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 \( a = 9.1609(7)\,\text{Å}, \quad b = 12.6764(8)\,\text{Å}, \quad c = 9.6868(10)\,\text{Å} \) and \( \beta = 106.771(7)^\circ \). An open framework structure having tunnel-type cavities is observed.

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Table 1 Crystal and experimental data

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>H₂Co₂O₄P₄</td>
</tr>
<tr>
<td>Formula weight</td>
<td>467.76</td>
</tr>
<tr>
<td>Crystal system</td>
<td>monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>( P2_1/c, \ Z = 4 )</td>
</tr>
<tr>
<td>( a )</td>
<td>9.1609(7)Å</td>
</tr>
<tr>
<td>( b )</td>
<td>12.6764(8)Å</td>
</tr>
<tr>
<td>( c )</td>
<td>9.6868(10)Å</td>
</tr>
<tr>
<td>( \beta )</td>
<td>106.771(7)Å</td>
</tr>
<tr>
<td>( V )</td>
<td>1077.06(15)Å²</td>
</tr>
<tr>
<td>( D )</td>
<td>2.885 Mg/cm³</td>
</tr>
<tr>
<td>( \theta_{\text{ex}} )</td>
<td>30.02° with Mo Kα</td>
</tr>
<tr>
<td>( R )</td>
<td>0.0382</td>
</tr>
<tr>
<td>( (\Delta\sigma)_{\text{ex}} )</td>
<td>0.001</td>
</tr>
<tr>
<td>( (\Delta\rho)_{\text{ex}} )</td>
<td>1.111 e⁻³</td>
</tr>
<tr>
<td>( (\Delta\rho)_{\text{std}} )</td>
<td>−1.093 e⁻³</td>
</tr>
<tr>
<td>Measurement</td>
<td>DipLabo Kappa</td>
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<tr>
<td>Program system</td>
<td>Denzo</td>
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<tr>
<td>Structure determination</td>
<td>SHELXS-97</td>
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<tr>
<td>Refinement</td>
<td>fullmatrix: SHELXL-97</td>
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Phosphates were studied extensively owing to their wide range of applications such as piezoelectric, magnetic, luminescence, ceramics and superionic 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 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 CoCl₂ was solved and refined in the space group \( I \) centered 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 \( P2_1/a \) in the presence of Co atoms.

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

\[ 2\text{CoCl}_2 + 4\text{H}_3\text{PO}_4 + 2\text{H}_2\text{O} \rightarrow \text{H}_2\text{Co}_2\text{P}_4\text{O}_{14} + 6\text{HCl} + 4\text{H}_2\text{O} \]
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 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

Acknowledgements

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References


Table 2 Atomic coordinates and equivalent temperature factors (Å²)

<table>
<thead>
<tr>
<th>Atom</th>
<th>x</th>
<th>y</th>
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<tbody>
<tr>
<td>Co1</td>
<td>0.75030(3)</td>
<td>0.25490(3)</td>
</tr>
<tr>
<td>Co2</td>
<td>0.74784(4)</td>
<td>0.38553(3)</td>
</tr>
<tr>
<td>O3</td>
<td>0.6388(2)</td>
<td>0.21142(15)</td>
</tr>
<tr>
<td>P4</td>
<td>0.53444(8)</td>
<td>0.29120(6)</td>
</tr>
<tr>
<td>O5</td>
<td>0.5638(3)</td>
<td>0.33153(17)</td>
</tr>
<tr>
<td>O6</td>
<td>0.3494(3)</td>
<td>0.24783(3)</td>
</tr>
<tr>
<td>O7</td>
<td>0.5025(4)</td>
<td>0.3980(2)</td>
</tr>
<tr>
<td>P8</td>
<td>0.54163(8)</td>
<td>0.03837(16)</td>
</tr>
<tr>
<td>O9</td>
<td>0.6025(2)</td>
<td>0.02151(17)</td>
</tr>
<tr>
<td>O10</td>
<td>0.6156(3)</td>
<td>0.06642(2)</td>
</tr>
<tr>
<td>O11</td>
<td>0.6266(2)</td>
<td>0.09934(15)</td>
</tr>
<tr>
<td>O12</td>
<td>0.8835(2)</td>
<td>0.20750(15)</td>
</tr>
<tr>
<td>O13</td>
<td>0.9391(8)</td>
<td>0.27856(5)</td>
</tr>
<tr>
<td>O14</td>
<td>0.9393(3)</td>
<td>0.17526(16)</td>
</tr>
<tr>
<td>O15</td>
<td>1.1503(2)</td>
<td>0.23399(19)</td>
</tr>
<tr>
<td>O16</td>
<td>1.0462(2)</td>
<td>0.36873(17)</td>
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<td>P17</td>
<td>0.97722(6)</td>
<td>0.44508(16)</td>
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<tr>
<td>O18</td>
<td>1.10842(2)</td>
<td>0.46732(17)</td>
</tr>
<tr>
<td>O19</td>
<td>0.9113(3)</td>
<td>0.54898(18)</td>
</tr>
<tr>
<td>O20</td>
<td>0.8469(2)</td>
<td>0.11116(15)</td>
</tr>
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</table>

Ueq = (1/3)ΣΣi,jUij(ai·aj).

Table 3 Bond lengths (Å) and bond angles (°)

<table>
<thead>
<tr>
<th>Atoms</th>
<th>Length</th>
<th>Atoms</th>
<th>Length</th>
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</thead>
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<tr>
<td>P17-O18</td>
<td>1.491(2)</td>
<td>Co2-O3</td>
<td>2.1434(19)</td>
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<tr>
<td>P17-O20#e</td>
<td>1.533(2)</td>
<td>Co2-O18#a</td>
<td>2.028(2)</td>
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<tr>
<td>P4-O5</td>
<td>1.494(2)</td>
<td>Co1-O20</td>
<td>2.047(2)</td>
</tr>
<tr>
<td>P4-O6</td>
<td>1.549(3)</td>
<td>Co1-O12#d</td>
<td>2.094(3)</td>
</tr>
<tr>
<td>P8-O9#e</td>
<td>1.475(2)</td>
<td>Co1-O14</td>
<td>2.152(2)</td>
</tr>
<tr>
<td>P8-O11</td>
<td>1.512(2)</td>
<td>O11-Co1#e</td>
<td>2.047(2)</td>
</tr>
<tr>
<td>P13-O12</td>
<td>1.515(2)</td>
<td>O14-P13#e</td>
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</tr>
<tr>
<td>O(18)-P(17)-O(20)#e</td>
<td>1.332(12)</td>
<td>O(14)-#d-P(15)-O(12)</td>
<td>1.142(12)</td>
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<tr>
<td>O(18)-P(17)-O(19)</td>
<td>1.157(13)</td>
<td>O(18)-#e-Co(2)-O(30)</td>
<td>0.966(8)</td>
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<tr>
<td>O(20)-#e-P(17)-O(19)</td>
<td>1.079(12)</td>
<td>O(11)-Co(2)-O(20)</td>
<td>0.966(8)</td>
</tr>
<tr>
<td>O(18)-P(17)-O(16)</td>
<td>1.041(12)</td>
<td>O(20)-Co(1)-O(12)#d</td>
<td>0.973(8)</td>
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<tr>
<td>O(20)-#e-P(17)-O(16)</td>
<td>1.087(11)</td>
<td>P(8)-O(11)-Co(2)</td>
<td>1.318(12)</td>
</tr>
<tr>
<td>O(19)-#e-P(17)-O(16)</td>
<td>1.061(13)</td>
<td>Co(1)-#e-O(11)-Co(2)</td>
<td>0.979(9)</td>
</tr>
<tr>
<td>O(9)-#e-P(8)-O(11)</td>
<td>1.154(13)</td>
<td>P(17)-O(18)-Co(2)#b</td>
<td>1.411(14)</td>
</tr>
<tr>
<td>O(12)-P(13)-O(16)</td>
<td>1.084(11)</td>
<td>P(13)-O(12)-Co(2)</td>
<td>1.279(12)</td>
</tr>
</tbody>
</table>

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).