inorganic papers

Synthesis, crystal structure and vibrational spectra of a new diammonium zinc(II) dihydrogendiphosphate dihydrate, $(NH_4)_2Zn(H_2P_2O_7)_2 \cdot 2H_2O$

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Key indicators

Single-crystal X-ray study
$T = 301$ K
Mean σ(P–O) = 0.002 Å
R factor = 0.032
wR factor = 0.090
Data-to-parameter ratio = 11.5

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

$(NH_4)_2Zn(H_2P_2O_7)_2 \cdot 2H_2O$ is isostructural with its manganese homologue. Isolated almost-regular ZnO_6 octahedra form a layered structure. The IR and Raman spectra show bands characteristic of $H_2P_2O_7$ groups.

Comment

A large number of diphosphates with mineral cations are presently known and a systematic survey of the crystal structures has been reported (Durif, 1995).

We previously reported a series of compounds with the formula $K_2T(H_2P_2O_7)_2 \cdot 2H_2O$, where T = Mn (Alaoui *et al.*, 2003*a*), Co (Alaoui *et al.*, 2002), Ni (Alaoui *et al.*, 2004), Zn (Alaoui *et al.*, 2003*b*). In fact, the acidic diphosphates are of interest in many fields, for example, in some enzyme-catalysed reaction processes (Haromy *et al.*, 1984), as inhibitors in the formation and dissolution of apatite crystals *in vitro* (Mathew *et al.*, 1993), as additives in fertilizers (Frazier *et al.*, 1965, 1966), or even in medicine (Fleisch & Russell, 1972). We report here the synthesis, crystal structure and Raman study of the new dihydrogendiphosphate $(NH_4)_2Zn(H_2P_2O_7)_2 \cdot 2H_2O$, a homologue of $Mn_{0.5}NH_4H_2P_2O_7 \cdot H_2O$, which was published recently (Capitelli *et al.*, 2004).

Zn^{2+} cations lie on crystallographic inversion centres in the framework of $(NH_4)_2Zn(H_2P_2O_7)_2 \cdot 2H_2O$. Their octahedral coordination is composed of four O atoms from two bidendate
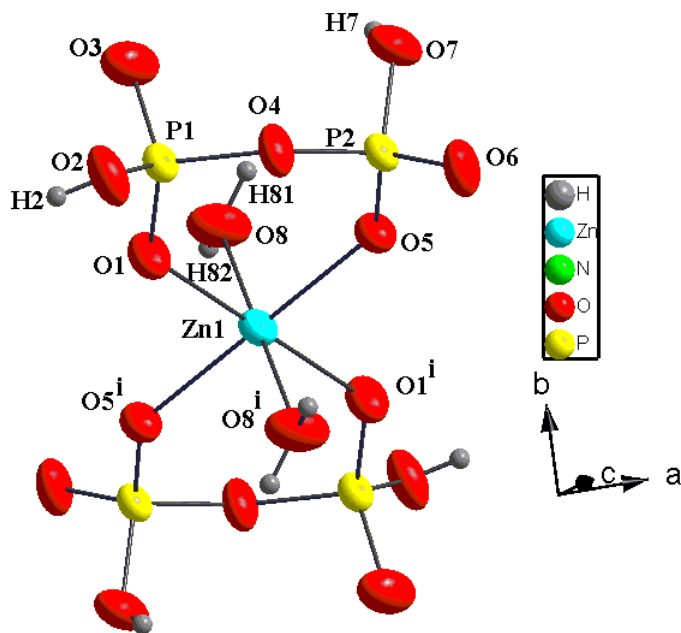
Figure 1
The coordination around P^V and Zn^{II} in $(NH_4)_2Zn(H_2P_2O_7)_2 \cdot 2H_2O$. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry code: (i) $-x$, $1 - y$, $-z$.]
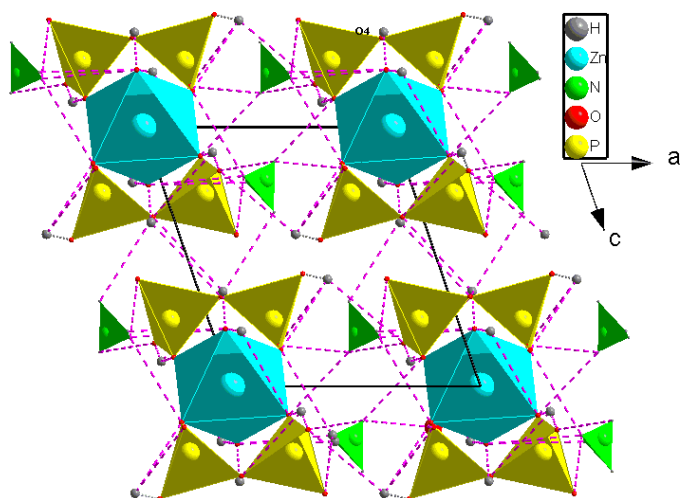
Figure 2
Projection of the title compound along the *b* axis. Colour key: yellow $H_2P_2O_7$ polyhedra, light blue ZnO_6 polyhedra, green NH_4^+ and small grey circles H atoms.

$H_2P_2O_7$ groups, with the remaining two O atoms being from the water molecules. This coordination scheme has almost regular D_{4h} idealized symmetry. The average Zn—O distance of 2.092 Å is in close agreement with the value of 2.084 Å for $K_2Zn(H_2P_2O_7)_2$·2H_2O (Alaoui *et al.*, 2003b). The ZnO_6 polyhedra are isolated in the structure, with Zn···Zn over 7 Å.

Each of the two unique P atoms is coordinated by four O atoms, two of which belong to hydroxyl groups, in a slightly distorted tetrahedral geometry. The two tetrahedra share an apex (O4) to form the $[H_2P_2O_7]^{2-}$ anion in a roughly eclipsed conformation. The average P—O distance of 1.533 Å can be compared to that found in $K_2H_2P_2O_7$ (1.537 Å; Larbot *et al.*, 1983) and $K_3H(H_2P_2O_7)_2$ (1.543 Å; Dumas, 1978). $H_2P_2O_7$ is generally characterized by the bridging P—O—P angle, which is 128.85 (6)°, a value close to that of 130.8° found in $K_2Zn(H_2P_2O_7)_2$·2H_2O and 130.3° in $K_4P_2O_7$·3H_2O (Robertson & Calvo, 1967). Fig. 1 illustrates the oxygen coordination around P^V and Zn^{II} in the title compound.

The crystal structure might thus be described as a complex made of isolated $[Zn(H_2O)_2(H_2P_2O_7)_2]^{2-}$ and NH_4^+ ions interacting with each other through an intricate hydrogen-bonding network, as shown in Fig. 2. There are three kinds of such interactions (see Table 2), *viz.* four bonds from ammonium, two from the dihydrogendiphosphate ion and another two from water oxygen. The longest hydrogen bonds occur between the hydroxyl species of the $[H_2P_2O_7]$ groups.

The interpretation of the Raman spectrum can be made in terms of the PO_2 group, the POH bond, the POP bridge and NH_4^+ and H_2O (Sarr & Diop, 1987). The assignment of bands appearing in the spectrum is reported in Table 3. These data confirm the presence of the different entities in $(NH_4)_2Zn(H_2P_2O_7)_2$·2H_2O, especially in the region 990–1220 cm^{-1}, with four bands attributed to the terminal stretching modes of $(P_2O_7)^{4-}$ anions. The band observed at 1036 cm^{-1} and attributed to the symmetric terminal P—O stretching vibration of the PO_2 group was observed at

1048 cm^{-1} in $Mg_{0.5}KH_2P_2O_7$·H_2O (Capitelli *et al.*, 2004). The δPO_2, δPO—H, δPO_2 and δH_2O are observed in the 350–670 cm^{-1} region, as reported in the literature (Sarr & Diop, 1987, Capitelli *et al.*, 2004).

Note added in proof: the structure of the same compound has been reported independently by another research group (Capitelli *et al.*, 2005).

Experimental

Three solutions have been mixed in a beaker to prepare the title compound: NH_4OH (20 ml, 0.1 *M*), $ZnCl_2$·4H_2O (20 ml, 0.1 *M*) and $K_4P_2O_7$ (30 ml, 0.1 *M*). The mixture was stirred for 1 d and allowed to stand for two to three weeks. At the end of this time, large prismatic colourless crystals deposited, which were filtered off and washed with a water–ethanol solution (20:80). The Raman spectrum of the title compound was measured in a back-scattering arrangement, under room conditions, using a high throughput holographic imaging spectrograph with a volume transmission grating, a holographic notch filter and a 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 power was operated at 40 mW and the exposure time was 60 s with 10 accumulations.

Crystal data

$(NH_4)_2Zn(H_2P_2O_7)_2$·2H_2O	$Z = 1$
$M_r = 489.40$	$D_x = 2.168$ Mg m^{-3}
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 7.0074 (9)$ Å	Cell parameters from 2048
$b = 7.339 (1)$ Å	reflections
$c = 7.796 (1)$ Å	$\theta = 2.8–29.8°$
$\alpha = 81.24 (1)°$	$\mu = 2.15$ mm^{-1}
$\beta = 71.08 (1)°$	$T = 301 (2)$ K
$\gamma = 88.15 (1)°$	Prism, colourless
$V = 374.78 (9)$ Å^3	$0.26 \times 0.18 \times 0.08$ mm

Data collection

Oxford Diffraction Xcalibur diffractometer with Sapphire CCD detector	2491 measured reflections
	1495 independent reflections
	1402 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.036$
Absorption correction: analytical (*CrysAlis RED*; Oxford Diffraction, 2001)	$\theta_{max} = 26.4°$
	$h = -8 \rightarrow 8$
	$k = -9 \rightarrow 6$
$T_{min} = 0.605$, $T_{max} = 0.847$	$l = -9 \rightarrow 9$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0631P)^2 + 0.1969P]$
$R[F^2 > 2\sigma(F^2)] = 0.032$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.090$	$(\Delta/\sigma)_{max} = 0.001$
$S = 1.06$	$\Delta\rho_{max} = 0.78$ e Å^{-3}
1495 reflections	$\Delta\rho_{min} = -0.72$ e Å^{-3}
130 parameters	
H-atom parameters constrained	

Table 1
Selected bond lengths (Å).

Zn1—O1	2.0816 (18)	P1—O4	1.6056 (19)
Zn1—O5	2.0888 (17)	P2—O6	1.4950 (19)
Zn1—O8	2.108 (2)	P2—O5	1.5040 (17)
P1—O1	1.4930 (18)	P2—O7	1.5521 (19)
P1—O3	1.506 (2)	P2—O4	1.5997 (19)
P1—O2	1.5476 (18)		

Table 2
Hydrogen-bonding geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O2—H2···O6[i]	0.896 (10)	1.610 (12)	2.495 (3)	169 (4)
O7—H7···O3[ii]	0.895 (10)	1.642 (15)	2.510 (3)	162 (4)
O8—H81···O3[iii]	0.842 (10)	1.948 (10)	2.788 (3)	176 (3)
O8—H82···O6[iv]	0.844 (10)	1.928 (11)	2.770 (3)	175 (4)
N1—H11···O5[v]	0.896 (9)	2.177 (12)	3.037 (3)	161 (2)
N1—H12···O2[iv]	0.897 (9)	1.978 (11)	2.859 (3)	167 (2)
N1—H13···O5	0.896 (9)	2.080 (13)	2.963 (3)	169 (3)
N1—H14···O7[iii]	0.894 (9)	2.089 (10)	2.977 (3)	172 (2)

Symmetry codes: (i) $1 + x, y, z$; (ii) $-x, -y, -z$; (iii) $x, 1 + y, z$; (iv) $-x, 1 - y, -1 - z$; (v) $-1 - x, 1 - y, -z$.

Table 3
Raman spectrum (cm^{-1}).

Raman frequency	Mode assignment
3344.7	OH stretching
3220	NH stretching
2850	NH_4^+ combination modes
1670	OH_2 bending
1340	OH_2 bending
1450	NH_4^+ bending
1034.9−1192.4	P—O stretching
970.6	asymmetric P—O—P stretching
907.6	asymmetric P—O—P stretching
748.2	symmetric P—O—P stretching
473.6−578.5	P—O bending modes and NH_4^+ torsional oscillation

All H atoms were located in a difference Fourier map. H atoms of the water molecules were refined with constrained geometry (Nardelli, 1999). H atoms of the NH_4^+ ion were refined with constrained geometry for tetrahedra, with an N—H distance of 0.9 Å. The O—H distances in the water molecules were constrained to 0.85 Å, with O—H—O angles of 108°. The displacement parameters of all H atoms were constrained to $1.2U_{eq}$ of the parent atoms.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2001); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2001); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *SHELXL97*.

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