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**CHARACTERIZATION AND CRYSTAL STRUCTURE OF A NEW LAYERED CADMIUM DIPHOSPHATE:  $\text{KCdHP}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$** **S. Kouass<sup>1</sup>, A. Selmi<sup>2,3</sup>, H. Chebbi<sup>4,5</sup>, A. Guesmi<sup>5,6</sup>**<sup>1</sup>*Laboratoire des Matériaux Utiles, Institut National de Recherche et d'Analyse Physico-chimique Sidi-Thabet, 2020 Tunis, Tunisia*<sup>2</sup>*Université de Gafsa, Faculté des Sciences, Unité de Recherche Matériaux, Energie et Energies Renouvelables MEER, Sidi Ahmed Zarroug, 2112 Gafsa, Tunisia*<sup>3</sup>*Université de Carthage, Faculté des Sciences de Bizerte, Laboratoire de Chimie des Matériaux, 7021 Zarzouna, Bizerte, Tunisia*<sup>4</sup>*Université de Tunis, Institut Préparatoire aux Etudes d'Ingénieurs de Tunis, Rue Jawaher Lel Nehru, 1089 Montfleury, Tunis, Tunisia*

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A new potassium cadmium hydrogen diphosphate dihydrate,  $\text{KCdHP}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$  (**1**), has been synthesized by slow evaporation at room temperature and characterized by FT-IR, Raman, TG-DTA, and single crystal X-ray diffraction. Compound (**1**) crystallizes in the orthorhombic *Pcmm* space group with the unit cell parameters  $a = 6.5814(8) \text{ \AA}$ ,  $b = 7.9428(9) \text{ \AA}$ ,  $c = 15.961(6) \text{ \AA}$ ,  $V = 834.4(3) \text{ \AA}^3$  and  $Z = 4$ . Its structure consists of polyhedral layers parallel to the *ab* plane where each  $\text{CdO}_6$  octahedron (*m* position) shares four edges with three different diphosphate groups. In the Cd octahedron, two oxygen atoms residing in (*m*) special positions belong to coordinated water molecules. These layers are joint by  $\text{K}^+$  cations (*4c* Wyckoff position) and hydrogen bonds, leading thus to a two-dimensional framework. The structural model is supported by the bond-valence-sum validation tool as calculated valences are close to the formal oxidation numbers.

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**Keywords:** crystal structure, cadmium diphosphate, Bond-Valence-Sum, FT-IR, Raman.**INTRODUCTION**

Open framework phosphates are investigated as a part of the enrichment of the materials domain by new structures with particular topologies exhibiting many physical properties such as ionic conduction, adsorption, catalysis, etc. Many members of the chemical system  $\text{K—Cd—P—O}$  have particular structures, e.g.  $\text{K}_4\text{Cd}_3(\text{HPO}_4)_4(\text{H}_2\text{PO}_4)_2$  is an open-framework cadmium phosphate [ 1 ];  $\text{KCdPO}_4 \cdot 6\text{H}_2\text{O}$  belongs to the series of struvite analogs [ 2 ];  $\text{Cd}_{0.5}\text{Ce}_2(\text{PO}_4)_3$  with monazite structure type is known as a promising class used to immobilize wastes from nuclear power plants [ 3 ], etc. This paper focuses on the synthesis, characterization and crystal structure of a new layered cadmium phosphate  $\text{KCdHP}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$  (**1**). The structural model is additionally supported by Bond-Valence-Sum (BVS) validation tool [ 4 ].

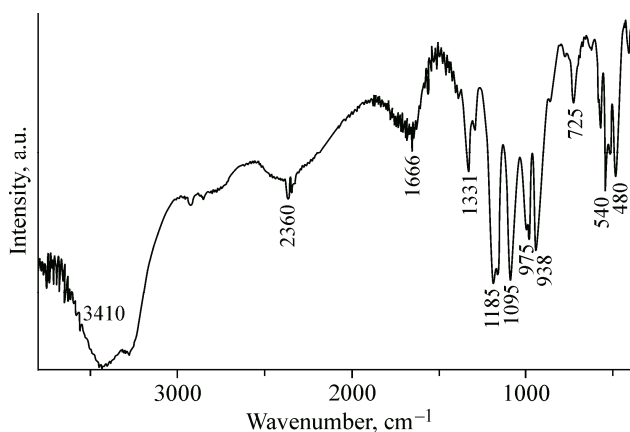


Fig. 1. FT-IR spectrum of **1**

### EXPERIMENTAL

**Materials and measurements:** All chemicals were purchased commercially and used without further purification. The infrared spectrum was recorded in the range 4000–400  $\text{cm}^{-1}$  employing a Perkin-Elmer spectrometer in KBr pellet; the Raman spectrum was registered on a LabRAM HR (Horiba JobinYvon) spectrometer. Thermogravimetric (TG) and differential thermal analyses (DTA) were made on a Setaram SETSYS 16/18 instrument in argon atmosphere, sample weight: 8.5 mg, heating rate 5  $^{\circ}\text{C min}^{-1}$ , temperature range 30–500  $^{\circ}\text{C}$ . The X-ray diffraction analysis of (**1**) was performed on an automated four-circle diffractometer Enraf-Nonius CAD-4 with a graphite-monochromated  $\text{MoK}_{\alpha}$  radiation source ( $\lambda = 0.71073 \text{ \AA}$ ).

**Synthesis of  $\text{KCdHP}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$  (**1**):** Crystals of **1** were grown at room temperature by slow evaporation of a water-ethanol (80/20) solution containing a stoichiometric mixture of  $\text{CdCO}_3$ , KCl and  $\text{Na}_4\text{P}_2\text{O}_7$ . The solution was stirred for three hours and left to stand at room temperature (293 K). Crystals suitable for X-ray analysis were formed after five days.

**X-ray crystallographic analysis.** The crystallographic data of **1**:  $\text{CdH}_5\text{KO}_9\text{P}_2$ ,  $FW = 362.48 \text{ g} \cdot \text{mol}^{-1}$ ,  $T = 293 \text{ K}$ , crystal size  $0.20 \times 0.15 \times 0.10 \text{ mm}$ , orthorhombic,  $Pcmm$ ,  $a = 6.5814(8) \text{ \AA}$ ,  $b = 7.9428(9) \text{ \AA}$ ,  $c = 15.961(6) \text{ \AA}$ ,  $V = 834.4(3) \text{ \AA}^3$ ,  $Z = 4$ ,  $\mu(\text{MoK}_{\alpha}) = 3.52 \text{ mm}^{-1}$ , a total of 1507 reflections, 791 observed reflections ( $I \geq 2\sigma(I)$ ), 68 parameters,  $\text{GOOF} = 1.21$ ,  $R_{\text{int}} = 0.023$ ,  $R_1(I \geq 2\sigma(I)) = 0.021$ ,  $wR_2(I \geq 2\sigma(I)) = 0.056$ , max/min diff. peak  $1.04/-0.60 \text{ e} \text{ \AA}^{-3}$ .

The structure was solved by the direct methods with SHELXS-97 and expanded using Fourier techniques [5]. The positions of two independent H atoms at O3 and O4 of the coordinated water

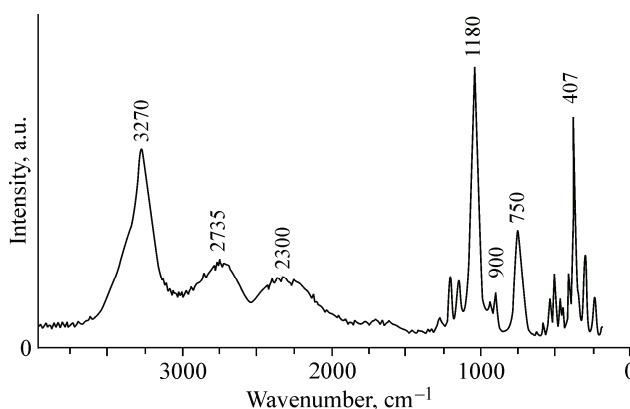


Fig. 2. Raman spectrum of **1**

molecules were located from difference Fourier maps and they were refined with displacement parameters fixed as  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$ . The formula obtained at this stage remained unbalanced, namely  $\{\text{KCdP}_2\text{O}_7 \cdot 2\text{H}_2\text{O}\}$  ( $Z = 4$ ), the coordinates of one more H atom per formula had to be localized. The only reasonable position for the additional H atom was found at O6, which had a low bond-valence-sum and enough space for OH. A structural model including a refined half-occupied position for this H6 atom with  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$  gave reasonable geometric parameters for a hydrogen bond toward O6(i) atom. CIF file containing complete information about the structure of **1** was deposited with the Cambridge Crystallographic Data Center (No. 1052452); the file is freely available upon request from the following web site: [http://www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

## RESULTS AND DISCUSSION

**FT-IR and Raman spectroscopic analyses:** In analogy with earlier vibrational studies of hydrate diphosphates [6–10], the IR spectrum of the title compound (Fig. 1) shows many absorption bands in the region  $3500\text{--}1600\text{ cm}^{-1}$  that correspond both to the vibrations of water molecules and hydroxyl groups. As for phosphate groups, the bands observed at  $1185$  and  $1095\text{ cm}^{-1}$  are assigned to the asymmetric stretching vibration  $\nu_{\text{as}}(\text{PO}_3)$  while the band at  $975\text{ cm}^{-1}$  is attributed to the symmetric  $\nu_{\text{s}}(\text{PO}_3)$ . Those ranging within  $940\text{--}720\text{ cm}^{-1}$  are due to stretching POP modes. Finally, the asymmetric  $\nu_{\text{as}}(\text{PO}_3)$  and symmetric  $\nu_{\text{s}}(\text{PO}_3)$  bending vibrations appear at  $540$  and  $480\text{ cm}^{-1}$ .

With regard to the Raman spectrum (Fig. 2), the bands in the region  $3400\text{--}1500\text{ cm}^{-1}$  are due to the vibrations modes of water molecules and hydroxyl groups. The strong band at  $1180\text{ cm}^{-1}$  is attributed to the symmetric stretching vibration  $\nu_{\text{s}}(\text{PO}_3)$ . The stretching modes of the POP bridge are observed at  $751\text{ cm}^{-1}$ . The last bands in the interval  $600\text{--}350$  are due to the bending vibrations of the terminal  $\text{PO}_3$  groups.

**Thermal analyses:** Two curves corresponding to TG-DTA analysis of **1** are given in Fig. 3. The DTA curve shows a major endothermic peak at  $\sim 210\text{ }^\circ\text{C}$  followed by a series of small endothermic peaks in a wide temperature range. These peaks are accompanied with two inseparable weight losses obviously observed on the TG curve. The first weight loss is attributed to the release of the two water molecules, while the second corresponds to the degradation of the anhydrous compound to a condensed phosphate with a release of a half of water molecule per formula unit. The total experimental and theoretical weight losses are in good accord:  $\%_{\text{exp}} = 12.35$ ,  $\%_{\text{th}} = 12.41$ ; these results agree well with the structural study.

**Single crystal X-ray diffraction analysis.** The asymmetric unit is illustrated in Fig. 4. The Cd atom is six-coordinated, four oxygen atoms form an almost regular square around the central Cd atom and the oxygen atoms of two water molecules (Ow) are located in the axial positions of the Cd octahedron. The Cd—Ow distances are slightly longer than those of Cd—O—P contacts. The shortest intra- and inter-layer Cd $\cdots$ Cd separations are  $5.450$  and  $7.418\text{ \AA}$ , respectively.

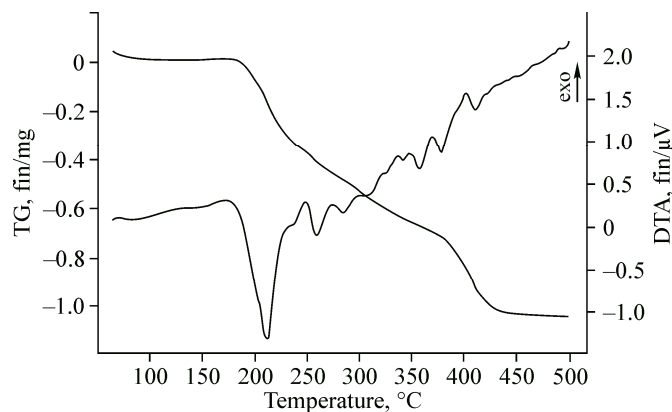


Fig. 3. TG—DTA curves of **1**

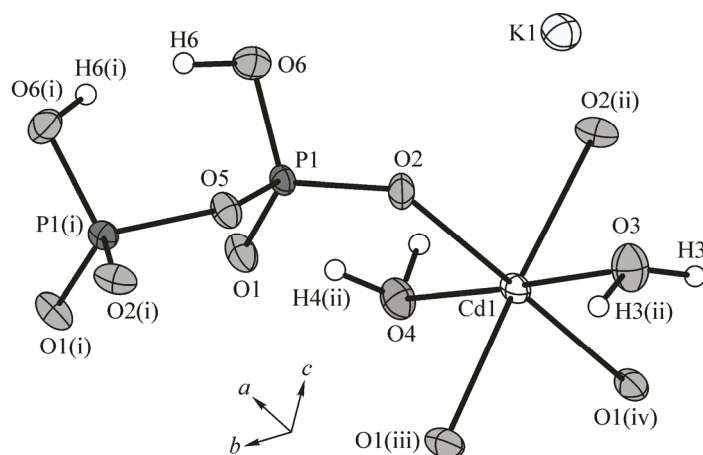


Fig. 4. The asymmetric unit with atom labeling scheme. Some symmetry-related O atoms are included to show the full coordination polyhedra around the Cd and P atoms. Displacement ellipsoids are drawn at the 50% probability level.

(Symmetry codes: (i)  $x, -y+3/2, z$ ; (ii)  $x, -y+1/2, z$ ; (iii)  $x-1/2, -y+1, -z+1/2$ ; (iv)  $x-1/2, y-1/2, -z+1/2$ )

The  $\text{PO}_4$  tetrahedra are linked by the bridging oxygen O5 atom to form the diphosphate groups. Inside the  $\text{PO}_4$  tetrahedron, the P—O distances vary from 1.505(2) to 1.611(1) Å. The shortest distances correspond to the terminal P—O1 bond, whereas the intermediate one [1.536(2) Å] is related to the P—OH bond, and the largest distance corresponds to the P—O5 of the bridging oxygen atom. The value of the O—P—O angles vary between 103.3(1) and 115.4(1)° whereas the angle of the P—O5—P bridge equals 134.3(2)°. These values are in conformity with the results found in the literature [11–14]. The bond-valence-sum BVS calculations for all atoms are close to their oxidation states: Cd1: 2.09, P1: 4.93, K: 0.98, O1: 1.88, O2: 1.85, O3: 2.35, O4: 2.35, O5: 2.26, O6: 1.93, H3: 1.07, H4: 1.09, H6: 1.02 v.u. (valence unit).

The crystal packing of the title compound consists of polyhedral layers parallel to the  $ab$  plane where each  $\text{CdO}_6$  octahedron shares four corners with three different diphosphate groups (Fig. 5). These layers are joined by  $\text{K}^+$  cations and hydrogen bonds, thus leading to a two-dimensional framework.

The three hydrogen bonds in the structure involve four oxygen atoms and are of two types and have two locations. Those involving the two oxygen atoms of the coordinated water molecules as donors strengthen the cohesion in the  $ab$  plane. The oxygen atoms of the hydroxyl groups act as acceptors within the polyhedral layers and donors and acceptors between the polyhedral sheets with the

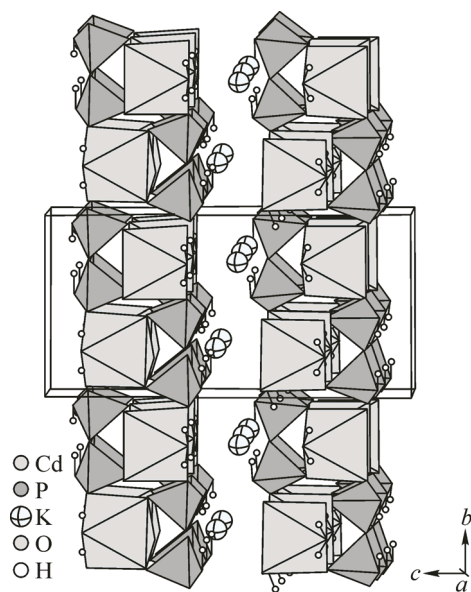


Fig. 5. The polyhedral layers in the studied compound

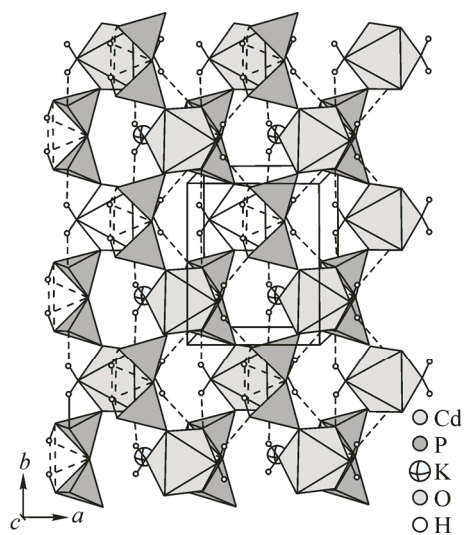


Fig. 6. Perspective view of the structure showing the hydrogen bonds (dashed lines) and the location of the alkali metal cations

strongest hydrogen bond, thus reinforcing the cohesion of the framework and creating, with the polyhedra, channels hosting the alkali cations (Fig. 6).

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