inorganic papers

(NH$_4$)$_2$[Ni(H$_2$P$_2$O$_7$)$_2$(H$_2$O)$_2$]

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Key indicators

Diammonium nickel(II) dihydrogendiphosphate(V) dihydrate is a member of the isotypic series (NH$_4$)$_2$$T$(H$_2P_2O_7$)$_2$·2H$_2$O ($T$ = Mn, Co or Zn). Isolated almost-regular NiO$_6$ octahedra form a layered structure. The Raman spectrum shows bands characteristic of H$_2$P$_2$O$_7$ groups.

Comment

Recently, we published the structures of two acidic diphosphates (NH$_4$)$_2$Zn(H$_2$P$_2$O$_7$)$_2$·2H$_2$O (Essehli *et al.*, 2005*a*) [which was published at the same time by Capitelli *et al.* (2005)] and (NH$_4$)$_2$Co(H$_2$P$_2$O$_7$)$_2$·2H$_2$O (Essehli *et al.*, 2005*b*). These two dihydrogenediphosphates are isotypic with (NH$_4$)$_2$Mn(H$_2$P$_2$O$_7$)$_2$·2H$_2$O (Capitelli *et al.*, 2004). The present paper deals with the preparation and crystal structure of the likewise isotypic Ni member of this series.

Ni^{2+} cations lie on crystallographic inversion centres in the framework of the crystal structure. The metal atoms constitute a primitive, nearly hexagonal lattice. They are octahedrally surrounded by four O atoms from two bidendate H$_2$P$_2$O$_7$ groups and by two O atoms from the water molecules. This coordination scheme has almost regular D_{4h} idealized symmetry. The NiO$_6$ polyhedra are isolated in the framework
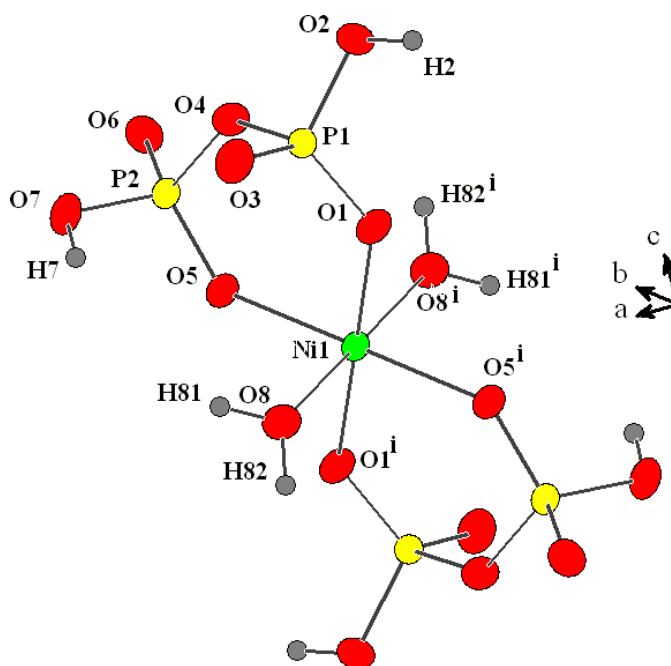
Figure 1
The coordination scheme around Ni^{II} and P^V in (NH$_4$)$_2$Ni(H$_2$P$_2$O$_7$)$_2$·2H$_2$O. The probability level of the anisotropic displacement ellipsoids is 50%. [Symmetry code: (i) $-x$, $1-y$, $-z$.]
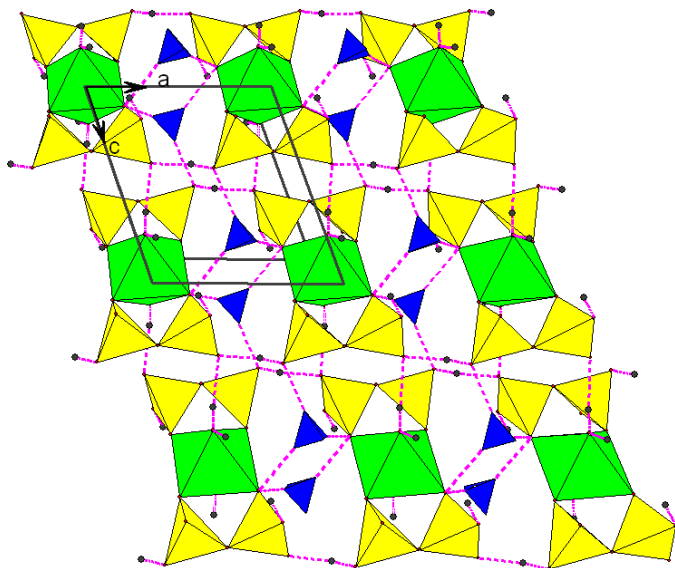
Figure 2
Projection of the crystal structure along [010]. Yellow polyhedra: $H_2P_2O_7$, green: NiO_6, blue: NH_4; dark grey spheres: H atoms. Dashed lines represent hydrogen bonds.

of $(NH_4)_2Ni(H_2P_2O_7)_2 \cdot 2H_2O$, with $Ni \cdots Ni$ distances over 7 Å. The average Ni—O distance of 2.071 Å is in close agreement with the average T—O distances in the isotypic compounds of 2.084 (T = Zn) and 2.106 Å (T = Co), or 2.033 Å for a similar coordination of Ni^{2+} in $SrNiP_2O_7$ (El Bali *et al.*, 2001).

Each of the two unique P atoms is coordinated in a distorted tetrahedral geometry by four O atoms, two of which belong to hydroxyl groups. The two tetrahedra share an apex (O4) to form the $H_2P_2O_7^{2-}$ diphosphate anion in a roughly eclipsed conformation. The average P—O distance of 1.545 Å is the same as for the isotypic Co member and is comparable to the average distances observed for other diphosphates: 1.533 Å in $(NH_4)_2Zn(H_2P_2O_7)_2 \cdot 2H_2O$, 1.537 Å in $K_2H_2P_2O_7$ (Larbot *et al.*, 1983) and 1.543 Å in $K_3H(H_2P_2O_7)_2$ (Dumas, 1978).

The P—O—P bridging angle of the bent di-hydrogendiphosphate anion in $(NH_4)_2Ni(H_2P_2O_7)_2 \cdot 2H_2O$ is 130.4 (1)°. This is close to the values observed in $(NH_4)_2Co(H_2P_2O_7)_2 \cdot 2H_2O$ [131.3 (1)°], $(NH_4)_2Zn(H_2P_2O_7)_2 \cdot 2H_2O$ [128.85 (6)°], $(NH_4)_2Mn(H_2P_2O_7)_2 \cdot 2H_2O$ (131.7°), $K_2Zn(H_2P_2O_7)_2 \cdot 2H_2O$ (130.8°; Alaoui Tahiri *et al.*, 2003) and $K_4P_2O_7 \cdot 3H_2O$ (130.3°; Robertson & Calvo, 1967).

Fig. 1 illustrates the oxygen coordination scheme around Ni^{II} and P^{V} in the title compound.

The crystal structure of $(NH_4)_2Ni(H_2P_2O_7)_2 \cdot 2H_2O$ might be thus described as a complex made of isolated $[Ni(H_2O)_2(H_2P_2O_7)]^{2-}$ and NH_4^+ ions interacting with each other through intricate hydrogen bonding, as shown in Fig. 2. There are three kinds of hydrogen bonds (see Table 2), *viz.* four bonds from ammonium, two from the dihydrogendiphosphate units and another two from water molecules. Note that the longest hydrogen bonds occur between the hydroxyl species of the $H_2P_2O_7$ groups.

The interpretation and assignment of Raman bands of $(NH_4)_2Ni(H_2P_2O_7)_2 \cdot 2H_2O$ (see Table 3) can be made in terms of PO_2 groups, POH groups, the P—O—P bridge, as well as NH_4^+ and H_2O (Sarr & Diop, 1987). These data confirm the presence of the different entities in the title compound. The region between 990 and 1200 cm^{-1} shows vibration bands that are characteristic for diphosphates, *viz.* the terminal stretching modes of the $P_2O_7^{4-}$ anions. The band observed at 1043 cm^{-1} is attributed to the symmetric terminal P—O stretching vibration of the PO_2 group. This vibration was observed at 1036 cm^{-1} in $(NH_4)_2Zn(H_2P_2O_7)_2 \cdot 2H_2O$. The δPO_2, δPO—H, δPO_2 and δH_2O modes are observed in the region 350–670 cm^{-1} as reported in the literature (Sarr & Diop, 1987; Essehli *et al.*, 2005a).

Experimental

Crystals of the title compound were obtained from a mixture of three aqueous solutions, namely NH_4OH (20 ml, 0.1 *M*), $NiCl_2 \cdot 6H_2O$ (20 ml, 0.1 *M*) and $K_4P_2O_7$ (30 ml, 0.1 *M*). The mixture was stirred for a day and allowed to stand for around three weeks. At the end of this time, large prismatic light green crystals were deposited, which were filtered off and washed with a water–ethanol solution (20:80). The Raman spectrum of the title compound was measured at room conditions in a back-scattering arrangement using a high-throughput holographic imaging spectrograph with volume transmission grating, holographic notch filter and thermoelectrically cooled CCD detector (Physics Spectra), with the 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

$(NH_4)_2[Ni(H_2P_2O_7)_2(H_2O)_2]$	$Z = 1$
$M_r = 482.74$	$D_x = 2.137$ Mg m^{-3}
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 7.0344$ (9) Å	Cell parameters from 2066
$b = 7.3214$ (9) Å	reflections
$c = 7.792$ (1) Å	$\theta = 3.0$–29.8°
$\alpha = 81.53$ (1)°	$\mu = 1.81$ mm^{-1}
$\beta = 70.91$ (1)°	$T = 301$ (2) K
$\gamma = 88.21$ (1)°	Prism, light green
$V = 375.03$ (8) Å^3	$0.28 \times 0.18 \times 0.14$ mm

Data collection

Oxford Diffraction Xcalibur diffractometer with Sapphire CCD detector	2491 measured reflections
	1496 independent reflections
	1409 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.027$
Absorption correction: analytical (*CrysAlis RED*; Oxford Diffraction, 2001)	$\theta_{max} = 26.4°$
	$h = -8 \rightarrow 4$
	$k = -9 \rightarrow 9$
$T_{min} = 0.632$, $T_{max} = 0.786$	$l = -9 \rightarrow 9$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0733P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.033$	$+ 0.3934P]$
$wR(F^2) = 0.107$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.08$	$(\Delta/\sigma)_{max} = 0.043$
1496 reflections	$\Delta\rho_{max} = 0.80$ e Å^{-3}
130 parameters	$\Delta\rho_{min} = -0.49$ e Å^{-3}
H-atom parameters constrained	

Table 1
Selected bond lengths (Å).

Ni1—O1^i	2.069 (2)	P1—O3	1.513 (2)
Ni1—O1	2.069 (2)	P1—O2	1.560 (2)
Ni1—O5	2.070 (2)	P1—O4	1.613 (2)
Ni1—O5^i	2.070 (2)	P2—O6	1.504 (2)
Ni1—O8	2.075 (2)	P2—O5	1.510 (2)
Ni1—O8^i	2.075 (2)	P2—O7	1.559 (2)
P1—O1	1.499 (2)	P2—O4	1.604 (2)

Symmetry codes: (i) $-x, 1-y, -z$.

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O2—H2$\cdots$O6^{ii}	0.897 (10)	1.615 (13)	2.502 (3)	169 (4)
O7—H7$\cdots$O3^{iii}	0.901 (10)	1.639 (14)	2.525 (3)	167 (4)
O8—H81$\cdots$O3^{iv}	0.846 (10)	1.950 (10)	2.795 (3)	177 (3)
O8—H82$\cdots$O6^{v}	0.847 (10)	1.943 (11)	2.789 (3)	177 (4)
N1—H11$\cdots$O5^{vi}	0.895 (9)	2.161 (11)	3.038 (4)	167 (3)
N1—H12$\cdots$O2^{v}	0.896 (9)	2.008 (13)	2.869 (4)	161 (3)
N1—H13$\cdots$O5	0.896 (10)	2.101 (16)	2.966 (4)	162 (3)
N1—H14$\cdots$O7^{iv}	0.899 (10)	2.096 (11)	2.984 (4)	169 (3)

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

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

Raman bands	Mode assignment
3310	OH stretching
3264	NH stretching
2531	NH$_4^+$ combination modes
1684	OH$_2$ bending
1313	OH$_2$ bending
1448	NH$_4^+$ bending
1162–1044	P—O stretching
966	asymmetric P—O—P stretching
906	asymmetric P—O—P stretching
755	symmetric P—O—P stretching
536–455	P—O bending modes and NH$_4^+$ torsional oscillation

All H atoms were located in a difference Fourier map. Water H atoms were refined with constrained geometry (Nardelli, 1999), *viz.* O—H distances were constrained to 0.85 Å and H—O—H angles to 107°; the H$\cdots$H distance was constrained to 1.365 Å, thus leading to the angle of 107°. H atoms of NH$_4$ were refined with constrained geometry for tetrahedra, with an N—H distance of 0.9 Å. H atoms of the OH groups were refined with the O—H distance constrained to 0.9 Å. 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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