

# The synthesis and structure of a chiral 1D aluminophosphate chain compound: $d\text{-Co(en)}_3[\text{AlP}_2\text{O}_8] \cdot 6.5\text{H}_2\text{O}$

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## Abstract

A new chiral one-dimensional (1D) aluminophosphate chain compound  $[d\text{-Co(en)}_3][\text{AlP}_2\text{O}_8] \cdot 6.5\text{H}_2\text{O}$  (designated AIPO-CJ22) has been hydrothermally synthesized by using the optically pure  $d\text{-Co(en)}_3\text{I}_3$  complex as the template. Single-crystal structural analysis reveals that its structure is built up from alternating connection of  $\text{AlO}_4$  and  $\text{PO}_2(=\text{O}_2)$  tetrahedra to form corner-shared  $\text{Al}_2\text{P}_2$  four-membered ring (4-MR) chains. The  $d\text{-Co(en)}_3^{3+}$  complex cations extended along the  $2_1$  screw axis interact with the inorganic chains through hydrogen-bonds of  $\text{N}\cdots\text{O}$  atoms in a helical fashion. Optical rotation measurement shows that AIPO-CJ22 is chiral as with  $d\text{-Co(en)}_3^{3+}$  complex cations. Crystal data: orthorhombic,  $I2_12_12_1$ ,  $a = 8.5573(8)$  Å,  $b = 22.613(2)$  Å,  $c = 22.605(2)$  Å,  $Z = 8$ ,  $R_1 = 0.067$ ,  $wR_2 = 0.1291$ , and Flack parameter:  $-0.02(3)$ . CCDC number: 254179.

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**Keywords:** Aluminophosphate; Hydrothermal synthesis; 1D chain; Chiral structure; Metal complex

## 1. Introduction

There are considerable interests in the synthesis of chiral inorganic framework materials for their potential applications in enantio-selective separation and catalysis [1,2]. Chirality can possibly be imprinted on such structures by using rigid chiral templates. In recent years, racemic metal complexes have been used as the templates to synthesize some open-framework and related structures with chiral substructure features. Examples are known as aluminophosphates  $[\text{Co(en)}_3][\text{Al}_3\text{P}_4\text{O}_{16}] \cdot 3\text{H}_2\text{O}$  [3],  $[\text{Co}(\text{tn})_3][\text{Al}_3\text{P}_4\text{O}_{16}] \cdot 2\text{H}_2\text{O}$  [4] and  $[\text{Co(en)}_3][\text{AlP}_2\text{O}_8] \cdot x\text{H}_2\text{O}$  [5], zincophosphates  $[\text{Co(en)}_3][\text{Zn}_8\text{P}_6\text{O}_{24}\text{Cl}] \cdot \text{H}_2\text{O}$  [6],  $[\text{Co(en)}_3]_2[\text{Zn}_6\text{P}_8\text{O}_{32}\text{H}_8]$  [6] and  $[\text{Co}(\text{dien})_2][\text{Zn}_2(\text{HPO}_4)_4] \cdot \text{H}_2\text{O}$  [7]. These compounds are intrinsically all achiral because of the existence of enantiomers of chiral metal complexes in the as-synthesized products. Our group has systematically investigated the role of chiral metal complexes in determining the stereo-specificity between the host and guest [8].

So far, only a few chiral metal phosphates have been prepared in the presence of optically pure chiral complex  $d\text{-Co(en)}_3\text{I}_3$  as the template, such as gallium phosphate  $[d\text{-Co(en)}_3][\text{H}_3\text{Ga}_2\text{P}_4\text{O}_{16}]$  [9], aluminophosphate  $[d\text{-Co(en)}_3][\text{Al}_3\text{P}_4\text{O}_{16}] \cdot 3\text{H}_2\text{O}$  [10] and zinc phosphate  $[d\text{-Co(en)}_3][\text{Zn}_3(\text{HPO}_4)_4]$  [11]. In this work, we report a chiral aluminophosphate chain compound  $[d\text{-Co(en)}_3][\text{AlP}_2\text{O}_8] \cdot 6.5\text{H}_2\text{O}$  (designated AIPO-CJ22) by using  $d\text{-Co(en)}_3\text{I}_3$  complex as the template. Interestingly, the  $d\text{-Co(en)}_3^{3+}$  complex cations interact with the inorganic chains via H-bondings in a helical fashion. Optical rotation measurement shows that the complex cations involved in the as-synthesized product predominantly have  $\Lambda$ -configuration, which is the same as that of the  $d\text{-Co(en)}_3\text{I}_3$  complex.

## 2. Experimental section

### 2.1. Synthesis and characterization

Large single crystals of AIPO-CJ22 were hydrothermally prepared from a reaction mixture of  $\text{Al}(\text{iPrO})_3$ ,

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*d*-Co(en)<sub>3</sub>I<sub>3</sub>, H<sub>3</sub>PO<sub>4</sub>, tetramethylammonium hydroxide (TMA(OH)) and H<sub>2</sub>O. Typically, 0.204 g Al(*i*PrO)<sub>3</sub> was dissolved in 8 mL of H<sub>2</sub>O and then 0.150 g *d*-Co(en)<sub>3</sub>I<sub>3</sub> and 0.2 mL of H<sub>3</sub>PO<sub>4</sub> (85 wt%) were added subsequently with stirring. Finally, 2.9 mL of TMA(OH) (10% aq.) was added to the above reaction mixture with stirring. The resulting homogenous mixture with the pH value of 7.0 was transferred into a Teflon-lined stainless steel autoclave, and kept statically at 110 °C for 3 days. Orange rod-like single crystals were obtained and washed with distilled water and then air-dried.

X-ray powder diffraction (XRD) data were collected on a Siemens D5005 diffractometer with CuK $\alpha$  radiation ( $\lambda = 1.54418 \text{ \AA}$ ). The elemental analysis was conducted on a Perkin-Elmer 2400 element analyzer. Inductively coupled plasma (ICP) analysis was performed on a Perkin-Elmer Optima 3300DV spectrometer. A Perkin-Elmer TGA 7 unit was used to carry out the thermo-gravimetric analysis (TGA) in the air with a heating rate 10 °C/min. WZZ-1S automatic polarimeter was used to characterize the optical specific rotation of the solution of AIPO-CJ22 dissolved in HNO<sub>3</sub>.

## 2.2. Determination of crystal structure

A suitable single crystal of AIPO-CJ22 with dimension  $0.4 \times 0.3 \times 0.3 \text{ mm}^3$  was selected for single-crystal X-ray diffraction analysis. Structure analysis was performed on a Siemens SMART CCD diffractometer using graphite-monochromated MoK $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). The data were collected at temperature of  $20 \pm 2 \text{ }^\circ\text{C}$ . Intensity data of 13,482 reflections in which 5382 were independent ( $-11 \leq h \leq 11$ ,  $-29 \leq k \leq 18$ ,  $-29 \leq l \leq 30$ ) were collected in the  $\omega$  scan mode ( $R_{\text{int}} = 0.1364$ ). Data processing was accomplished with the SAINT processing program [12]. The structure was solved in the space group of  $I2_12_12_1$  by the direct methods and refined on  $F^2$  by full-matrix least-squares using SHELXTL-97 [13]. We also tried to solve the structure in the space group of  $I-42d$  and the same chains can be obtained with Co(en)<sub>3</sub><sup>3+</sup> complex cations greatly disordered. However, the optical rotation measurement showed that *d*-Co(en)<sub>3</sub><sup>3+</sup> complex cations were predominantly involved in AIPO-CJ22, so we thought that the space group of  $I2_12_12_1$  is more preferred. No absorption correction was applied. The heaviest atoms Al, P and Co were easily located and then non-hydrogen atoms (C, N and O) were placed from subsequent Fourier-difference map. The H atoms attached to the metal complex cations were placed geometrically and refined using a riding model, while the H atoms attached to the water were not located. All non-hydrogen atoms were refined anisotropically. Experimental details for the structure determination are presented in Table 1. The final atomic coordinates and

Table 1  
Crystal data and structure refinement

|  |   |
|--|---|
| Identification code                    | AIPO-CJ22   |
| Empirical formula                      | C <sub>6</sub> H <sub>37</sub> N <sub>6</sub> CoAlP <sub>2</sub> O <sub>14.50</sub>       |
| Formula weight                         | 573.27  |
| Temperature                            | 293(2) K  |
| Wavelength                             | 0.71073 Å   |
| Crystal system, space group            | Orthorhombic, $I2_12_12_1$  |
| Unit cell dimensions                   | $a = 8.5573(8) \text{ \AA}$<br>$b = 22.613(2) \text{ \AA}$<br>$c = 22.605(2) \text{ \AA}$ |
| Volume                                 | $4374.2(7) \text{ \AA}^3$   |
| Z, calculated density                  | 8, 1.741 Mg/m <sup>3</sup>  |
| Absorption coefficient                 | $1.050 \text{ cm}^{-1}$   |
| $F(000)$                               | 2408  |
| Crystal size                           | $0.4 \times 0.3 \times 0.3 \text{ mm}$  |
| Theta range for data collection        | $2.54\text{--}28.23^\circ$  |
| Limiting indices                       | $-11 \leq h \leq 11$ , $-29 \leq k \leq 18$ ,<br>$-29 \leq l \leq 30$                     |
| Reflections collected/unique           | 13482/5382 [ $R_{\text{int}} = 0.1364$ ]  |
| Completeness to $\theta = 28.23$       | 99.8%   |
| Refinement method                      | Full-matrix least-squares on $F^2$  |
| Data/restraints/parameters             | 5382/18/279   |
| Goodness-of-fit on $F^2$               | 0.857   |
| Final $R$ indices [ $I > 2\sigma(I)$ ] | $R_1 = 0.067$ , $wR_2 = 0.1291$   |
| $R$ indices (all data)                 | $R_1 = 0.1574$ , $wR_2 = 0.1570$  |
| Absolute structure parameter           | $-0.02(3)$  |
| Largest diff. peak and hole            | 1.230 and $-0.715 \text{ e. \AA}^{-3}$  |

the selected bond distances and angles are given in Tables 2 and 3, respectively.

## 3. Results and discussion

### 3.1. Characterization

Fig. 1 shows the experimental XRD pattern of AIPO-CJ22, which is consistent with the simulated one generated based on structural data, proving the phase purity of the as-synthesized product.

The results of elemental analysis are consistent with the theoretical values calculated by the single-crystal structural analysis. Found for AIPO-CJ22: Al, 4.80; P, 12.01; Co, 10.23; C, 13.51; H, 8.21; N, 14.56 wt%. Calcd.: Al, 4.71; P, 10.80; Co, 10.28; C, 12.57; H, 6.51; N, 14.66 wt%.

The TG analysis (Fig. 2) indicates that the lattice H<sub>2</sub>O molecules are lost between 90 and 190 °C in two distinct stages with a total weight loss of 20.51 wt% (calcd. 20.41 wt%). The first weight loss of 9.42 wt% (calcd. 9.42 wt%) corresponds to the loss of three mole H<sub>2</sub>O molecules without H-bonds with the framework or the cobalt complex, and the second weight loss of 11.09 wt% (calcd. 10.99 wt%) corresponds to the loss of the three and half mole H<sub>2</sub>O molecules sharing H-bonds with the inorganic framework or the complexes

Table 2

Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for AIPO-CJ22.  $U(\text{eq})$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor

|       | x         | y       | z       | $U(\text{eq})$ |
|-------|-----------|---------|---------|----------------|
| Co(1) | 2500      | 4787(1) | 0       | 23(1)          |
| Co(2) | 0         | 7500    | 2334(1) | 21(1)          |
| Al(1) | -3757(4)  | 5000    | 2500    | 16(1)          |
| Al(2) | 1275(4)   | 5000    | 2500    | 17(1)          |
| P(1)  | -1260(3)  | 4554(1) | 1593(1) | 21(1)          |
| P(2)  | -6231(3)  | 5909(1) | 2045(1) | 22(1)          |
| O(1)  | -2605(7)  | 4912(2) | 1873(2) | 27(1)          |
| O(2)  | -5771(7)  | 5962(3) | 1396(2) | 38(2)          |
| O(3)  | 2378(7)   | 5470(2) | 2071(2) | 36(2)          |
| O(4)  | -838(7)   | 4839(3) | 1017(2) | 40(2)          |
| O(5)  | -1726(7)  | 3908(2) | 1546(2) | 32(2)          |
| O(6)  | -6677(7)  | 6493(2) | 2334(3) | 38(2)          |
| O(7)  | 137(7)    | 4585(2) | 2021(2) | 37(2)          |
| O(8)  | -4878(6)  | 5631(2) | 2419(2) | 29(1)          |
| O(1W) | 0         | 7500    | 494(6)  | 125(5)         |
| O(2W) | 7500      | 6614(6) | 0       | 110(4)         |
| O(3W) | 5000      | 2500    | 973(5)  | 91(4)          |
| O(4W) | 4135(13)  | 7022(4) | 833(4)  | 112(4)         |
| O(5W) | 8674(10)  | 3498(3) | 422(3)  | 77(2)          |
| O(6W) | 5839(8)   | 3251(3) | 1846(3) | 42(2)          |
| O(7W) | -3274(7)  | 5694(3) | 744(2)  | 41(2)          |
| O(8W) | 1790(20)  | 2919(6) | 8(12)   | 272(9)         |
| C(1)  | -1180(14) | 6481(4) | 1779(4) | 49(3)          |
| C(2)  | -2438(14) | 6930(4) | 1713(4) | 48(3)          |
| C(3)  | -705(10)  | 7702(4) | 3541(3) | 35(2)          |
| C(4)  | 4825(14)  | 4279(5) | 742(5)  | 64(3)          |
| C(5)  | 1827(11)  | 5984(3) | 219(4)  | 33(2)          |
| C(6)  | 3413(13)  | 4170(6) | 1022(5) | 70(4)          |
| N(1)  | -255(9)   | 6638(3) | 2317(3) | 39(2)          |
| N(2)  | -1652(10) | 7527(4) | 1754(3) | 48(2)          |
| N(3)  | -1532(9)  | 7593(3) | 2977(3) | 46(2)          |
| N(4)  | 4679(9)   | 4739(3) | 261(3)  | 37(2)          |
| N(5)  | 1948(9)   | 5425(3) | 558(3)  | 40(2)          |
| N(6)  | 2072(8)   | 4202(3) | 613(3)  | 34(2)          |

[10]. The weight loss of 26.49 wt% (calcd. 31.49 wt%) in the region of 190–600 °C is due to the decomposition of ethylene diamine in the complex. The lower value is probably due to the retention of carbon in the residues.

### 3.2. Description of the structure

The asymmetric unit of AIPO-CJ22 (Fig. 3) contains two crystallographically distinct P atoms. P(1) and P(2) each share two oxygen atoms with adjacent Al atoms (P–O bond lengths: 1.538(6)–1.566(6) Å), leaving two terminal P=O groups (P=O bond lengths: 1.497(6)–1.524(6) Å). There are two unique Al sites locating on the two-fold axis, and both adopt a tetrahedral geometry by sharing four oxygen atoms with adjacent P atoms. The Al–O bond lengths are in the range of 1.721(6)–1.737(5) Å and O–Al–O angles are in the range of 106.9(3)–113.5(4)°. Two unique Co sites locate on the two-fold axis. In addition, there are eight

Table 3

Selected bond lengths [Å] and angles [°] for AIPO-CJ22

|                   |          |                   |          |
|-------------------|----------|-------------------|----------|
| Co(1)–N(6)        | 1.951(7) | Co(1)–N(4)        | 1.959(7) |
| Co(1)–N(5)        | 1.975(7) | Co(2)–N(2)        | 1.929(8) |
| Co(2)–N(1)        | 1.962(6) | Co(2)–N(3)        | 1.969(8) |
| Al(1)–O(8)        | 1.729(5) | Al(1)–O(1)        | 1.737(5) |
| Al(2)–O(3)        | 1.721(6) | Al(2)–O(7)        | 1.734(6) |
| P(1)–O(4)         | 1.497(6) | P(1)–O(5)         | 1.517(6) |
| P(1)–O(7)         | 1.538(6) | P(1)–O(1)         | 1.544(6) |
| P(2)–O(6)         | 1.521(5) | P(2)–O(2)         | 1.524(6) |
| P(2)–O(3)#2       | 1.550(6) | P(2)–O(8)         | 1.566(6) |
| O(8)#1–Al(1)–O(8) | 112.6(4) | O(8)–Al(1)–O(1)#1 | 107.9(2) |
| O(8)–Al(1)–O(1)   | 108.8(2) | O(1)#1–Al(1)–O(1) | 110.9(4) |
| O(3)–Al(2)–O(3)#1 | 113.5(4) | O(3)–Al(2)–O(7)   | 106.9(3) |
| O(3)#1–Al(2)–O(7) | 109.0(3) | O(7)–Al(2)–O(7)#1 | 111.6(4) |
| O(4)–P(1)–O(5)    | 114.6(4) | O(4)–P(1)–O(7)    | 109.9(4) |
| O(5)–P(1)–O(7)    | 107.0(3) | O(4)–P(1)–O(1)    | 108.0(3) |
| O(5)–P(1)–O(1)    | 109.8(3) | O(7)–P(1)–O(1)    | 107.3(3) |
| O(6)–P(2)–O(2)    | 114.2(4) | O(6)–P(2)–O(3)#2  | 110.3(3) |
| O(2)–P(2)–O(3)#2  | 106.6(3) | O(6)–P(2)–O(8)    | 107.6(3) |
| O(2)–P(2)–O(8)    | 111.2(3) | O(3)#2–P(2)–O(8)  | 106.9(3) |
| P(1)–O(1)–Al(1)   | 144.8(3) | P(2)#3–O(3)–Al(2) | 146.9(4) |
| P(1)–O(7)–Al(2)   | 148.6(4) | P(2)–O(8)–Al(1)   | 143.0(4) |

Symmetry transformations used to generate equivalent atoms: #1  $x, -y + 1, -z + 1/2$  #2  $x - 1, y, z$  #3  $x + 1, y, z$ .

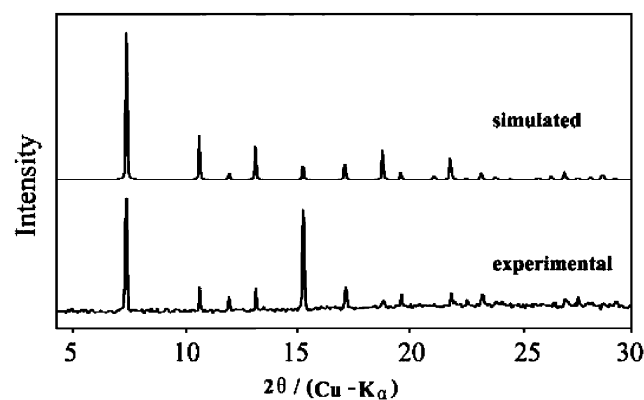


Fig. 1. Experimental and simulated X-ray powder diffraction patterns of AIPO-CJ22.

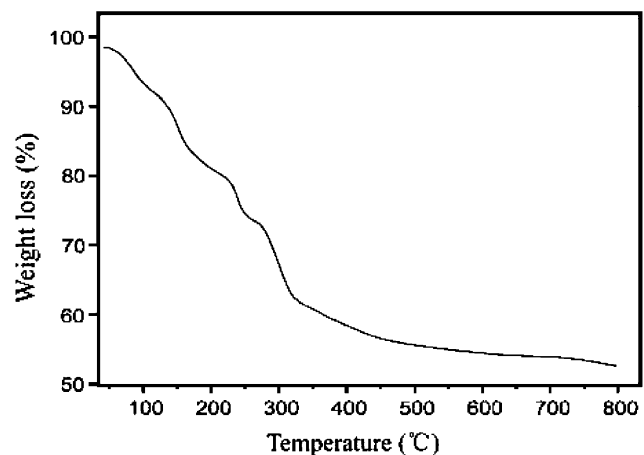


Fig. 2. Thermal-gravimetric analysis curve for AIPO-CJ22.

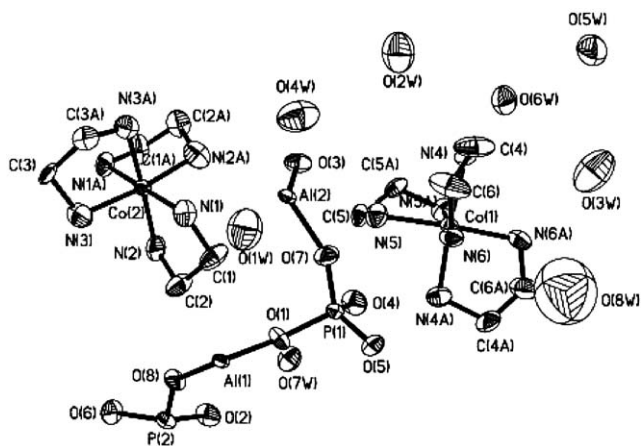


Fig. 3. ORTEP plot of AlPO-CJ22. Thermal ellipsoids are given at 50% probability.

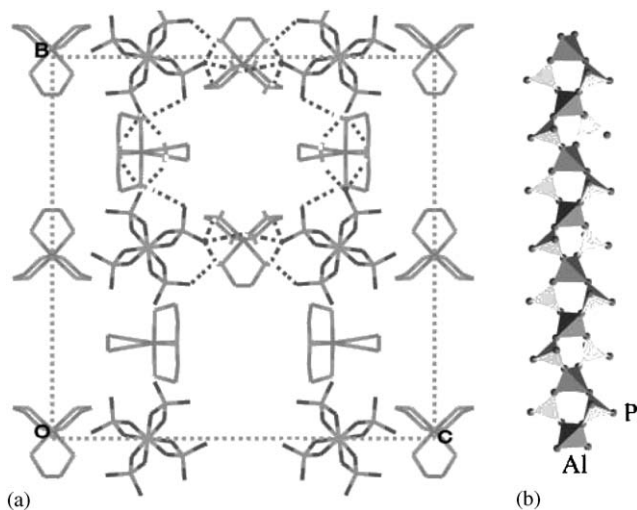


Fig. 4. (a) The structure of AlPO-CJ22 viewed along the [100] direction and (b) The corner-shared 4-MR aluminophosphate chain.

crystallographically unique  $O_w$  sites, while  $O(1w)$ ,  $O(2w)$  and  $O(3w)$  are on the two-fold axis and  $O(8w)$  is disordered over two sites.

The structure of AlPO-CJ22 is based on an anionic aluminophosphate chain  $[AlP_2O_8]^{3-}$  with corner-shared 4-MRs formed by  $AlO_4$  and  $PO_2(=O)_2$  tetrahedra (Fig. 4). This type of 1D chain, denoted AlPO-CSC [14–16] is one of the fundamental chains in the known aluminophosphate structures [17–20]. Charge neutralizing is achieved by the optically pure  $d-Co(en)_3^{3+}$  cations tightly packed between the inorganic chains. So far, AlPO-CJ22 is the first aluminophosphate chain templated by optically pure  $d-Co(en)_3I_3$  complex. Its structure is analogue to that of the reported  $[Co(en)_3][AlP_2O_8] \cdot xH_2O$  [5], in which greatly disordered racemic  $Co(en)_3^{3+}$  cations are located between the chains. The structures of inorganic chains in these two compounds are the same, while AlPO-CJ22, templated

by the optically pure  $d-Co(en)_3I_3$  complex, crystallizes in a chiral space group of  $I2_12_12_1$  and  $[Co(en)_3][AlP_2O_8] \cdot xH_2O$ , templated by  $dl-Co(en)_3Cl_3$  complex, is solved in the space group of  $I-42d$  with achiral characters. This means that the chirality of AlPO-CJ22 is defined by the chirality of  $d-Co(en)_3^{3+}$  complex cations locating between the chains.

Strikingly, the  $d-Co(en)_3^{3+}$  complex cations following  $2_1$  screw axis along the [100] direction interact with the aluminophosphate chains through extensive H-bonds in a helical fashion (Fig. 5). So far, there are few reports on the helical H-bond formed by the inorganic host and organic guest. A notable example is the H-bonded helix formed by the organic amine template and the inorganic network in a 2D layered aluminophosphate with  $Al_2P_3O_{12}^{3-}$  stoichiometry, reported by our group [21]. In AlPO-CJ22, the nitrogen atoms of the complex cations, acting as the H-bonding donors, form weak H-bonds with the terminal oxygen atoms of the chain. One  $Co(1)(en)_3^{3+}$  complex cation forms three H-bonds with  $O(6)$  atom ( $O(6) \cdots N$  distances: 2.946(9)–3.079(10) Å) and one H-bond with  $O(6w)$  ( $N(3) \cdots O(6w)$  distance: 2.978(10) Å). One  $Co(2)(en)_3^{3+}$  complex cation forms three H-bonds with  $O(4)$  and one H-bond with  $O(2)$ ,

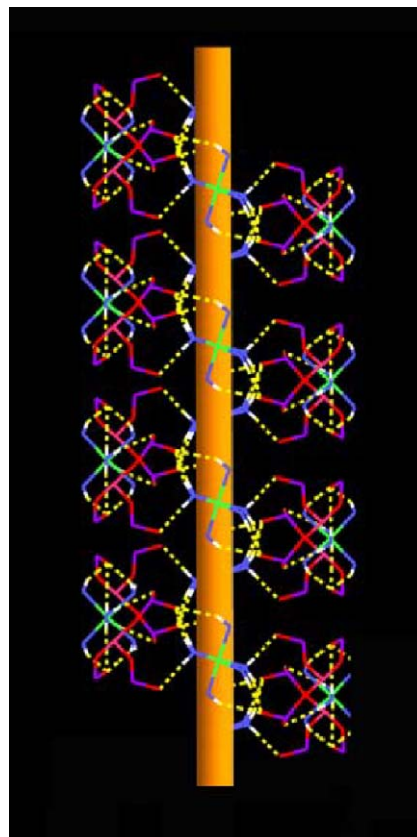


Fig. 5. Helical H-bonds between the  $d-Co(en)_3^{3+}$  complex cations and the aluminophosphate chains. All carbon atoms are omitted for clarity. P: purple, Al: pink, Co: green, O: red, N: blue and H: white.

Table 4  
Hydrogen-bonds parameters for AlPO-CJ22 [ $\text{\AA}$  and deg]

| D–H...A              | $d(\text{D–H})$ | $d(\text{H...A})$ | $d(\text{D...A})$ | $\angle(\text{DHA})$ |
|----------------------|-----------------|-------------------|-------------------|----------------------|
| N(1)–H(1C)...O(6)#2  | 0.9             | 2.26              | 3.079(10)         | 151.5                |
| N(2)–H(2C)...O(6)#3  | 0.9             | 2.09              | 2.946(9)          | 158.0                |
| N(3)–H(3C)...O(6)#3  | 0.9             | 2.12              | 2.956(9)          | 154.6                |
| N(3)–H(3D)...O(6W)#4 | 0.9             | 2.13              | 2.978(10)         | 157.2                |
| N(4)–H(4C)...O(4)#1  | 0.9             | 2.29              | 3.063(9)          | 144.2                |
| N(4)–H(4D)...O(7W)#2 | 0.9             | 2.16              | 2.988(9)          | 152.9                |
| N(5)–H(5C)...O(4)    | 0.9             | 2.07              | 2.918(9)          | 157.7                |
| N(5)–H(5D)...O(2)#2  | 0.9             | 2.15              | 2.978(9)          | 152.7                |
| N(6)–H(6C)...O(4)    | 0.9             | 2.17              | 3.018(9)          | 155.8                |

Symmetry transformations used to generate equivalent atoms: #1  $-x + 1/2, y, -z$  #2  $x + 1, y, z$  #3  $-x - 1, -y + 3/2, z$  #4  $x - 1, -y + 1, -z + 1/2$ .

and the O...N distances are within 2.918(9)–3.063(9)  $\text{\AA}$ . In addition, N(4) atom of  $\text{Co}(\text{en})_3^{3+}$  complex cation also forms a weak H-bond with O(7w), and the N(4)...O(7w) distance is 2.988(9)  $\text{\AA}$ . H-bonding information is summarized in Table 4.

Furthermore, the optical rotation measurement reveals that cobalt complex cations with  $\Lambda$ -configuration are predominantly involved in the as-synthesized product of AlPO-CJ22. This result can be further confirmed by the following experiments. The use of *l*-Co(en)<sub>3</sub>I<sub>3</sub> as the template under similar reaction condition as we mentioned above leads to the formation of [*l*-Co(en)<sub>3</sub>][AlP<sub>2</sub>O<sub>8</sub>]·6.5H<sub>2</sub>O, which is analogue to AlPO-CJ22. Optical specific rotation measurement also shows that the complex cations involved in the as-synthesized product predominantly possess the  $\Delta$ -configuration. Otherwise, when we use racemic cobalt complex *dl*-Co(en)<sub>3</sub>Cl<sub>3</sub> as the template under similar condition, the formed product is [*dl*-Co(en)<sub>3</sub>][AlP<sub>2</sub>O<sub>8</sub>]·6.5H<sub>2</sub>O rather than [*d*-Co(en)<sub>3</sub>][AlP<sub>2</sub>O<sub>8</sub>]·6.5H<sub>2</sub>O or [*l*-Co(en)<sub>3</sub>][AlP<sub>2</sub>O<sub>8</sub>]·6.5H<sub>2</sub>O. Even though it is difficult to perform quantitative measurements of optical activity of the product, above results indicate that no significant racemization of *d*-Co(en)<sub>3</sub><sup>3+</sup> cations occurs under our synthesis conditions of AlPO-CJ22. Of course, it may be unavoidable that trace of *d*-Co(en)<sub>3</sub><sup>3+</sup> or *l*-Co(en)<sub>3</sub><sup>3+</sup> cations decompose or racemize.

#### 4. Conclusions

A chiral 1D aluminophosphate chain compound, [*d*-Co(en)<sub>3</sub>][AlP<sub>2</sub>O<sub>8</sub>]·6.5H<sub>2</sub>O, has been hydrothermally synthesized in the system of Al(*i*PrO)<sub>3</sub>–H<sub>3</sub>PO<sub>4</sub>–*d*-Co(en)<sub>3</sub>I<sub>3</sub>–TMAOH–H<sub>2</sub>O. Its inorganic chains are built up by alternation of AlO<sub>4</sub> and PO<sub>2</sub>(=O)<sub>2</sub> tetrahedra, which are separated by the charge-balancing Co(en)<sub>3</sub><sup>3+</sup> cations. Extensive H-bonds are formed between the amino groups of the complex cations and the terminal oxygen atoms in the chain, arraying in a helical fashion.

Automatic polarimeter measurement indicates that *d*-Co(en)<sub>3</sub><sup>3+</sup> complex cations are predominantly involved in the products.

#### 5. Supplementary material

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC\_254179. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: 44 1223 336 033; E-mail: deposit@ccdc.cam.ac.uk).

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