Hydrothermal Synthesis and Structural Characterization of Four Layered Vanadyl(IV) Phosphate Hydrates $A(VO)_2(PO_4)_2{\cdot}4H_2O$ (A = Co, Ca, Sr, Pb)

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The single crystals of four vanadyl(IV) phosphate hydrates $A(VO)_2(PO_4)_2{\cdot}4H_2O$ (A = Co, Ca, Sr, Pb) were grown hydrothermally at 230 °C and were characterized by single-crystal X-ray diffraction and thermal analysis. Crystal data: $Co(VO)_2(PO_4)_2{\cdot}4H_2O$, tetragonal, $I4/mmm$, $a = 6.264$ (1) Å, $c = 13.428$ (4) Å, $V = 526.9$ (2) Å^3, $Z = 2$, and $R = 0.0527$; $Ca(VO)_2(PO_4)_2{\cdot}4H_2O$, triclinic, $P1$, $a = 6.3484$ (8) Å, $b = 6.350$ (1) Å, $c = 6.597$ (1) Å, $\alpha = 106.81$ (2)°, $\beta = 94.09$ (1)°, $\gamma = 90.02$ (1)°, $V = 253.86$ (8) Å^3, $Z = 1$, and $R = 0.0221$; $Sr(VO)_2(PO_4)_2{\cdot}4H_2O$, monoclinic, Cc, $a = 9.026$ (2) Å, $b = 9.010$ (3) Å, $c = 12.841$ (3) Å, $\beta = 100.19$ (2)°, $V = 1027.8$ (1) Å^3, $Z = 4$, and $R = 0.0350$; $Pb(VO)_2(PO_4)_2{\cdot}4H_2O$, monoclinic, Cc, $a = 9.030$ (3) Å, $b = 9.021$ (2) Å, $c = 12.874$ (4) Å, $\beta = 100.16$ (2)°, $V = 1032.3$ (5) Å^3, $Z = 4$, and $R = 0.0307$. All four structures contain layers of vanadium phosphorus oxide with the water molecules and divalent metal cations between the layers. The layer is a 4-connected net in which corner-sharing vanadium oxygen polyhedra and phosphate tetrahedra alternate. In $Co(VO)_2(PO_4)_2{\cdot}4H_2O$ the vanadium is 5-coordinated in form of square pyramids. In the Ca, Sr, and Pb compounds, the vanadium oxygen polyhedra are distorted octahedra. The Co compound contains units of linear V═O—Co—O═V. The structure of the Ca compound reported in this work is a triclinic polymorph of the rare mineral sincosite. The Sr and Pb compounds are isostructural. The four structures are discussed along with the parent $VOPO_4{\cdot}2H_2O$.

Introduction

We have recently reported hydrothermal synthesis and structural characterization of a number of new compounds in the ternary vanadium phosphate system.[1–6] Among these compounds the layered mixed-valence vanadyl phosphate hydrates $A_{0.5}VOPO_4{\cdot}xH_2O$ (A = Na, $x = 2$; A = K, $x = 1.5$)[3] are particularly interesting, since they were originally prepared by redox intercalation reactions of $VOPO_4{\cdot}2H_2O$ with metal iodides in aqueous solutions, and they are the first intercalation reactions in which the charge transfer proceeds chemically but not electrochemically.[7,8] On the basis of X-ray powder diffraction, it was reported that the basic tetragonal structure of $VOPO_4{\cdot}2H_2O$ was essentially maintained and cations were incorporated into the interlayer spaces. Detailed structural information was unavailable since the intercalation reaction often yields polycrystalline products that are difficult to characterize. Interestingly, the phases prepared by the hydrothermal method crystallize in a lower symmetry than that from the intercalation reaction (triclinic vs tetragonal), although they have similar alkali metal and water contents. Since it was reported that $VOPO_4{\cdot}2H_2O$ also underwent redox intercalation reactions with $MI_{2(aq)}$ (M = Mg, Mn, Co, Ni, Zn), it is of interest to pursue the hydrothermal synthesis of the analogues containing divalent metal cations. Single crystals of $Ni(VO)_2(PO_4)_2{\cdot}3H_2O$ and $Co(VO)_2(PO_4)_2{\cdot}4H_2O$ have been obtained hydrothermally. Their Ni/Co and water contents are different from those prepared by the intercalation reaction. The Ni compound, which crystallizes in a new structural type, consists of units of one NiO_6 and two VO_6 octahedra sharing a common oxygen.[6] In contrast, the basic structure of $VOPO_4{\cdot}2H_2O$ is maintained in the Co compound. Attempts to grow crystals of the Mg, Mn, and Zn compounds have been unsuccessful. However, crystals of the Ca, Sr, and Pb compounds can be readily obtained. We report here the hydrothermal synthesis and structural characterization of four vanadyl(IV) phosphate hydrates $A(VO)_2(PO_4)_2{\cdot}4H_2O$ (A = Co, Ca, Sr, Pb). Their crystal structures are discussed along with the parent $VOPO_4{\cdot}2H_2O$.

Table I. Crystallographic Data for $Co(VO)_2(PO_4)_2{\cdot}4H_2O$ (I), $Ca(VO)_2(PO_4)_2{\cdot}4H_2O$ (II), $Sr(VO)_2(PO_4)_2{\cdot}4H_2O$ (III), and $Pb(VO)_2(PO_4)_2{\cdot}4H_2O$ (IV)

	I	II	III	IV
chem formula	$H_8CoO_{14}P_2V_2$	$H_8CaO_{14}P_2V_2$	$H_8SrO_{14}P_2V_2$	$H_8PbO_{14}P_2V_2$
fw	454.8	436.0	483.5	603.1
space group	$I4/mmm$ (No. 139)	$P1$ (No. 1)	Cc (No. 9)	Cc (No. 9)
a, Å	6.264 (1)	6.3484 (8)	9.026 (2)	9.030 (3)
b, Å		6.350 (1)	9.010 (3)	9.021 (2)
c, Å	13.428 (4)	6.597 (1)	12.841 (3)	12.874 (4)
α, deg		106.81 (2)		
β, deg		94.09 (1)	100.19 (2)	100.16 (2)
γ, deg		90.02 (1)		
V, Å^3	526.9 (2)	253.86 (8)	1027.8 (1)	1032.3 (5)
Z	2	1	4	4
T, °C	24	24	24	24
λ, Å	0.710 73	0.710 73	0.710 73	0.710 73
ρ_{calcd}, g/cm^3	2.867	2.852	3.125	3.880
μ, cm^{-1}	36.16	26.69	71.32	185.0
2θ range, deg	2.5–55	2.5–55	2.5–55	2.5–55
$R(F_o)^a$	0.0527	0.0221	0.0350	0.0307
$R_w(F_o)^b$	0.0715	0.0248	0.0357	0.0304

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

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Table II. Positional Parameters and Equivalent Isotropic Thermal Parameters (Å^2 × 100) for $Co(VO)_2(PO_4)_2 \cdot 4H_2O$ (I), $Ca(VO)_2(PO_4)_2 \cdot 4H_2O$ (II), $Sr(VO)_2(PO_4)_2 \cdot 4H_2O$ (III), and $Pb(VO)_2(PO_4)_2 \cdot 4H_2O$ (IV)

	x	*y*	*z*	U_{eq}^a		*x*	*y*	*z*	U_{eq}^a
Compound I									
Co	0.5	0.5	0	1.3 (1)	O(1)	0.5	0.5	0.841 (1)	1.8 (3)
V	0.5	0.5	0.7219 (2)	0.6 (1)	O(2)	0.803 (1)	0.5	0.6824 (5)	1.8 (2)
P	0	0.5	0.75	0.6 (1)	O(3)^{b,c,d}	0.782 (3)	0.684 (3)	0	3.0 (5)
Compound II									
Ca	0.6502 (2)	0.9010 (2)	0.4983 (2)	1.57 (3)	O(8)	0.8192 (5)	0.7560 (5)	0.1738 (5)	0.87 (9)
V(1)	0.3422	0.8625	0.9413	0.58 (2)	O(9)	1.1632 (5)	0.4687 (5)	0.1868 (5)	0.99 (9)
V(2)	0.8504 (1)	0.4292 (1)	0.1218 (1)	0.59 (2)	O(10)	0.5459 (6)	0.4344 (5)	0.1875 (5)	1.0 (1)
P(1)	0.3425 (2)	0.3978 (2)	0.0367 (2)	0.61 (3)	O(11)	0.8708 (5)	0.1351 (5)	0.1720 (5)	0.98 (9)
P(2)	0.8430 (2)	0.8987 (2)	0.0235 (2)	0.56 (3)	O(12)^b	0.8516 (6)	0.5597 (6)	0.5017 (5)	1.4 (1)
O(1)	0.3839 (6)	0.9241 (5)	1.1944 (5)	1.2 (1)	H(12A)	0.7724	0.4634	0.5401	5.0
O(2)	0.3508 (6)	0.5342 (5)	0.8775 (5)	1.0 (1)	H(12B)	0.9718	0.5109	0.5369	5.0
O(3)	0.0313 (5)	0.8279 (5)	0.8876 (5)	1.0 (1)	O(13)^b	0.5340 (6)	0.2701 (5)	0.5342 (5)	1.6 (1)
O(4)	0.3142 (6)	1.1589 (5)	0.8991 (5)	1.1 (1)	H(13A)	0.4124	0.3635	0.6235	5.0
O(5)	0.6473 (5)	0.8743 (5)	0.8653 (5)	0.9 (1)	H(13B)	0.5388	0.3256	0.4191	5.0
O(6)^b	0.3090 (5)	0.7744 (5)	0.5608 (5)	1.2 (1)	O(14)^b	0.0079 (6)	0.0624 (6)	0.5403 (5)	1.7 (1)
H(6A)	0.2599	0.8897	0.5531	5.0	H(14A)	0.0078	0.1522	0.4607	5.0
H(6B)	0.2517	0.6506	0.4537	5.0	H(14B)	0.0706	−0.0356	0.4631	5.0
O(7)	0.8354 (7)	0.3571 (6)	−0.1299 (6)	1.7 (1)					
Compound III									
Sr	0.73479	0.1909 (1)	0.27927	1.36 (3)	O(10)	0.557 (1)	0.2542 (8)	1.1023 (6)	1.1 (2)
V(1)	0.8576 (3)	0.1068 (2)	0.9834 (2)	0.74 (6)	O(11)^b	0.8324 (9)	0.0874 (9)	0.7912 (7)	1.5 (2)
V(2)	0.8826 (3)	0.6111 (2)	1.0722 (2)	0.72 (6)	H(11A)	0.7737	0.1340	0.7196	5.0
P(1)	0.6214 (5)	0.3563 (2)	1.0259 (3)	0.74 (7)	H(11B)	0.9241	0.0667	0.7626	5.0
P(2)	0.6216 (5)	0.8566 (2)	1.0278 (3)	0.67 (6)	O(12)^b	0.945 (1)	0.6017 (9)	1.2603 (6)	1.5 (2)
O(1)	0.875 (1)	0.1131 (9)	1.1093 (7)	1.4 (3)	H(12A)	0.9626	0.6442	1.3258	5.0
O(2)	0.700 (1)	0.2662 (9)	0.9470 (7)	1.4 (3)	H(12B)	0.8457	0.5566	1.2384	5.0
O(3)	0.998 (1)	−0.0544 (9)	0.9548 (7)	1.5 (3)	O(13)^b	0.624 (1)	0.4597 (8)	0.2780 (7)	1.6 (2)
O(4)	0.6966 (9)	−0.0497 (8)	0.9509 (6)	1.0 (2)	H(13A)	0.6330	0.5436	0.3234	5.0
O(5)	1.011 (1)	0.2545 (9)	0.9545 (7)	1.2 (2)	H(13B)	0.5866	0.4978	0.2065	5.0
O(6)	0.847 (1)	0.6225 (9)	0.9477 (8)	1.7 (3)	O(14)^b	0.990 (1)	0.307 (1)	0.2777 (7)	1.9 (3)
O(7)	0.735 (1)	0.4563 (9)	1.0963 (6)	1.5 (3)	H(14A)	1.0529	0.2848	0.2374	5.0
O(8)	0.738 (1)	0.7674 (9)	1.1045 (7)	1.3 (3)	H(14B)	0.9869	0.4099	0.2824	5.0
O(9)	1.044 (1)	0.4556 (9)	1.0999 (7)	1.4 (3)					
Compound IV									
Pb	0.73479	0.19037 (5)	0.27927	1.95 (2)	O(9)	1.039 (1)	0.457 (1)	1.0974 (8)	1.2 (2)
V(1)	0.8570 (3)	0.1096 (2)	0.9829 (2)	0.81 (6)	O(10)	0.552 (1)	0.256 (1)	1.1013 (8)	1.2 (2)
V(2)	0.8805 (3)	0.6120 (3)	1.0718 (2)	0.88 (6)	O(11)^{b,e}	0.829 (1)	0.091 (1)	0.7915 (8)	1.5 (3)
P(1)	0.6193 (5)	0.3583 (4)	1.0252 (4)	0.85 (8)	H(11A)	0.7620	0.1107	0.7403	5.0
P(2)	0.6190 (4)	0.8591 (4)	1.0272 (4)	0.85 (8)	O(12)^b	0.937 (1)	0.601 (1)	1.2586 (8)	1.7 (3)
O(1)	0.876 (1)	0.113 (1)	1.1086 (8)	1.7 (3)	H(12A)	0.9899	0.7072	1.2733	5.0
O(2)	0.697 (1)	0.268 (1)	0.9471 (9)	1.4 (3)	H(12B)	0.9496	0.5324	1.2992	5.0
O(3)	0.996 (1)	−0.053 (1)	0.9549 (7)	1.3 (3)	O(13)^{b,e}	0.618 (1)	0.464 (1)	0.2753 (8)	1.9 (3)
O(4)	0.694 (1)	−0.046 (1)	0.9498 (8)	1.4 (3)	H(13A)	0.5344	0.4253	0.1995	5.0
O(5)	1.008 (1)	0.258 (1)	0.9541 (9)	1.3 (3)	O(14)^b	0.993 (1)	0.307 (1)	0.2795 (8)	1.7 (3)
O(6)	0.846 (1)	0.622 (1)	0.947 (1)	1.9 (3)	H(14A)	1.0927	0.3181	0.2622	5.0
O(7)	0.731 (1)	0.459 (1)	1.0972 (8)	1.3 (3)	H(14B)	0.9810	0.1896	0.2829	5.0
O(8)	0.735 (1)	0.768 (1)	1.1033 (9)	1.2 (3)					

[a] U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor. The thermal parameters for all the H atoms are fixed. [b] Water oxygen atom. [c] The H atoms are not located. [d] The occupancy factor is 0.5. [e] Only one H atom is located.

Experimental Section

Synthesis. Reagent grade chemicals were used as received. The condition for the crystal growth of $Sr(VO)_2(PO_4)_2 \cdot 4H_2O$ consisted of a mixture of 0.101 g of V_2O_3, 0.122 g of V_2O_5, 0.716 g of $Sr(OH)_2 \cdot 8H_2O$, 0.6 mL of 85% H_3PO_4, and 11 mL of H_2O in a 23-mL Teflon-lined autoclave (molar ratio Sr:V:P = 1:1:∼3). The reaction vessel was maintained at 230 °C and autogenous pressure for 4 d before slow cooling at 5 °C/h to room temperature. Visual microscopic inspection showed that there were many light green tabular crystals in the product. A single-crystal X-ray diffraction study showed the crystal to be the new compound $Sr(VO)_2(PO_4)_2 \cdot 4H_2O$ (vide infra). Subsequently, it was found that $Sr(VO)_2(PO_4)_2 \cdot 4H_2O$ could be obtained as a major product by heating a mixture of 0.445 g of VO_2, 0.709 g of $Sr(OH)_2 \cdot 8H_2O$, 1.2 mL of 85% H_3PO_4, and 10.5 mL of H_2O (molar ratio Sr:V:P = 1:2:∼6.5) under similar reaction conditions. The product was filtered, washed with water, rinsed with acetone, and dried in a desiccator at ambient temperature. As shown by X-ray powder analysis, the green product was always contaminated with a small amount of unidentified impurities. The intensity of the most intense reflection of the impurities was about 5% that of the major phase, and all other reflections in the diffraction pattern corresponded well with that calculated from the single-crystal data. The amounts of Sr, V, and P were determined by using an ICP-AE spectrometer after dissolving a sample in dilute aqua regia. Anal. Calcd for $Sr(VO)_2(PO_4)_2 \cdot 4H_2O$: Sr, 18.12; V, 21.07; P, 12.81. Found: Sr, 18.3; V, 21.6; P, 12.7.

The crystal growth of the Co, Ca, and Pb compounds were achieved under the following conditions. For $Co(VO)_2(PO_4)_2 \cdot 4H_2O$, a mixture of 0.200 g of CoO, 0.200 g of V_2O_3, 0.243 g of V_2O_5, 1.5 mL of 85% H_3PO_4, and 8.5 mL of H_2O (molar ratio Co:V:P = 1:2:∼2.5) was heated in a 23-mL Teflon-lined autoclave at 230 °C for 5 days before slow cooling at 10 °C/h to room temperature. The product was a mixture of green tabular crystals of the Co compound and unidentified materials. For $Ca(VO)_2(PO_4)_2 \cdot 4H_2O$, a mixture of 0.175 g of $Ca(OH)_2$, 0.377 g of VO_2, 0.232 g of V_2O_5, 1.5 mL of 85% H_3PO_4, and 10.5 mL of H_2O was heated at 230 °C for 4 days (molar ratio Ca:V:P = 1:3:∼9). In addition to the green rhombic tabular crystals of $Ca(VO)_2(PO_4)_2$[9] and dark green low-quality square tabular crystals, a very small amount of bluish green tabular crystals of $Ca(VO)_2(PO_4)_2 \cdot 4H_2O$ also crystallized from the reaction mixture. The dark green crystals are often very thin and platy. Preliminary X-ray study on a dark green crystal shows that

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Table III. Selected Bond Lengths (Å) and Bond Valence Sums (Σs) for $Co(VO)_2(PO_4)_2{\cdot}4H_2O$ (I), $Ca(VO)_2(PO_4)_2{\cdot}4H_2O$ (II), $Sr(VO)_2(PO_4)_2{\cdot}4H_2O$ (III), and $Pb(VO)_2(PO_4)_2{\cdot}4H_2O$ (IV)

Compound I							
Co–O(1)	2.14 (1) (2×)	Co–O(3)	2.11 (2) (4×)	P–O(2)	1.532 (8) (4×)		
Σs(Co–O) = 1.89				Σs(P–O) = 5.03			
V–O(1)	1.60 (1)	V–O(2)	1.971 (9) (4×)				
Σs(V–O) = 4.06							
Compound II							
Ca–O(1)	2.566 (4)	Ca–O(5)	2.477 (4)	P(1)–O(2)	1.545 (4)	P(1)–O(4)	1.529 (3)
Ca–O(6)	2.414 (4)	Ca–O(8)	2.402 (4)	P(1)–O(9)	1.543 (4)	P(1)–O(10)	1.547 (3)
Ca–O(12)	2.522 (4)	Ca–O(13)	2.408 (4)	Σs(P(1)–O) = 4.91			
Ca–O(14)	2.455 (4)			P(2)–O(3)	1.534 (4)	P(2)–O(5)	1.542 (3)
Σs(Ca–O) = 1.86				P(2)–O(8)	1.539 (4)	P(2)–O(11)	1.539 (3)
V(1)–O(1)	1.603 (3)	V(1)–O(2)	2.006 (3)	Σs(P(2)–O) = 4.95			
V(1)–O(3)	1.981 (3)	V(1)–O(4)	1.987 (3)	O(6)–H(6A)	0.809	O(6)–H(6B)	0.945
V(1)–O(5)	2.042 (3)	V(1)–O(6)	2.402 (3)	O(12)–H(12A)	0.893	O(12)–H(12B)	0.865
Σs(V(1)–O) = 4.03				O(13)–H(13A)	1.076	O(13)–H(13B)	0.927
V(2)–O(7)	1.585 (4)	V(2)–O(8)	2.015 (3)	O(14)–H(14A)	0.879	O(14)–H(14B)	0.807
V(2)–O(9)	2.001 (3)	V(2)–O(10)	2.009 (4)				
V(2)–O(11)	1.991 (4)	V(2)–O(12)	2.400 (4)				
Σs(V(2)–O) = 4.11							
Compound III							
Sr–O(1)	2.80 (1)	Sr–O(4)	2.620 (8)	P(1)–O(2)	1.56 (1)	P(1)–O(3)	1.537 (9)
Sr–O(6)	2.785 (9)	Sr–O(10)	2.604 (8)	P(1)–O(7)	1.536 (9)	P(1)–O(10)	1.535 (9)
Sr–O(11)	2.653 (8)	Sr–O(12)	2.707 (9)	Σs(P(1)–O) = 4.90			
Sr–O(13)	2.618 (8)	Sr–O(14)	2.535 (9)	P(2)–O(4)	1.544 (9)	P(2)–O(5)	1.546 (9)
Σs(Sr–O) = 1.87				P(2)–O(8)	1.535 (9)	P(2)–O(9)	1.54 (1)
V(1)–O(1)	1.598 (9)	V(1)–O(2)	2.018 (9)	Σs(P(2)–O) = 4.91			
V(1)–O(3)	2.003 (9)	V(1)–O(4)	2.015 (8)	O(11)–H(11A)	1.063	O(11)–H(11B)	0.981
V(1)–O(5)	2.004 (9)	V(1)–O(11)	2.44 (1)	O(12)–H(12A)	0.912	O(12)–H(12B)	0.977
Σs(V(1)–O) = 3.99				O(13)–H(13A)	0.949	O(13)–H(13B)	0.984
V(2)–O(6)	1.58 (1)	V(2)–O(7)	1.989 (9)	O(14)–H(14A)	0.855	O(14)–H(14B)	0.930
V(2)–O(8)	2.01 (1)	V(2)–O(9)	2.004 (9)				
V(2)–O(10)	2.015 (9)	V(2)–O(12)	2.382 (8)				
Σs(V(2)–O) = 4.14							
Compound IV							
Pb–O(1)	2.82 (1)	Pb–O(4)	2.63 (1)	P(1)–O(2)	1.55 (1)	P(1)–O(3)	1.53 (1)
Pb–O(6)	2.78 (1)	Pb–O(10)	2.645 (9)	P(1)–O(7)	1.54 (1)	P(1)–O(10)	1.55 (1)
Pb–O(11)	2.677 (9)	Pb–O(12)	2.77 (1)	Σs(P(1)–O) = 4.89			
Pb–O(13)	2.68 (1)	Pb–O(14)	2.56 (1)	P(2)–O(4)	1.56 (1)	P(2)–O(5)	1.54 (1)
Σs(Pb–O) = 1.70				P(2)–O(8)	1.54 (1)	P(2)–O(9)	1.53 (1)
V(1)–O(1)	1.60 (1)	V(1)–O(2)	2.03 (1)	Σs(P(2)–O) = 4.89			
V(1)–O(3)	2.00 (1)	V(1)–O(4)	2.02 (1)	O(11)–H(11A)	0.834	O(12)–H(12A)	1.073
V(1)–O(5)	1.99 (1)	V(1)–O(11)	2.44 (1)	O(12)–H(12B)	0.803	O(13)–H(13A)	1.179
Σs(V(1)–O) = 3.99				O(14)–H(14A)	0.969	O(14)–H(14B)	1.070
V(2)–O(6)	1.59 (1)	V(2)–O(7)	2.00 (1)				
V(2)–O(8)	2.01 (1)	V(2)–O(9)	1.99 (1)				
V(2)–O(12)	2.37 (1)	V(2)–O(10)	2.01 (1)				
Σs(V(2)–O) = 4.10							

it crystallizes in the orthorhombic space group *Pnma* and is structurally similar to $Ca(VO)_2(PO_4)_2{\cdot}4H_2O$ but with less calcium content. However, the structure has not been fully determined due to the disordering of the calcium atoms and water molecules. For $Pb(VO)_2(PO_4)_2{\cdot}4H_2O$, 0.600 g of PbO, 0.101 g of V_2O_3, 0.123 g of V_2O_5, 0.6 mL of 85% H_3PO_4, and 11 mL of H_2O was heated at 230 °C for 4 days (molar ratio Pb:V:P = 1:1:~3.3). Reactions to prepare single-phase products using starting materials in the molar ratio A:V = 1:2 and excess H_3PO_4 have been performed. Powder X-ray diffraction combined with visual microscopic inspection showed that the products for the Pb compound were always contaminated with unidentified materials and yellow crystals of $Pb(VO_2)PO_4$,[10] and the Co and Ca compounds could only be obtained as a minor product despite of numerous attempts at the synthesis. However, a small amount of the crystals of $Co(VO)_2(PO_4)_2{\cdot}4H_2O$ and $Pb(VO)_2(PO_4)_2{\cdot}4H_2O$ could be manually separated from the impurities for ICP analysis owing to the differences in color and size. Anal. Calcd for $Co(VO)_2(PO_4)_2{\cdot}4H_2O$: Co, 12.96; V, 22.40; P, 13.62. Found: Co, 12.5; V, 22.9; P, 13.0. Calcd for $Pb(VO)_2(PO_4)_2{\cdot}4H_2O$: Pb, 34.36; V, 16.89; P, 10.27. Found: Pb, 34.5; V, 16.8; P, 10.7. All the title compounds appeared air-stable in the laboratory atmosphere for at least several days and were checked by powder X-ray diffraction.

Thermal Analysis. Thermogravimetric (TG) and differential thermal (DT) analyses (a Du Pont thermal analyzer) were performed on powder samples of $Sr(VO)_2(PO_4)_2{\cdot}4H_2O$ in flowing N_2. The weight loss occurs in several steps between ~120 and ~540 °C, which corresponds to dehydration of the sample; this dehydration is also seen in DTA by endothermic peaks at 200, 250, 320, and 500 °C. A large exothermic peak on DTA occurs at ~700 °C, which has no counterpart in the TGA curve. In order to characterize the decomposition product, experiments were performed in which $Sr(VO)_2(PO_4)_2{\cdot}4H_2O$ was heated in flowing N_2 at 400, 600, and 750 °C for 16 h followed by furnace-cooling to room temperature, respectively. The brown product from the reaction at 400 °C was poorly crystalline. At 600 °C the sample changed to green and became a mixture of $Sr(VO)_2(PO_4)_2$ and unidentified materials. The reaction at 750 °C yielded a green polycrystalline product of $Sr(VO)_2(PO_4)_2$ only. The compound $Sr(VO)_2(PO_4)_2$, which is isostructural to $Ca(VO)_2(PO_4)_2$, has been characterized by powder and single-crystal X-ray diffraction.[11]

TG analysis was also performed in flowing N_2 on crushed samples of manually selected crystals of $Co(VO)_2(PO_4)_2{\cdot}4H_2O$. The dehydration product has not been characterized because of the limited amount of the sample.

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(11) Lee, T. C.; Lii, K. H. Unpublished research.

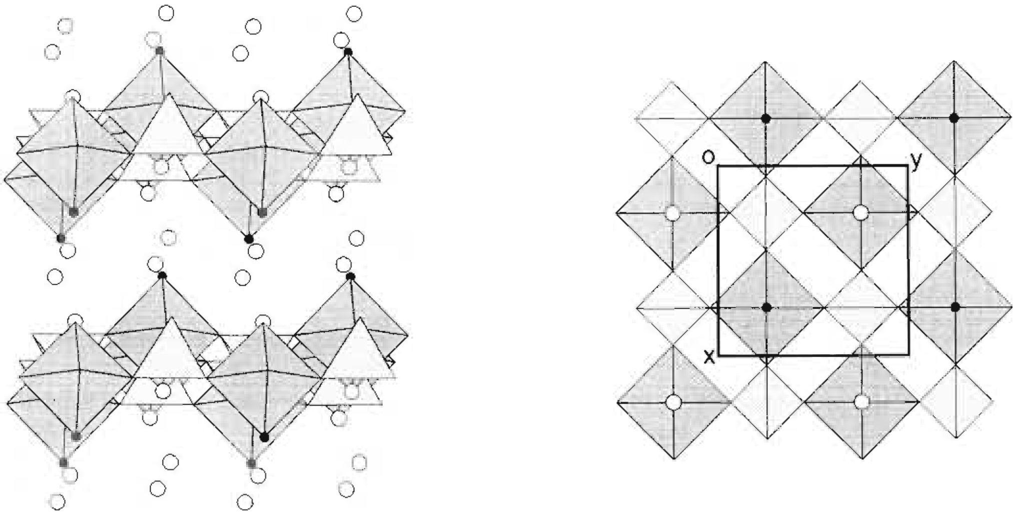

Figure 1. Left: (a) Structure of $VOPO_4{\cdot}2H_2O$. The open and solid circles represent the water oxygens and the vanadyl oxygens, respectively. H atoms are not shown. Right: (b) Section of a layer as viewed along the *c* axis.

Single-Crystal X-ray Diffraction. Four green crystals having the dimensions of 0.20 × 0.06 × 0.04 mm for $Co(VO)_2(PO_4)_2{\cdot}4H_2O$, 0.14 × 0.13 × 0.08 mm for $Ca(VO)_2(PO_4)_2{\cdot}4H_2O$, 0.18 × 0.18 × 0.08 mm for $Sr(VO)_2(PO_4)_2{\cdot}4H_2O$, and 0.22 × 0.18 × 0.08 mm for $Pb(VO)_2(PO_4)_2{\cdot}4H_2O$ 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 all four crystals were corrected for *Lp* 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 from the SHELXTL PLUS program package.[12] On the basis of the systematic absences for the Co, Sr, and Pb compounds, statistical analysis of the intensity data, and successful solution and refinement of the structures, the space groups were determined to be $I4/mmm$ for the Co compound, $P1$ for the Ca compound, and Cc for both the Sr and Pb compounds. Diret methods (SHELXTL PLUS) were used to locate the metal atoms with the remaining non-hydrogen atoms being found from successive difference maps. The hydrogen atoms were located by careful scrutiny of the difference maps and were included in the refinement. The hydrogen atoms of the Co compound could not be located, since the water oxygen O(3) was disordered in two sites with equal occupancy. The hydrogen atoms of the Pb compound could only be partially located. Although the layers of the Ca compound appears very close to centric, the refinement of the structure in $P\bar{1}$ was unsuccessful because the Ca metal and water solvate could not be refined. Tests for chirality were made for the Ca, Sr, and Pb compounds by adding to the least-squares refinement one additional parameter, called η. Refinement of η tended strongly to +1 for the Ca and Pb compounds, indicating that the configurations were correct. The low η value (+0.07) for the Sr compound could be associated with enantiomorphic twinning. All four structures were refined by full-matrix least-squares refinement based on *F* values. All of the non-hydrogen atoms were refined with anisotropic temperature factors. The atomic coordinates and isotropic thermal parameters for the hydrogen atoms were fixed. The multiplities of Co, Ca, Sr, and Pb atoms were all allowed to vary but did not deviate significantly from full occupancy. Corrections for anomalous dispersion and secondary extinction were applied. Neutral-atom scattering factors for all atoms were taken from standard sources.[13] Calculations were performed on a DEC MicroVAX II computer system using SHELXTL–PLUS programs.

Results and Discussion

Thermal Analysis. The observed total weight difference between room temperature and 600 °C agrees well with the calculated value for $Co(VO)_2(PO_4)_2{\cdot}4H_2O$ (calcd/found = 15.84%/15.8%), but is somewhat lower for $Sr(VO)_2(PO_4)_2{\cdot}4H_2O$ (calcd/found = 14.89%/13.3%). $Co(VO)_2(PO_4)_2{\cdot}4H_2O$ shows water loss in two equal steps near 250 and 380 °C, although the four water molecules are crystallogrpahically equivalent. Below ~540 °C $Sr(VO)_2(PO_4)_2{\cdot}4H_2O$ decomposes in a manner which is not clear to us. The exothermic peak at ~700 °C in the DTA curve can be interpreted by a recrystallization reaction, which means that the structure formed between ~120 and ~540 °C is metastable and at higher temperature transforms into $Sr(VO)_2(PO_4)_2$.

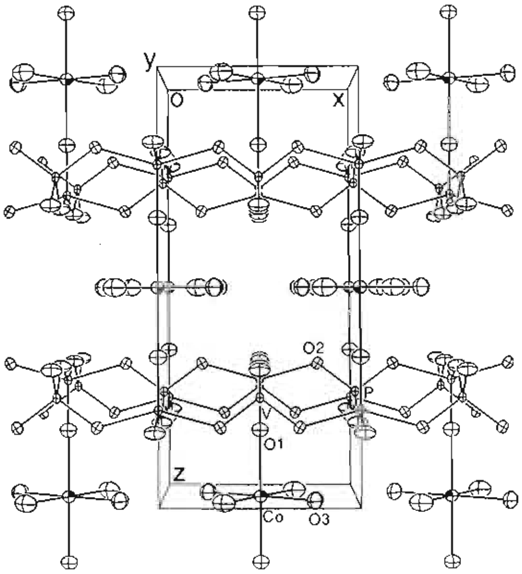

Figure 2. Structure of $Co(VO)_2(PO_4)_2{\cdot}4H_2O$. Thermal ellipsoids with shaded segments are Co atoms. H atoms are not shown.

Structure. The crystallographic data for the four compounds are listed in Table I. The atomic coordinates, thermal parameters, selected bond distances, and bond valence sums[14] are listed in Tables II and III. The coordination numbers of Ca^{2+}, Sr^{2+}, and Pb^{2+} are determined on the basis of the maximum gap in the cation–oxygen distances ranked in increasing order. The Ca^{2+} cation is coordinated by seven oxygen atoms, the eighth Ca–O bond length is 3.117 Å. Both the Sr^{2+} and Pb^{2+} cations are coordinated by eight oxygen atoms. The ninth Sr–O and Pb–O bond lengths are 3.29 and 3.22 Å, respectively. Bond valence sums for the V, P, Ca, Sr, and Co atoms are in good accordance with their formal oxidation states. The value for Pb is somewhat lower.

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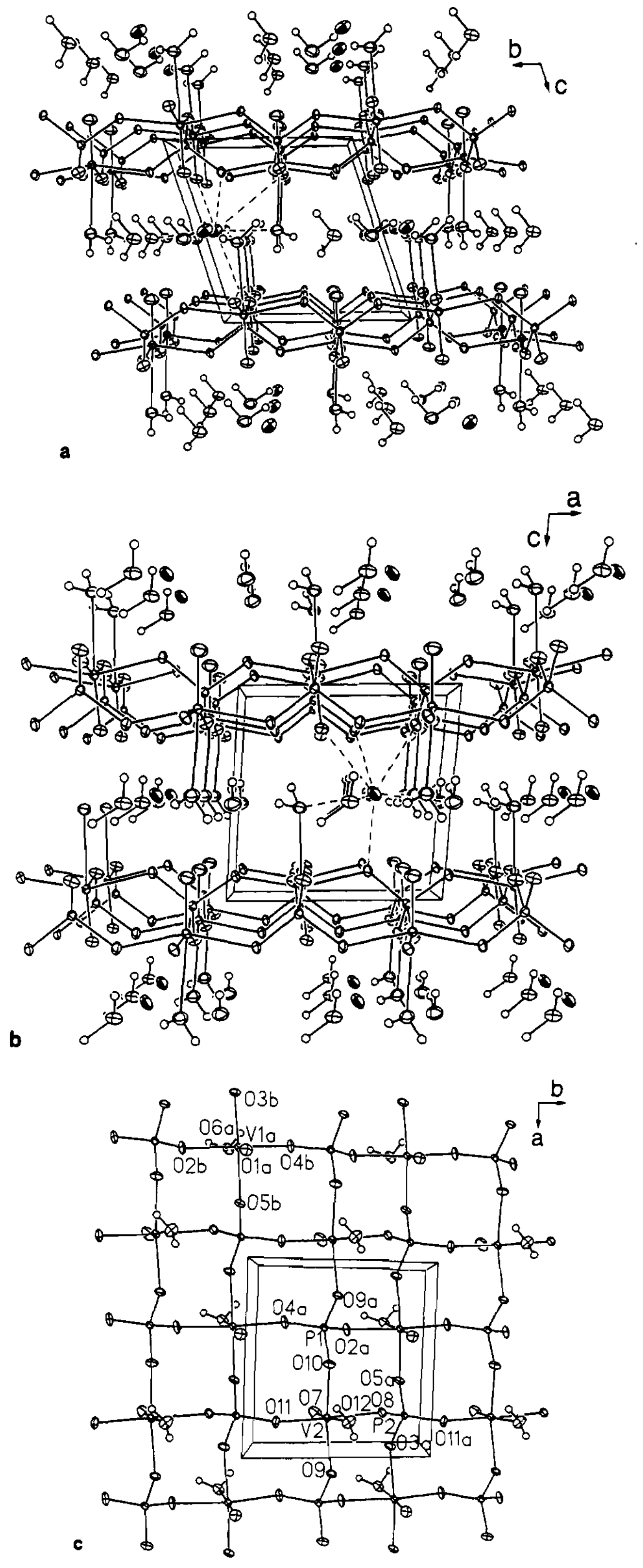

Figure 3. Structure of $Ca(VO)_2(PO_4)_2{\cdot}4H_2O$ as viewed (a) along the *a* axis and (b) along the *b* axis. A section of a 4-connected net is shown in part c. Thermal ellipsoids with shaded segments are Ca atoms. Small open circles are H atoms. The Ca–O bonds are represented by dashed lines.

The structures are closely related to that of $VOPO_4{\cdot}2H_2O$,[15,16] which has a tetragonal unit cell with parameters $a = 6.21$ Å, $c = 7.40$ Å, and $Z = 2$. The structure of $VOPO_4{\cdot}2H_2O$ contains layers of vanadium oxygen octahedra and phosphate tetrahedra with the water molecules between the layers (Figure 1). The layer is a 4-connected net in which corner-sharing vanadium and phosphorus polyhedra alternate. Each vanadium octahedron shares its four equatorial oxygen atoms with four different PO_4 groups. The two remaining axial oxygens consist of a vanadyl oxygen and a water oxygen coordinated trans to it. The second water molecule is located between two phosphate groups and is linked by hydrogen bonds to two layers simultaneously. Along the [110] direction the vanadyl oxygens alternately point up and down relative to a layer. The incorporation of Co^{2+}, Ca^{2+}, Sr^{2+}, and Pb^{2+} does not change the water content, but leads to reduction of V^{5+} to V^{4+} and alters the way in which the layers pack in the lattice. The interlayer separations for the Co, Ca, Sr, and Pb compounds are respectively 6.71, 6.30, 6.32, and 6.34 Å, which are considerably shorter than that in $VOPO_4{\cdot}2H_2O$. On incorporation of the cations, the layers become negatively charged and are brought closer together by electrostatic interaction with the interlayer metal cations. The interlayer separations in the Ca, Sr, and Pb compounds are comparable to that in $K_{0.5}VOPO_4{\cdot}1.5H_2O$ (6.38 Å), but shorter than that in $Na_{0.5}VOPO_4{\cdot}2H_2O$ (6.53 Å). In contrast, the separation in the Co compound is much longer.

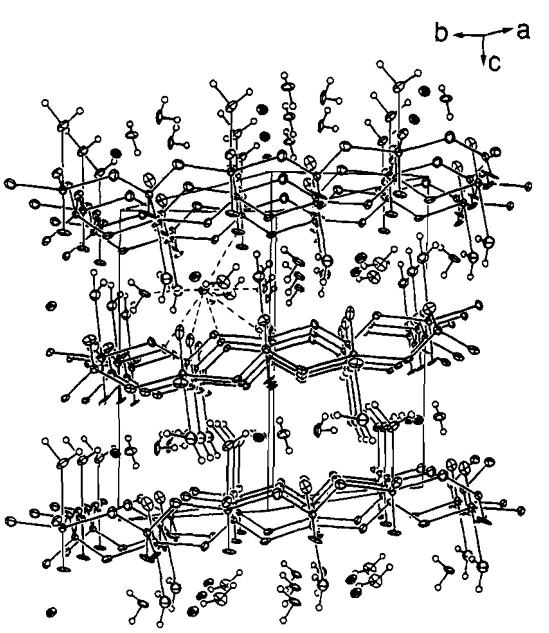

Figure 4. $Sr(VO)_2(PO_4)_2{\cdot}4H_2O$ structure as viewed along the [110] direction. Thermal ellipsoids with shaded segments are Sr atoms. Small open circles are H atoms. The Sr–O bonds are represented by dashed lines.

The vanadium phosphorus oxide layers in $Co(VO)_2(PO_4)_2{\cdot}4H_2O$, $Ca(VO)_2(PO_4)_2{\cdot}4H_2O$, $Sr(VO)_2(PO_4)_2{\cdot}4H_2O$, and $VOPO_4{\cdot}2H_2O$ stack in different ways. $Sr(VO)_2(PO_4)_2{\cdot}4H_2O$ and $Pb(VO)_2(PO_4)_2{\cdot}4H_2O$ are isostructural. Although the layer stackings in $Ca(VO)_2(PO_4)_2{\cdot}4H_2O$, $Na_{0.5}VOPO_4{\cdot}2H_2O$, and $K_{0.5}VOPO_4{\cdot}1.5H_2O$ are the same, the *c* axis of the Na compound is 2 times as long as the *c* axes in the other two, since the Na compound is centrosymmetric and the Na^+ ion is at a general position. In the parent $VOPO_4{\cdot}2H_2O$, each V=O group is directed toward the water molecule which is weakly coordinated trans to the V=O group of an adjacent layer. The $Ca(VO)_2(PO_4)_2{\cdot}4H_2O$ structure is formed by a relative displacement of adjacent layers in the $VOPO_4{\cdot}2H_2O$ structure parallel to one of the unit cell edges by ~3.1 Å ($=\vec{a}/2$). If the displacement is along the diagonal direction by ~4.4 Å ($=(\vec{a} + \vec{b})/2$), then the $Co(VO)_2(PO_4)_2{\cdot}4H_2O$ structure is formed. For the $Sr(VO)_2(PO_4)_2{\cdot}4H_2O$ structure, the displacement is approximately parallel to the diagonal direction by ~2.2 Å ($=(\vec{a} + \vec{b})/4$).

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As shown in Figure 2, the bonding scheme of the V atom in $Co(VO)_2(PO_4)_2 \cdot 4H_2O$ is rather different. It is 5-coordinate in which the stereochemistry is square pyramidal. A very short vanadium to oxygen bond defines the vanadyl group V═O, and four equatorial V—O bonds are equivalent. In the Ca, Sr, and Pb compounds, the water molecule as the sixth ligand is weakly bonded trans to V═O to produce a distorted octahedron (Figures 3 and 4). The crystal structure of $Co(VO)_2(PO_4)_2 \cdot 4H_2O$ is particularly interesting. The Co atom is coordinated by six oxygen atoms including two trans vanadyl oxygens from adjacent layers and four equatorial water oxygens such that linear V═O—Co—O═V chains are formed. The coordination octahedra around the Co atom has D_{4h} symmetry, with the 4-fold rotation axis passing through the linear chain. In $Ca(VO)_2(PO_4)_2 \cdot 4H_2O$ the Ca^{2+} ions and water molecules are located between the V–P–O layers, and run in rows parallel to the *a* and *b* axes. Views of the $Sr(VO)_2(PO_4)_2 \cdot 4H_2O$ structure along the [110] and [1$\bar{1}$0] directions show the large cavities where the Sr^{2+} ions and water molecules are located.

We note that the crystal structure of $Ca(VO)_2(PO_4)_2 \cdot 4H_2O$ that we have determined is a triclinic polymorph of the rare mineral sincosite. The mineral was first found in a black carbonaceous shale from Sincos, Peru. Chemical analyses on one sample by Schaller in 1924 yielded the formula $V_2O_4 \cdot CaO \cdot P_2O_5 \cdot 5H_2O$.[17] However, from analytical data of second sample the quantity of water is estimated to be 4 H_2O. In 1984, Shitov et al.[18] reported that sincosite of the Lower Cambrian carbonaceous shales from Kazakhstan contains four water molecules instead of five and had the tetragonal space group $P4_2/n$ with $a = 9.08$ Å and $c = 12.66$ Å. Interestingly, microprobe analysis of sincosite from the Black Hills of South Dakota by Zolensky in 1985 gave the formula $Ca(VO)_2(PO_4)_2 \cdot 5H_2O$.[19] Its powder diffraction pattern was collected using a Gandolf camera. The pattern was indexed by analogy with the meta-autunite structure with tetragonal cell parameters $a = 8.895$ (3) Å and $c = 12.727$ (2) Å. However, its detailed structure has not been determined due to the low quality of the natural mineral. A comparison of the calculated powder pattern of our synthetic calcium compound to that of sincosite reported by Zolensky indicates that the crystal structures are similar and that the naturally occurring mineral has a higher symmetry.

The hydrothermal techniques that we have used are useful for the crystal growth of the layered vanadyl phosphate hydrates $A(VO)_2(PO_4)_2 \cdot xH_2O$. However, the phases that we have obtained have different crystal symmetries or compositions from those prepared by redox intercalation reactions of $VOPO_4 \cdot 2H_2O$ with metal iodides in aqueous solutions. The Co compound is particularly interesting since its framework contains the interesting magnetic moiety V═O—Co—O═V. The synthesis of new transition metal–vanadium phosphate frameworks is currently under investigation.

Acknowledgment. Support for this study by the National Science Council and the Institute of Chemistry, Academia Sinica, is gratefully acknowledged.

Supplementary Material Available: Tables giving crystal data and details of the structure determination, anisotropic thermal parameters, and bond angles (11 pages). Ordering information is given on any current masthead page.

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