

[Co(H₂O)(HPO₄)]·H₂O: The Layered Divalent Metal Monohydrogenphosphate Structure

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A new layered divalent metal monohydrogenphosphate [Co(H₂O)(HPO₄)]·H₂O (1) was hydrothermally synthesized from the reaction of CoCl₂·6H₂O with H₃PO₄ in the presence of *cis*-Pt(NH₃)₂Cl₂ and ethylenediamine. The structure features extensive intra- and inter-layer hydrogen bonding among the hydrogenphosphate anion, the coordinated water and the crystallization water. X-ray crystallographic parameters for 1 are orthorhombic *Pnma* (# 62), *a* = 1.7528(2), *b* = 0.56158(7), *c* = 0.47867(6) nm, *V* = 0.47116(9) nm³, *Z* = 4

Keywords hydrothermal reaction, monohydrogenphosphate, hydrogen bonding, structure

Introduction

Since the pioneer works of Clearfield and coworkers in the 1960s,^{1,2} layered metal phosphates have attracted much attention due to their applications on ion exchange, intercalation, heterogeneous catalysis and sorption.³⁻⁷ Among the numerous lamellar phases, the prototypical tetravalent metal hydrogenphosphates represented by Zr(HPO₄)₂·H₂O (*α*-ZrP) occupy a prominent position in this area.⁸ These compounds feature protic hydrogen atoms on the layers, and can provide a convenient entry to a large number of new lamellar phases via intercalation or ion exchange.^{6,9-13}

We have been interested in the synthesis of new open-framework structures of transition metal phosphates, borophosphates and inorganic-organic hybrid oxides by molecular templating reactions. In an attempt to

synthesize some new cobalt phosphate compounds using *cis*-Pt(NH₃)₂Cl₂ as a template, we obtained a new hydrated layered compound [Co(H₂O)(HPO₄)]·H₂O (1). Thus far, this compound has proven to be inaccessible by a direct hydrothermal reaction of CoCl₂·6H₂O with Na₂HPO₄. Herein, we report the synthesis and structural characterization of [Co(H₂O)(HPO₄)]·H₂O, the first layered divalent metal monohydrogenphosphate.

Experimental

Synthesis and characterization

The chemicals were purchased from either Aldrich or Strem and used as obtained. All manipulations were performed in air. The elemental analysis was performed on a Perkin-Elmer, Model 240C elemental analyzer. The FT-IR spectrum was recorded on a Nicolet 750 FT-IR spectrometer in the KBr matrix in the range of 400—4000 cm⁻¹. The diffuse reflectance UV/VIS spectrum was measured on a Varian Cary 1E spectrophotometer equipped with a 73-mm diameter integrating sphere. The semi-quantitative analysis of Co, P and O contents was performed on single crystal samples with a JEOL 5800 LV scanning electron microscope (SEM) equipped with an X-ray microanalysis attachment and the H-atoms content of the compound was determined by a Model 240C elemental analyzer.

A mixture of 30 mg (0.126 mmol) of CoCl₂·6H₂O, 38 mg (0.126 mmol) of *cis*-Pt(NH₃)₂Cl₂, 110

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mg (1.80 mmol) of ethylenediamine and 115 mg (1.00 mmol) of 85% H_3PO_4 was sealed in a thick wall Pyrex tube. The reaction was carried out at 110 °C for 7 d to afford purple single crystals of $[\text{Co}(\text{H}_2\text{O})(\text{HPO}_4)] \cdot \text{H}_2\text{O}$ with 50% yield. Semi-quantitative elemental analysis showed the Co, P and O contents in the $[\text{Co}(\text{H}_2\text{O})(\text{HPO}_4)] \cdot \text{H}_2\text{O}$ were 29.4%, 16.6% and 53.7%, respectively, and the elemental analysis gave H content in the compound as 2.71%, which was in agreement with calculated values of 30.89% (Co), 16.23% (P), 50.26% (O) and 2.62% (H) based on the formula of $[\text{Co}(\text{H}_2\text{O})(\text{HPO}_4)] \cdot \text{H}_2\text{O}$ revealed by single-crystal structure analysis.

The phase identity and homogeneity of **1** were confirmed by comparing its experimental X-ray powder diffraction patterns of the bulk material with those calculated from the single crystal X-ray data.

X-Ray data collection, structure solution and refinement

A brilliant purple platelet single crystal of $[\text{Co}(\text{H}_2\text{O})(\text{HPO}_4)] \cdot \text{H}_2\text{O}$ having approximate dimensions of 0.18 mm × 0.08 mm × 0.02 mm was selected from the reaction product and mounted on a thin glass fiber using epoxy cement. All measurements were made on a Siemens SMART 1000 CCD diffractometer with graphite

monochromated Mo K_α radiation ($\lambda = 0.071073$ nm) operating at 50 kV and 35 mA.

The data were collected at -100 °C using a narrow frame method with scan widths of 0.3 in ω and exposure times of 20 s. A hemisphere of intensity data was collected in 1081 frames with the crystal to detector distance of 50.4 mm. Frames were integrated with the Siemens SAINT program.¹⁴ A semi-empirical absorption correction based upon simulated Ψ -scans was applied to the data set.

The unit cell constants corresponding to a primitive orthorhombic cell with dimensions of $a = 1.7528(2)$, $b = 0.56158(7)$, $c = 0.47867(6)$ nm, $V = 0.47116(9)$ nm³ were obtained from a least squares refinement using 1851 reflections in full θ range. Of the 2495 reflections which were collected, 613 were unique ($R_{\text{int}} = 0.041$). The weighting scheme was based on counting statistics and included a factor ($p = 0.031$) to down-weight the intense reflections. $\sigma w (|F_o| - |F_c|)^2$ versus $|F_o|$, reflection order in data collection, $\sin\theta/\lambda$ and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 9.5×10^{-4} and -6.5×10^{-4} e⁻/nm³, respectively. Details of the data collection, structure solution and refinement are given in Table 1.

Table 1 Results of crystal data and structure refinement

| | |
|------------------------------------|---|
| Empirical formula | $[\text{Co}(\text{H}_2\text{O})(\text{HPO}_4)] \cdot \text{H}_2\text{O}$ |
| Formula weight | 190.94 |
| Color/shape | purple/platelet |
| Crystal system | orthorhombic |
| Space group | $Pnma$ (# 62) |
| | $a = 1.7528(2)$ nm, $\alpha = 90^\circ$ |
| | $b = 0.56158(7)$ nm, $\beta = 90^\circ$ |
| | $c = 0.47867(6)$ nm, $\gamma = 90^\circ$ |
| V | 0.47116(9) nm ³ |
| Z | 4 |
| Density (calculated) | 2.692 mg/mm ³ |
| Absorption coefficient | 3.992 mm ⁻¹ |
| $F(000)$ | 380.00 |
| Crystal size | 0.18 mm × 0.08 mm × 0.02 mm |
| θ | 1.16 to 27.00 |
| Reflections collected | 2495 |
| Independent/observed refl. | 613 ($R_{\text{int}} = 0.041$)/408 ($I > 3\sigma(I)$) |
| Absorption collection | Semi-empirical from simulated psi-scans |
| Range of relative. transm. factors | 1.00, 0.7636 |
| Final R indices $I > 3\sigma(I)$ | $R = 0.0397$, $wR = 0.0476$ |
| Goodness-of-fit on F | 1.476 |
| Weighting scheme | $W = 1/[\sigma^2(F_o) + 0.00024 F_o ^2]$ |
| Largest difference peak and hole | 9.5×10^{-4} and -6.5×10^{-4} e ⁻ ·nm ⁻³ |

Results and discussion

The title compound was synthesized by a hydrothermal reaction of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ with H_3PO_4 in the presence of $\text{cis-Pt}(\text{NH}_3)_2\text{Cl}_2$. The reaction pH value can be adjusted by adding of an appropriate amount of ethylenediamine (en). Interestingly, when the aqueous solution of the same starting materials ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, H_3PO_4 , $\text{cis-Pt}(\text{NH}_3)_2\text{Cl}_2$ and $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$) were refluxed together in the general atmosphere, a mixture containing $\text{Co}_3(\text{PO}_4)_2 \cdot n\text{H}_2\text{O}$, $[\text{Co}(\text{en})_3]\text{Cl}_2$ and some unidentified Pt complexes obtained. Although the exact role of the platinum complex in the formation of **1** is unknown at this moment, elimination of this molecule from the above mentioned hydrothermal reaction leads to the formation of a blue, three-dimensional open framework structure $(\text{enH}_2)[\text{Co}(\text{PO}_4)]_2$ (**2**). This result could be considered as the template effect of the Pt complex $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$. Careful examinations of several single crystals of **1** on SEM-EDAX showed no Pt or Cl in the sample.

The refined atomic coordinates and equivalent isotropic displacement parameters are illustrated in Table 2, and the selected bond distances and bond angles data are shown in Table 3. From the structure refinement, the asymmetric unit is shown to contain a total of ten atoms, *i. e.* one cobalt atom, one phosphorus atom, five oxygen atoms and three hydrogen atoms. The latter is located directly from the difference Fourier maps. Eight of the ten atoms, Co, P, O(1), O(3), O(4), O(5), H(2) and H(3), are situated on a crystallographic mirror plane with 1/2 occupancy. The O(2) and H(1) are localized in the general position with 1 occupancy. Fig. 1 shows the structure of one individual $[\text{Co}(\text{H}_2\text{O})(\text{HPO}_4)]$ layer, which consist of CoO_6 and PO_4 units connected by Co—O—Co and P—O—Co bonds. Interestingly, there are no P—O—P bonds. The cobalt atom is in an octahedral coordination environment, bonded to six oxygen atoms. The Co—O distances range from 0.2053(6) to 0.2200(4) nm, with O—Co—O angles ranging from $67.6(2)^\circ$ to $175.5(2)^\circ$. Each phosphorus atom is in a tetrahedral coordination environment, bonded to four oxygen atoms. The P—O distances range from 0.1526(6) to 0.1556(4) nm, with O—P—O angles ranging from $103.7(3)^\circ$ to $111.8(2)^\circ$. The CoO_6 octahedra and PO_4 tetrahedra link by corner- and edge-sharing to form a two-dimensional arrangement parallel to the bc-

plane (b: *b* axis; c: *c* axis; Fig. 1). Of the four oxygen atoms around the phosphorus atom, two O(2) are triply bridging and bonded to two Co-atoms, O(1) is doubly bridging and bonded to one Co-atom and O(3) is terminal oxygen atom, whereas for the cobalt, of the six oxygen atoms, five [four O(2) and one O(1)] are from the PO_4 tetrahedra and one is from the water molecule O(4). The water O atom is always situated in opposition to the oxygen atom O(1) position. On the other hand, the layer can be described as a two-dimensional array of CoO_6 octahedra formed parallel to the bc-plane by sharing their four equatorial corners with one another. Then, each PO_4 tetrahedron shares the corners and an edge of its base with the fifth oxygen atom on a CoO_6 octahedron and three other neighboring CoO_6 octahedra as shown in Fig. 1. The sixth position of each CoO_6 octahedron is occupied by one water molecule O(4), thus giving a $[\text{Co}(\text{H}_2\text{O})(\text{PO}_4)]$ layer. The water molecule simultaneously forms hydrogen bonds with O(1) and O(2) from closest PO_4 groups, which gives rise to extended intralayer hydrogen bonding. Because the PO_4 tetrahedra are located alternatively above and below the $[\text{Co}(\text{H}_2\text{O})(\text{PO}_4)]$ layer, the water molecules [O(4)] coordinated to the Co atoms are either pointing up or down. Furthermore, the crystallization water molecules O(5) are situated on the top of the trenches formed by every two neighboring P—O groups and hydrogen-bonded to the adjacent terminal oxygen atoms [O(3)] from the PO_4 tetrahedra (Fig. 2). The $[\text{Co}(\text{H}_2\text{O})(\text{HPO}_4)] \cdot \text{H}_2\text{O}$ layers make an ABAB... stacking sequence in the crystallographic *a*-direction (*a*: axis) with adjacent layers slightly displaced from each other so that the length of the *a*-axis is equal to twice of the basal spacing for this material.

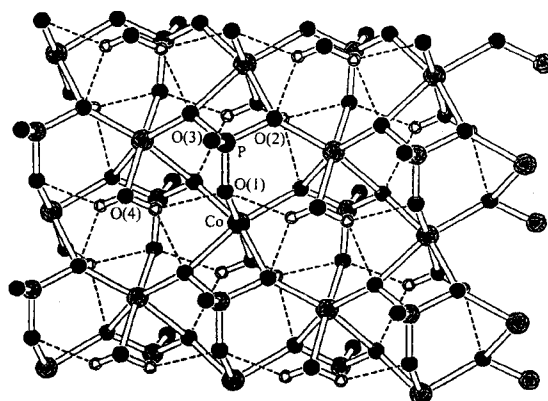


Fig. 1 Structure of an individual $[\text{Co}(\text{H}_2\text{O})(\text{HPO}_4)]$ layer, showing the intralayer hydrogen bonds.

Table 2 Atomic coordinates and thermal parameter ($\text{nm}^2 \times 10^2$)

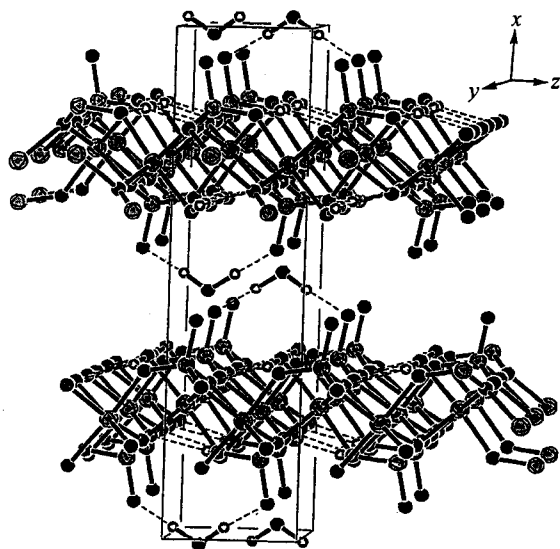
| Atom | <i>x</i> | <i>y</i> | <i>z</i> | B_{eq}^a | Occ ^b |
|------|------------|-----------|-----------|-------------------|------------------|
| Co | 0.23957(6) | 0.2500 | 0.6126(2) | 0.46(2) | 1/2 |
| P | 0.3467(1) | 0.2500 | 0.1817(4) | 0.42(4) | 1/2 |
| O(1) | 0.3340(3) | 0.2500 | 0.866(1) | 0.7(1) | 1/2 |
| O(2) | 0.3081(2) | 0.0321(7) | 0.3245(8) | 0.75(9) | 1 |
| O(3) | 0.4326(3) | 0.2500 | 1.243(1) | 0.5(1) | 1/2 |
| O(4) | 0.1459(3) | 0.2500 | 0.317(1) | 0.7(1) | 1/2 |
| O(5) | 0.5157(4) | 0.2500 | 0.743(1) | 2.3(2) | 1/2 |
| H(1) | 0.1600 | 0.1043 | 0.2354 | 0.9421 | 1 |
| H(2) | 0.4814 | 0.2500 | 0.9265 | 0.9421 | 1/2 |
| H(3) | 0.4819 | 0.2500 | 0.5460 | 0.9421 | 1/2 |

^a Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $B_{\text{eq}} = 8/3\pi^2 [U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}(aa^*bb^*)\cos\gamma + 2U_{13}(aa^*cc^*)\cos\beta + 2U_{23}(bb^*cc^*)\cos\alpha]$;

^b Occ.: occupancy.

Table 3 Selected bond distances (nm) and bond angles ($^\circ$)

| Bond distance | | | | | |
|---------------|-----------|--------------|-----------|-------------|-----------|
| Co—O(1) | 0.2053(6) | Co—O(2) | 0.2200(4) | Co—O(2) | 0.2058(4) |
| Co—O(2) | 0.2058(4) | Co—O(2) | 0.2200(4) | Co—O(4) | 0.2169(6) |
| P—O(1) | 0.1526(6) | P—O(2) | 0.1556(4) | P—O(3) | 0.1535(6) |
| O(1)···O(4) | 0.2840(1) | O(1)···O(5) | 0.3239(9) | O(2)···O(4) | 0.2951(6) |
| O(2)···O(4) | 0.3012(6) | O(2)···O(4) | 0.3095(9) | O(3)···O(5) | 0.2802(9) |
| O(3)···O(5) | 0.2951(3) | O(4)···O(5) | 0.3110(1) | | |
| Bond angle | | | | | |
| O(1)-Co-O(2) | 86.0(2) | O(1)-Co-O(2) | 92.0(1) | | |
| O(1)-Co-O(2) | 86.0(2) | O(1)-Co-O(4) | 175.5(2) | | |
| O(2)-Co-O(2) | 95.87(9) | O(2)-Co-O(2) | 163.4(2) | | |
| O(2)-Co-O(2) | 67.6(2) | O(2)-Co-O(4) | 90.2(2) | | |
| O(2)-Co-O(2) | 100.7(2) | O(1)-P-O(2) | 111.8(2) | | |
| O(1)-P-O(2) | 111.8(2) | O(1)-P-O(3) | 109.4(3) | | |
| O(2)-P-O(2) | 103.7(3) | O(2)-P-O(3) | 110.0(2) | | |
| Co-O(1)-P | 134.6(4) | Co-O(2)-P | 124.4(2) | | |

**Fig. 2** Unit cell packing diagram of $[\text{Co}(\text{H}_2\text{O})(\text{HPO}_4)] \cdot \text{H}_2\text{O}$

The protons H^+ , which balance the negative charge of the lamellar framework, are disorderly trapped on the oxygens from the PO_4 or the H_2O , and can not be localized.

The diffuse reflectance UV/VIS spectrum for **1** shows a broad band centered around 545 nm, attributable to the spin-allowed $4\text{T}_1\text{g}(\text{F}) \rightarrow 4\text{T}_1(\text{P})$ electronic transition of the Co^{2+} ion (d^7) in an octahedral environment. The infrared spectrum of **1** contains medium to strong $\text{P}=\text{O}$ and $\text{P}-\text{O}$ vibrations at 1465, 1435, 1103, 1041, and 943 cm^{-1} . In addition, the OH stretching bands appear as very broad peaks at 3404 and 3229 cm^{-1} . A weak peak at 1618 cm^{-1} and a medium peak at 1590 cm^{-1} can be both attributed to water bending vibrations. The X-ray powder diffraction patterns for the compound show a series of $h00$ ($h = 2n$) reflections, indicative of typical layered compound with a high degree of orientation preference. The most intense peak

can be indexed into the 200 reflection with the $d_{200} = 0.877$ nm, corresponding to the length of half the a -axis. The three other peaks observed are all from the $h00$ family with $n = 4, 6$ and 10 . The total intensity of the latter three is less than 10% compared to that of the first reflection.

In summary, a new layer divalent metal hydrogen-phosphate compound has been synthesized and characterized. The formation of **1** attests to the already diverse structural chemistry of cobalt phosphate compounds.^{15,16} The most interesting feature of **1** is the extensive intra- and inter-layer hydrogen bonding between the hydrogen-phosphate anion, the coordinate water and the crystallization water.

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