Two caesium vanadium hydrogenphosphates with tunnelled structures: Cs$_2$V$_2$O$_3$(PO$_4$)(HPO$_4$) and Cs$_2$[(VO)$_3$(HPO$_4$)$_4$(H$_2$O)].H$_2$O

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Two caesium vanadium hydrogenphosphates with tunnelled structures: \(\text{Cs}_2\text{V}_2\text{O}_5(\text{PO}_4)(\text{HPO}_4)\) and \(\text{Cs}_2[(\text{VO})_3(\text{HPO}_4)_4(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}\)

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Dicaesium divanadium trioxide phosphate hydrogenphosphate, \(\text{Cs}_2\text{V}_2\text{O}_5(\text{PO}_4)(\text{HPO}_4)\), (I), and dicaesium tris[oxido-vanadate(IV)] hydrogenphosphate dihydrate, \(\text{Cs}_2[(\text{VO})_3(\text{HPO}_4)_2(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}\), (II), crystallize in the monoclinic system with all atoms in general positions. The structures of the two compounds are built up from \(\text{VO}_6\) octahedra and \(\text{PO}_4\) tetrahedra. In (I), infinite chains of corner-sharing \(\text{VO}_6\) octahedra are connected to \(\text{V}_2\text{O}_{10}\) dimers by phosphate and hydrogenphosphate groups, while in (II) three vanadium octahedra share vertices leading to \(\text{V}_5\text{O}_{18}(\text{H}_2\text{O})\) trimers separated by hydrogenphosphate groups. Both structures show three-dimensional frameworks with tunnels in which Cs\(^+\) cations are located.

Comment

Vanadium phosphates and hydrogenphosphates have been extensively studied because of their interesting properties in catalysis, for example, the oxidation of light hydrocarbons into maleic anhydride, in low-dimensional magnetism and in ion exchange (Boudin et al., 2000). Previous studies involving hydrothermal preparation of vanadium phosphate compounds with insertion of Cs\(^+\) cations led to the isolation of several different structural types. The \(V^V\) phase \(\text{Cs}(\text{VO}_2)(\text{HPO}_4)\) was first isolated (Preuss et al., 1975) and then its structure proposed many years later (Amorós et al., 1988). Subsequently, the \(V^{III}\) compounds \(\text{Cs}_2\text{H}(\text{PO}_4)(\text{H}_2\text{O})\) (Klinkert et al., 1988) and \(\text{Cs}_2[\text{V}_2(\text{PO}_4)(\text{H}_2\text{O})]_2\) (Haushalter et al., 1993), and the mixed-valence \(V^{IV}/V^V\) compounds \(\text{Cs}(\text{VO}_2)(\text{HPO}_4)(\text{H}_2\text{O})\) (Haushalter et al., 1994) and \(\text{Cs}_2\text{Cs}(\text{VO}_2)(\text{HPO}_4)(\text{H}_2\text{O})\) (Le Fur et al., 2001) were also isolated. The most interesting remains \(\text{Cs}_2[\text{V}_2\text{O}_5(\text{PO}_4)_3] \cdot 4.5\text{H}_2\text{O}\), due to its high degree of porosity which leads to ion-exchange properties (Khan et al., 1996). During our current investigations, the mixed phosphate/hydrogenphosphate \(\text{Cs}_2\text{V}_2\text{O}_5(\text{PO}_4)(\text{HPO}_4)_3\) (I), and the hydrogenphosphate \(\text{Cs}_2[\text{V}_2\text{O}_5(\text{HPO}_4)_2(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}\), (II), have been synthesised and their structures solved using single-crystal X-ray diffraction.

The asymmetric unit of (I) contains 17 crystallographically independent non-H atoms: two \(V\) atoms with different oxidation states (\(V^1 +4\) and \(V^2 +5\)), two \(P\) atoms (P1 and P2) forming phosphate and hydrogenphosphate groups, respectively, and two Cs and 11 O atoms (Fig. 1a). The VPO framework consists of \([\text{V}_2\text{O}_{10}]_\oplus\) dimers connected through phosphate bridges to \([\text{V}_\text{II}^{IV}\text{O}(\text{HPO}_4)_2]\) infinite chains of corner-sharing \(\text{VO}_6\) octahedra that run along \(a\) (Fig. 2a). This results

Figure 1
The asymmetric unit and vanadium coordination spheres of (a) (I) [symmetry codes: (i) \(-x, 1-y, -z\); (ii) \(1+x, y, z\); (iii) \(1-x, 1-y, 1+z\); (iv) \(x, \frac{1}{2}-y, \frac{1}{2}+z\); and (b) (II) [symmetry codes: (i) \(-x, -y, -z\); (ii) \(x, -\frac{1}{2}-y, -\frac{1}{2}+z\); (iii) \(1-x, -y, -z\); (iv) \(x, \frac{1}{2}-y, \frac{1}{2}+z\)]. Displacement ellipsoids are drawn at the 50% probability level.
in a three-dimensional framework in which tunnels develop along \( c \) that interconnect tunnels running along \( a \). The Cs\(^+\) ions lie inside the tunnels (Fig. 2b). Within the dimer, the two VO\(_6\) octahedra [1.629 (2) Å \( \leq d_{V-O} \leq 2.339 \) (2) Å] are connected by edge sharing. In the infinite chains, alternating V=O\( \cdot \cdot \cdot \)V bonds are observed \([d_{V-O} = 1.618 (2) \text{ Å} \text{ and } d_{V-O} = 2.389 (2) \text{ Å}]\), with a V–O–V angle at the shared O1 atom of 129.11 (11)°. The four equatorial O atoms of the octahedra \([1.958 (2) \text{ Å} \leq d_{V-O} \leq 2.002 (2) \text{ Å}]\) are shared with phosphate and hydrogenphosphate groups. The phosphate groups share two O atoms with V2 atoms in the dimer and the other two with V1 atoms in the chain. In the hydrogenphosphate groups, two O atoms are shared with the vanadium chain and one with a dimer. The last O atom (O7) is unshared and the P1–O7 distance [1.588 (2) Å] is long enough to suggest the presence of an acidic H atom connected to this O atom. None of the H atoms were located in the structure analysis. The bond-valence-sum calculation gives values of 4.09 and 4.88 for V1 and V2, respectively, indicating formal oxidation states of +4 for V1 and +5 for V2. The structure of (I) can be compared to that of Cs(V2O3)(HPO4)2(H2O) described by Haushalter et al. (1994). Both structures are built up from infinite chains of corner-sharing vanadium octahedra and present tunnels, running along the infinite chain, occupied by Cs\(^+\) cations. In the case of Cs(V2O3)(HPO4)2(H2O), the chains are connected directly by hydrogenphosphate groups, generating narrow tunnels, while in (I) the tunnels are larger due to the presence of the V2O10 dimers which act as spacing agents. In both structures, mixed valence is observed. In (I), the tetravalent V atoms are observed in the chains and the pentavalent V atoms in the dimer, while in the case of Cs(V2O3)(HPO4)2(H2O) there is an alternation of V\(^{IV}\) and V\(^{V}\) within the infinite chain which is evidenced by the quite distinct V\( \cdot \cdot \cdot \)O distances.

The asymmetric unit of (II) contains three crystallographically independent V\(^{IV}\) atoms in octahedral environments and four hydrogenphosphate anions (Fig. 1b). V1 is coordinated to one terminal oxide O atom, four phosphate O atoms and a water molecule, while V2 and V3 are coordinated to one terminal oxide O atom, four phosphate O atoms and one oxide O atom from an adjacent vanadyl group. The short V=O bonds are in the range 1.592 (2) Å \( \leq d_{V=O} \leq 1.618 (2) \text{ Å} \) and the equatorial distances are in the range 1.959 (2) Å \( \leq d_{V-O} \leq 2.018 (2) \text{ Å} \), while the long V\( \cdot \cdot \cdot \)O bonds are in the range 1.97 (2) Å \( \leq d_{V-O} \leq 2.07 (2) \text{ Å} \).
distances are in the range 2.244 (2) Å ≤ d_{P–O} ≤ 2.634 (2) Å. Within the hydrogenphosphate groups, two sets of distances are observed. The first corresponds to O atoms shared with V atoms [1.493 (2) Å ≤ d_{P–O} ≤ 1.535 (2) Å] and the second to longer P–O distances to unshared O atoms [1.562 (2) Å ≤ d_{P–O} ≤ 1.599 (2) Å] that are presumed to be protonated. No H atoms could be located in the structure analysis. The three vanadium octahedra share vertices to form a distorted trimer. Each hydrogenphosphate group is linked to two vanadium octahedra through μ₂-oxygen bridges. One O atom is shared with another trimer and the last one is a terminal OH group. This leads to a three-dimensional framework (Fig. 3) with tunnels running along a in which Cs⁺ cations and water molecules are located. Similar trimers have already been encountered in H₃N(CH₂)₂NH₂[(VO)₂(OH)₂(H₂O)(PO₄)₂] (Soghomonian et al., 1993), in which the trimers are built up from a central square pyramid in which the vanadium shares O atoms from the basal plane with two adjacent V atoms in octahedral coordination. The trimer observed in (II) is actually more similar to that of the phosphite-containing compound (C₆H₅N₃)₃[(VO)₃(H₂O)(HPO₄)₃]·H₂O (Zhang et al., 2005), as shown in Fig. 4. The differences between the two structures are in the slightly different tilting of the phosphorus–oxygen groups. This may have its origin in the nature of the counter-cations: quasi-spherical Cs⁺ in our structure and nonsymmetric propylenediammonium in the phosphite compound.

**Experimental**

Both title compounds were prepared by hydrothermal treatment starting from mixtures of vanadium(V) oxide, caesium carbonate, oxalic acid, phosphoric acid and water. For the preparation of (I), a mixture of V₂O₅ (1 mmol), H₂C₂O₄·2H₂O (0.92 mmol), Cs₂CO₃ (2 mmol), H₃PO₄ (17 mmol) and water (170 mmol) was loaded in a 23 ml-capacity Teflon-lined stainless steel Parr hydrothermal reaction vessel and heated at 393 K for 3 d. After slow cooling of the reaction vessel to room temperature, pale-green crystals were recovered by vacuumfiltration, washed with water and dried in a desiccator.

For the preparation of (II), a mixture of V₂O₅ (1 mmol), H₂C₂O₄·2H₂O (0.92 mmol), Cs₂CO₃ (2 mmol), H₃PO₄ (0.25 ml of an 85% solution) and water (4.75 ml) was loaded into a vessel as in the preparation of (I) and heated at 493 K for 72 h. The final product, a mixture of black and green crystals, was filtered off, rinsed with water and dried in a desiccator. Green crystals, corresponding to (II), were manually selected for single-crystal X-ray data collection. Attempts to obtain a pure phase remain unsuccessful.

**Compound (I)**

**Crystal data**

Cs₂[V₂O₅(PO₄)(H₂O)]

Mᵣ = 605.64

Monoclinic, P₂₁/c

a = 8.9180 (2) Å

b = 16.9479 (4) Å

c = 7.2199 (1) Å

b = 99.092 (1)°

**Data collection**

Nonius KappaCCD area-detector diffractometer

Absorption correction: multi-scan (SADABS; Sheldrick, 2002)

Tₘᵢₙ = 0.251, Tₘₐₓ = 0.277

18070 measured reflections

5051 independent reflections

4170 reflections with I > 2σ(I)

Rₘᵢₙ = 0.022

**Refinement**

\( R[F^2 > 2\sigma(F^2)] = 0.033 \)

wR(F²) = 0.055

S = 1.14

5051 reflections

154 parameters

H-atom parameters not defined

Δρₘₐₓ = 1.70 e Å⁻³

Δρₘᵢₙ = −2.53 e Å⁻³

**Compound (II)**

**Crystal data**

Cs₃[(VO)₃(HPO₄)₃(H₂O)]·H₂O

Mᵣ = 878.52

Monoclinic, P₂₁/c

a = 12.5465 (1) Å

b = 11.9181 (1) Å

c = 12.6531 (1) Å

b = 96.7859 (6)°

V = 1878.77 (3) Å³

Z = 4

Mo Kα radiation

μ = 5.72 mm⁻¹

T = 293 K

0.30 × 0.25 × 0.19 mm

5051 reflections

Δρₘₐₓ = 1.70 e Å⁻³

Δρₘᵢₙ = −2.53 e Å⁻³


Gautier et al. · Cs₂[V₂O₅(PO₄)(H₂O)] and Cs₃[(VO)₃(HPO₄)₃(H₂O)]·H₂O
Data collection

Nonius KappaCCD area-detector diffractometer
Absorption correction: empirical (using intensity measurements) (SADABS; Sheldrick, 2002)

\[ T_{	ext{min}} = 0.208, \quad T_{	ext{max}} = 0.293 \]

Refinement

\[ R[F^2 > 2\sigma(F^2)] = 0.039 \]
\[ wR(F^2) = 0.095 \]
\[ S = 1.02 \]
12989 reflections
272 parameters

H-atom parameters not defined
\[ \Delta p_{\text{max}} = 3.64 \text{ e/Å}^3 \]
\[ \Delta p_{\text{min}} = -3.14 \text{ e/Å}^3 \]

In both title compounds, the H atoms on the hydrogenphosphate groups and the water molecules could not be located from difference Fourier maps. The largest electron-density peaks in the final difference Fourier syntheses are close to Cs atoms in both structures [at distances of 0.64 and 0.59 Å for compounds (I) and (II), respectively].

For both compounds, data collection: COLLECT (Nonius, 1998); cell refinement: DIRAX/LSQ (Duisenberg, 1998); data reduction: EVALCCD (Duisenberg, 1998); program(s) used to solve structure: SIR97 (Altomare et al., 1999); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: DIAMOND (Brandenburg, 2005); software used to prepare material for publication: WinGX (Farrugia, 1999).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ3221). Services for accessing these data are described at the back of the journal.

References