Hydrothermal Synthesis and Structure of Dihydrated Cobalt Pyrophosphates

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H₂Co₂P₄O₁₄ crystals were synthesized by a hydrothermal technique. They crystallized in a monoclinic system with cell parameters $a = 9.1609(7)\text{\AA}$, $b = 12.6764(8)\text{\AA}$, $c = 9.6868(10)\text{\AA}$ and $\beta = 106.771(7)^\circ$. An open framework structure having tunnel-type cavities is observed.

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Phosphates were studied extensively owing to their wide range of applications such as piezoelectric, magnetic, luminescence, ceramics and superionics application.¹⁻³ Subsequently, there were also reports on pyrophosphates exhibiting simple framework structure with relatively high ionic conductivity values.⁴ Recently, there are also reports on hydrated phosphates.⁵ Here, we report a new group of hydrated cobalt-bearing pyrophosphates, which is paramagnetic in nature at ambient condition.

H₂Co₂P₄O₁₄ crystals were synthesized by hydrothermal processing. The growth of phosphates by the hydrothermal technique is relatively new and is quite complicated for these compounds, because of the highly corrosive and volatile nature of phosphorus at higher temperature. Following earlier methods, the present experiments were carried out in Morey type autoclaves provided with Teflon liners, in the temperature and pressure range of 230 – 265°C and 60 – 100 bars. All reagents used in the synthesis process were of Analar grade with 99.9% purity from Merck. The desired quantity of CoCl₃ was dissolved in 10 ml of 0.25 M of EDTA solution and the mixture was taken in Teflon liners, then 6 ml of 85% H₃PO₄ was added. The crystallization was carried out by spontaneous nucleation controlled through a slow and programmed rate of heating. The authors were able to synthesize H₂Co₂P₄O₁₄ crystals under the following experimental conditions: molar ratio, Co₂O₃ : P₂O₅ : H₂O = 1 – 1.5 : 10 – 12 : 8 – 10; T , 260°C; P , 80 bars; duration = 8 – 10 days.

The following reaction could explain the formation of H₂Co₂P₄O₁₄:

The crystals obtained by this method were of good quality, exhibiting translucent luster with well developed morphology. The sizes of crystals range from 0.5 to 3 mm with pink color.

A single crystal of H₂Co₂P₄O₁₄ of dimensions 0.2 × 0.2 × 0.2 mm was chosen for X-ray diffraction studies. The crystal and experimental data are given in Table 1. The structure was solved by direct methods and refined by full-matrix least

squares methods with anisotropic temperature factors for the non-H atoms. H atoms were generated by a difference Fourier map and were placed at a distance of 0.98 Å from the parent atom. The maximum peak lies at the nearest distances of 0.76 Å, 1.58 Å, 1.85 Å and 1.92 Å from the atoms Co1, O3, O11 and O5, respectively. The final coordinates and equivalent thermal parameters of non-H atoms are listed in Table 2. Table 3 gives selected bond distances and bond angles; they agree with their standard values. Figure 1 represents the ORTEP diagram of the molecule with thermal ellipsoids at 50% probability. Crystal structure has an additional feature of a pseudo I -centred lattice translation of (0.5, 0.5, 0.5) for all the atoms except O7, O10, O16 and O19, respectively. But the structure could not be solved and refined in the space group $I2/a$.

The polymerization of phosphate with Co has revealed its coordination and packing mode. Each Co atom has coordination with six pyrophosphate oxygen atoms *i.e.*, from two O-atoms of one terminal pyrophosphate. This coordination environment resembles a distorted hexahedron representation or six membered ring column. Also, the Co–O–Co–O ring

Table 1 Crystal and experimental data

Formula	H ₂ Co ₂ O ₁₄ P ₄
Formula weight	467.76
Crystal system	monoclinic
Space group	$P2_1/c$, $Z = 4$
a	9.1609(7)Å
b	12.6764(8)Å
c	9.6868(10)Å
β	106.771(7)Å
V	1077.06(15)Å ³
D_x	2.885 Mg/cm ³
θ_{max}	30.02° with Mo K_α
R	0.0382
$(\Delta/\sigma)_{\text{max}}$	0.001
$(\Delta\rho)_{\text{max}}$	1.111 eÅ ⁻³
$(\Delta\rho)_{\text{min}}$	– 1.093 eÅ ⁻³
Measurement	DipLabo Kappa
Program system	Denzo
Structure determination	SHELXS-97
Refinement	fullmatrix: SHELXL-97

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Table 2 Atomic coordinates and equivalent temperature factors ($\text{\AA}^2$)

Atom	x	y		
Co1	0.75030(3)	0.25490(3)	-0.24969(3)	0.00847(13)
Co2	0.74781(4)	0.08553(3)	-0.00442(3)	0.00884(13)
O3	0.6188(2)	0.21742(15)	-0.1140(2)	0.0114(4)
P4	0.51443(8)	0.29103(6)	-0.06417(7)	0.01059(17)
O5	0.5638(3)	0.31532(17)	0.0935(2)	0.0170(4)
O6	0.3494(3)	0.2478(3)	-0.1042(3)	0.0414(8)
O7	0.5025(4)	0.3980(2)	-0.1468(3)	0.0475(10)
P8	0.54163(8)	0.03871(6)	0.22708(7)	0.01098(17)
O9	0.6025(2)	-0.02151(17)	-0.1125(2)	0.0201(5)
O10	0.6158(3)	-0.0646(2)	0.3013(3)	0.0294(6)
O11	0.6626(2)	0.09934(15)	0.1822(2)	0.0128(4)
O12	0.8835(2)	0.20750(15)	0.1142(2)	0.0107(4)
P13	0.99318(8)	0.27895(5)	0.06757(7)	0.00888(16)
O14	0.9303(3)	0.17526(16)	0.4196(2)	0.0162(4)
O15	1.1502(3)	0.22399(19)	0.0886(3)	0.0209(5)
O16	1.0462(2)	0.36873(17)	0.1838(2)	0.0178(4)
P17	0.97722(8)	0.44506(5)	0.28156(7)	0.00920(16)
O18	1.1084(2)	0.46732(17)	0.4108(2)	0.0169(4)
O19	0.9113(3)	0.54082(18)	0.1868(3)	0.0237(5)
O20	0.8469(2)	0.11116(15)	-0.1829(2)	0.0117(4)

$$U_{eq} = (1/3) \sum_i \sum_j U_{ij} (a_i^* a_j^*) (a_i a_j).$$

Table 3 Bond lengths ($\text{\AA}$) and bond angles ($^\circ$)

Atoms	Length	Atoms	Length
P17-O18	1.491(2)	Co2-O3	2.1434(19)
P17-O20#e	1.513(2)	Co2-O18#a	2.028(2)
P4-O5	1.494(2)	Co1-O20	2.047(2)
P4-O6	1.549(3)	Co1-O12#d	2.094(2)
P8-O9#c	1.475(2)	Co1-O14	2.152(2)
P8-O11	1.512(2)	O11-Co1#e	2.047(2)
P13-O12	1.515(2)	O14-P13#e	1.499(2)
O(18)-P(17)-O(20)#e	113.32(12)	O(14)#d-P(13)-O(12)	114.32(12)
O(18)-P(17)-O(19)	115.77(13)	O(18)#a-Co(2)-O(20)	95.66(8)
O(20)#e-P(17)-O(19)	107.93(12)	O(11)-Co(2)-O(20)	166.45(8)
O(18)-P(17)-O(16)	104.51(12)	O(20)-Co(1)-O(12)#d	97.13(8)
O(20)#e-P(17)-O(16)	108.71(11)	P(8)-O(11)-Co(2)	131.87(12)
O(19)-P(17)-O(16)	106.13(13)	Co(1)#e-O(11)-Co(2)	97.99(8)
O(9)#c-P(8)-O(11)	115.45(13)	P(17)-O(18)-Co(2)#b	141.01(14)
O(12)-P(13)-O(16)	108.24(11)	P(13)-O(12)-Co(2)	127.91(12)

represents a four membered ring column. These condensed phosphates have been extended linearly and interlinked *via* metal coordination, which in turn exhibits three dimensional open framework structure. Tunnel-type cavities are observed in the molecular packing diagram along the *a* axis. By suitable

Fig. 1 ORTEP diagram of the molecule at 50% probability. Symmetry transformations used to generate equivalent atoms: #a $(-x + 2, y - 1/2, -z + 1/2)$, #b $(-x + 2, y + 1/2, -z + 1/2)$, #c $(-x + 1, -y, -z)$, #d $(x, -y + 1/2, z - 1/2)$, #e $(x, -y + 1/2, z + 1/2)$.

modification in the synthetic procedure, we can have the participation of alkali metal ions in the cavity as expected for the ion transport mechanism.⁶

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