Thus, the close Se⋯Se distance may be the result of crystal packing forces.

Concluding Remarks

Thus far, all Mo/Se phases isolated contain recognizable $[Mo_3(\mu_2\text{-}Se_2)_3(\mu_3\text{-}Se)]^{4+}$ clusters connected by bridging selenide or polyselenide ligands. This extraordinarily stable $[Mo_3(\mu_2\text{-}Se_2)_3(\mu_3\text{-}Se)]^{4+}$ trinuclear core contains a triangular cavity created by the selenium atoms of the $\mu_2\text{-}Se_2^{2-}$ ligands which has the hitherto unrecognized property of attracting negatively charged species such as Se^{2-} or Se_x^{2-} ligands.

Hydrothermal synthesis with polychalcogenide ligands is a feasible and convenient technique to novel cluster or polymeric phases. Our work in this system alone points to an enormous wealth of new and different K/Mo/Se phases to be discovered. This synthesis is applicable to any cation/metal/chalcogenide system and thus has a very broad scope. We believe that future work in this new area of chalcogenide synthesis will lead to an abundance of novel structure types which may rival, in number, those of zeolites.

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Supplementary Material Available: Tables of crystallographic data and structure refinement for $K_2Mo_3Se_{18}$ and $K_8Mo_9Se_{40}\cdot 4H_2O$, calculated and observed X-ray powder diffraction patterns, atomic coordinates of all atoms, and anisotropic and isotropic thermal parameters of all atoms for $K_2Mo_3Se_{18}$ and all non-hydrogen atoms for $K_8Mo_9Se_{40}\cdot 4H_2O$ (18 pages); listings of calculated and observed $(10F_o/10F_c)$ structure factors (41 pages). Ordering information is given on any current masthead page.

Contribution from the Institute of Chemistry, Academia Sinica, Taipei, and Departments of Chemistry, National Taiwan Normal University, Taipei, and National Chung Hsing University, Taichung, Taiwan, Republic of China

Hydrothermal Synthesis and Structural Characterization of Two Calcium Vanadium(III) Phosphates: $Ca_2V(PO_4)(HPO_4)_2\cdot H_2O$ and $Ca_2V(PO_4)(P_2O_7)$

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The new phosphate $Ca_2V(PO_4)(HPO_4)_2\cdot H_2O$ and the dehydrated compound $Ca_2V(PO_4)(P_2O_7)$ have been synthesized hydrothermally at 230 and 450 °C, respectively, and characterized by single-crystal X-ray diffraction and thermogravimetric analysis. Crystal data: $Ca_2V(PO_4)(HPO_4)_2\cdot H_2O$, monoclinic, $C2/c$, $a = 7.531$ (2) Å, $b = 15.522$ (4) Å, $c = 9.149$ (2) Å, $\beta = 113.52$ (2)°, $Z = 4$, $R = 0.0215$ for 954 unique reflections; $Ca_2V(PO_4)(P_2O_7)$, monoclinic, $P2_1/c$, $a = 6.391$ (2) Å, $b = 6.6362$ (9) Å, $c = 19.071$ (2) Å, $\beta = 99.26$ (2)°, $Z = 4$, $R = 0.029$ for 1389 unique reflections. The structure of the hydrated compound consists of ${}^1_\infty[V(PO_4)_{2/2}(HPO_4)_{4/2}]$ along the [101] direction, which are held together by hydrogen bonding and O–Ca–O bonds. The structure of the dehydrated compound contains intersecting channels where the calcium atoms are located. The framework consists of corner-sharing VO_6 octahedra, PO_4 tetrahedra, and P_2O_7 groups. The connectivity formula is ${}^3_\infty Ca_2[V(PO_4)_{2/2}(P_2O_7)_{1/3}(P_2O_7)_{2/3}]$.

Introduction

We have recently found a number of new compounds in the alkali-metal vanadium phosphate system using high-temperature solid-state reactions. Compounds such as $Cs_2V_3P_4O_{17}$,[1] β-$K_2V_3P_4O_{17}$,[2] $A_2VOP_2O_7$ (A = Cs, Rb),[3] AVP_2O_7 (A = Li–Cs),[4–6] $NaVOPO_4$,[7] and $RbV_3P_4O_{17+x}$[8] were isolated. These phosphates often adopt tunnel or layer structures with the alkali-metal cations located in the tunnels or between the layers. Since the nature of the alkali-metal cations plays an important role in the crystal structures of these compounds, we have been interested in the synthesis and structural characterization of vanadium phosphates with divalent cations. Recently, we synthesized $Zn_2VO(PO_4)_2$ which contains a dimer of edge-sharing ZnO_5 square pyramids.[9] However, our efforts to grow crystals of vanadium phosphates containing alkaline-earth metals by the solid-state method have been unsuccessful, probably due to their very high melting points. Since the hydrothermal method is particularly suited for the synthesis of low-temperature phases and is also useful for the crystal growth, we have also been applying hydrothermal techniques to the synthesis of vanadium phosphates. Recent examples of vanadium phosphates from hydrothermal reactions include $K_2(VO)_2P_3O_9(OH)_3\cdot 1.125H_2O$,[10] $K_2(VO)_3(HPO_4)_4$,[11] β-$LiVOPO_4$,[12] $A_{0.5}VOPO_4\cdot xH_2O$ (A = Na, $x = 2.0$; A = K, $x = 1.5$),[13] and $Ni_{0.5}VOPO_4\cdot 1.5H_2O$.[14] We have extended our research aimed at synthesizing vanadium phosphates containing alkaline-earth metals by the hydrothermal method. At this time, we are able to grow crystals of calcium vanadium phosphates. To our knowledge, calcium vanadium phosphates are rare and up to now only the mineral sincosite, $Ca(VO)_2(PO_4)_2\cdot 5H_2O$, has been reported.[15] This paper describes the hydrothermal synthesis and structural characterization of $Ca_2V(PO_4)(HPO_4)_2\cdot H_2O$ and the dehydrated compound $Ca_2V(PO_4)(P_2O_7)$.

Experimental Section

Synthesis. $Ca(OH)_2$ (GR, Merck), $Ca_3(PO_4)_2$ (Merck), V_2O_3 (99.9%, Cerac), P_2O_5 (99.9%, Cerac), and H_3PO_4 (85%, Merck) were used as received. The conditions for the crystal growth of $Ca_2V(PO_4)(HPO_4)_2\cdot H_2O$ were as follows. A mixture of 1.0460 g of $Ca(OH)_2$ (14.12

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mmol), 0.5038 g of V_2O_3 (3.361 mmol), and 10 mL of 7.5 M H_3PO_4 was placed in a 23-mL Teflon-lined autoclave (Parr Instruments). The reaction vessel was maintained at 230 °C under autogenous pressure for 5 days and then cooled at 10 °C/h to room temperature. The product was filtered off, washed with water, rinsed with acetone, and dried in a desiccator at ambient temperature. Powder X-ray diffraction analysis of the green product indicated that a single phase of $Ca_2V(PO_4)(HPO_4)_2{\cdot}H_2O$ had been produced. The amounts of Ca, V, and P in the product were determined by using an ICP-AE spectrometer after dissolving the sample in dilute aqua regia. Anal. Calcd for $Ca_2V(PO_4)(HPO_4)_2{\cdot}H_2O$: Ca, 18.3; V, 11.7; P, 21.3. Found: Ca, 18.8; V, 11.7; P, 21.4. The solid-state reaction of $Ca_3(PO_4)_2$, V_2O_3, and P_2O_5 (molar ratio Ca:V:P:O = 2:1:3:11) in an alumina crucible, which was sealed in a quartz glass tube, at 1000 °C for 2 days gave a green polycrystalline product, which had the same X-ray powder pattern as that prepared by dehydration of $Ca_2V(PO_4)(HPO_4)_2{\cdot}H_2O$ at 700 °C (vide infra). However, efforts to grow crystals of the dehydrated compound by the solid-state method were unsuccessful, probably due to its very high melting point. Subsequently, the hydrothermal technique was attempted. The hydrothermal reaction of 0.3426 g of $Ca(OH)_2$ (4.625 mmol), 0.1574 g of V_2O_3 (1.050 mmol), and 2.0 mL of 7.5 M H_3PO_4 in a sealed quartz glass tube (i.d., o.d. = 8, 10 mm) at 450 °C for 2 days followed by slow cooling at 40 °C/h to room temperature yielded green crystals of the dehydrated compound $Ca_2V(PO_4)(P_2O_7)$. The degree of fill in the glass tube was found to be 50%, including the volume of undissolved solid. The glass tube was heated in a pressure vessel in which the pressure inside the tube was balanced by an external pressure to keep the tube intact. The resulting green crystalline product was removed, washed with water, rinsed with acetone, and dried in a desiccator at ambient temperature. Powder X-ray diffraction analysis of the green solid indicated a single phase of $Ca_2V(PO_4)(P_2O_7)$. Anal. Calcd for $Ca_2V(PO_4)(P_2O_7)$: Ca, 20.04; V, 12.73; P, 23.23. Found: Ca, 19.3; V, 12.4; P, 23.8.

Table I. Crystallographic and Experimental Parameters for $Ca_2V(PO_4)(HPO_4)_2{\cdot}H_2O$ (I) and $Ca_2V(PO_4)(P_2O_7)$ (II)

	I	II
formula	$H_4Ca_2O_{13}P_3V$	$Ca_2O_{11}P_3V$
fw	436.04	400.01
cryst syst	monoclinic	monoclinic
space group	$C2/c$	$P2_1/c$
a, Å	7.531 (2)	6.391 (2)
b, Å	15.522 (4)	6.6362 (9)
c, Å	9.149 (2)	19.071 (2)
β, deg	113.52 (2)	99.26 (2)
V, Å^3	980.6 (5)	798.3 (3)
Z	4	4
ρ_{calcd}, g/cm^3	2.953	3.328
μ, cm^{-1}	25.6	31.1
transm coeff		0.898–0.999
T, °C	24	24
radiation (λ, Å)	Mo Kα (0.710 73)	Mo Kα (0.709 30)
2θ range, deg	2.5–55	2.5–55
no. of data collected	1895 ($+h,+k,\pm l$)	2902 ($\pm h,+k,+l$)
no. of unique data	1139	1829
no. of data used in refinement	954	1389
R^a	0.0215	0.029
$R_w{}^b$	0.0206	0.034

$^a R = \sum ||F_o| - |F_c|| / |F_o|$. $^b R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$, $w^{-1} = \sigma^2(F_o)$.

Table II. Atomic Coordinates and Equivalent Isotropic Thermal Parameters (Å^2 × 10^2) for $Ca_2V(PO_4)(HPO_4)_2{\cdot}H_2O$

atom	x	y	z	$U_{eq}{}^a$
Ca	0.27178 (8)	0.50903 (3)	0.06319 (7)	1.18 (2)
V	0.25	0.25	0.5	0.60 (2)
P(1)	0	0.39741 (6)	0.25	0.66 (3)
P(2)	0.1703 (1)	0.15158 (4)	0.15179 (8)	0.76 (2)
O(1)	0.1848 (3)	0.3442 (1)	0.3433 (2)	1.14 (6)
O(2)	0.0375 (3)	0.4528 (1)	0.1293 (2)	1.44 (7)
O(3)	0.0872 (3)	0.0609 (1)	0.1212 (2)	1.34 (7)
O(4)	0.0345 (3)	0.2225 (1)	0.0546 (2)	1.14 (6)
O(5)	0.2522 (3)	0.1667 (1)	0.3322 (2)	1.27 (7)
O(6)	0.3374 (3)	0.1448 (1)	0.0904 (2)	1.72 (7)
H(6)^b	0.9069	0.6865	0.0898	8 (2)
O(7)	0.5	0.3994 (2)	0.25	1.8 (1)
H(7)^b	0.5730	0.3679	0.2256	5 (1)

$^a U_{eq}$ is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor. ^{b}The atomic coordinates for both H atoms are fixed.

Table III. Atomic Coordinates and Equivalent Isotropic Thermal Parameters (Å^2) for $Ca_2V(PO_4)(P_2O_7)$

atom	x	y	z	$B_{iso}{}^a$
Ca(1)	0.67011 (18)	0.64524 (19)	0.07768 (6)	0.95 (4)
Ca(2)	0.67074 (18)	−0.01060 (16)	0.27244 (7)	0.81 (4)
V	0.94683 (13)	0.14427 (13)	0.12229 (5)	0.33 (3)
P(1)	0.42809 (21)	0.15421 (20)	0.08817 (7)	0.41 (5)
P(2)	0.17104 (22)	−0.20579 (20)	0.04854 (7)	0.49 (5)
P(3)	0.18400 (21)	−0.01081 (19)	0.27365 (7)	0.38 (5)
O(1)	0.9807 (6)	−0.1271 (5)	0.08165 (19)	0.61 (13)
O(2)	0.2728 (5)	0.2026 (5)	0.13890 (19)	0.60 (4)
O(3)	0.3098 (6)	−0.3427 (5)	0.09743 (19)	0.94 (14)
O(4)	0.6340 (5)	0.0590 (5)	0.12566 (19)	0.69 (14)
O(5)	0.4696 (6)	0.3267 (5)	0.04101 (19)	0.74 (14)
O(6)	0.9070 (6)	0.2820 (5)	0.02645 (19)	0.71 (14)
O(7)	0.3121 (6)	−0.0121 (6)	0.03447 (19)	0.71 (14)
O(8)	0.9856 (6)	0.0354 (5)	0.21851 (19)	0.73 (14)
O(9)	0.3267 (6)	−0.1680 (6)	0.24845 (20)	0.87 (14)
O(10)	0.9081 (6)	0.4193 (5)	0.15898 (19)	0.58 (13)
O(11)	0.3143 (5)	0.1757 (5)	0.29667 (19)	0.76 (14)

$^a B_{iso}$ is the mean of the principal axes of the thermal ellipsoid.

Thermal Analysis. Thermogravimetric (TG) analysis, using a Du Pont 951 thermogravimetric analyzer, was performed on a powder sample of $Ca_2V(PO_4)(HPO_4)_2{\cdot}H_2O$. The experiment was performed in flowing N_2 with a heating rate of 5 °C/min. In order to characterize the decomposition product, an experiment was performed in which $Ca_2V(PO_4)(HPO_4)_2{\cdot}H_2O$ was heated in flowing N_2 at 700 °C for 12 h. The product of this heat treatment was analyzed by powder X-ray diffraction.

Single-Crystal X-ray Diffraction. Two green crystals having the dimensions of 0.14 × 0.16 × 0.18 mm for $Ca_2V(PO_4)(HPO_4)_2{\cdot}H_2O$ and 0.05 × 0.05 × 0.20 mm for $Ca_2V(PO_4)(P_2O_7)$ were selected for indexing and intensity data collection on a Nicolet R3m/V four-circle diffractometer and an Enraf-Nonius CAD4 diffractometer with κ-axis geometry using monochromated Mo Kα radiation, respectively. Axial oscillation photographs along the three axes were taken to check the symmetry properties and unit cell parameters. The intensity data for $Ca_2V(PO_4)(P_2O_7)$ were corrected for Lp and absorption effects, but no absorption corrections were applied to $Ca_2V(PO_4)(HPO_4)_2{\cdot}H_2O$. Corrections 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.[16] On the basis of the systematic absences, statistical analyses of the intensity data, and successful solution and refinement of the structures, the space groups were determined to be $C2/c$ and $P2_1/c$ for $Ca_2V(PO_4)(HPO_4)_2{\cdot}H_2O$ and $Ca_2V(PO_4)(P_2O_7)$, respectively. Direct methods (SHELXTL PLUS) were used to locate the metal atoms of $Ca_2V(PO_4)(HPO_4)_2{\cdot}H_2O$, with the remaining non-hydrogen atoms being found from successive difference Fourier maps. Bond strength calculations were carried out to help locate any hydrogen atoms. Two oxygen atoms were found to be considerably undersaturated; valence sums of 1.25 and 0.43 valence unit were calculated for O(6) and O(7). The value for O(7) is typically associated with the presence of two hydrogen atoms. The other value suggested that O(6) is bonded to a hydrogen atom. The hydrogen atoms were located by careful scrutiny of a difference map. Subsequent refinement, including the atomic coordinates and anisotropic thermal parameters for all non-hydrogen atoms and isotropic thermal parameters for hydrogen atoms, converged at $R = 0.0215$ and $R_w = 0.0206$. Extinction effects were not observed. NRCVAX programs[17] were used in the solution and refinement of the structure of $Ca_2V(PO_4)(P_2O_7)$. The final cycle of refinement of all positional parameters, anisotropic thermal parameters for all atoms, and isotropic extinction coefficients led to convergence with $R = 0.029$ and $R_w = 0.034$, respectively. The multiplicities of Ca for both compounds were allowed to refined but did not deviate significantly from full occupancy. Therefore, the calcium metal sites were considered fully occupied in the final cycles of refinement. Neutral-atom scattering factors for all atoms were taken from standard sources.[18] Anomalous dispersion corrections were applied.

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Table IV. Bond Distances (Å) and Bond Valence Sums ($\sum s$) for $Ca_2V(PO_4)(HPO_4)_2 \cdot H_2O$

Ca–O(1)	2.935 (2)	Ca–O(2)	2.257 (2)
Ca–O(2)	2.367 (2)	Ca–O(3)	2.359 (2)
Ca–O(3)	2.565 (2)	Ca–O(3)	2.769 (2)
Ca–O(5)	2.660 (2)	Ca–O(6)	2.725 (2)
Ca–O(7)	2.535 (2)		
	$\sum s$(Ca–O) = 2.03		
V–O(1)	1.968 (2) (2×)[a]	V–O(4)	2.042 (2) (2×)
V–O(5)	2.013 (2) (2×)		
	$\sum s$(V–O) = 2.94		
P(1)–O(1)	1.549 (2) (2×)	P(1)–O(2)	1.512 (2) (2×)
	$\sum s$(P(1)–O) = 5.05		
P(2)–O(3)	1.521 (2)	O(2)–O(4)	1.524 (2)
P(2)–O(5)	1.532 (2)	P(2)–O(6)	1.573 (3)
	$\sum s$(P(2)–O) = 4.96		
O(6)–H(6)	0.834	O(7)–H(7)	0.830 (2×)

[a] Number of times the distance occurs per formula unit.

Table V. Bond Distances (Å) and Bond Valence Sums ($\sum s$) for $Ca_2V(PO_4)(P_2O_7)$

Ca(1)–O(1)	2.486 (4)	Ca(1)–O(3)	2.394 (4)
Ca(1)–O(4)	2.915 (4)	Ca(1)–O(5)	2.512 (4)
Ca(1)–O(5)	2.304 (4)	Ca(1)–O(6)	3.087 (4)
Ca(1)–O(10)	2.491 (4)	Ca(1)–O(11)	2.391 (4)
	$\sum s$(Ca(1)–O) = 1.88		
Ca(2)–O(2)	2.533 (4)	Ca(2)–O(3)	2.705 (4)
Ca(2)–O(4)	2.809 (4)	Ca(2)–O(8)	2.422 (4)
Ca(2)–O(9)	2.411 (4)	Ca(2)–O(9)	2.309 (4)
Ca(2)–O(10)	2.835 (4)	Ca(2)–O(11)	2.697 (4)
Ca(2)–O(11)	2.474 (4)		
	$\sum s$(Ca(2)–O) = 1.94		
V–O(1)	1.986 (4)	V–O(2)	2.092 (4)
V–O(4)	2.089 (4)	V–O(6)	2.023 (4)
V–O(8)	1.950 (4)	V–O(10)	1.985 (4)
	$\sum s$(V–O) = 2.86		
P(1)–O(2)	1.527 (3)	P(1)–O(4)	1.530 (4)
P(1)–O(5)	1.505 (4)	P(1)–O(7)	1.604 (4)
	$\sum s$(P(1)–O) = 4.93		
P(2)–O(1)	1.549 (4)	P(2)–O(3)	1.488 (4)
P(2)–O(6)	1.523 (4)	P(2)–O(7)	1.617 (4)
	$\sum s$(P(2)–O) = 4.91		
P(3)–O(8)	1.542 (4)	P(3)–O(9)	1.514 (4)
P(3)–O(10)	1.567 (4)	P(3)–O(11)	1.517 (4)
	$\sum s$(P(3)–O) = 5.00		

Results and Discussion

Thermal Analysis. The TG analysis on $Ca_2V(PO_4)(HPO_4)_2 \cdot H_2O$ shows a one-step weight loss from 400 to 700 °C with a maximum slope at 600 °C. The weight loss (8.1%) corresponds to the loss of two water molecules and can be compared with the calculated value of 8.26%. On the basis of powder X-ray analysis, the product of dehydration at 700 °C is $Ca_2V(PO_4)(P_2O_7)$.

Structure. The crytallographic data for both compounds are listed in Table I. The atomic coordinates, thermal parameters, selected bond distances, and bond valence sums[19] are listed in Tables II–V. Bond valence sums for the cations in both compounds are in good accord with their formal oxidation states. Both structures are new structure types.

$Ca_2V(PO_4)(HPO_4)_2 \cdot H_2O$. The structure consists of infinite chains of corner-sharing VO_6 octahedra, PO_4 tetrahedra, and HPO_4 groups, as shown in Figure 1. The PO_4 and HPO_4 groups form bridges over adjacent VO_6 octahedra, forming ${}^{1}_{\infty}[V(PO_4)_{2/2}(HPO_4)_{4/2}]$ along the [101] direction. The coordination sphere of the V atom, which lies on a site of $\bar{1}$ symmetry, is an almost regular octahedron typical of V^{3+}. As shown in Figure 2, adjacent infinite chains are held together by hydrogen bonding through water molecules and the HPO_4 groups to form layers within the *ac* plane. The oxygen-to-oxygen distances in the hydrogen bonds are 2.821 (3) Å for O(6)–O(4) and 2.952 (2) Å for O(7)–O(1). Atom O(4) of the HPO_4 group acts as a hydrogen-bond acceptor from the hydrogen atom of a HPO_4 group in an adjacent chain. The hydrogen atoms of the water molecule are hydrogen bonded to two PO_4 groups in two different chains.

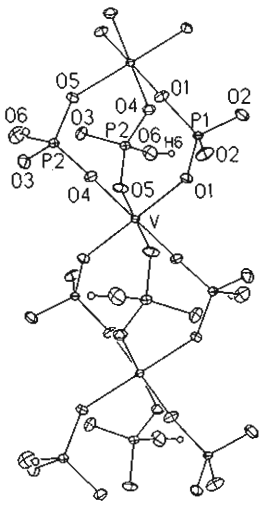

Figure 1. Section of an infinite chain of corner-sharing VO_6 octahedra, PO_4 tetrahedra, and HPO_4 groups in $Ca_2V(PO_4)(HPO_4)_2 \cdot H_2O$. Thermal ellipsoids are shown at the 60% probability level.

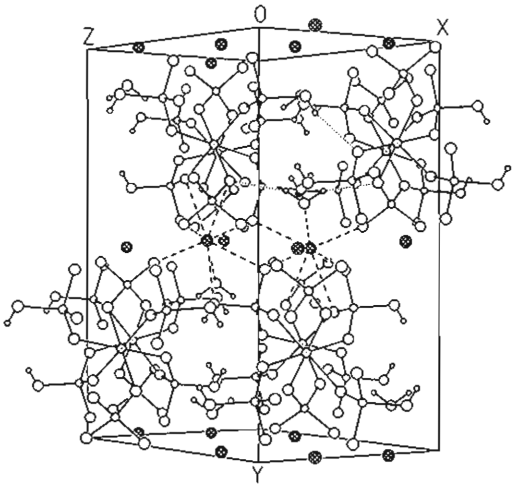

Figure 2. View of the $Ca_2V(PO_4)(HPO_4)_2 \cdot H_2O$ structure along the [101] direction: cross-hatched circles, Ca atoms; dotted circles, V atoms; medium open circles, P atoms; large open circles, O atoms; small open circles, H atoms. The hydrogen bonds and O–Ca–O bonds are represented by dotted and dashed lines, respectively.

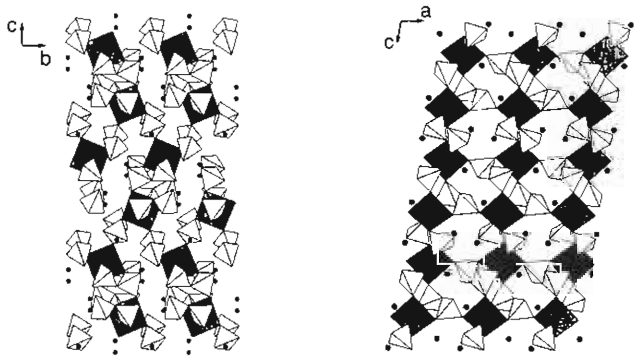

Figure 3. Structure of $Ca_2V(PO_4)(P_2O_7)$ as viewed (a, left) along the *a* axis and (b, right) along the *b* axis. In this representation, the corners of octahedra and tetrahedra are O^{2-} ions and the V and P ions are at the center of each octahedron and tetrahedron, respectively. Solid circles are Ca^{2+} ions.

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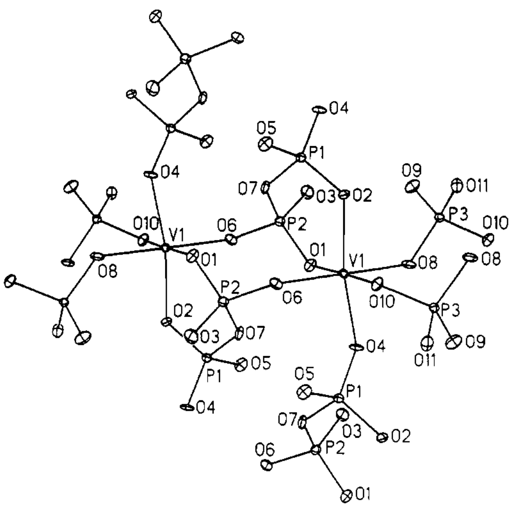

Figure 4. Structure of $Ca_2V(PO_4)(P_2O_7)$ showing the coordination of PO_4 and P_2O_7 ligands around VO_6 octahedra. Thermal ellipsoids are shown at the 60% probability level.

Connection between adjacent layers is provided by O–Ca–O bonds, as shown by the dashed lines in Figure 2. The water molecules are also coordinated to the Ca atoms. Thus, in the TG analysis the release of one lattice water molecule, which occurs at rather high temperature, is not resolved from the second step corresponding to the condensation of two HPO_4 groups to a P_2O_7 group. The coordination number (CN) of Ca is assinged on the basis of two criteria: the maximum gap in the Ca–O distances and the bond valence sums for Ca. Therefore, the Ca atom is coordinated by nine oxygen atoms with an average Ca–O distance of 2.575 Å.

$Ca_2V(PO_4)(P_2O_7)$. The structure of this compound, viewed along the *a* and *b* axes, is shown in Figure 3. It contains intersecting channels where the Ca^{2+} cations are located. The framework consists of corner-sharing VO_6 octahedra, PO_4 tetrahedra, and P_2O_7 groups. The conversion of $Ca_2V(PO_4)(HPO_4)_2 \cdot H_2O$ to $Ca_2V(PO_4)(P_2O_7)$ is difficult to explain mechanistically. To our knowledge, $Ca_2V(PO_4)(P_2O_7)$ is the first vanadium phosphate containing both PO_4 and P_2O_7 groups in the structure. As shown in Figure 4, each VO_6 octahedron shares its corners with two PO_4 and three P_2O_7 groups. One of the diphosphate groups is coordinated to the V atom as a bidentate ligand. The VO_6 octahedron in the dehydrated compound is more distorted than that in the hydrate as shown by the V–O bond lengths. Each phosphate group shares two corners with two VO_6 octahedra, with the remaining two oxygen atoms being bonded to the Ca atoms. Each diphosphate group is bonded to a V atom as a chelate and bonded to two V atoms as a monodentate ligand. The remaining two oxygen atoms of the diphosphate group are bonded to the Ca atoms only. The PO_4 tetrahedra of a P_2O_7 group are in a semieclipsed configuration. The P atoms are displaced away from the bridging oxygen atoms, O(7), so that one longer and three shorter P–O bonds are formed. The P(1)–O(7)–P(2) bond angle is 130.8 (2)°. Atoms Ca(1) and Ca(2) occupy sites within the channels and are eight- and nine-coordinated, with average Ca–O distances of 2.572 and 2.577 Å, respectively. The connectivity formula can be represented as $^{3}_{\infty}Ca_2[V(PO_4)_{2/2}(P_2O_7)_{1/3}(P_2O_7)_{2/3}]$.

Hydrothermal techniques are useful for the synthesis of new phases in the form of single crystals suitable for structure analysis. $Ca_2V(PO_4)(HPO_4)_2 \cdot H_2O$, which contains hydrogen phosphate groups and a water of hydration, was synthesized under mild conditions. Interestingly, crystals of the dehydrated compound, $Ca_2V(PO_4)(P_2O_7)$, were obtained under much more vigorous conditions. This research shows that the use of different *PT* conditions can aid the search for new crystalline phases.

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Supplementary Material Available: Tables of anisotropic thermal parameters and bond angles (5 pages); tables of observed and calculated structure factors for both compounds (13 pages). Ordering information is given on any current masthead page.

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1,4-Phenylene-Bridged 1,3,2,4,6-Thia- and 1,3,2,4,6-Selenaphosphatriazinyl Diradicals: Preparation, Spin Distributions, and Solid-State Structures

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The 1,4-phenylene-bridged bis(1,3,2,4,6-thiaphosphatriazine) and bis(1,3,2,4,6-selenaphosphatriazine) compounds $(ClEN_3PPh_2C)C_6H_4(CPPh_2N_3ECl)$ (E = S, Se) have been prepared by the reactions of 1,4-phenylenebis(phosphimidoylamidine), $(Me_3Si)_2NPPh_2(Me_3SiN)CC_6H_4C(NSiMe_3)PPh_2N(SiMe_3)_2$, with SCl_2 and $SeCl_4$. Reduction of these *E*-chloro derivatives with triphenylantimony affords the corresponding bis(thiaphosphatriazinyl) and bis(selenaphosphatriazinyl) diradicals, $(EN_3PPh_2C)C_6H_4(CPPh_2N_3E)$ (E = S, Se). The ESR spectra of these materials in CH_2Cl_2 are consistent with noninteracting radicals, an observation suggested to arise from association of radicals through a single terminus. The solid-state structure of the selenium compound, $(SeN_3PPh_2C)C_6H_4(CPPh_2N_3Se)$, reveals association through both termini to produce a centrosymmetric dimer. Association occurs through Se–N rather than Se–Se linkages. Crystals of $C_{32}H_{24}N_6P_2Se_2 \cdot 2CH_3CN$ belong to the rhombohedral space group $R\bar{3}$; fw = 794.6, a = 34.431 (12) Å, c = 17.513 (4) Å, and Z = 9.

Introduction

There is growing interest in the study of heterocyclic thiazyl and selenazyl radicals, in particular the factors that control the nature and strength of their association, both in solution and in the solid state.[1] Such interactions are known to provide pathways for structural change[2,3] and, in suitably designed cases, provide solid-state structures with interesting electrical and magnetic properties.[4,5] Within the context of both these issues, we recently

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