Inorg. Chem. **1998,** *37,* 5844−5850

Syntheses, Structures, and Magnetic Properties of Metal(II) Phosphates with $M(OH)(PO_4)^{2-}$ Layers (M = Ni, Co, Mg)

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Received May 27, 1998

A series of compounds with a novel phosphate layer of the composition $M^{II}(OH)(PO_4)^{2-}$ (M = Ni, Co, Mg) were hydrothermally prepared. Structures of compounds $Na(H_3O)_2\{Ni_4(OH)_4(HPO_4)_3(H_2PO_4)\}$ (**1**) and $(H_3O)\{Co_2(OH)_2(HPO_4)(H_2PO_4)\}$ (**4**) were determined by the single-crystal X-ray diffraction. Crystal data for **1**: monoclinic $P2_1$, $a = 8.374(1)$ Å, $b = 12.810(3)$ Å, $c = 8.407(4)$ Å, $\beta = 106.19(2)°$, $Z = 2$. Cyrstal data for **4**: orthorhombic, *Pcab*, $a = 8.443(2)$ Å, $b = 13.093(4)$ Å, $c = 15.484(4)$ Å, $Z = 8$. The phosphate layers of these compounds have similar structures but belong to different layer groups. They are composed of zigzag chains of MO_6 octahedra sharing skew edges, and the chains are linked by shared corners and also by bridging PO_4 tetrahedra. The space between the layers is occupied by sodium and oxonium ions in **1** and by only oxonium ions in **4**. Both **1** and **4** are paramagnetic with antiferromagnetic transition at 6 and 5 K, respectively. A lithium analogue of **1**, $Li_{0.39}H_{1.61}Ni(OH)(PO_4)(H_2O)_{0.5}$ (isostructural with **1**), a nickel phosphate without alkali cations $H_2Ni(OH)(PO_4)(H_2O)_{0.5}$ (isostructural with **4**), and a magnesium phosphate $Na_{0.27}H_{1.73}Mg(OH)(PO_4)(H_2O)_{0.5}$ (isostructural with **1**) were also identified by powder X-ray diffraction.

Introduction

Layered phosphates of zirconium[1] and vanadium[2] have been extensively studied and many of them are known to have notable ion-exchange ability or interlayer ionic mobility.[3] If layered phosphates of other transition metals are prepared, they will give further possibilities of chemical applications. Though recent preparative efforts, especially with hydrothermal techniques, have yielded a variety of phosphates and arsenates of transition metals other than zirconium and vanadium, only a few of them have been reported to have layered structures.[4−8] In this article, we describe a new family of the phosphate with the layers $M^{II}(OH)(PO_4)^{2-}$ (M = Mg, Ni, Co). These phosphates are obtained when metal hydroxide sols are used as the metal sources of the hydrothermal reactions.

Experimental Section

Instruments. Hydrothermal reactions were carried out in a Teflon vessel (50 cm^3) enclosed in a stainless autoclave. The ICP analyses and X-ray fluorescent analyses (XFA) were performed with a Seiko SPS-7000 analyzer and Seiko SEA 2010 spectrometer (Rh target, 15 kV), respectively. Infrared spectra were recorded on a Hitachi I-3000 spectrometer using KBr pellets. Magnetic susceptibilities were measured on a Quantum Design MPMS-5S SQUID susceptometer with a magnetic field of 5 kG after zero-field cooling.

$Na(H_3O)_2\{Ni_4(OH)_4(HPO_4)_3(H_2PO_4)\}$ (=$Na_{0.25}H_{1.75}Ni(OH)(PO_4)(H_2O)_{0.5}$) (1). Pellets of NaOH (0.20 g, 5.0 mmol) were added to the solution of $NiCl_2 \cdot 6H_2O$ (0.48 g, 2.0 mmol) in 5.1 mL of water to yield a green sol of nickel hydroxide. The mixture of the sol and phosphoric acid (0.40 g, 3.5 mmol, 85%) was heated at 150 °C under autogenous pressure. After 60 h, it was cooled to room temperature at the rate of 5 °C/h. The final pH of the reaction solution was 1.8−2.5. A light green powder of **1** was collected by filtration, washed with water, and dried in air. Yield: 69% based on nickel. The X-ray powder diffraction of the product showed reflections only of **1**. The Na/Ni molar ratio determined by the ICP analysis was 0.24. The P/Ni molar ratio by XFA was 1.01. IR (cm^{-1}): 3432 (s), 1630 (m), 1140 (s), 1062 (s), 998 (s), 868 (s), 834 (w), 794 (s), 598 (m), 572 (s). The compound does not dissolve in neutral water but decomposes in acidic or alkaline solutions.

Single crystals of **1** for X-ray studies were obtained under modified reaction conditions. In addition to the materials described for the preparation of the powder sample, 1,4-diazabicycro[2,2,2]octadiene (DABCO) was added (molar ratio, DABCO/Ni = 0.5) and the mixture was heated at 170 °C for 60 h. The reaction yielded unidentified compounds along with the crystals of **1**.

The products of the reaction depended on the ratio of the starting compounds. The reaction with smaller amounts of sodium and phosphate ions yielded $Ni_3(PO_4)_2 \cdot 8H_2O$ (vivianite)[9] while excess of NaOH resulted in the formation of an unidentified compound.

$Li_{0.39}H_{1.61}Ni(OH)(PO_4)(H_2O)_{0.5}$ (2). A similar procedure described for **1** with $LiOH \cdot H_2O$ (0.38 g, 9.0 mmol), $NiCl_2 \cdot 6H_2O$ (0.95 mg, 4.0 mmol), water (10.1 mL), and 85% H_3PO_4 (0.86 g, 7.5 mmol) gave a light green powder of **2**. Yield: 37% based on nickel. X-ray powder diffraction indicated that **2** was the only product of the reaction. The Li/Ni molar ratio 0.39 was determined by ICP.

$H_2Ni(OH)(PO_4)(H_2O)_{0.5}$ (3). An aqueous solution of $N(CH_3)_4OH$ (0.37 g, 4.0 mmol, 10%) was reacted with the solution of $NiCl_2 \cdot 6H_2O$ (0.48 mg, 2.0 mmol) in water (1.8 mL) to yield a green sol of $Ni(OH)_2$. To the mixture was added 85% H_3PO_4 (0.46 mg, 4.0 mmol), and the mixture was processed as described for **1** to yield a light green powder of **3**. The compound was obtained only as a mixture with a

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small amount of $Ni_3(PO_4)_2{\cdot}8H_2O$[9] and identified only by X-ray powder diffraction.

$(H_3O)\{Co_2(OH)_2(HPO_4)(H_2PO_4)\}$ (=$H_2Co(OH)(PO_4)(H_2O)_{0.5}$) (4). A similar procedure described for **1** with NaOH (0.20 g, 5.0 mmol), $CoCl_2{\cdot}6H_2O$ (0.48 g, 2.0 mmol), water (6.9 mL), and 85% H_3PO_4 (0.58 g, 5.0 mmol) yielded light purple-red plates of **4**. The reaction temperature was 160 °C. The pH of the final solution was 1.9−2.3. Yield: 31% based on cobalt. No sodium was detected by ICP analysis. The P/Co molar ration by XFA was 1.07. IR (cm^{-1}): 3338 (m), 3152 (m), 1630 (m), 1302 (w), 1114 (s), 1032 (s), 914 (s), 896 (s), 786 (m), 744 (s), 584 (s), 546 (w), 532 (w).

If a larger amount of NaOH was used in the reaction system, red-purple rods of $NaCo_3(PO_4)_2(HPO_4)$ (alluaudite-type structure)[10] were formed instead of **4**. Therefore, it was not possible to prepare a sodium-containing cobalt phosphate like **1**. The product was sensitive also to the reaction temperature. The reaction carried out at 170 °C yielded an unidentified blue material.

$Na_{0.27}H_{1.73}Mg(OH)(PO_4)(H_2O)_{0.5}$ (5). A similar procedure described for **1** with NaOH (0.20 g, 5.0 mmol), DABCO (0.11 g, 1.0 mmol), $MgCl_2{\cdot}6H_2O$ (0.40 g, 2.0 mmol), water (6.9 mL), and 85% H_3PO_4 (415.0 mg, 3.6 mmol) yielded colorless powder of **5**. Yield: 82% based on magnesium. The reaction temperature was 160 °C. The pH of the final solution was 5.1−5.4. The Na/Mg ratio was determined by ICP analysis to be 0.27. In a reaction where smaller amount of water (5.0 mL) was used, the compound obtained showed the X-ray diffraction pattern of the alluaudite-type structure.[10] When a larger amount of NaOH was used, the product was colorless rods of $MgHPO_4{\cdot}3H_2O$ (newberyite).[11] Attempts to prepare a lithium analogue were unsuccessful.

Structure Study of 1. A crystal of **1** with the dimensions 0.3 × 0.03 × 0.02 mm was used for X-ray studies. The intensity data of all 7942 reflections within the 2θ range 6−55° were measured on a Rigaku AFC5R diffractometer. The reflection data were empirically corrected for absorption by the ψ-scan method (relative transmission factor 0.946−0.975). Systematic absences indicated that the space group was $P2_1/m$ or $P2_1$, and the structure was solved only when the latter was assumed. Averaging the equivalent reflections, where the reflections hkl and $\bar{h}\bar{k}\bar{l}$ were treated as independent reflections, yielded 3972 independent reflections ($R_{int}(F^2) = 0.075$). The positions of Ni and P atoms were determined by the direct method (SHELXS-86[12]). Sodium and oxygen atoms were located by the Fourier method (SHELXS-76[13]). Full-matrix refinement was performed on F^2 with the program ANYBLK,[14] where 3139 averaged reflections ($I \geq \sigma(I)$) were used. Anisotropic temperature factors were used for nickel and phosphorus atoms, and isotropic ones for oxygen atoms. Hydrogen atoms were not included in the calculation. Flack's x parameter was included in the refinement, and was converged at $x = 0.72(4)$, indicating the crystal was twinned.[15] The refined structure indicated the possibility of the space group to be $P2_1/a$. However, when the space group $P2_1/a$ was assumed, the refinement of the structure with disorders for the atoms that were not fit to the symmetry (Na, O9, and O10) gave much higher R values ($R = 0.116$ and $R_w = 0.168$ based on F^2) for the same reflection set. Therefore, we concluded that the space group of **1** was $P2_1$. Sodium atoms between the layers were distinguished from the oxygen atoms by their Brese−O'Keffe bond-valence sums.[16] Because the two sodium positions (Na(1) and Na(2)) were only 0.65(2) Å apart from each other, sodium atoms were considered to be disordered in these two positions. If the occupancies of the sodium atoms were refined independently, they were converged to 0.56(3) for Na(1) and 0.36(3) for Na(2). In the final refinement, the occupations of the neighboring sodium positions were constrained so that the sum of them was 1.0.

Structure Study of 4. All single crystals of **4** that we could prepare were small, and the size of the crystal used for the X-ray study was marginal (0.4 × 0.02 × 0.02 mm). All 19720 reflections in the 2θ range $6° \leq 2\theta \leq 60°$ were measured on a Rigaku AFC7R diffractometer in the $2\theta-\omega$ scan mode. A slight decay of intensities of standard reflections was observed and the intensity data were linearly corrected (3.2% at the end of the data collection). The space group was unequivocally determined to be that of No. 61 from the systematic absences. Among the six possible settings of the axes, the setting *Pcab* was selected for easier comparison with the structures of **1** though the standard setting of the space group was *Pbca*. Averaging the equivalent reflections yielded 2809 reflections ($R_{int}(F^2) = 0.281$), where the low agreement of the equivalent reflections was due to the low intensities of the reflections. If the reflections with $|F_o|^2 > \sigma(F_o^2)$ were compared, the agreement was reasonable ($R_{int}(F^2) = 0.089$). Cobalt and phosphorus atoms were located using the direct method (SAPI91[17]), and the oxygen atoms were located by difference Fourier method (SHELXS-76[13]). Finally, all non-hydrogen atoms were anisotropically refined on F^2 against 1702 observed reflections ($I \geq \sigma(I)$) with the program ANYBLK.[14]

Thermal Analyses. Well ground powder (ca. 50 mg) of the samples **1**, **4**, and **5** was pressed into a pellet and placed in a gold boat. It was heated at a constant temperature for 1 day under a nitrogen atmosphere, and the change of the weight was measured. This process was repeated. In each cycle, the sample was heated at the temperature ca. 20 °C higher than in the previous cycle. The heating temperature was 75 °C in the initial cycle and 320 °C in the last cycle.

Ion Exchange. Powdered sample of **1** (ca. 100 mg) was stirred in an aqueous solution (0.1 M, 25 mL) of LiCl or NaCl for 5 days. The product was filtered off, washed with water, and dried in air at ambient temperature. The ratio of Ni/Na(/Li) of the product was determined by the ICP analysis after it was dissolved in a dilute hydrochloric acid. Attempts of the intercalation of ammonium cations or pyridine molecules was unsuccessful because the reactions of **1** with aqueous solution of NH_4Cl or pyridine resulted in the dissolution of **1**.

Results and Discussion

Preparation. The new compounds reported here were all prepared only when hydroxide sol was prepared in situ in the first step. If $NiCl_2{\cdot}6H_2O$ was reacted with phosphoric acid followed by the addition of sodium hydroxide solution, the yield of **1** was none or very slight. If $NaHCO_3$ was substituted for NaOH in the reaction described for the preparation of **1**, hydroxide sol was not formed in the first stage and the hydrothermal reaction of the mixture did not yield **1**. These observations indicate that the products are kinetically controlled. Another support for the kinetic control is the observation that the reactions with very similar procedures and compositions did not always give the same mixture of the products. The nature and structure of the sol are strongly affected by the local pH of the solution, which cannot be well controlled in the present preparations.

Reactions of the hydroxide sols with phosphoric acid yield a variety of phosphates depending on the reaction conditions as described in the Experimental Section. Especially the alluaudite-type compounds of cobalt and magnesium ($NaM_3(PO_4)_2(HPO_4)$, M = Co and Mg) are formed under very similar conditions to those for **4** and **5**, and some experiments yielded a mixture of the two compounds. The compounds **4** and **5** have a hydroxo group coordinated to the metal atom while the formation of the alluaudite-type compounds requires the complete replacement of the coordinating water molecules (or hydroxo groups) by phosphate anions. Therefore, higher pH of the solution, where

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Table 1. Crystallographic Data for **1** and **4**[a]

	1	**4**
empirical formula	$H_{15}NaNi_4O_{22}P_4$	$H_8Co_2O_{11}P_2$
fw	747.01	363.87
space group	$P2_1$ (No. 4)	*Pcab* (No. 61)
Z	2	8
ρ_{calc}/g cm^{-3}	2.871	2.824
T/K	296	296
λ/Å	0.7107	0.7107
μ/mm^{-1}	4.794	4.300
$R(F_o^2)$, $R_w(F_o^2)$[b]	0.0687, 0.0862	0.0791, 0.0745

[a] Cell parameters are given in Table 6. [b] $R(F_o^2) = \sum||F_o|^2 - |F_c|^2|/\sum|F_o|^2$, $R(F_o^2) = \sum w(|F_o|^2 - |F_c|^2)^2/\sum w|F_o|^4$, $w = 1/\{\sigma(|F_o|^2)^2 + p^2|F_o|^4\}$, where $p = 0.0079$ for **1** and 0.0076 for **4**.

Table 2. Positional and (Equivalent) Isotropic Thermal Parameters of **1**

atom	*x*/*a*	*y*/*b*	*z*/*c*	U_{eq} or U_{iso}
Ni(ax)	0.3015(2)	0.11447	0.0057(2)	0.0101(8)
Ni(ay)	0.1928(2)	−0.11513(13)	−0.0062(2)	0.0096(9)
Ni(bx)	0.6828(2)	0.1114(2)	−0.0076(2)	0.0106(7)
Ni(by)	−0.1959(2)	−0.1166(2)	−0.0196(2)	0.0096(7)
P(1x)	0.5546(4)	0.2844(4)	0.2064(4)	0.009(2)
P(1y)	−0.0426(5)	−0.2936(4)	−0.2075(4)	0.012(2)
P(2x)	0.5666(5)	−0.0485(4)	0.2219(4)	0.009(2)
P(2y)	−0.0649(5)	0.0549(4)	−0.2299(4)	0.0089(15)
O(1ax)	0.3842(11)	−0.0234(8)	0.1312(10)	0.010(2)
O(1ay)	0.1110(11)	0.0234(8)	−0.1276(10)	0.012(2)
O(1bx)	0.6740(9)	−0.0303(6)	0.1026(9)	0.010(2)
O(1by)	−0.1942(9)	0.0221(6)	−0.1403(9)	0.009(2)
O(2x)	0.5207(10)	0.1880(7)	0.0916(9)	0.009(2)
O(2y)	−0.0248(11)	−0.1903(8)	−0.1132(10)	0.016(2)
O(3ax)	0.6818(11)	0.3573(8)	0.1732(9)	0.016(2)
O(3ay)	−0.1858(12)	−0.3570(9)	−0.1877(10)	0.022(2)
O(3bx)	0.3930(9)	0.3396(7)	0.2063(9)	0.012(2)
O(3by)	0.1153(11)	−0.3536(7)	−0.1757(10)	0.023(2)
O(4x)	0.4419(10)	0.0654(8)	−0.1679(10)	0.014(2)
O(4y)	0.0387(10)	−0.0687(7)	0.1524(10)	0.012(2)
O(5x)	0.2105(10)	0.2498(8)	−0.1284(10)	0.009(2)
O(5y)	0.2930(11)	−0.2508(8)	0.1357(10)	0.014(2)
O(6x)	0.6269(9)	0.2377(6)	0.3895(9)	0.018(2)
O(6y)	−0.1011(9)	−0.2667(6)	−0.4024(9)	0.014(2)
O(7x)	0.6259(10)	0.0200(7)	0.3774(9)	0.018(2)
O(7y)	−0.0997(9)	−0.0090(6)	−0.3963(9)	0.012(2)
O(8x)	0.5783(11)	−0.1670(8)	0.2697(10)	0.012(2)
O(8y)	−0.0778(12)	0.1683(9)	−0.2690(11)	0.019(2)
O(9)	0.3853(11)	0.0865(7)	0.5133(11)	0.037(2)
O(10)	0.0881(9)	−0.1349(6)	−0.5354(9)	0.024(2)
Na(1)	0.3711(11)	0.2891(10)	0.4647(10)	0.023(3)
Na(2)	0.341(2)	0.337(2)	0.448(2)	0.033(5)

Table 3. Selected Interatomic Distances (Å) of **1**[a]

Bond Distances of Ni−O and P−O

	p = a		p = b	
	r = x, s = y	r = y, s = x	r = x, s = y	r = y, s = x
Ni(*pr*)−O(1*pr*)	2.075(9)	2.067(10)	2.048(8)	2.048(8)
Ni(*pr*)−O(1*ps*)	2.041(9)	2.061(9)	2.062(8)	2.022(8)
Ni(*pr*)−O(2*r*)	2.010(8)	2.036(9)	2.033(9)	2.047(9)
Ni(*pr*)−O(3*ps*)^{i}	2.060(10)	2.005(9)	1.996(8)	2.014(8)
Ni(*pr*)−O(4*r*)	2.205(9)	2.182(9)	2.171(8)	2.178(8)
Ni(*pr*)−O(5*r*)	2.092(9)	2.143(10)	2.107(10)[b]	2.139(9)[b]
P(1*r*)−O(2*r*)	1.545(9)	1.529(10)		
P(1*r*)−O(3*pr*)	1.500(10)	1.495(11)	1.526(8)	1.488(9)
P(1*r*)−O(6*r*)	1.604(8)	1.612(8)		
P(2*r*)−O(1*pr*)	1.539(9)	1.538(9)	1.541(8)	1.541(8)
P(2*r*)−O(7*r*)	1.538(8)	1.577(8)		
P(2*r*)−O(8*r*)	1.566(11)	1.487(11)		

Other Interatomic Distances

Na(1)−Na(2)	0.66(2)	Na(2)−O(7y)^{i}	2.77(2)
Na(1)−O(3bx)	2.322(11)	Na(2)−O(8x)^{i}	2.28(2)
Na(1)−O(6x)	2.486(12)	O(3ay)−O(9)^{i}	2.874(12)
Na(1)−O(6y)^{i}	2.288(10)	O(4x)−O(9)	2.602(12)
Na(1)−O(8x)^{i}	2.225(11)	O(4y)−O(10)	2.678(11)
Na(1)−O(9)	2.63(2)	O(6x)−O(10)^{i}	2.869(11)
Na(2)−O(3bx)	2.194(15)	O(6y)−O(10)	2.756(11)
Na(2)−O(6x)	2.87(2)	O(7x)−O(9)	2.715(12)
Na(2)−O(6y)^{i}	2.35(2)	O(7y)−O(10)	2.732(11)
Na(2)−O(7x)^{i}	2.74(2)		

[a] Symmetry code: i, $-x$, $y + 1/2$, $-z$. [b] The distance is for Ni(b*r*)-O(5*s*)^{i}.

more phosphate ions are deprotonated, is favorable for the formation of alluaudite-type compounds. This is consistent with the observation in the cobalt system that the alluaudite-type compound was obtained when the molar ratio $NaOH/H_3PO_4$ was higher than 1.13. Because of the formation of the alluaudite-type compound, the reaction condition for new cobalt phosphates was limited to lower $NaOH/H_3PO_4$ ratios, and the cobalt phosphate with incorporated sodium ions such as **1** could not be prepared.

The lack of the alluaudite-type compound in the nickel system can be explained by the slow substitution rate of the nickel complexes. For the formation of the alluaudite-type compound, all water molecules and hydroxo groups around the nickel ion must be replaced before the nickel ions precipitate as **1** or **3**. The substitution rate is expected to be similar to the water exchange rate of the corresponding hexaaqua metal ion, which is in the order Co^{2+} (3.2×10^6 s^{-1}) > Mg^{2+} (5.3×10^5 s^{-1}) > Ni^{2+} (3.4×10^4 s^{-1}).[18] Probably the substitution rate of the nickel complex is too slow for the formation of the alluaudite-type compound. Because the alluaudite-type compound is not produced, we can prepare both **1** containing sodium ions and **3** with no sodium ions by using a wider range of the $NaOH/H_3PO_4$ ratio.

Structures. The results of single-crystal X-ray studies of **1** and **4** are given in Tables 1−5, and the ORTEP drawings are shown in Figures 1 and 2. The cell parameters of the new layer compounds are summarized in Table 6. The interlayer distances of **1** and **5**, which contain sodium ions between the layers, are 0.2−0.3 Å larger than those of others containing only oxonium ions or containing oxonium and lithium ions.

The compounds **1** and **4** contain layers of a new structural type composed of the condensed MO_6 octahedra and the PO_4 tetrahedra (Figures 3−5). The MO_6 octahedra form zigzag chains running along the *a* axis by sharing skew edges as shown in Figure 6a. The chains of the new phosphates are structurally different from those of the alluaudite-type structure though both are composed of MO_6 octahedra sharing skew edges. The isolated chains with the same structural motif as observed in **1** and **4** are found in $LiCo_2P_3O_{10}$, where the chains are connected with P_3O_{10} groups.[19] In **1** and **4**, the chains are merged with each other to form a layer extending along the *ab* plane. Because the chains cannot be merged if they are made of regular octahedra aligned on a plane (Figure 6a), they are slightly puckered as shown in Figures 4 and 5, and the octahedra comprising the chain are deformed. Adjacent chains are linked not only through the shared oxygen atoms but also through the bridging PO_4 tetrahedra. Figure 6b illustrates the layer obtained in this way with the highest possible symmetry. The symmetry of a single layer can be clearly expressed by the concept of the layer group.[20] The layer illustrated in Figure 6b belongs to the layer group $p(2_1/m)(2_1/a)(2/b)$. However, the stacking of the

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(19) (a) Erragh, F.; Boukhari, A.; Holt, E. M. *Acta Crystallogr. C* **1996**, *52*, 1867. (b) Rissouli, K.; Benkhoujia, K.; Sadel, A.; Bettach, M.; Zahir, M.; Giorgi, M.; Pierrot, M.; Drillon, M. *Eur. J. Solid State Inorg. Chem.* **1997**, *34*, 221.

Table 4. Positional and Equivalent Isotropic Thermal Parameters of **4**

atom	x/a	y/b	z/c	U_{eq}
Co(a)	−0.03727(11)	0.11113(8)	0.25756(7)	0.0092(5)
Co(b)	0.35005(14)	0.11941(8)	0.26304(6)	0.0092(5)
P(1)	0.1535(3)	0.28893(14)	0.36508(12)	0.0086(9)
P(2)	0.1510(3)	−0.05980(14)	0.36629(12)	0.0082(9)
O(1a)	0.0057(6)	−0.0349(4)	0.3093(4)	0.010(3)
O(1b)	0.3068(6)	−0.0251(4)	0.3240(3)	0.008(3)
O(2)	0.1556(8)	0.1894(3)	0.3114(3)	0.010(3)
O(3a)	−0.2184(6)	0.1356(4)	0.3392(3)	0.015(3)
O(3b)	0.4913(6)	0.1623(4)	0.3614(4)	0.014(3)
O(4)	0.1625(8)	0.0664(4)	0.1736(3)	0.011(3)
O(5)	−0.0915(7)	0.2463(5)	0.1835(3)	0.011(2)
O(6)	0.1807(7)	0.2585(4)	0.4635(3)	0.018(3)
O(7)	0.1554(8)	−0.1720(3)	0.3896(3)	0.013(3)
O(8)	0.1325(7)	0.0049(4)	0.4521(3)	0.015(3)
O(9)	0.3986(7)	0.0814(5)	0.5112(4)	0.027(4)

Table 5. Interatomic Distances of **4**[a]

Co(a)−O(1a)	2.105(5)	P(1)−O(2)	1.545(5)
Co(a)−O(1b)^{i}	2.144(5)	P(1)−O(3a)^{iii}	1.519(5)
Co(a)−O(2)	2.097(6)	P(1)−O(3b)^{iv}	1.512(6)
Co(a)−O(3a)	2.010(5)	P(1)−O(6)	1.592(5)
Co(a)−O(4)	2.209(6)	P(2)−O(1a)	1.545(6)
Co(a)−O(5)	2.158(6)	P(2)−O(1b)	1.538(5)
Co(b)−O(1a)^{ii}	2.051(5)	P(2)−O(7)	1.514(5)
Co(b)−O(1b)	2.146(5)	P(2)−O(8)	1.583(5)
Co(b)−O(2)	2.025(6)	O(3b)−O(9)	2.668(8)
Co(b)−O(3b)	2.014(5)	O(4)−O(9)^{v}	2.574(7)
Co(b)−O(4)	2.215(6)	O(8)−O(9)	2.625(8)
Co(b)−O(5)^{iii}	2.203(6)	O(9)−O(9)^{vi}	2.757(12)

[a] Symmetry code: i, $x - 1/2$, $-y$, $1/2 - z$; ii, $x + 1/2$, $-y$, $-z + 1/2$; iii, $x + 1/2$, $1/2 - y$, z; iv, $x - 1/2$, $1/2 - y$, z; v, $1 - x$, $-y$, $1 - z$; vi, $1/2 - x$, y, $z + 1/2$.

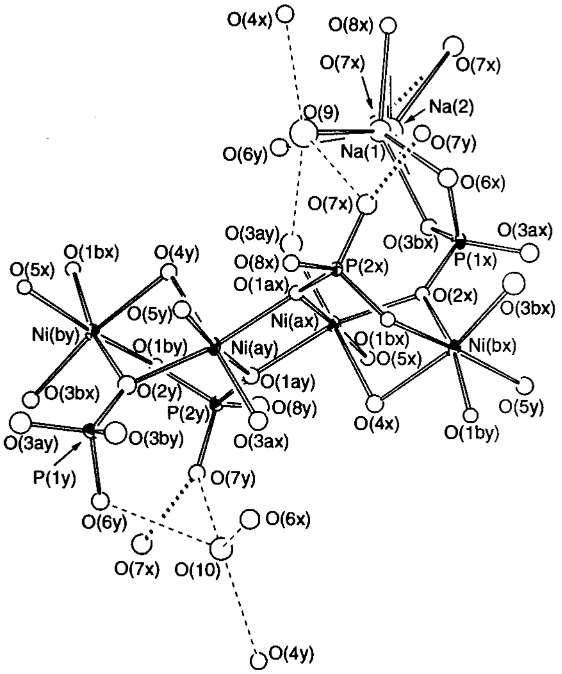

Figure 1. ORTEP drawing of **1** with 50% probability ellipsoids illustrating the coordination around nickel and phosphorus atoms and cations between the layers. Hydrogen atoms are not drawn. Thin broken lines show the O(oxonium ion)−O(layer) distances less than 2.9 Å. Thick broken lines indicate the interlayer O−O distances less than 2.9 Å. These short O−O distances indicate the possibility of the hydrogen bond.

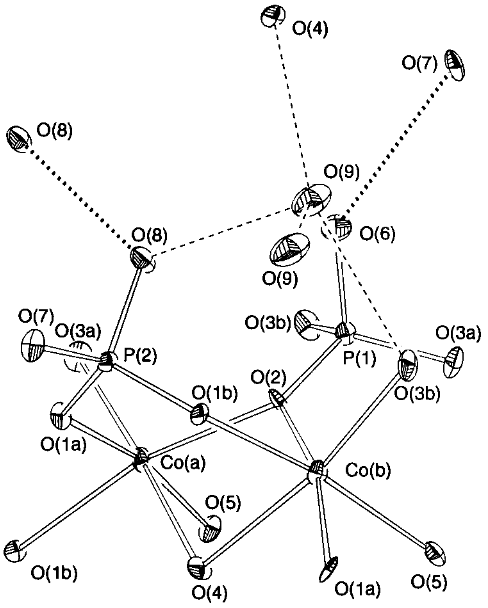

Figure 2. ORTEP drawing of **4** with 50% probability ellipsoids illustrating the coordination around cobalt and phosphorus atoms and cations between the layers. Hydrogen atoms are not drawn. Thin broken lines show the O(oxonium ion)−O(layer) distances less than 2.9 Å. Thick broken lines indicate the interlayer O−O distances less than 2.9 Å. These short O−O distances indicate the possibility of the hydrogen bond.

layers and the arrangements of the cations between the layers are not consistent with this symmetry, and the real layer structures of **1** and **4** have no mirror perpendicular to the *a* axis. The removal of a mirror plane from the point group $(2/m)(2/m)(2/m)$ requires lowering of the symmetry to the monoclinic system $2/m$ or the loss of the inversion center, which results the point group $mm2$. The latter case is realized in **4**, where the layer belong to the layer group $p2_1ab$, having no inversion symmetry. On the other hand, the structure of the layer in **1** is very close to that belonging to the monoclinic layer space group $p1(2_1/a)1$. The real structure of **1** is, however, a little deformed and has a lower symmetry ($p12_11$). Therefore, the layers of **1** and **4** have the same basic structure but are deformed in different ways.

Independent atoms in the hypothetical layer illustrated in Figure 6b are one metal atom (M = Ni, Co), two phosphorus atoms, and eight oxygen atoms (O(1)−O(8)). The atomic labels for **1** and **4** were derived from those for this symmetric structure. In the structure of **1**, the loss of the mirror plane perpendicular to the *a* axis causes the distinction of the atoms denoted by the letters "a" and "b" and the loss of the inversion center gives the distinction between the atoms with the label "x" and those with "y". Similarly, in the structure of **4** the letters a and b are used to distinguish the atoms related by the pseudo-mirror plane. In the compound **4**, adjacent layers are related by a screw axis running along the *b* axis while in **1** they are related by the lattice translation along the *c* axis.

The positions of protons could not be determined directly by the X-ray structure studies. Because the compounds are prepared in acidic conditions, the oxygen atoms between the layers cannot be hydroxide anions and in the following discussion we regard them to be water molecules that can accommodate one more proton. Then, the chemical formula

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(20) The layer group is a set of the symmetry operations observed in a layer. It contains all point-group operations and translational operations along the two axes parallel to the layer. Therefore, the layer group is similar to the space group, but lacks the translational symmetry along the third axis. Vainshtein, B. K. *Fundamentals of Crystals. Symmetry, and Methods of Structural Crystallography*; Springer: Berlin, 1994; Section 2.7.4.

Table 6. Cell Parameters of $A_2M(OH)(PO_4)(H_2O)_{0.5}$

compd	A_2	M	a/Å	b/Å	c/Å	β/deg	V/Å^3	d/Å^a
1^b	$Na_{0.25}H_{1.75}$	Ni	8.374(1)	12.810(3)	8.407(4)	106.19(2)	866.1(5)	8.07
2^c	$Li_{0.39}H_{1.61}$	Ni	8.343(2)	12.847(5)	8.109(3)	105.69(2)	836.8(4)	7.81
5^c	$Na_{0.27}H_{1.73}$	Mg	8.451(6)	12.925(6)	8.438(5)	106.34(3)	884.5(8)	8.10
4^b	H_2	Co	8.443(2)	13.093(4)	15.484(4)	90	1711.8(8)	7.74
3^d	H_2	Ni	8.364(7)	12.889(7)	15.538(12)	90	1675.3(18)	7.77

[a] Distance between the phosphate layers. [b] Cell parameters determined by the diffraction of a single crystal (monochromated Mo Kα radiation). [c] Cell parameters determined by X-ray powder diffraction measured on a Mac-Science MXP3TA diffractometer (monochromated Cu Kα radiation). [d] Cell parameters determined by X-ray powder diffraction measured on a Rigaku Geigerflex RAD-1A diffractometer (Cu Kα radiation).

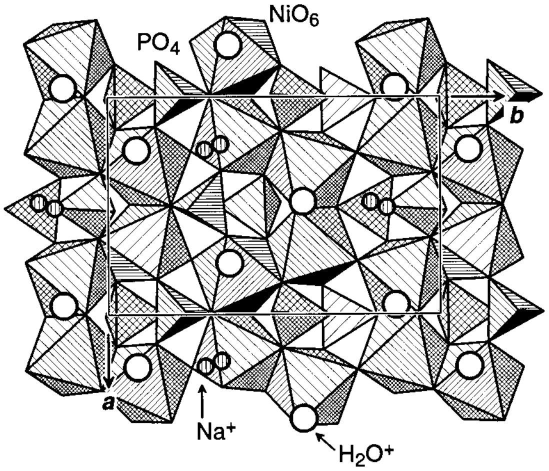

Figure 3. Structure of **1** projected on the *ab* plane, illustrating a phosphate layer and cations between layers. Hydrogen atoms are not drawn. Oxygen atoms between layers form oxonium cations.

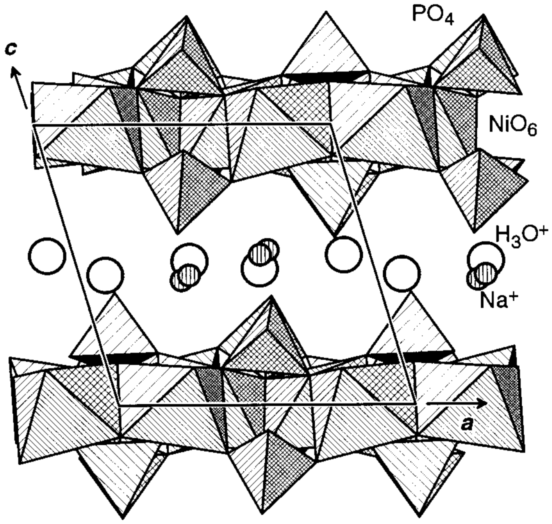

Figure 4. Stacking of the phosphate layers in **1** projected on the *ac* plane. Hydrogen atoms are not drawn. Oxygen atoms between layers form oxonium cations.

of **1** and **4** are expressed as $NaH_{11}Ni_4O_4(PO_4)_4(H_2O)_2$ and $H_{12}Co_4O_4(PO_4)_4(H_2O)_2$, respectively, because magnetic studies have confirmed that the oxidation number of the metals is +2 in both **1** and **4**. The oxygen atoms of **1** and **4**, to which the protons can be connected, are classified as follows, where *n* is the total number of the sites for protons.

Group A (O(1)−O(3)): Oxygen atoms bridging a phosphorus atom and one or two metal atoms ($n = 6$).

Group B (O(4) and O(5)): Atoms bridging two metal atoms ($n = 4$).

Group C (O(6)−O(8)): Atoms bound only to a phosphorus atom ($n = 6$).

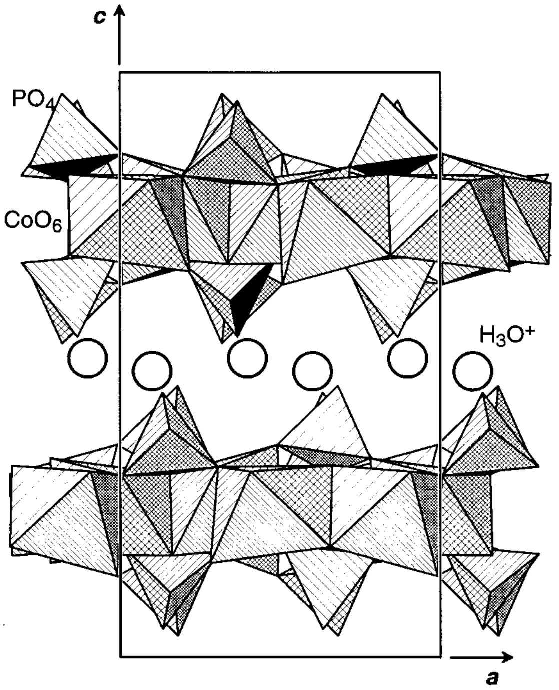

Figure 5. Stacking of the phosphate layers in **4** projected on the *ac* plane. Hydrogen atoms are not drawn. Oxygen atoms between layers form oxonium cations.

Group D (O(9) and later): Water molecules between the layers ($n = 2$).

Because the atoms of group A are bonded to both phosphorus(V) and metal(II) atoms, they are expected to have the least tendency to bond with protons. The absence of protons on the oxygen atoms of group A is supported by their shorter M−O bond distances (2.00−2.08 Å in **1** and 2.01−2.15 Å in **4)** compared to those of the group B atoms (2.09−2.21 Å in **1** and 2.16−2.22 Å in **4**). Then, the only possible way to distribute protons in **4** is to put one in each position of group B, C, and D, which leads to the chemical formula $(H_3O)\{Co_2(OH)_2(HPO_4)(H_2PO_4)\}$, where the part within the braces shows the phosphate layer.

In **1**, one of these protons is removed. At present, definite discussion on the positions of the protons is not possible, but there is some indication from the P−O distances. One of the oxygen atom O(8y) in the group D has an extremely short P−O distance (1.487(11) Å) than the distances of other group D atoms (1.536(8)−1.613(8) Å, average 1.58 Å). Comparison of these distances with those in the crystalline H_3PO_4 (P−O(terminal) 1.494 Å, P−OH 1.547−1.551 Å)[21] suggests that a proton is removed from the O(8y) atom to give the formula $Na(H_3O)_2\{Ni_4(OH)_4(HPO_4)_3(H_2PO_4)\}$.

All oxygen atoms in the phosphate layer of **1** and **4** make OH groups except for those bridging phosphorus and metal

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(21) Blessing, R. H. *Acta Crystallogr. B* **1988**, *44*, 334.

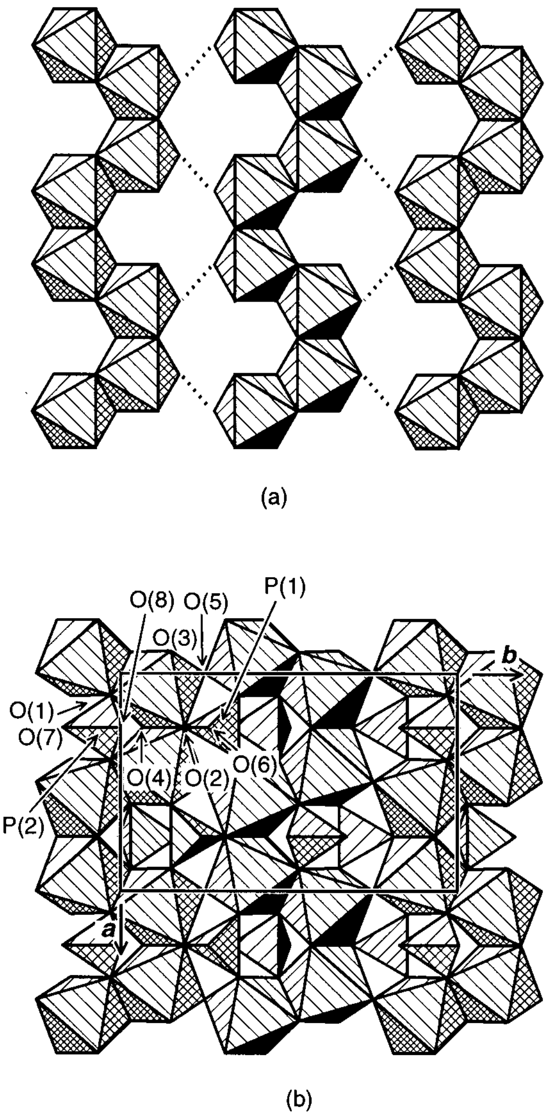

Figure 6. (a) Zigzag chains composed of perfect octahedra sharing skew edges. The chains are arranged on a plane. (b) Idealized phosphate layer of **1** and **4**. The structure belongs to the layer group $p(2_1/m)(2_1/a)(2/b)$. The coordinates are obtained by averaging the coordinates of **4**. The illustration shows also the labeling scheme for **1** and **4**.

atoms. This structural feature distinguishes the present compounds from the alluaudite-type phosphate ($NaCo_3(PO_4)_2(HPO_4)$)[10] and $KCo_2(AsO_4)(HAsO_4)$.[22] The abundance of the OH groups is related to the acidic condition for the preparation of **1** and **4** as discussed above.

Ion Exchange. The structure of **1** suggests that sodium or oxonium cations can be replaced by other monovalent cations. The reaction of **1** ($=Na_{0.25}H_{1.75}Ni(OH)(PO_4)(H_2O)$) with aqueous solution of LiCl (0.1 M) resulted in the incorporation of small amount of lithium, yielding the compound $Na_{0.23}Li_{0.06}H_{1.71}Ni(OH)(PO_4)(H_2O)$. The substantial invariance of the sodium amount indicates that sodium cations are strongly hold between the phosphate layers. The reaction of **1** with aqueous solution of NaCl yielded no or a very slight increase of the sodium cations in the compound, suggesting that the positions for sodium cations are already full in **1**.

Thermal Decomposition. The weight changes of the samples **1**, **4**, and **5** are plotted in Figure 7. The total weight loss of **1** was 5.5% after it had been heated to 206 °C. The amount is close to the weight of interlayer water molecules (4.9%), and the powder X-ray diffraction after the heating was similar to that before heating, indicating that the layer structure was maintained and interlayer water molecules were lost. Further heating caused drastic changes of the color at 215 °C from light green to brownish yellow. After heated at 256 °C, the powder pattern showed only a few weak reflections indicating most of the sample became amorphous. Therefore, the compound **1** loses interlayer water molecules until the temperature reaches ca. 206 °C, and further heating destroys the layer structure with the change of color.[23] The cobalt compound **4** showed similar changes. The color of the sample was changed from light red-purple to dark blue at 176 °C, and the total weight loss at the temperature was 6.2%, which was a little lager than the weight of interlayer water molecule (5.2%).

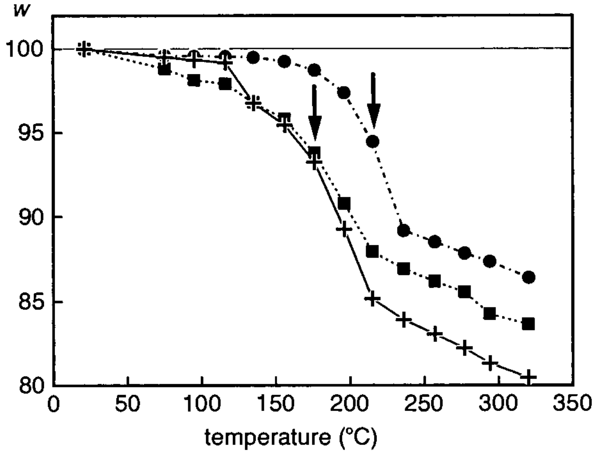

Figure 7. The weight changes of **1** (●), **4** (■), and **5** (+) with the temperature increase. Relative weights in percentage are shown where the values before heat are 100%. The arrows attached to the curves for **1** and **4** indicate the temperature where the colors of the samples changed.

Magnetic Properties. In Figure 8, the magnetic susceptibilities of **1** and **4** are plotted and the magnetic properties are summarized in Table 7. At higher temperatures (50−350 K), both of the compounds obey the Curie−Weiss law. The magnetic susceptibilities have the maximums at low temperatures, indicating antiferromagnetic ordering of metal ions. The alluaudite-type phosphate $NaCo_3(PO_4)(HPO_4)_2$ also show similar magnetic behavior, but the transition temperature is much higher than those of **1** and **4** (Table 7).[10] While in the alluaudite-type phosphate the chains comprised of CoO_6 octahedra sharing their skew edges are linked by PO_4 tetrahedra, in **1** and **4** similar chains are combined with each other by the direct connection through the shared oxygen atoms along with the connection by PO_4 tetrahedra. Therefore, the magnetic interactions between the metal atoms in **1** and **4** are expected to be stronger than those in the alluaudite-type if we assume the magnetic interactions are transmitted through oxygen bridges. However, the transition temperatures and the θ values indicate that the magnetic interactions are much stronger in the alluaudite-type.

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(22) Horng, J. C.; Liao, F. L.; Wang, S. L. *Eur. J. Solid State Inorg. Chem.* **1996**, *33*, 471.

(23) After the sample **1** was heated at 206 °C, the cell parameters *a*, *b*, and *c* decreased by 0.6%, 0.4%, and 0.4%, respectively. The observed small decrease of the *c* parameter indicates that the interlayer distance is mainly determined by the interlayer O−O contacts and/or Na−O contacts. This indication is supported by a short contact of phosphate groups in the neighboring layers. The interlayer O(7x)−O(7y) distance is as short as 2.57 Å (Figure 1), and it is reasonable that the interlayer distance does not decrease explicitly even water molecules between the layers are removed.

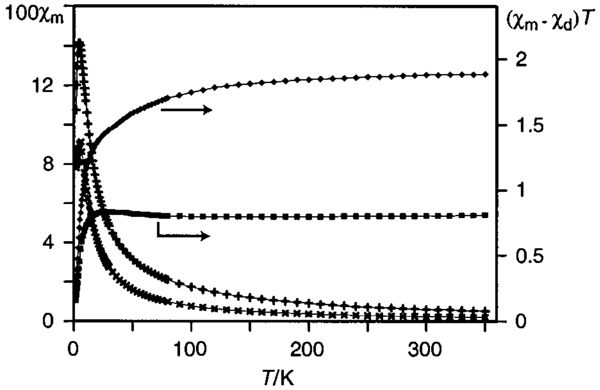

Figure 8. Temperature dependence of the magnetic susceptibility χ_m of **1** (×) and **4** (+) and the $(\chi_m - \chi_d)T$ values of **1** (■) and **4** (◆), where the values of χ_d are given in Table 7. All values are for 1 mol of metal atoms in the emu unit.

These observations suggest that the superexchange through PO_4 tetrahedra is more effective than through oxo bridges as discussed in vanadium phosphates.[24]

Table 7. Magnetic Properties of **1** and **4**

compd	C/(cm^3 K/mol)^a	θ/K^a	$10^4\ \chi_d{}^a$	$\mu/\mu_B{}^b$	χ_{max}/K^c
1	1.172(1)	3.27(4)	3.21(4)	3.061(1)	5.6
4	2.84(1)	−11.3(3)	1.7(5)	4.77(1)	4.8
alluaudite^d	3.28	26	−	5.13	25

[a] The values for **1** and **4** were obtained by the least-squares fitting of the observed susceptibility data above 50 K for 1 mol of metal atoms to an equation $\chi_m = C/(T - \theta) + \chi_d$. The values for alluaudite were taken from ref 10, where the equation $\chi_m = C/(T - \theta)$ was applied for the data above 150 K. [b] Magnetic moment calculated by the relation $\mu^2 = 3k_BC/N$. [c] Temperature of the maximum magnetic susceptibility. [d] $NaCo_3(PO_4)(HPO_4)_2$ with the alluaudite-type structure. All values are from ref 10.

Conclusion

The reactions of hydroxide sol of nickel, cobalt, and magnesium with phosphoric acid yield a novel family of metal(II) phosphates with layered structures. The structure determinations of nickel and cobalt phosphates have revealed that the layers in them are structurally very similar. However, they belong to the different space groups, and the symmetries of the layers, which can be well described by the concept of the layer group, are different. The X-ray powder diffraction has shown that all the phosphates of the new family are isostructural with **1** or **4**, depending on the existence of the interlayer sodium cations.

Acknowledgment. We thank Dr. Tsuchiya and Professor Otsuka at Low-Temperature Center of The University of Tokyo for measuring SQUID data. We thank Mac-Science for the measurements of powder X-ray diffraction. We thank Dr. Eun at The University of Tokyo for assistance in measurements with the ICP emission spectrometer.

Supporting Information Available: A polyhedral drawing of **4** (1 page). Two X-ray crystallographic files, in CIF format, are also available on the Internet only. Access and ordering information is given on any current masthead page.

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(24) Villeneuve, G.; Suh, K. S.; Amorós, P.; Casañ-Pastor, N.; Beltrán-Porter, D. *Chem. Mater.* **1992**, *4*, 108.