in **4**. Oxygen atoms are represented by circles of arbitrary radius and the metal atoms with 50% probability.

in the present compounds are, therefore, tentatively assigned to the region 920–600 cm⁻¹. Bands in the range 400–300 cm⁻¹ are attributed to the bending modes of Sb–O and those in the range 200–80 cm⁻¹ to the external modes.

Conclusion

The four new vanadates of antimony, ASbV₂O₈ (A = K, Rb, Tl or Cs), prepared by solid state synthesis have been unambiguously characterized by single crystal X-ray diffraction. It is only the chemical vapour transport technique that has enabled the isolation of these materials in the form of single crystals suitable for X-ray diffraction. While the cesium compound is two dimensional in nature, the other three compounds have three dimensional frameworks with one dimensional channels. The counter cations A⁺ occupy the channels and the interlayer region. The large size and requirement for higher co-ordination of cesium seems to favour the two dimensional structure. A partial assignment of the infrared and Raman spectra of the polycrystalline samples has been made. It would be interesting to synthesize and study similar vanadates of other pentavalent metals with octahedral co-ordination, such as niobium and tantalum. We have made some progress in this direction and the results will be published later.

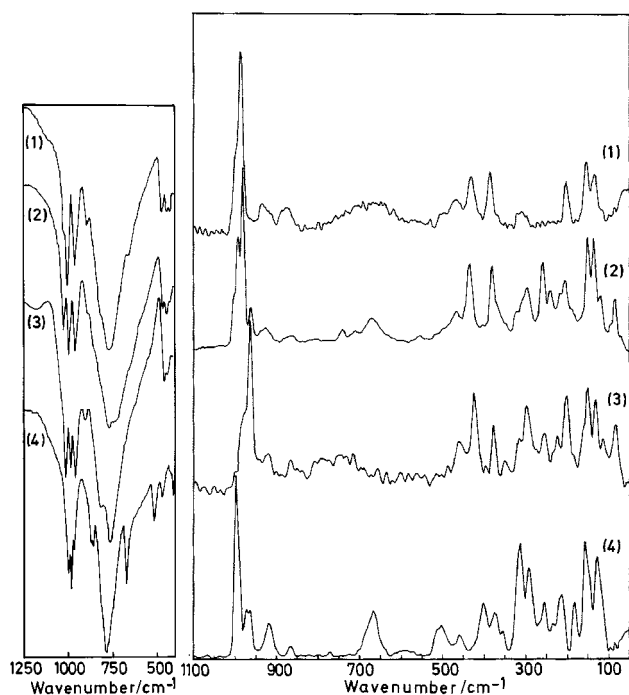


Fig. 7 Infrared (left) and Raman (right) spectra of ASbV₂O₈ compounds, 1 to 4.

Experimental

Synthesis

The compounds **1** to **4** were prepared in the polycrystalline form by solid state reaction in open air; KSbV₂O₈ was prepared from a stoichiometric mixture of KSb(OH)₆ and V₂O₅. The mixture was initially heated at 400 °C for 12 h and then the temperature was raised in steps of 50 °C to 600 °C and the duration of heating at each step was about 9 h. Thus the reaction was carried out for a total duration of 2 d with three intermittent grindings. Similarly the other three compounds were prepared from stoichiometric mixtures of Sb₂O₅, V₂O₅ and decomposable salts, Rb₂CO₃/Cs₂CO₃/TiNO₃, at a maximum temperature of 700 °C.

Crystal growth

Single crystals of the compounds were grown from their polycrystalline samples by chemical vapour transport (CVT) using SbCl₅ as the transporting agent. The compound SbCl₅ was initially sealed in thin glass capillary tubes of low melting (≈300 °C) glass. About 0.2 to 0.3 g of powdered ASbV₂O₈ compounds were sealed, along with sealed capillary tubes containing SbCl₅, in an evacuated quartz tube of 1.3 cm diameter and 12 cm length. These quartz tubes were heated in a tubular furnace such that the sample was at the maximum temperature of its formation, 600/700 °C, and the other end of the tube was at a colder zone which was about 100 °C less. At 600/700 °C the capillary tubes burst to provide SbCl₅ vapour as transporting agent inside the sealed quartz tube. A bunch of transparent block shaped crystals grew at the colder end of the quartz tube after 4 d of heating.

X-Ray diffraction and crystal structure

The powder X-ray diffraction (XRD) patterns of polycrystalline samples of compounds **1** to **4** were recorded on Rigaku Miniflex diffractometer using Ni-filtered Co-Kα (1.7902 Å) radiation. Silicon was used as external standard.

Single crystals suitable for X-ray diffraction were isolated from the bunch of the crystals grown by the CVT method.

Diffraction data for the single crystals of the compounds **1** to **4** were collected at 293 ± 2 K on an Enraf-Nonius CAD4 diffractometer. There was no detectable decay during the data collection according to the intensities of three reflections measured at regular intervals. Absorption corrections based on azimuthal scans of reflections with angle $\chi \approx 90^\circ$ were applied to all the four data sets. The space groups were determined from systematic absences. For compounds **1** and **2** the centrosymmetric *Pnma* was chosen over non-centrosymmetric *Pna2*₁. The choice was found to be correct by the successful refinement. The structure solution and refinement were done using the programs SHELXS 86 and SHELXL 93 respectively.²⁸ The metal atoms were first located by direct methods. Refinement of their positions and subsequent Fourier difference maps led to the location of oxygen atoms. All the atoms were refined by full matrix least squares based on F^2 . For compounds **1** and **2** the anisotropic refinement of all the atoms of the asymmetric unit proceeded smoothly to give acceptable *R* values and the final Fourier difference maps did not have chemically significant features. For **3** all the atoms except one vanadium atom, V(1), were refined anisotropically. For **3** and **4** the *R* values were found to be 0.044 and 0.054 respectively and the final Fourier difference maps showed about 20 peaks with electron density >1 e Å⁻³. These peaks were found to be ghosts of existing atoms indicating severe absorption problems. Therefore an additional absorption correction using the DIFABS program²⁹ was applied to isotropically refined data sets for these two compounds. The final anisotropic refinement carried out using the corrected data of the two compounds led to improved *R* values (Table 1) and reduced electron density of ghost peaks. Several attempts were made to grow better crystals of **3** and **4** but were unsuccessful.

CCDC reference number 186/1081.

See <http://www.rsc.org/suppdata/dt/1998/3013/> for crystallographic files in .cif format.

Spectroscopy

The infrared spectra of these compounds were recorded on a Bruker 17S 66V FT-IR spectrometer. The samples were ground with dry KBr and pressed into transparent discs. The Raman spectra were recorded on an RFS 100 FT Raman spectrometer with a FRA 106 FT Raman accessory provided with a CaF₂ beam splitter; a Nd:YAG laser operating at an output of 200 mW for a 1064 nm line was used as the excitation source.

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