

$K_2M(H_2P_2O_7)_2 \cdot 2H_2O$ ($M = Ni, Cu, Zn$): orthorhombic forms and Raman spectra

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Received 12 August 2005
Accepted 8 November 2005
Online 30 November 2005

The crystal structures of three isotopic orthorhombic dihydrogendiphosphates, namely dipotassium copper(II)/nickel(II)/zinc(II) bis(dihydrogendiphosphate) dihydrate, $K_2M(H_2P_2O_7)_2 \cdot 2H_2O$ ($M = Cu, Ni$ and Zn), have been refined from single-crystal data. The M^{2+} and K^+ cations are located at sites of m symmetry, and the P atoms occupy general positions. These compounds also exist in triclinic forms with very similar structural features. The structures of both forms are compared, as well as the geometry of the MO_6 octahedron, which is considerably elongated towards the water molecules for $M = Ni$ and Cu . Such elongation has not been observed among the other representatives of the family. A Raman study of the whole series $K_2M(H_2P_2O_7)_2 \cdot 2H_2O$ ($M = Mn, Co, Ni, Cu, Zn$ and Mg) is reported.

Comment

Acidic metal diphosphates are known particularly for their biological applications, notably their role in some enzyme-catalyzed reaction processes (Haromy *et al.*, 1984). They are used as inhibitors in the formation and dissolution of apatite crystals *in vitro* (Mathew *et al.*, 1993), and as additives in fertilizers (Frazier *et al.*, 1965, 1966) or even in medicine (Fleisch & Russell, 1972). The present work is a continuation of our investigation of the system $(A,M)_x(H_2P_2O_7)_y \cdot zH_2O$, where A is an alkaline earth or ammonium and M is a divalent 3d transition metal (including Zn). We have previously reported the compounds $(NH_4)_2M(H_2P_2O_7)_2 \cdot 2H_2O$ with $M = Co$ (Essehli *et al.*, 2005a), Ni (Essehli *et al.*, 2005b) and Zn (Essehli *et al.*, 2005c), as well as four $K_2M(H_2P_2O_7)_2 \cdot 2H_2O$ compounds with $M = Mn$ (Alaoui Tahiri *et al.*, 2003), Co

(Alaoui Tahiri *et al.*, 2002), Zn (Tahiri *et al.*, 2003) and Ni (Tahiri *et al.*, 2004). The K,Mg analogue has been studied by others (Harcharras, Capitelli *et al.*, 2003). The known $K_2M(H_2P_2O_7)_2 \cdot 2H_2O$ compounds are either orthorhombic ($Pnma$) for $M = Mn$ and Co , or triclinic ($P\bar{1}$) for $M = Ni, Zn$ and Mg . New orthorhombic structures for $M = Cu, (I), Ni, (II),$ and $Zn, (III)$, are described here, establishing that both crystalline forms exist for $M = Ni$ and Zn .

The packing of the orthorhombic $K_2M(H_2P_2O_7)_2 \cdot 2H_2O$ structure is shown in Fig. 1. The basic building units of the structure, *viz.* $(H_2P_2O_7)_2M(H_2O)_2$ octahedra (Fig. 2), are connected by either $K-O$ bonds or $O-H \cdots O$ hydrogen bonds (Tables 1, 2 and 3). The long $M \cdots M$ distances (Table 4)

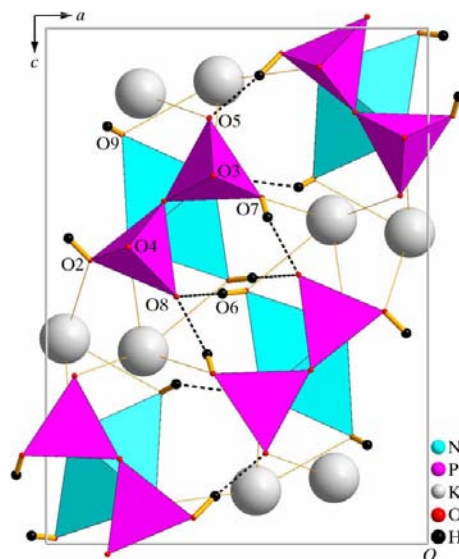


Figure 1
The packing in orthorhombic $K_2Ni(H_2P_2O_7)_2 \cdot 2H_2O$, viewed along the b axis. Thin solid lines indicate bonds to K and dashed black lines are hydrogen bonds. Not all seven O atoms closest to K are visible in this projection.

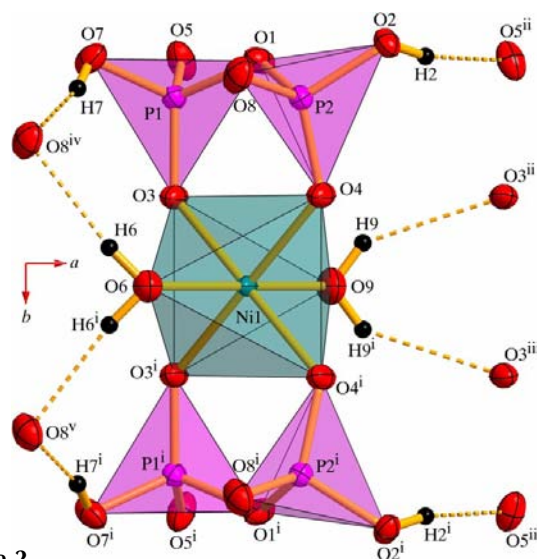


Figure 2
The basic $(H_2P_2O_7)_2Ni(H_2O)_2$ building unit. Hydrogen bonds are indicated by dashed lines. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (i) $x, \frac{1}{2} - y, z$; (ii) $\frac{1}{2} + x, y, \frac{1}{2} - z$; (iii) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} - z$; (iv) $1 - x, 1 - y, 1 - z$; (v) $1 - x, \frac{1}{2} + y, 1 - z$.]

correspond to the fact that the building units are not directly connected, and distances of the same magnitude are found in $\text{K}_2\text{CuP}_2\text{O}_7$ (5.276 Å for $\text{Cu}\cdots\text{Cu}$; El Maadi *et al.*, 1995) or $\text{KCo}(\text{HP}_2\text{O}_7)\cdot 2\text{H}_2\text{O}$ (5.347 Å for $\text{Co}\cdots\text{Co}$; Harcharras, Goubitz *et al.*, 2003). However, there are no isolated octahedral units in these compounds and the metal cations are linked *via* an O—P—O bridge. Isolated building units exist in $(\text{NH}_4)_2\text{Zn}(\text{H}_2\text{P}_2\text{O}_7)_2\cdot 2\text{H}_2\text{O}$ (Essehli *et al.*, 2005c) with a longer $\text{Zn}\cdots\text{Zn}$ distance of 7.007 Å, due to the larger size of the NH_4^+ cation.

The K^+ cations occupy two symmetry-independent positions (K1 and K2) in the mirror plane. Each position is coordinated by seven O atoms, forming strongly distorted monocapped octahedra. The P atoms occupy two symmetry-independent general positions (P1 and P2), both corresponding to a slightly distorted tetrahedral conformation with typical average P—O distances (Table 4). The two tetrahedra share a vertex to form the diphosphate unit, with bridging P—O—P angles of 127.44 (13), 127.35 (10) and 129.32 (13)° for $M = \text{Cu}$, Ni and Zn , respectively.

The M^{2+} cations are located in the mirror plane within an octahedral coordination environment formed by two $\text{H}_2\text{P}_2\text{O}_7$ groups and two water molecules (O6 and O9). There is virtually no difference in the geometry of the MO_6 octahedra for $M = \text{Cu}$ and Ni (Table 4). For $M = \text{Zn}$, however, the octahedron is less elongated along the $M\text{—O}6$ and $M\text{—O}9$ bonds by approximately 0.2 Å. This influences not only the octahedral angles but also the length of the hydrogen bonds, which are all shorter for $M = \text{Zn}$ (Tables 2 and 3). The elongation of the MO_6 octahedron towards the water molecules has been observed in all structures of the $\text{K}_2M(\text{H}_2\text{P}_2\text{O}_7)_2\cdot 2\text{H}_2\text{O}$ family but is most pronounced in the present orthorhombic structures for $M = \text{Cu}$ and Ni (Table 5). There is almost no elongation in the triclinic structure for $M = \text{Ni}$, but this difference cannot be attributed to the difference in symmetry since the Zn member shows a similar elongation in both forms. One could speculate that this is a result of stronger hydrogen bonding when the elongation is larger, but the data actually show that the reverse is true (Tables 2 and 3). Another reason for the elongation could be a better saturation of the K^+ cation, as the $\text{K}\text{—O}6$ and $\text{K}\text{—O}9$ distances are longer by 0.1 Å for the Zn member. However, the other O atoms compensate for this change and similar bond-valence sums (Brown & Altermatt, 1985) around the K^+ cations are observed for all the reported compounds (Table 5). We do not currently have an explanation for the elongated octahedra of the orthorhombic Ni and Cu compounds.

The cell volume of the orthorhombic form of $\text{K}_2M(\text{H}_2\text{P}_2\text{O}_7)_2\cdot 2\text{H}_2\text{O}$ is approximately four times larger than in the triclinic form. The triclinic cell can be transformed into a fourfold cell with angles differing from 90° by several degrees. In this transformed cell, the packing along the b axis (Fig. 3) reveals that the main difference from the orthorhombic form is the uniform orientation of the basic $(\text{H}_2\text{P}_2\text{O}_7)_2M(\text{H}_2\text{O})_2$ building unit. Although no hint of orthorhombic symmetry exists in the fourfold structure, the hydrogen bonding and even the coordination of K remains very similar in both forms.

This is achieved by different rotation of the PO_4 tetrahedra. The distances in the MO_6 octahedron and bond-valence sums for K are given in Table 5. We do not see systematic behaviour in the MO_6 elongation. On the other hand, the bond-valence sums seem to be regularly smaller for triclinic compounds. This indicates rather tighter connection of the basic building units in the orthorhombic compounds. The possible small differences in bond-valence sums for M cannot be reliably compared because of different atomic types of the central M atom.

The structures of both crystalline forms were determined at ambient temperature, suggesting that it is the method of synthesis rather than a phase transition that is responsible for the existence of a specific form. Up to now, the targeted preparation of either the triclinic or orthorhombic phase has been unsuccessful. The triclinic form sometimes accompanies the orthorhombic form as a minor component. The possibility of a phase transition near room temperature was excluded by measuring the cell parameters of the orthorhombic Ni representative between 270 and 330 K. Our results suggest that the orthorhombic forms for $M = \text{Mn}$, Co and Mg , as well as the triclinic form for $M = \text{Cu}$, probably exist and remain to be discovered.

Raman spectra of the series of dihydrogendiphosphates $\text{K}_2M(\text{H}_2\text{P}_2\text{O}_7)_2\cdot 2\text{H}_2\text{O}$ ($M = \text{Mn}$, Co , Ni , Cu , Zn and Mg) collected under conditions of ambient pressure and temperature are shown in Fig. 4. The number of observed modes varies from 32 to 39 bands, significantly smaller than expected, especially for the orthorhombic structures. This may be attributed to the accidental degeneracy of a number of modes. Moreover, some weak bands are most likely overlapped by much stronger bands, and other bands are observed as weak shoulders. The interpretation of the Raman spectra can be made in terms of PO_2 groups, P—OH bonds, P—O—P bridges and H_2O (Sarr & Diop, 1987; Harcharras, Assaoudi *et al.*, 2003). Broad bands in the region of the stretching vibrations of water molecules are observed above 3000 cm^{-1} . The

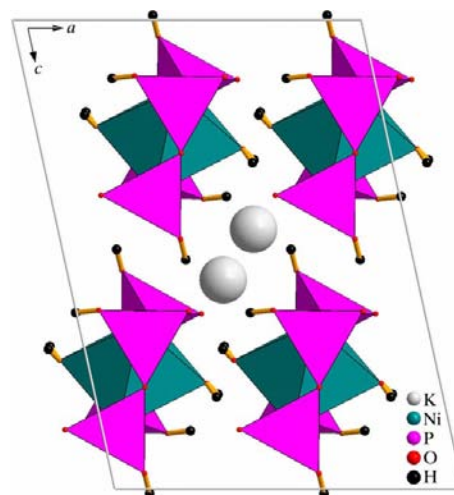


Figure 3

The triclinic form of $\text{K}_2\text{Ni}(\text{H}_2\text{P}_2\text{O}_7)_2\cdot 2\text{H}_2\text{O}$, transformed into a fourfold supercell with cell parameters $a = 9.6625$ (8) Å, $b = 11.3100$ (9) Å, $c = 13.4952$ (9) Å, $\alpha = 81.23^\circ$, $\beta = 77.59^\circ$, $\gamma = 88.06^\circ$ and $V = 1423.47$ (79) Å³.

frequencies of ν_{OH} are observed as very weak bands around 2525 cm^{-1} . Bending vibrations ρ_{OH} are located between 1300 and 1370 cm^{-1} . The band observed at 637.5 cm^{-1} is attributed to the libration of water molecules $\rho(\text{H}_2\text{O})$. In the region 990 – 1220 cm^{-1} , five to six bands attributed to the terminal stretching modes of the $(\text{P}_2\text{O}_7)^{4-}$ anions are observed. For all samples, the bands in the 1040 – 1055 cm^{-1} region are attributed to the symmetric terminal P–O stretching vibration of the PO_2 group, as observed at 1048 cm^{-1} in $\text{K}_2\text{Mg}(\text{H}_2\text{P}_2\text{O}_7)_2 \cdot 2\text{H}_2\text{O}$ (Harcharras, Capitelli *et al.*, 2003). The bridge vibrations give Raman peaks for the symmetric and anti-symmetric modes in the ranges 730 – 760 and 880 – 970 cm^{-1} , respectively. The weak band observed in $\text{K}_2\text{Mg}(\text{H}_2\text{P}_2\text{O}_7)_2 \cdot 2\text{H}_2\text{O}$, at 790.5 cm^{-1} , has been attributed to the ν_{P-OH} mode (Harcharras, Assaaoudi *et al.*, 2003; Ben Moussa *et al.*, 2000; Assaaoudi *et al.*, 2002). This band was observed at 797 cm^{-1} in $\text{Na}_4\text{Mg}_2(\text{H}_2\text{P}_2\text{O}_7)_4 \cdot 8\text{H}_2\text{O}$ (Harcharras, Assaaoudi *et al.*, 2003), but was absent in $\text{K}_2\text{Mg}(\text{H}_2\text{P}_2\text{O}_7)_2 \cdot 2\text{H}_2\text{O}$ (Harcharras, Capitelli *et al.*, 2003) and did not appear in the present compounds either. The Raman modes between 40 and 350 cm^{-1} are attributed to the external, torsional and P–O–P deformation modes. The δ_{POP} band is observed between 309 and 317 cm^{-1} ; this band was observed at 300 cm^{-1} in $\text{K}_2\text{Mg}(\text{H}_2\text{P}_2\text{O}_7)_2 \cdot 2\text{H}_2\text{O}$ (Harcharras, Capitelli *et al.*, 2003) and at 317 cm^{-1} in $\text{Na}_4\text{Mg}_2(\text{H}_2\text{P}_2\text{O}_7)_4 \cdot 8\text{H}_2\text{O}$ (Harcharras, Assaaoudi *et al.*, 2003). The rocking and the PO_2 deformation modes are observed in the region 330 – 640 cm^{-1} (Sarr & Diop, 1987; Harcharras, Goubitz *et al.*, 2003). Most of the peaks shift in frequency with increasing M^{2+} radius. For example, $\nu_s(\text{POP})$, observed as a strong band in $\text{K}_2\text{Ni}(\text{H}_2\text{P}_2\text{O}_7)_2 \cdot 2\text{H}_2\text{O}$ and centred at 757 cm^{-1} , decreases in frequency and occurs at 731 cm^{-1} in the Mg compound.

Overall, we note that the Raman spectra have the same general appearance with some differences. As an example, the $\text{K}_2\text{Ni}(\text{H}_2\text{P}_2\text{O}_7)_2 \cdot 2\text{H}_2\text{O}$ spectrum has more than one $\nu_s(\text{POP})$ band around 752 cm^{-1} and looks similar to the spectrum of triclinic $\text{K}_2\text{Mg}(\text{H}_2\text{P}_2\text{O}_7)_2 \cdot 2\text{H}_2\text{O}$. Three $\nu_{as}(\text{POP})$ modes are observed in $\text{K}_2M(\text{H}_2\text{P}_2\text{O}_7)_2 \cdot 2\text{H}_2\text{O}$ ($M = \text{Co}, \text{Ni}$ and Zn), as opposed to only one in $\text{K}_2\text{Cu}(\text{H}_2\text{P}_2\text{O}_7)_2 \cdot 2\text{H}_2\text{O}$ and $\text{K}_2\text{Mn}(\text{H}_2\text{P}_2\text{O}_7)_2 \cdot 2\text{H}_2\text{O}$. More bands were observed in the spectra of

$\text{K}_2M(\text{H}_2\text{P}_2\text{O}_7)_2 \cdot 2\text{H}_2\text{O}$ ($M = \text{Mn}, \text{Co}, \text{Cu}, \text{Zn}$) than in the spectrum of the Ni compound. These changes are not completely understood and may be due to some overlapping of bands and/or orientation of crystals. The spectrum of the Zn compound resembles those of the Co and Mn compounds and is quite distinct from that of the Ni phase.

Experimental

Single crystals of $\text{K}_2M(\text{H}_2\text{P}_2\text{O}_7)_2 \cdot 2\text{H}_2\text{O}$ ($M = \text{Ni}, \text{Cu}$ and Zn) were prepared by dissolution of the following reactants (Alaoui Tahiri *et al.*, 2002, 2003; Tahiri *et al.*, 2003, 2004): $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (0.16 g, 0.7 mmol) in $\text{K}_4\text{P}_2\text{O}_7$ (0.3 g, 0.9 mmol); $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.13 g, 7.5 mmol) in $\text{K}_4\text{P}_2\text{O}_7$ (0.5 g, 1.5 mmol); $\text{ZnCl}_2 \cdot 6\text{H}_2\text{O}$ (0.10, 0.7 mmol) in $\text{K}_4\text{P}_2\text{O}_7$ (0.5 g, 1.5 mmol). The volume ratio of water/solution was 8:2. In each case, the mixture was stirred for 12 h and the resulting solution was allowed to stand at room temperature. After a few days, light-green, light-blue and colourless crystals deposited for $M = \text{Ni}, \text{Cu}$ and Zn , respectively. The crystals were filtered off and washed with an 80% ethanol–water solution. The crystals for $M = \text{Ni}$ were of excellent quality, while only intergrown crystals were recovered for the other compounds, *viz.* $M = \text{Cu}$ and Zn . Raman spectra were measured in a back-scattering arrangement, on both compression and decompression. They were collected at room temperature using a high-throughput holographic imaging spectrograph with volume transmission grating, holographic notch filter and thermoelectrically cooled CCD detector (Physics Spectra), with a resolution of 4 cm^{-1} . A Ti^{3+} sapphire laser pumped by an argon ion laser was tuned at 785 nm . The laser was operated at 65 mW , except for the Cu compound (6 mW), and the laser beam was focused to a spot size of 5 mm to excite the sample. The spectrometer and the Raman spectra were calibrated using the Raman modes of diamond and sulfur, as well as the neon emission spectrum. An exposure time of 10 s was used with 50 accumulations.

Compound (I), $M = \text{Cu}$

Crystal data

$\text{K}_2\text{Cu}(\text{H}_2\text{P}_2\text{O}_7)_2 \cdot 2\text{H}_2\text{O}$
 $M_r = 529.7$
 Orthorhombic, $Pnma$
 $a = 9.9128(4)\text{ \AA}$
 $b = 10.7830(3)\text{ \AA}$
 $c = 13.4209(5)\text{ \AA}$
 $V = 1434.56(9)\text{ \AA}^3$
 $Z = 4$
 $D_x = 2.452\text{ Mg m}^{-3}$

Mo $K\alpha$ radiation
 Cell parameters from 17123 reflections
 $\theta = 3.2$ – 26.6°
 $\mu = 2.63\text{ mm}^{-1}$
 $T = 292\text{ K}$
 Fragment, light blue
 $0.14 \times 0.09 \times 0.06\text{ mm}$

Data collection

Oxford Sapphire-2 CCD diffractometer
 ω scans
 Absorption correction: analytical [CrysAlis RED (Oxford Diffraction, 2004), using a multifaceted crystal model]
 $T_{\min} = 0.616, T_{\max} = 0.765$

17123 measured reflections
 1572 independent reflections
 1244 reflections with $I > 3\sigma(I)$
 $R_{\text{int}} = 0.039$
 $\theta_{\max} = 26.6^\circ$
 $h = -12 \rightarrow 12$
 $k = -13 \rightarrow 13$
 $l = -16 \rightarrow 16$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.024$
 $wR(F^2) = 0.071$
 $S = 1.12$
 1572 reflections
 125 parameters
 H atoms treated by a mixture of independent and constrained refinement

Weighting scheme based on measured s.u.'s
 $w = 1/[\sigma^2(I) + 0.0016I^2]$
 $(\Delta/\sigma)_{\max} = 0.009$
 $\Delta\rho_{\max} = 0.46\text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.68\text{ e \AA}^{-3}$

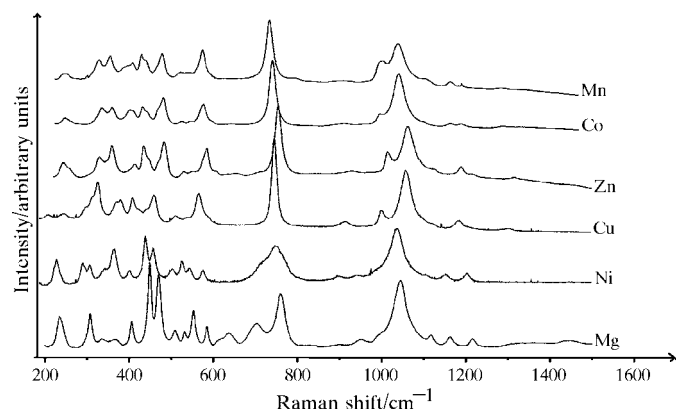


Figure 4
 Raman spectra for $\text{K}_2M(\text{H}_2\text{P}_2\text{O}_7)_2 \cdot 2\text{H}_2\text{O}$ ($M = \text{Mn}, \text{Co}, \text{Ni}, \text{Cu}, \text{Zn}$ and Mg).

Table 1

Hydrogen-bond geometry (Å, °) for (I).

| <i>D</i> —H... <i>A</i> | <i>D</i> —H | H... <i>A</i> | <i>D</i> ... <i>A</i> | <i>D</i> —H... <i>A</i> |
|--------------------------|-------------|---------------|-----------------------|-------------------------|
| O7—H7...O8 ⁱ | 0.81 (3) | 1.73 (3) | 2.536 (3) | 168 (3) |
| O6—H6...O8 ⁱ | 0.82 (3) | 2.05 (3) | 2.863 (3) | 174 (3) |
| O2—H2...O5 ⁱⁱ | 0.81 (2) | 1.72 (2) | 2.525 (3) | 172 (3) |
| O9—H9...O3 ⁱⁱ | 0.81 (3) | 2.24 (3) | 2.922 (3) | 142 (3) |

Symmetry codes: (i) $-x + 1, -y + 1, -z + 1$; (ii) $x + \frac{1}{2}, y, -z + \frac{3}{2}$.**Compound (II), *M* = Ni***Crystal data*

| | |
|----------------------------------|--|
| $K_2Ni(H_2P_2O_7)_2 \cdot 2H_2O$ | Mo <i>K</i> α radiation |
| $M_r = 524.8$ | Cell parameters from 15622 reflections |
| Orthorhombic, <i>Pnma</i> | $\theta = 3.0$ – 26.6° |
| $a = 9.9117$ (3) Å | $\mu = 2.47$ mm ⁻¹ |
| $b = 10.7736$ (3) Å | $T = 292$ K |
| $c = 13.4219$ (5) Å | Prism, light green |
| $V = 1433.25$ (8) Å ³ | $0.29 \times 0.19 \times 0.14$ mm |
| $Z = 4$ | |
| $D_x = 2.431$ Mg m ⁻³ | |

Data collection

| | |
|--|--|
| Oxford Sapphire-2 CCD diffractometer | 15622 measured reflections |
| ω scans | 1543 independent reflections |
| Absorption correction: analytical [CrysAlis RED (Oxford Diffraction, 2004), using a multi-faceted crystal model] | 1418 reflections with $I > 3\sigma(I)$ |
| $T_{min} = 0.363, T_{max} = 0.559$ | $R_{int} = 0.024$ |
| | $\theta_{max} = 26.6^\circ$ |
| | $h = -12 \rightarrow 12$ |
| | $k = -13 \rightarrow 13$ |
| | $l = -16 \rightarrow 16$ |

Refinement

| | |
|--|--|
| Refinement on F^2 | Weighting scheme based on measured s.u.'s |
| $R[F^2 > 2\sigma(F^2)] = 0.025$ | $w = 1/[\sigma^2(I) + 0.0036I^2]$ |
| $wR(F^2) = 0.089$ | $(\Delta/\sigma)_{max} = 0.008$ |
| $S = 1.31$ | $\Delta\rho_{max} = 0.26$ e Å ⁻³ |
| 1543 reflections | $\Delta\rho_{min} = -0.33$ e Å ⁻³ |
| 124 parameters | |
| H atoms treated by a mixture of independent and constrained refinement | |

Table 2

Hydrogen-bond geometry (Å, °) for (II).

| <i>D</i> —H... <i>A</i> | <i>D</i> —H | H... <i>A</i> | <i>D</i> ... <i>A</i> | <i>D</i> —H... <i>A</i> |
|--------------------------|-------------|---------------|-----------------------|-------------------------|
| O7—H7...O8 ⁱ | 0.82 (2) | 1.73 (2) | 2.535 (2) | 168 (3) |
| O6—H6...O8 ⁱ | 0.82 (2) | 2.04 (2) | 2.852 (2) | 173 (2) |
| O2—H2...O5 ⁱⁱ | 0.82 (2) | 1.72 (2) | 2.522 (2) | 168 (3) |
| O9—H9...O3 ⁱⁱ | 0.82 (2) | 2.23 (2) | 2.923 (3) | 143 (2) |

Symmetry codes: (i) $-x + 1, -y + 1, -z + 1$; (ii) $x + \frac{1}{2}, y, -z + \frac{3}{2}$.**Compound (III), *M* = Zn***Crystal data*

| | |
|----------------------------------|--|
| $K_2Zn(H_2P_2O_7)_2 \cdot 2H_2O$ | Mo <i>K</i> α radiation |
| $M_r = 531.5$ | Cell parameters from 24193 reflections |
| Orthorhombic, <i>Pnma</i> | $\theta = 3.7$ – 26.5° |
| $a = 9.7699$ (2) Å | $\mu = 2.82$ mm ⁻¹ |
| $b = 10.9749$ (3) Å | $T = 292$ K |
| $c = 13.4201$ (3) Å | Prism, colourless |
| $V = 1438.95$ (6) Å ³ | $0.17 \times 0.12 \times 0.06$ mm |
| $Z = 4$ | |
| $D_x = 2.453$ Mg m ⁻³ | |

Data collection

| | |
|--|--|
| Oxford Sapphire-2 CCD diffractometer | 24193 measured reflections |
| ω scans | 1566 independent reflections |
| Absorption correction: analytical [CrysAlis RED (Oxford Diffraction, 2004), using a multi-faceted crystal model] | 1403 reflections with $I > 3\sigma(I)$ |
| $T_{min} = 0.513, T_{max} = 0.714$ | $R_{int} = 0.032$ |
| | $\theta_{max} = 26.5^\circ$ |
| | $h = -12 \rightarrow 12$ |
| | $k = -13 \rightarrow 13$ |
| | $l = -16 \rightarrow 16$ |

Refinement

| | |
|--|--|
| Refinement on F^2 | Weighting scheme based on measured s.u.'s |
| $R[F^2 > 2\sigma(F^2)] = 0.030$ | $w = 1/[\sigma^2(I) + 0.0016I^2]$ |
| $wR(F^2) = 0.090$ | $(\Delta/\sigma)_{max} = 0.005$ |
| $S = 1.74$ | $\Delta\rho_{max} = 0.40$ e Å ⁻³ |
| 1566 reflections | $\Delta\rho_{min} = -0.63$ e Å ⁻³ |
| 124 parameters | |
| H atoms treated by a mixture of independent and constrained refinement | |

Table 3

Hydrogen-bond geometry (Å, °) for (III).

| <i>D</i> —H... <i>A</i> | <i>D</i> —H | H... <i>A</i> | <i>D</i> ... <i>A</i> | <i>D</i> —H... <i>A</i> |
|--------------------------|-------------|---------------|-----------------------|-------------------------|
| O7—H7...O8 ⁱ | 0.81 (2) | 1.73 (2) | 2.531 (3) | 176 (2) |
| O6—H6...O8 ⁱ | 0.81 (1) | 2.00 (1) | 2.793 (3) | 168 (2) |
| O2—H2...O5 ⁱⁱ | 0.80 (1) | 1.71 (1) | 2.504 (3) | 169 (2) |
| O9—H9...O3 ⁱⁱ | 0.80 (2) | 2.12 (2) | 2.862 (3) | 155 (2) |

Symmetry codes: (i) $-x + 1, -y + 1, -z + 1$; (ii) $x + \frac{1}{2}, y, -z + \frac{3}{2}$.**Table 4**

Comparison of bond lengths for compounds (I)–(III) (Å).

Atoms O6 and O9 belong to water molecules.

| Atom1 | Atom2 | <i>M</i> = Cu | <i>M</i> = Ni | <i>M</i> = Zn |
|----------|------------------------|---------------|---------------|---------------|
| <i>M</i> | O3 | 1.9788 (19) | 1.9785 (14) | 2.0818 (19) |
| <i>M</i> | O4 | 1.984 (2) | 1.9879 (15) | 2.074 (2) |
| <i>M</i> | O6 | 2.324 (3) | 2.313 (2) | 2.113 (3) |
| <i>M</i> | O9 | 2.405 (4) | 2.398 (3) | 2.189 (3) |
| P1 | O1 | 1.598 (2) | 1.6004 (16) | 1.599 (2) |
| P1 | O3 | 1.505 (2) | 1.5017 (14) | 1.504 (2) |
| P1 | O5 | 1.485 (2) | 1.4893 (15) | 1.487 (2) |
| P1 | O7 | 1.551 (2) | 1.5539 (16) | 1.550 (2) |
| P2 | O1 | 1.615 (2) | 1.6136 (16) | 1.613 (2) |
| P2 | O2 | 1.546 (2) | 1.5452 (15) | 1.542 (2) |
| P2 | O4 | 1.512 (2) | 1.5050 (16) | 1.505 (2) |
| P2 | O8 | 1.487 (2) | 1.4917 (16) | 1.498 (2) |
| K1 | O2 ⁱⁱⁱ | 2.753 (2) | 2.7545 (15) | 2.718 (2) |
| K1 | O3 | 2.820 (2) | 2.8215 (16) | 2.829 (2) |
| K1 | O4 ^{iv} | 2.964 (2) | 2.9698 (16) | 3.055 (2) |
| K1 | O9 | 2.859 (3) | 2.862 (3) | 2.963 (3) |
| K2 | O4 ^v | 3.081 (2) | 3.0741 (17) | 3.011 (2) |
| K2 | O5 ^{iv} | 2.749 (2) | 2.7440 (16) | 2.714 (2) |
| K2 | O6 ^v | 2.885 (3) | 2.889 (2) | 2.978 (3) |
| K2 | O7 | 2.732 (2) | 2.7294 (16) | 2.709 (2) |
| <i>M</i> | <i>M</i> ^{iv} | 5.7397 (7) | 5.7399 (5) | 5.7257 (6) |

Symmetry codes: (iii) $\frac{3}{2} - x, 1 - y, \frac{1}{2} + z$; (vi) $-\frac{1}{2} + x, y, \frac{3}{2} - z$; (v) $1 - x, 1 - y, 1 - z$.

The H atoms were located in difference Fourier maps and their coordinates were refined independently by constraining the O—H distances to 0.82 (1) Å. $U_{iso}(H)$ values were calculated as $1.2U_{eq}$ of the parent atom. No extinction correction was required.

For all compounds, data collection: *CrysAlis CCD* (Oxford Diffraction, 2004); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2004); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SIR2002* (Burla *et al.*, 2003); program(s) used to refine structure: *JANA2000* (Petříček *et al.*, 2000); molecular graphics:

Table 5

Comparison of bond lengths (Å) in the MO_6 octahedra of the $K_2M(H_2P_2O_7) \cdot 2H_2O$ series. Bond-valence sums (BVS) for the seven-coordinated K atoms and for the octahedrally coordinated M atom are also listed.

OW denotes the O atoms of water molecules; o and t denote orthorhombic and triclinic structures, respectively.

| | $M = Ni, o$ | $M = Ni, t$ | $M = Zn, o$ | $M = Zn, t$ | $M = Cu, o$ | $M = Co, o$ | $M = Mg, t$ |
|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|
| $M-O$ | 1.9785 (14) | 2.055 (3) | 2.0818 (19) | 2.081 (4) | 1.9788 (19) | 2.0926 (10) | 2.0530 (13) |
| $M-O$ | 1.9785 (14) | 2.055 (3) | 2.0818 (19) | 2.081 (4) | 1.9788 (19) | 2.0926 (10) | 2.0530 (13) |
| $M-O$ | 1.9879 (15) | 2.052 (3) | 2.074 (2) | 2.057 (3) | 1.984 (2) | 2.0884 (10) | 2.0592 (17) |
| $M-O$ | 1.9879 (15) | 2.052 (3) | 2.074 (2) | 2.057 (3) | 1.984 (2) | 2.0884 (10) | 2.0592 (17) |
| $M-OW$ | 2.313 (2) | 2.067 (3) | 2.113 (3) | 2.116 (3) | 2.324 (3) | 2.1537 (15) | 2.0998 (14) |
| $M-OW$ | 2.398 (3) | 2.067 (3) | 2.189 (3) | 2.116 (3) | 2.405 (4) | 2.1017 (15) | 2.0998 (14) |
| BVS (K1)† | 1.03 | 0.89 | 1.02 | 0.91 | 1.04 | 1.19 | 0.85 |
| BVS (K2) | 1.07 | | 1.12 | | 1.06 | 1.02 | |
| BVS (M) | 2.03 | 2.10 | 2.06 | 2.15 | 2.08 | 1.94 | 2.17 |

† Bond-valence parameters for K–O, Zn–O and Mg–O taken from Brown & Altermatt (1985); those for Ni–O and Cu–O taken from Liu & Thorp (1993); those for Co–O taken from Wood & Palenik (1998).

DIAMOND (Brandenburg & Putz, 2005); software used to prepare material for publication: JANA2000.

This work was supported by the Grant Agency of the Czech Republic (grant No. 202/03/0430). A part of this work was supported financially by a grant from the National Science Foundation (DMR 0231291 to FIU).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BC1079). Services for accessing these data are described at the back of the journal.

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