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Hydrothermal Synthesis and Crystal Structure of a New Layered Phosphate, $K_2Co_3(P_2O_7)_2 \cdot 2H_2O$

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A novel pyrophosphate, $K_2Co_3(P_2O_7)_2 \cdot 2H_2O$, has been synthesized by hydrothermal techniques and characterized by single crystal X-ray diffraction. Crystals suitable for structure determination were grown by slow cooling from 700°C under an external pressure of 3 kbar, though the phase may be synthesized in pure polycrystalline form under much milder conditions (220°C and 30 bar). The compound adopts the monoclinic space group $P2_1/a$ with $a = 9.229(2)$, $b = 8.110(1)$, $c = 9.122(4)$ Å, $\beta = 99.31(4)°$. The structure was solved by Patterson and Fourier methods, and refined to final agreement factors $R = 0.023$, $R_w = 0.025$. The structure has a layered nature, composed of *cis*-edge-sharing chains of CoO_6 octahedra running parallel to the *b*-direction, linked together by P_2O_7 groups to form two-dimensional sheets in the *ab* plane. Adjacent sheets are separated in the *c*-direction by potassium ions. The ammonium analog of the title compound has also been synthesized. © 1990 Academic Press, Inc.

Introduction

We have recently reported the syntheses and structures of two new layered phosphate materials, $KMn_2O(PO_4)(HPO_4)$ (*1*) and $NH_4Mn_2O(PO_4)(HPO_4) \cdot H_2O$ (*2*). Both compounds were synthesized hydrothermally and have related structures, being based on edge-sharing chains of MnO_6 octahedra linked by PO_4 tetrahedra to form two dimensional sheets which are separated by the larger cations. Layered materials are of interest for their ion exchange properties, and for the possible intercalation of guest species between the layers, a property that is well documented for the phosphates of vanadium (*3*), for example.

The present paper is an extension of our earlier work on the layered Mn(III) phosphates mentioned above. We chose to study another relatively poorly explored system, the mixed phosphates of cobalt, where the only structurally characterized phase previously reported is $NH_4CoPO_4 \cdot H_2O$, itself adopting a layer-like structure (*4*). Here, we report the synthesis and structure of a new layered cobalt pyrophosphate, $K_2Co_3(P_2O_7)_2 \cdot 2H_2O$, and its ammonium analog.

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Experimental

Synthesis and Characterization

Single crystals of $K_2Co_3(P_2O_7)_2 \cdot 2H_2O$ were grown by a hydrothermal technique. A mixture of 0.54 g KH_2PO_4 and 0.25 g $CoCl_2 \cdot 6H_2O$ (molar ratio 4 : 1) was added to 6 ml water and sealed in a 6-in.-long, $\frac{1}{4}$-in.-diameter gold tube. This was heated to 700°C under an external N_2 atmosphere of 3 kbar and held for 12 hr. Subsequent cooling to room temperature, at a rate of 10° hr^{-1}, produced well-formed bright pink crystals with dimensions up to 3 mm. These were filtered, washed with water, and dried in air at room temperature. This route provided the best method of obtaining single crystals of the phase. However, a pure polycrystalline sample of the compound was prepared under less extreme conditions, viz. heating the same starting mixture in a Teflon-lined stainless steel autoclave at 250°C for 3 days. By experience, it was found necessary to use an excess of KH_2PO_4 in order to avoid the preferred formation of $Co_7(HPO_4)_4(PO_4)_2$ (*5*). Both syntheses described above produced a homogeneous product having an X-ray powder pattern as detailed in Table I. A LAZY PULVERIX (*6*) simulation of the pattern is given for comparison. Quantitative X-ray microanalysis, using a JEOL TEMSCAN 2000FX system, gave a composition Co/P = 0.76(5), P/K = 2.1(2). Thermogravimetric analysis, on a DuPont 951/1090B system, revealed a continuous weight loss of 5.7% between 300 and 600°C. This is in excellent agreement with that calculated for the loss of water in the proposed formula, $K_2Co_3(P_2O_7)_2 \cdot 2H_2O$. The product of this treatment was amorphous.

TABLE I

X-RAY POWDER DIFFRACTION PATTERN OF $K_2Co_3(P_2O_7)_2 \cdot 2H_2O$

h	k	l	d_{obsd}	d_{calcd}	I_{obsd}	I_{calcd}
0	0	1	9.08	9.002	vs	100
1	1	−1	5.32	5.296	m	21
1	1	1	4.83	4.792	m	27
2	0	−1	4.34	4.357	w	3
2	1	0	3.93	3.971	w	1
0	1	2		3.936		2
2	1	1	3.45	3.457	m	13
1	1	2		3.440		12
1	2	1	3.36	3.349	m	24
2	1	−2	3.214	3.211	s	50
2	2	0	3.021	3.028	w	3
2	0	2	2.979	2.9699	s	17
2	2	−1		2.9684		39
0	1	3	2.810	2.8142	m	9
1	1	−3		2.8118		2
2	1	2		2.7888		22
2	2	1	2.788	2.7813	s	9
1	2	2		2.7721		9
2	0	−3	2.713	2.7155	m	4
1	3	0		2.5916		3
0	3	1	2.591	2.5891	m	4
3	1	−2		2.5872		9
2	1	−3	2.571	2.5750	w	4
1	3	1	2.461	2.4605	m	15
3	2	−1	2.425	2.4266	m	8
0	2	3	2.413	2.4120	w	5
4	0	0	2.277	2.2769	w	5
3	1	−3	2.259	2.2402	m	12
4	1	0	2.186	2.1921	w	4
1	1	−4		2.1878		5
2	0	−4	2.158	2.1612	w	5
4	1	−2	2.106	2.1040	w	5
2	1	−4	2.086	2.0833	w	3
			. . . + 81 lines to 2θ = 60.00°			

Note. Unobservable lines with $I_{calcd} < 5$ not included. I_{obsd} is a visually estimated value. Data were collected on a Philips PW1710 diffractometer with Cu$K\alpha$ radiation.

Structure Determination and Refinement

Single crystal X-ray diffraction data were collected on an Enraf–Nonius CAD4 diffractometer. The unit cell was determined on the basis of 25 reflections in the range 15° < θ < 25°. Details of the subsequent data collection and refinement are given in Table II. The structure was solved by a combination of Patterson and Fourier methods. The positions of Co(1), Co(2), K(1), and P(1) were determined from the Patterson map, and the remaining nonhy-

TABLE II

DATA COLLECTION AND REFINEMENT PARAMETERS

Formula weight	319.5
Space group	$P2_1/a$
a(Å)	9.229(2)
b(Å)	8.110(1)
c(Å)	9.122(4)
β(°)	99.31(4)
V(Å^3)	673.8
D_{calcd} (g cm^{-3} ($Z = 2$))	3.149
F(000)	558
μ(Mo$K\alpha$) (cm^{-1})	48.3
Crystal size (mm)	0.30 × 0.50 × 0.10
θ min, max (deg)	0.0–40.0
Scan width (deg)	$1.35 + 0.35 \tan \theta$
Scan speed: min, max (deg min^{-1})	0.8–5.5
Total data	7328
Total unique data	4156
Observed data ($I > 3\sigma(I)$)	3851
Absorption correction: min, max	1.00, 1.87
No. of parameters	124
Weights (3-term Chebyshev parameters)	11.7, −8.0, 9.2
Extinction parameter	229(5)
Final rms shift/error	0.10
Max residual electron density (eÅ^{-3})	0.6
Final R, R_w	0.023, 0.025

drogen atoms from successive difference Fourier maps. An analysis of the oxygen atom valence sums (*7*) at this stage suggested probable sites for hydrogen atoms, discrepancies being observed for O(7) (0.45 valence units), O(2) (1.69 v.u.), and O(8) (1.89 v.u.). These figures are indicative of O(7) being the water molecule, with hydrogen bonds being formed for O(2) and O(8). Careful scrutiny of the difference Fourier map revealed two suitable candidates for hydrogen atoms, which were included in the refinement for the final least-squares cycles. Convergence was achieved at $R = 0.023$, $R_w = 0.025$ for a total of 124 parameters. Weights were calculated according to a three-term Chebyshev polynomial (*8*). All crystallographic data analysis was carried out using the Oxford CRYSTALS system (*9*). Figures were drawn using the program STRUPLO84 (*10*).

Results and Discussion

Final atomic coordinates, anisotropic thermal parameters, and selected bond distances and angles are given in Tables III, IV, and V, respectively. A view of the structure along [100] is shown in Fig. 1, from which the layer-like nature is readily apparent. Figure 2 shows an alternative, [010], view parallel to these layers, while Fig. 3 shows a plan view of one of the layers, along [001]. Each layer consists of edge-sharing chains of CoO_6 octahedra running parallel to *b*, interconnected by bridging pyrophosphate groups, to form continuous sheets in the *ab* plane. Interlayer linkages are made via the potassium ions and via hydrogen bonds. The Co(1) octahedron shares *trans* edges with two Co(2) octahedra, while the Co(2) octahedron shares *cis* edges with adjacent Co(1) and Co(2) oc-

TABLE III

FINAL ATOMIC COORDINATES AND ISOTROPIC/EQUIVALENT ISOTROPIC THERMAL PARAMETERS FOR $K_2Co_3(P_2O_7)_2 \cdot 2H_2O$

Atom	x/a	y/b	z/c	U(iso)/U(equiv)
Co(1)	0.5000	0.0000	0.5000	0.0077
Co(2)	0.00301(1)	0.14106(1)	0.36634(1)	0.0078
K(1)	0.52232(2)	0.22557(3)	0.92540(2)	0.0176
P(1)	0.79055(2)	0.19783(2)	0.60177(2)	0.0061
P(2)	0.26520(2)	0.06848(2)	0.19785(2)	0.0072
O(1)	0.38804(7)	0.12591(7)	0.31977(7)	0.0100
O(2)	0.36280(6)	0.13646(7)	0.63700(7)	0.0093
O(3)	0.88878(6)	0.07555(7)	0.53883(6)	0.0087
O(4)	0.63743(6)	0.20410(7)	0.51051(7)	0.0091
O(5)	0.76597(7)	0.12459(7)	0.76174(6)	0.0097
O(6)	0.30974(8)	0.05807(8)	0.04659(7)	0.0125
O(7)	0.84379(8)	0.0067(1)	0.22668(8)	0.0151
O(8)	0.12179(7)	0.15853(8)	0.19798(7)	0.0116
H(1)	0.230(3)	0.023(3)	0.734(3)	0.032(5)
H(2)	0.201(3)	−0.008(4)	0.865(4)	0.040(8)

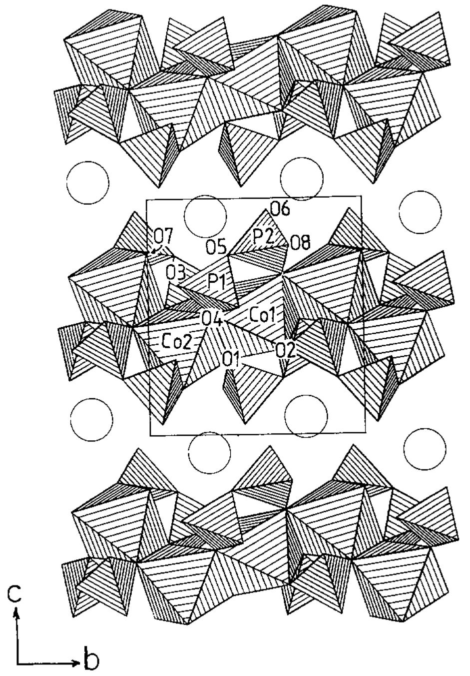

FIG. 1. View of the $K_2Co_3(P_2O_7)_2 \cdot 2H_2O$ structure along [100]. The K^+ ions are represented by open circles.

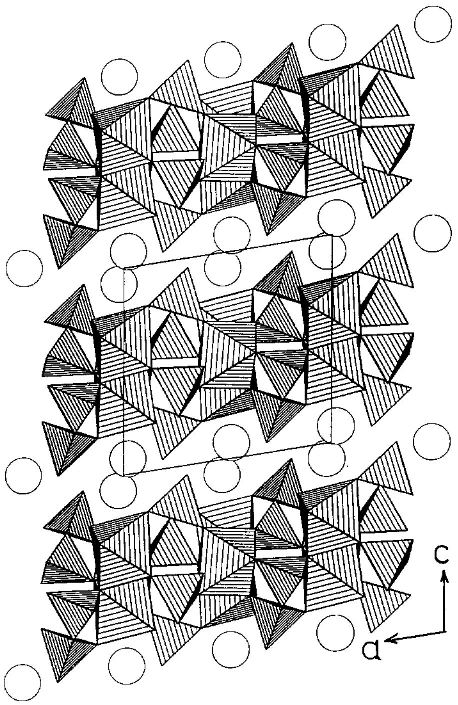

FIG. 2. View of the $K_2Co_3(P_2O_7)_2 \cdot 2H_2O$ structure along [010], for comparison with Fig. 1.

TABLE IV

ANISOTROPIC THERMAL PARAMETERS[a] FOR $K_2Co_3(P_2O_7)_2 \cdot 2H_2O$

Atom	U(11)	U(22)	U(33)	U(23)	U(13)	U(12)
Co(1)	0.00730(5)	0.00678(5)	0.00924(6)	0.00117(3)	−0.00082(4)	−0.00059(3)
Co(2)	0.00754(4)	0.00748(4)	0.00838(4)	−0.00031(2)	0.00131(3)	0.00022(2)
K(1)	0.01732(7)	0.02012(8)	0.01534(7)	−0.00153(5)	−0.00019(5)	0.00163(6)
P(1)	0.00532(6)	0.00586(6)	0.00727(6)	−0.00010(4)	0.00094(5)	0.00004(4)
P(2)	0.00711(7)	0.00876(7)	0.00604(6)	0.00060(5)	0.00078(5)	−0.00062(5)
O(1)	0.0106(2)	0.0095(2)	0.0107(2)	0.0008(1)	−0.0026(2)	−0.0022(2)
O(2)	0.0101(2)	0.0073(2)	0.0122(2)	0.0011(1)	0.0024(2)	0.0025(1)
O(3)	0.0090(2)	0.0082(2)	0.0110(2)	0.0004(1)	0.0036(1)	0.0023(1)
O(4)	0.0065(2)	0.0092(2)	0.0128(2)	0.0016(1)	−0.0015(1)	−0.0000(1)
O(5)	0.0132(2)	0.0091(2)	0.0081(2)	0.0002(1)	0.0024(2)	−0.0020(2)
O(6)	0.0170(2)	0.0174(2)	0.0081(2)	0.0008(2)	0.0050(2)	−0.0019(2)
O(7)	0.0163(2)	0.0229(3)	0.0121(2)	−0.0008(2)	0.0009(2)	−0.0096(2)
O(8)	0.0092(2)	0.0163(2)	0.0126(2)	0.0040(2)	0.0028(2)	0.0036(2)

[a] The U's are defined by $\exp[-2\pi^2(U_{11}h^2a^{*2} + \ldots . 2U_{23}klb^*c^*)]$.

tahedra. The pyrophosphate group acts as a bidentate ligand to Co(1), thus producing a fairly bent P_2O_7 group (P1)–O(5)–P(2) = 127.17°). This is unusual for a pyrophosphate of a rather small divalent ion, and leads to relatively long bridging P–O bonds of 1.625 and 1.645 Å for P(1) and P(2), respectively. These may be compared with those in, for example, $Mn_2P_2O_7$ (*11*)—1.582 Å and $Co_2P_2O_7$ (*12*)—1.600 and 1.566 Å, where the P_2O_7 group is allowed to take up a more linear configuration. In all cases, the bridging P–O bonds are, of course, much longer than the terminal ones, as expected on theoretical grounds (*13*). The potassium ion is best described as eight coordinate, with K–O distances in the range 2.678–3.223 Å, and no further oxygens within 3.6 Å.

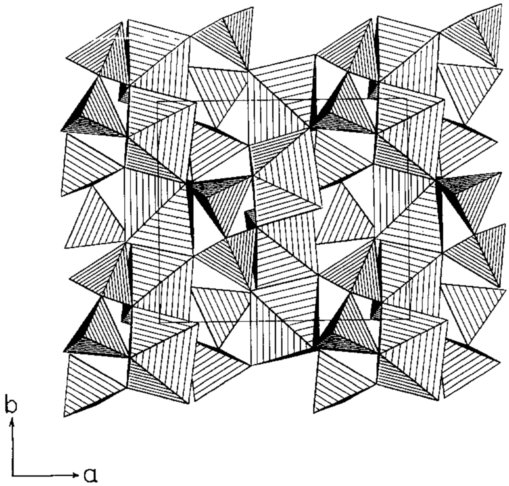

FIG. 3. View of the $K_2Co_3(P_2O_7)_2 \cdot 2H_2O$ structure along [001], showing a plan view of one of the layers.

There are no previously reported analogs of this phase; a compound of stoichiometry "$K_2Ca_3(P_2O_7)_2 \cdot 2H_2O$" has been previously reported (*14*), but the powder X-ray pattern of this phase bears no relation to the present case, and lack of structural analysis may cast some doubt upon the authenticity of its composition. Our attempts to prepare analogs using other transition metals were unsuccessful. However, the corresponding ammonium compound, $(NH_4)_2Co_3(P_2O_7)_2 \cdot 2H_2O$, was prepared by a method analogous to that for the title compound, viz. by reacting a 4 : 1 molar ratio of $CoCl_2 \cdot 6H_2O$ and $NH_4H_2PO_4$ hydrothermally at 250°C for 3

TABLE V

SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (deg) AND POLYHEDRAL EDGE LENGTHS (Å) FOR $K_2Co_3(P_2O_7)_2 \cdot 2H_2O$

		Distance	Angle	Edge
Co(1) octahedron				
Co(1)–O(1)	×2	2.065(1)		
Co(1)–O(2)	×2	2.214(1)		
Co(1)–O(4)	×2	2.078(1)		
O(1)–Co(1)–O(2)		×2	86.79(2)	2.942(1)
O(1)–Co(1)–O(2)		×2	93.21(2)	3.111(1)
O(1)–Co(1)–O(4)		×2	97.71(2)	3.120(1)
O(1)–Co(1)–O(4)		×2	82.29(2)	2.726(1)
O(2)–Co(1)–O(4)		×2	89.64(2)	3.000(1)
O(2)–Co(1)–O(4)		×2	91.36(2)	3.072(1)
Co(2) octahedron				
Co(2)–O(1)		2.175(1)		
Co(2)–O(3)		2.099(1)		
Co(2)–O(3)		2.134(1)		
Co(2)–O(4)		2.078(1)		
Co(2)–O(7)		2.089(1)		
Co(2)–O(8)		2.031(1)		
O(1)–Co(2)–O(3)			94.47(2)	3.139(1)
O(1)–Co(2)–O(3)			167.43(2)	
O(1)–Co(2)–O(4)			79.69(2)	3.120(1)
O(1)–Co(2)–O(7)			93.51(3)	2.896(1)
O(1)–Co(2)–O(8)			95.60(2)	3.118(1)
O(3)–Co(2)–O(3)			75.32(2)	2.586(1)
O(3)–Co(2)–O(4)			89.96(2)	2.953(1)
O(3)–Co(2)–O(7)			86.34(3)	2.865(1)
O(3)–Co(2)–O(8)			169.24(2)	
O(3)–Co(2)–O(4)			92.79(2)	3.050(1)
O(3)–Co(2)–O(7)			93.14(3)	3.067(1)
O(3)–Co(2)–O(8)			95.14(2)	3.075(1)
O(4)–Co(2)–O(7)			171.99(3)	
O(4)–Co(2)–O(8)			95.53(3)	3.043(1)
O(7)–Co(2)–O(8)			89.29(3)	2.896(1)
P_2O_7 group				
P(1)–O(2)		1.511(1)		
P(1)–O(3)		1.518(1)		
P(1)–O(4)		1.520(1)		
P(1)–O(5)		1.625(1)		
O(2)–P(1)–O(3)			113.05(3)	2.527(1)
O(2)–P(1)–O(4)			115.19(3)	2.560(1)
O(2)–P(1)–O(5)			104.77(3)	2.485(1)
O(3)–P(1)–O(4)			111.95(3)	2.518(1)
O(3)–P(1)–O(5)			106.23(3)	2.515(1)
O(4)–P(1)–O(5)			104.57(3)	2.489(1)
P(2)–O(1)		1.527(1)		
P(2)–O(5)		1.645(1)		
P(2)–O(6)		1.504(1)		
P(2)–O(8)		1.512(1)		

TABLE V—*Continued*

	Distance	Angle	Edge
O(1)–P(2)–O(5)		105.27(3)	2.522(1)
O(1)–P(2)–O(6)		113.85(4)	2.540(1)
O(1)–P(2)–O(8)		113.52(4)	2.541(1)
O(5)–P(2)–O(6)		103.64(3)	2.477(1)
O(5)–P(2)–O(8)		105.95(3)	2.521(1)
O(6)–P(2)–O(8)		113.39(4)	2.521(1)
P(1)–O(5)–P(2)		127.17(4)	
K(1) polyhedron			
K(1)–O(2)	2.891(1)		
K(1)–O(5)	3.007(1)		
K(1)–O(5)	2.856(1)		
K(1)–O(6)	2.760(1)		
K(1)–O(6)	2.762(1)		
K(1)–O(6)	3.223(1)		
K(1)–O(7)	3.034(1)		
K(1)–O(8)	2.678(1)		
Water molecule			
O(7)–H(1)	0.86(2)		
O(7)–H(2)	0.87(3)		
H(1)–O(7)–H(2)		97(3)	
Hydrogen bonding			
Donor–H–Acceptor	D---A	H---A	D---H---A
O(7)–H(1)---O(2)	2.701(1)	1.87(2)	165(2)
O(7)–H(2)---O(6)	2.712(1)	1.87(3)	162(3)

days. The product was a pale pink powder having an XRD pattern very similar to that of $K_2Co_3(P_2O_7)_2 \cdot 2H_2O$. X-ray microanalysis confirmed the heavy element ratio (Co/P = 0.78(4), P/K = 2.0(2)), and a TGA scan was used to confirm the water content. This revealed a weight loss of 14.6% compared to a calculated loss of only 13.9% for the removal of $2NH_3 + 2H_2O$. The product of this heat treatment, as shown by XRD and X-ray microanalysis, was $Co_7(PO_4)_2(HPO_4)_4$ (*5*)—a small degree of volatilization of P_2O_5 may account for the extra weight loss.

Despite the apparent potential for exchange of the interlayer ions in these phases, our attempts to carry out such transformations have proved unsuccessful. No exchange of potassium was observed for either sodium or ammonium, in 1 *M* solutions up to 80°C. Partial exchange for lithium was observed under these conditions, albeit with considerable loss of crystallinity.

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