Hydrothermal Synthesis and Crystal Structures of $Sr_2V(PO_4)_2(H_2PO_4)$ and $Sr_2Fe(PO_4)_2(H_2PO_4)$ *

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Two new phosphates, $Sr_2M(PO_4)_2(H_2PO_4)$ ($M = V^{III}$ or Fe^{III}), have been synthesised hydrothermally at 230 °C and characterized by single-crystal X-ray diffraction and thermal analysis. Crystal data: $Sr_2V(PO_4)_2(H_2PO_4)$, monoclinic, space group $C2/c$, $a = 11.078(3)$, $b = 11.742(3)$, $c = 8.951(3)$ Å, $\beta = 125.35(2)°$, $Z = 4$ and $R = 0.0356$; $Sr_2Fe(PO_4)_2(H_2PO_4)$, as above except $a = 11.082(2)$, $b = 11.737(2)$, $c = 8.961(2)$ Å, $\beta = 125.45(1)°$ and $R = 0.0273$. The two compounds are isostructural. The structure consists of ${}^{1}_{\infty}[M(PO_4)_{4/2}(H_2PO_4)_{2/2}]$ units along the [101] direction, held together by hydrogen bonding and O–Sr–O bonds. The interaction between the structural unit and the interstitial species has been evaluated using the valence-matching principle to account for the presence of an interstitial H_2O in the structure of the related compound $Ca_2V(PO_4)(HPO_4)_2{\cdot}H_2O$. Dehydration of the compounds at 750 and 650 °C yields $Sr_2V(PO_4)(P_2O_7)$ and $Sr_2Fe(PO_4)(P_2O_7)$, respectively.

We have been applying hydrothermal techniques to the synthesis of new phases in the transition-metal phosphate system and reported a number of new structures.[1–7] The hydrothermal method is useful for the synthesis of low-temperature phases and is particularly suited for crystal growth. We have also found that the use of different pressure and temperature conditions can aid the search for new phases. For example, $Ca_2V(PO_4)(HPO_4)_2{\cdot}H_2O$, which contains hydrogenphosphate groups and a water of hydration, was synthesised under mild conditions (230 °C, ≈20 bar). Interestingly, crystals of the dehydrated compound, $Ca_2V(PO_4)(P_2O_7)$, were obtained under much more vigorous conditions (450 °C, ≈700 bar).[6] Attempts to prepare analogues of the calcium compounds have yielded crystals of $Sr_2M(PO_4)_2(H_2PO_4)$ and $Sr_2M(PO_4)(P_2O_7)$ where M = V or Fe. The dihydrogenphosphates adopt a structure related to that of $Ca_2V(PO_4)(HPO_4)_2{\cdot}H_2O$. Both diphosphates are isostructural with $Ca_2V(PO_4)(P_2O_7)$. The present paper reports the synthesis and crystal structures of the dihydrogenphosphates $Sr_2M(PO_4)_2(H_2PO_4)$ (M = V or Fe).

Experimental

Synthesis.—Reagent-grade $Sr(OH)_2{\cdot}8H_2O$, V_2O_3, $FePO_4$ and 85% H_3PO_4, obtained from Merck, were used as received. Green crystals of $Sr_2V(PO_4)_2(H_2PO_4)$ were obtained by heating a mixture of $Sr(OH)_2{\cdot}8H_2O$, V_2O_3 (molar ratio Sr : V = 2 : 1), and 7.5 mol dm^{-3} H_3PO_4 (10 cm^3) in a Teflon-lined autoclave (23 cm^3) at 230 °C for 4 d before slow cooling at 5 °C h^{-1} to room temperature. The product was filtered off, washed with water, rinsed with ethanol, and dried at ambient temperature. Visual microscopic inspection showed that there were some green crystals in the product. A single-crystal X-ray diffraction study showed the green crystals to be the new compound $Sr_2V(PO_4)_2(H_2PO_4)$. Colourless crystals of $Sr_2Fe(PO_4)_2(H_2PO_4)$ were obtained under similar reaction conditions. The products were checked for purity by means of powder X-ray diffraction.

Thermal Analysis.—Thermogravimetric analysis (TGA), using a DuPont thermogravimetric analyser, was performed on a powder sample of $Sr_2V(PO_4)_2(H_2PO_4)$ in flowing N_2 at a heating rate of 10 °C min^{-1}. The TGA curve showed a one-step weight loss (3.35%) from 480 to 630 °C with a maximum slope at 560 °C, corresponding to the loss of one water molecule (calc. 3.51%). In order to characterize the decomposition products, an experiment was performed in which $Sr_2V(PO_4)_2(H_2PO_4)$ was heated in flowing N_2 at 750 °C for 12 h. On the basis of powder X-ray analysis, the product of dehydration was $Sr_2V(PO_4)(P_2O_7)$. Upon heating in air at 650 °C $Sr_2Fe(PO_4)_2(H_2PO_4)$ also decomposed to $Sr_2Fe(PO_4)(P_2O_7)$ and water.

Single-crystal X-Ray Diffraction.—Two crystals having dimensions 0.06 × 0.06 × 0.14 mm for $Sr_2V(PO_4)_2(H_2PO_4)$ and 0.08 × 0.10 × 0.16 mm for $Sr_2Fe(PO_4)_2(H_2PO_4)$ were selected for indexing and intensity data collection on a Nicolet R3m/V four-circle diffractometer using monochromated Mo-Kα radiation. Axial oscillation photographs along the three axes were taken to check the symmetry properties and unit-cell parameters. The intensity data for both crystals were corrected for Lorentz polarization and absorption effects. Correction for absorption effects were based on ψ scans of a few suitable reflections with χ values close to 90° using the program XEMP of the SHELXTL-PLUS program package.[8] Based on systematic absences, statistical analysis of the intensity data, and successful solution and refinement of the structures, the space groups were determined to be $C2/c$ for both crystals. Direct methods were used to locate the metal atoms with the remaining non-hydrogen atoms being found from successive difference maps. Bond-strength calculations were carried out to help locate any hydrogen atoms. Atom O(4) was found to be undersaturated; a sum of 1.45 valence units (v.u.s.) was calculated for O(4) in each structure. This suggested that a hydrogen atom is bonded to O(4). The hydrogen atom was located by scrutiny of a difference map. Both structures were refined by full-matrix least-squares refinement based on F values. All of the non-hydrogen atoms were refined with anisotropic thermal parameters. The atomic coordinates and isotropic thermal parameters for the hydrogen atoms in both structures were fixed. Corrections for secondary extinction were

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* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

Non-SI unit employed: bar = 10^5 Pa.

Table 1 Crystal data and intensity collection parameters[a] for $Sr_2V(PO_4)_2(H_2PO_4)$ and $Sr_2Fe(PO_4)_2(H_2PO_4)$

Formula	$Sr_2V(PO_4)_2(H_2PO_4)$	$Sr_2Fe(PO_4)_2(H_2PO_4)$
M	513.1	518.0
a/Å	11.078(3)	11.082(2)
b/Å	11.742(3)	11.737(2)
c/Å	8.951(3)	8.961(2)
β/°	125.35(2)	125.45(1)
U/Å^3	949.7(5)	949.5(3)
D_c/g cm^{-3}	3.589	3.624
F(000)	968	980
μ(Mo-Kα)/cm^{-1}	123.6	129.3
Reflections collected	1415	1309
Unique reflections [$I > 3\sigma(I)$]	792	843
g^b	0.000 58	0.00157
R^c	0.0356	0.0273
R'^d	0.0377	0.0278

[a] Details in common: monoclinic, space group $C2/c$; $Z = 4$; $T = 24$ °C; scan rate, 2–14.65°(ω) min^{-1}; scan mode θ–2θ; scan width/° 1.0 + Kα separation; 2θ range 2.5–55.0°; parameters refined 85. Weighting scheme of form $w^{-1} = \sigma^2(F) + gF^2$. [c] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [d] $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{\frac{1}{2}}$.

Table 2 Atomic coordinates for $Sr_2V(PO_4)_2(H_2PO_4)$ and $Sr_2Fe(PO_4)_2(H_2PO_4)$

Atom	X/a	Y/b	Z/c
$Sr_2V(PO_4)_2(H_2PO_4)$			
Sr	0.799 89(8)	0.459 40(6)	0.205 9(1)
V	0.25	0.25	0
P(1)	0.5	0.465 8(2)	0.25
P(2)	0.560 9(2)	0.191 1(2)	0.051 2(3)
O(1)	0.368 1(6)	0.397 2(5)	0.099 2(7)
O(2)	0.390 1(6)	0.190 4(5)	−0.049 5(7)
O(3)	0.362 8(6)	0.169 9(5)	0.243 2(7)
O(4)	0.568 5(6)	0.543 7(5)	0.177 4(8)
O(5)	0.593 6(6)	0.091 0(5)	−0.030 1(7)
O(6)	0.609 8(6)	0.305 9(5)	0.024 0(8)
$Sr_2Fe(PO_4)_2(H_2PO_4)$			
Sr	0.799 18(5)	0.460 11(4)	0.204 60(7)
Fe	0.25	0.25	0
P(1)	0.5	0.465 2(1)	0.25
P(2)	0.559 0(1)	0.190 4(1)	0.050 3(2)
O(1)	0.369 0(4)	0.396 1(3)	0.098 4(5)
O(2)	0.388 8(4)	0.189 9(3)	−0.050 3(4)
O(3)	0.363 1(4)	0.169 7(3)	0.243 0(4)
O(4)	0.568 0(4)	0.543 3(3)	0.177 2(5)
O(5)	0.591 6(4)	0.089 8(3)	−0.030 0(5)
O(6)	0.607 4(4)	0.306 5(3)	0.022 1(5)

applied. Neutral-atom scattering factors and corrections for anomalous dispersion were from ref. 9. All calculations were performed on a DEC MicroVAX II computer system using the SHELXTL-PLUS programs.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Table 3 Selected bond lengths (Å) and angles (°) for $Sr_2V(PO_4)_2(H_2PO_4)$ and $Sr_2Fe(PO_4)_2(H_2PO_4)$

$Sr_2V(PO_4)_2(H_2PO_4)$			
Sr–O(1$^{\rm I}$)	2.806(5)	Sr–O(2$^{\rm II}$)	2.521(6)
Sr–O(3$^{\rm III}$)	2.537(6)	Sr–O(4)	2.619(7)
Sr–O(5$^{\rm IV}$)	2.524(8)	Sr–O(5$^{\rm V}$)	2.870(6)
Sr–O(5$^{\rm II}$)	2.761(5)	Sr–O(6)	2.524(5)
V–O(1)	2.035(6) (2 ×)	V–O(2)	1.972(8) (2 ×)
V–O(3)	2.009(5) (2 ×)		
P(1)–O(1)	1.524(5) (2 ×)	P(1)–O(4)	1.551(8) (2 ×)
P(2)–O(2)	1.555(6)	P(2)–O(3$^{\rm VI}$)	1.538(6)
P(2)–O(5)	1.532(6)	P(2)–O(6)	1.524(7)
H–O(4$^{\rm VII}$)	0.88	H $\cdots$ O(6$^{\rm VIII}$)	1.63
O(1)–V–O(2)	90.5(3)	O(1)–V–O(3)	94.9(2)
O(2)–V–O(3)	90.0(3)	O(1)–P(1)–O(4)	113.0(3)
O(1)–P(1)–O(1$^{\rm VI}$)	116.2(4)	O(1)–P(1)–O(4$^{\rm VI}$)	103.4(3)
O(4)–P(1)–O(4$^{\rm VI}$)	107.7(5)	O(2)–P(2)–O(5)	105.3(3)
O(2)–P(2)–O(6)	109.7(3)	O(2)–P(2)–O(3$^{\rm VI}$)	109.6(4)
O(5)–P(2)–O(6)	113.5(5)	O(5)–P(2)–O(3$^{\rm VI}$)	109.1(3)
O(6)–P(2)–O(3$^{\rm VI}$)	109.5(3)	O(4$^{\rm VII}$)–H $\cdots$ O(6$^{\rm VIII}$)	162.2
H–O(4)–P(1)	121.7(7)		
$Sr_2Fe(PO_4)_2(H_2PO_4)$			
Sr–O(1$^{\rm I}$)	2.797(3)	Sr–O(2$^{\rm II}$)	2.526(4)
Sr–O(3$^{\rm III}$)	2.528(4)	Sr–O(4)	2.617(5)
Sr–O(5$^{\rm IV}$)	2.541(6)	Sr–O(5$^{\rm V}$)	2.862(4)
Sr–O(5$^{\rm II}$)	2.749(3)	Sr–O(6)	2.532(3)
Fe–O(1)	2.027(3) (2 ×)	Fe–O(2)	1.967(5) (2 ×)
Fe–O(3)	2.009(3) (2 ×)		
P(1)–O(1)	1.524(3) (2 ×)	P(1)–O(4)	1.550(5) (2 ×)
P(2)–O(2)	1.548(4)	P(2)–O(3$^{\rm VI}$)	1.542(4)
P(2)–O(5)	1.531(5)	P(2)–O(6)	1.539(4)
H–O(4$^{\rm VII}$)	1.11	H $\cdots$ O(6$^{\rm VIII}$)	1.36
O(1)–Fe–O(2)	90.3(2)	O(1)–Fe–O(3)	94.9(2)
O(2)–Fe–O(3)	90.1(2)	O(1)–P(1)–O(4)	112.6(2)
O(1)–P(1)–O(1$^{\rm VI}$)	115.7(3)	O(1)–P(1)–O(4$^{\rm VI}$)	104.2(2)
O(4)–P(1)–O(4$^{\rm VI}$)	107.5(3)	O(2)–P(2)–O(5)	105.3(2)
O(2)–P(2)–O(6)	109.3(2)	O(2)–P(2)–O(3$^{\rm VI}$)	110.1(3)
O(5)–P(2)–O(6)	113.9(3)	O(5)–P(2)–O(3$^{\rm VI}$)	108.8(2)
O(6)–P(2)–O(3$^{\rm VI}$)	109.3(2)	O(4$^{\rm VII}$)–H $\cdots$ O(6$^{\rm VIII}$)	168.8
H–O(4)–P(1)	116.6(3)		

Symmetry codes: I $1 - x, 1 - y, -z$; II $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$; III $\frac{1}{2} + x, \frac{1}{2} + y, z$; IV $\frac{3}{2} - x, \frac{1}{2} - y, -z$; V $\frac{3}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; VI $1 - x, y, \frac{1}{2} - z$; VII $-\frac{1}{2} + x, -\frac{1}{2} + y, z$; VIII $\frac{1}{2} - x, \frac{1}{2} - y, -z$.

Results and Discussion

The crystallographic data for both compounds are listed in Table 1. The atomic coordinates, selected bond distances, motif of mutual adjunction,[10] and bond-valence sums[11] are given in Tables 2–4. Both the V and Fe atoms are six-co-ordinated. The co-ordination number of Sr^{2+} was determined on the basis of the maximum gap in the Sr–O distances ranked in increasing order. In both compounds the strontium cation is co-ordinated by eight oxygen atoms and the ninth Sr–O bond length is ≈3.29 Å. Bond-valence sums for most atoms are in good accord with their formal oxidation states. The value for Fe is slightly higher. In the following paragraphs only $Sr_2V(PO_4)_2(H_2PO_4)$ will be discussed because the two compounds are isostructural. Besides the two compounds, a few pairs of isostructural phosphates of V^{III} and Fe^{III} have also been synthesised. For example, $Sr_2V(PO_4)(P_2O_7)$,[12] $Ca_2V(PO_4)(HPO_4)_2{\cdot}H_2O$,[6] $Ba_2V_3H(PO_4)_2(P_2O_7)_2$,[13] and AVP_2O_7 (A = alkali metal)[14] are isostructural with their iron(III) analogues. The very similar ionic radii for V^{III} and high-spin Fe^{III} should account for this close structural correspondence.

As shown in Fig. 1, the $Sr_2V(PO_4)_2(H_2PO_4)$ structure consists of layers of corner-sharing VO_6 octahedra, PO_4 tetrahedra, and H_2PO_4 groups in the ac plane with the strontium ions located between the layers. Adjacent layers are connected by O–Sr–O bonds and hydrogen bonding between PO_4 and H_2PO_4 groups. Each layer consists of infinite chains of VO_6 octahedra, PO_4 tetrahedra, and H_2PO_4 groups, as shown in Fig. 2 along the [101] direction. Connections between the infinite chains are provided by the hydrogen bonding between PO_4 and H_2PO_4 groups from adjacent layers and O–Sr–O bonds within a layer. The co-ordination sphere of the V atom, which lies on the site of $\bar{1}$ symmetry, is an almost regular octahedron typical of V^{3+}. The PO_4 and H_2PO_4 groups form bridges over adjacent VO_6 octahedra, forming ${}^{1}_{\infty}[V(PO_4)_{4/2}(H_2PO_4)_{2/2}]$ along the [101] direction (Fig. 3) where the superscript number (1) indicates the

Table 4 Motif of mutual adjunction, co-ordination number, and bond-valence sums (Σs) for $Sr_2V(PO_4)_2(H_2PO_4)$ and $Sr_2Fe(PO_4)_2(H_2PO_4)$

	O(1)	O(2)	O(3)	O(4)	O(5)	O(6)	Co-ordination no.	Σs*
Sr	1/1	1/1	1/1	1/1	3/3	1/1	8	2.05 (2.04)
V (Fe)	2/1	2/1	2/1				6	2.96 (3.13)
P(1)	2/1			2/1			4	4.96 (4.97)
P(2)		1/1	1/1		1/1	1/1	4	4.96 (4.93)
H				1/1		1/1	2	
Co-ordination no.	3	3	3	3	4	3		

* The values in parentheses are for $Sr_2Fe(PO_4)_2(H_2PO_4)$.

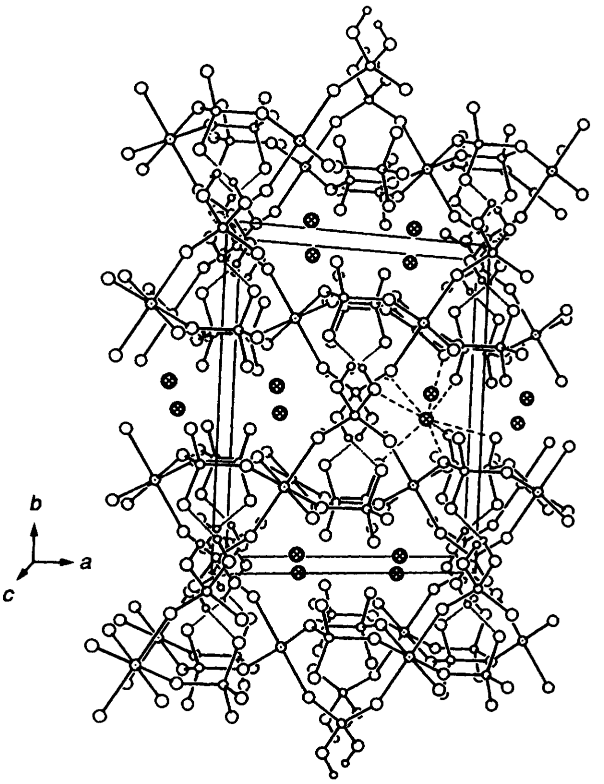

Fig. 1 View of the $Sr_2V(PO_4)_2(H_2PO_4)$ structure along the [001] direction: cross-hatched circles, Sr; dotted circles, V; large open circles, O; medium open circles, P; small open circles, H. The hydrogen bonds and O–Sr–O bonds are represented by dotted and dashed lines, respectively

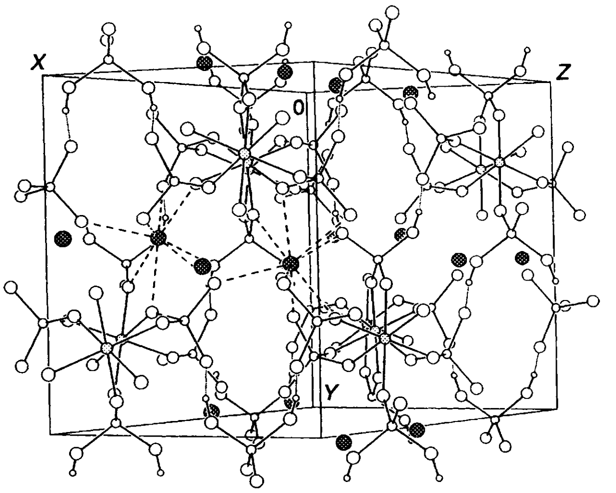

Fig. 2 View of the $Sr_2V(PO_4)_2(H_2PO_4)$ structure along the [101] direction

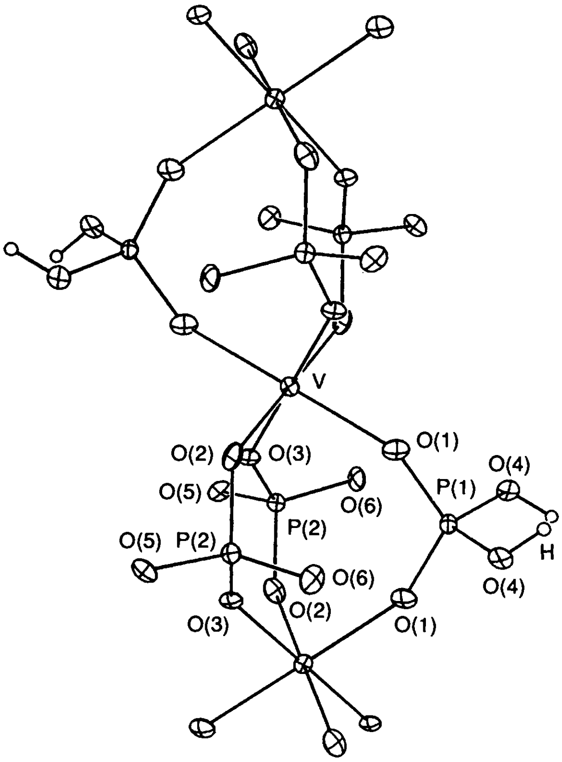

Fig. 3 Section of an infinite chain of corner-sharing VO_6 octahedra, PO_4 tetrahedra, and H_2PO_4 groups in $Sr_2V(PO_4)_2(H_2PO_4)$. Thermal ellipsoids are shown at the 60% probability level

dimensionality of the substructure in square brackets and the subscript 4/2 indicates that four PO_4 groups are co-ordinated to V, and each PO_4 group is bonded to two V atoms. Atom P(1) of the H_2PO_4 group sits on a two-fold axis and P(2) is at general positions. Atom O(6) of the PO_4 group acts as a hydrogen-bond acceptor from a H_2PO_4 group in an adjacent layer. The O(4)–H ••• O(6) bond angle is 162.2°. It is not clear to us why the hydrogen bond in the iron compound appears stronger and more symmetric than in the vanadium compound. In the dehydration experiments the release of one water molecule corresponds to the condensation of one H_2PO_4 with one PO_4 group in $Sr_2V(PO_4)_2(H_2PO_4)$ to give the P_2O_7 group in $Sr_2V(PO_4)(P_2O_7)$.

The compound $Ca_2V(PO_4)(HPO_4)_2{\cdot}H_2O$, which was synthesised under similar reaction conditions to those used for $Sr_2V(PO_4)_2(H_2PO_4)$, contains a water molecule of hydration which is co-ordinated to a calcium cation and also hydrogen bonded to the framework. The reason why an interstitial H_2O is structurally incorporated in this compound can be understood according to the arguments of Hawthorne.[15] For $Sr_2V(PO_4)_2(H_2PO_4)$, the structural units $V(PO_4)_2(H_2PO_4)$ are linked together by the interstitial species Sr^{2+}. The interaction between the structural unit and the interstitial species can be quantitatively evaluated using the valence-matching principle. The most stable structure will form when the Lewis-acid strength of the cation most closely matches the Lewis-base strength of the

Table 5 Details of the co-ordination of different anions in the structural unit of $Sr_2V(PO_4)_2(H_2PO_4)$*

Bonded atoms	Number of anions	Bonds needed
P	4 [2 $^{\mathrm{IV}}$O(5) and 2 $^{\mathrm{III}}$O(6)]	10
P + V	6 [2 $^{\mathrm{III}}$O(1), 2 $^{\mathrm{III}}$O(2), and 2 $^{\mathrm{III}}$O(3)]	6
P + H	2 [2 $^{\mathrm{III}}$O(4)]	2

Bonds needed to structural unit = 10 + 6 + 2 = 18
No. of H bonds to structural unit = 2 [2 H ··· O(6)]
No. of additional bonds needed = 18 − 2 = 16
Lewis basicity of structural unit = 4/16 = 0.25 v.u.
Lewis-acid strength for Sr^{2+} = 0.233 v.u.

* Roman superscript indicates the co-ordination numbers of the oxygen atoms.

Table 6 Details of the co-ordination of different anions in the structural unit of $Ca_2V(PO_4)(HPO_4)_2 \cdot H_2O$

Bonded atoms	Number of anions	Bonds needed
P	4 [2 $^{\mathrm{III}}$O(2) and 2 $^{\mathrm{IV}}$O(3)]	10
P + V	6 [2 $^{\mathrm{IV}}$O(1), 2 $^{\mathrm{III}}$O(4), and 2 $^{\mathrm{III}}$O(5)]	8
P + H	2 [2 $^{\mathrm{III}}$O(6)]	2

Bonds needed to structural unit = 10 + 8 + 2 = 20
No. of H bonds to structural unit = 2 [2 H ··· O(4)]
No. of additional bonds needed = 20 − 2 = 18
Lewis basicity of structural unit = 4/18 = 0.22 v.u.
Co-ordination number of the interstitial cation, Ca = 1(H_2O) + 8 O
Bonds from Ca to structural unit = (1 × 2) + 8 = 10
Effective Lewis acidity of Ca = 2/10 = 0.2 v.u.

structural unit. The calculation of the basicity of the structural unit $V(PO_4)_2(H_2PO_4)$ is illustrated in Table 5. The co-ordination number of each oxygen atom is assigned according to the refined crystal structure. The Lewis basicity of the structural unit is 0.25 v.u. Examination of the Lewis-acid strengths calculated by Brown[16] shows that Sr (0.233 v.u.) has a more appropriate Lewis acidity than do Ca (0.274 v.u.) and Ba (0.195 v.u.). The somewhat higher Lewis acidity of Ca can be moderated by the incorporation of an interstitial H_2O as a bond-valence transformer. The calculation for $Ca_2V(PO_4)(HPO_4)_2 \cdot H_2O$ is illustrated in Table 6. The moderated Lewis acidity of the complex interstitial species (0.2 v.u.) now better matches the Lewis basicity of the structural unit (0.22 v.u.) and thus a stable structure is formed.

Crystals of the barium analogue have also been obtained by the hydrothermal technique. Preliminary X-ray study shows that they are monoclinic with cell parameters similar to those of $Ca_2V(PO_4)(HPO_4)_2 \cdot H_2O$. Unfortunately, the crystals obtained are unsuitable for intensity data collection. Since it is of great interest to know the composition and structure of the barium compound, further attempts to grow single crystals are in progress.

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