metal-organic papers

# Bis(ethylenediammonium) diaquabis-[hydrogendiphosphato(3–)]nickelate(II): structure and vibrational spectroscopy

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In the crystal structure of the title compound, $(C_2N_2H_{10})_2[Ni(HP_2O_7)_2(H_2O)_2]$, each Ni cation is surrounded by two symmetry-related diphosphate anions and two symmetry-related water molecules within a distorted octahedron. The octahedra are connected *via* O—H···O hydrogen bonding into layers. The ethylenediammonium cations are located in the interlayer space and are connected by N—H···O hydrogen bonds to the anionic layers. The Ni cation and the two crystallographically independent ethylenediammonium cations are located on centres of inversion, whereas the diphosphate anion and the water molecule are located in general positions.

Comment

A bibliographical search shows that a large variety of diphosphates with inorganic cations exist. Their main crystallographic data have been reported by Durif (1995). However, compounds with organic cations have become of increasing interest in recent decades (Cheetham *et al.*, 1999, and references therein) because of their potential catalytic, adsorbent, ion-exchange or second-order non-linear optical properties (Clearfield *et al.*, 1998; Davis & Lobo, 1992; Breck, 1974; Venuto, 1994; Hlel & Smiri, 1999).

Among the large number of structurally characterized compounds, we mention the following diphosphates, where the organic cations are ethylenediammonium $(C_2H_{10}N_2)$, propylenediammonium $(C_3N_2H_{12})$ or ethanolammonium $(NH_3C_2H_4OH)$ and the diphosphate anion is $(HP_2O_7)^{3-}$ or $(H_2P_2O_7)^{2-}$: $(C_2H_{10}N_2)_3(HP_2O_7)_2 \cdot 2H_2O$ (Kamoun *et al.*, 1990), $(C_2H_{10}N_2)_2P_2O_7$ (Kamoun *et al.*, 1992), $(C_2H_{10}N_2)_2Cu_2(HP_2O_7)_2 \cdot 3H_2O$ (Gharbi *et al.*, 1994), $(NH_3C_2H_4OH)_2 \cdot H_2P_2O_7$ (Averbuch-Pouchot & Durif, 1992), $(C_2H_{10}N_2)H_2P_2O_7$ (Averbuch-Pouchot & Durif, 1993), $(C_2N_2H_{10})Ni(HP_2O_7)F$ (Yunling *et al.*, 2001) and $(C_3N_2H_{12})_2Ni(HP_2O_7)_2 \cdot 4H_2O$ (Gharbi & Jouini, 2004).

(I)
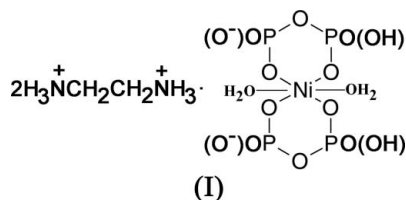
The present work is a part of our investigation of the systems $(Or)_xT(HP_2O_7)_2 \cdot 2H_2O$ (Or = organic cation and T = divalent 3d metal, also including Zn and Mg). Here, we report the synthesis, crystal structure and Raman study of the Ni member of this series, the title compound, (I), $[NH_3(CH_2)_2NH_3]_2Ni(HP_2O_7)_2 \cdot 2H_2O$ (abbreviated NiEnP), which contains ethylenediammonium cations.
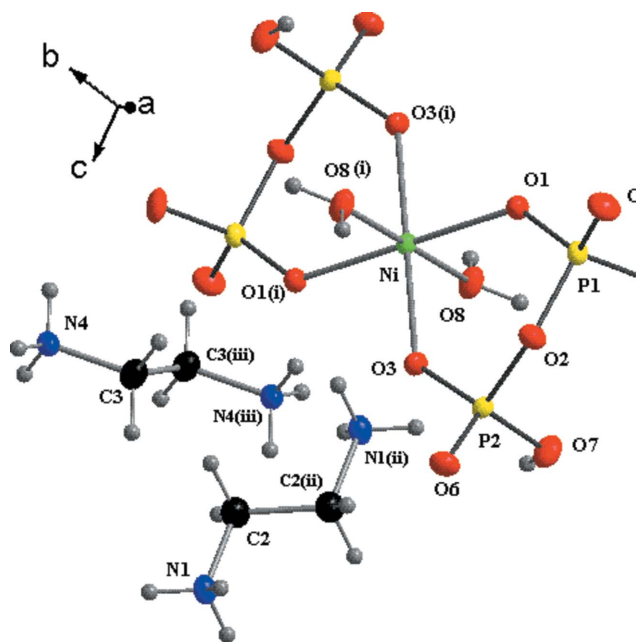
Figure 1
Perspective view of the asymmetric unit of the title compound, with the atom numbering; displacement ellipsoids are at the 50% probability level. [Symmetry codes: (i) $2-x, 2-y, -z$; (ii) $2-x, 2-y, 1-z$; (iii) $1-x, 1-y, 1-z$.]

The asymmetric unit of compound (I) consists of one Ni cation and two crystallographically independent ethylene-diammonium cations which are located on centres of inversion, and one diphosphate anion and one water molecule which occupy general positions (Fig. 1).

The Ni cations are each surrounded by two symmetry-related diphosphate anions and two symmetry-related water molecules within a distorted octahedron. The average Ni—O bond distance of 2.0729 Å is in the range of values observed in other Ni diphosphates, such as $(NH_4)_2Ni(H_2P_2O_7)_2 \cdot 2H_2O$ (mean Ni—O = 2.084 Å; Essehli et al., 2005b), $K_2Ni(H_2P_2O_7)_2 \cdot 2H_2O$ (mean Ni—O = 2.047 Å; Alaoui et al., 2004) and $(C_3N_2H_{12})_2Ni(HP_2O_7)_2 \cdot 4H_2O$ (mean Ni—O = 2.076 Å; Gharbi & Jouini, 2004). The cis-O—M—O bond angles range from 86.67 (6) to 93.33 (6)°, and the trans-O—M—O angles have values near to 180° (Table 1). These are similar to the values in other previously reported Ni^{II} diphosphates (Essehli et al., 2005b; Tahiri et al., 2004; Gharbi & Jouini, 2004).

The mean P—O distances within the hydrogen diphosphate group are 1.618 Å for the bridging P—O, 1.5207 Å for the terminal P—O and 1.5137 Å for the bridging P—OH bonds (Table 1). These distances are comparable with those observed in other diphosphates containing an HP_2O_7 group, e.g. $KMnP_2O_7 \cdot 2H_2O$ (Assaaoudi et al., 2002) or $KCoH-P_2O_7 \cdot 2H_2O$ (Harcharras et al., 2003). The P1—O2—P2 angle is 129.16 (1)°.

The Ni octahedra are connected via O—H···O hydrogen bonds into anionic layers which are located in the ab plane (Table 2 and Fig. 2). The anionic charge of the layers is balanced by the ethylenediammonium cations, which are located between the layers and which are connected to the O atoms of the diphosphate anions via N—H···O hydrogen bonds (Table 2 and Fig. 2).

We now discuss the vibrational spectroscopy results for compound (I). The Raman spectrum of (I) has been recorded and interpreted using factor group analysis. The compound crystallizes in the triclinic space group $P\bar{1}$, in which atoms Ni and O4 are located on 1c sites and all the other atoms are located on 2i sites. The irreducible representation of (I) in the C_i factor group (excluding 3 acoustic modes) leads to 81 A_g + 81 A_u modes. The A_g modes are Raman active and the A_u modes are IR active. The Raman spectrum of (I) is shown in Fig. 3. Its interpretation can be made on the basis of characteristic vibrations of –CH_2–, $(-NH_3)^+$, PO_3 and PO_2 groups, P—OH bond, POP bridge, and H_2O (Essehli et al., 2005a,b,c; Gharbi & Jouini, 2004; Sarr & Diop, 1987; Fernandez, Pizarro, Mesa, Lezama, Arriortua & Rojo, 2001; Fernandez, Pizarro, Mesa, Lezama, Arriortua, Olazcuaga & Rojo, 2001). Broad bands in the region 3290.3–3408.6 cm^{-1} show the presence of a hydrogen-bonding network. The stretching mode of the $(-NH_3)^+$ group in the ethylenediammonium cation appears at 3148.7 cm^{-1}. The band near 1466 cm^{-1} can be assigned to the $(-NH_3)^+$ bending vibration. This band is indicative of the presence of ethylenediammonium cations and is in good agreement with structural results (Fernandez, Pizarro, Mesa, Lezama, Arriortua & Rojo, 2001; Fernandez, Pizarro, Mesa, Lezama, Arriortua, Olazcuaga & Rojo, 2001). The stretching vibrations of the –CH_2– groups in the ethylenediammonium cations are observed in the Raman spectrum at 2982.6 and 2583.7 cm^{-1}.

Different groups of bands observed in the Raman spectrum can be attributed to the vibrational modes of the $(HP_2O_7)^{3-}$ anion. The band observed at 1119.1 cm^{-1} is attributed to the symmetric terminal P—O stretching vibration of the PO_2 group and that observed at 1182.8 cm^{-1} is due to the asymmetric terminal stretching vibration of the PO_2 group. The band observed at 1066.2 cm^{-1} is attributed to the symmetric terminal P—O stretching vibration of the PO_3 group. The band at 1034.8 cm^{-1} is attributed to the asymmetric terminal stretching vibration of the PO_3 group (Sarr & Diop, 1987). Three P—O—P bridge vibrations are observed in the Raman spectrum [$\nu_{as}(POP)$ = 920.3 and 970.3 cm^{-1}, and $\nu_s(P-O-P)$ = 760.6 cm^{-1}]. The modes located between 254.3 and 286.1 cm^{-1} can be attributed to the external torsional and P—O—P deformation modes. The P—O—P vibration is observed at 333.8 cm^{-1} and the rocking of the PO_2 and PO_3 deformation modes is observed between 495.8 and 606.6 cm^{-1} (Sarr & Diop, 1987).

Experimental

Ethylenediamine (5 ml, 100 mmol), nickel(II) chloride tetrahydrate (100 mmol), potassium pyrophosphate (100 mmol) and water (20 ml) were stirred in a beaker for 6 h and the mixture was then allowed to stand at room temperature for two weeks. Large prismatic pale-green crystals of (I) were obtained, which were filtered off and washed with
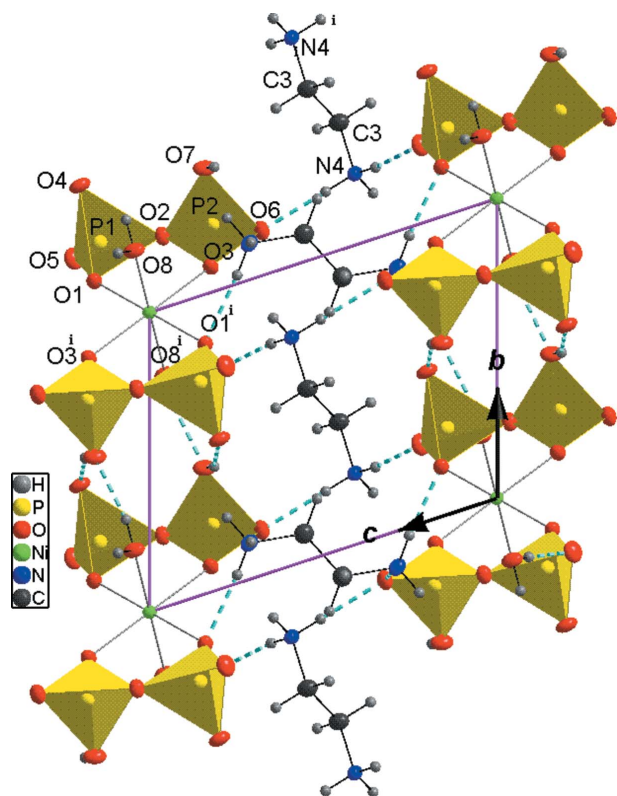
Figure 2
The layered structure of (I), viewed along the *a* axis. Yellow polyhedra indicate the $[P_2O_7]^{2-}$ anions. Intermolecular hydrogen bonds are shown as dashed lines. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry code: (i) $2 - x, 2 - y, -z$.]

a water–ethanol solution (20:80).

The Raman spectrum was collected in a back-scattering arrangement under ambient conditions using a high-throughput holographic imaging spectrograph with a 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 a power of 40 mW and the exposure time was 60 s with ten accumulations.

Crystal data

$(C_2H_{10}N_2)_2[Ni(HP_2O_7)_2(H_2O)_2]$	$Z = 1$
$M_r = 568.88$	$D_x = 1.946$ Mg m^{-3}
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 7.4898$ (9) Å	Cell parameters from 1929
$b = 7.5517$ (7) Å	reflections
$c = 9.7780$ (1) Å	$\theta = 3.0–29.2°$
$\alpha = 103.876$ (9)°	$\mu = 1.42$ mm^{-1}
$\beta = 111.190$ (1)°	$T = 301$ (2) K
$\gamma = 97.711$ (8)°	Prism, pale green
$V = 485.48$ (9) Å^3	$0.18 \times 0.10 \times 0.06$ mm

Data collection

Oxford Xcalibur diffractometer with Sapphire CCD area detector	1930 independent reflections
ω scans	1662 reflections with $I > 2\sigma(I)$
Absorption correction: analytical (*CrysAlis RED*; Oxford Diffraction, 2002)	$R_{int} = 0.035$
	$\theta_{max} = 26.4°$
	$h = -9 \rightarrow 9$
$T_{min} = 0.785$, $T_{max} = 0.920$	$k = -9 \rightarrow 9$
3240 measured reflections	$l = -11 \rightarrow 12$

Refinement

Refinement on F^2	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.033$	
$wR(F^2) = 0.089$	
$S = 1.03$	$w = 1/[\sigma^2(F_o^2) + (0.0576P)^2]$
1930 reflections	where $P = (F_o^2 + 2F_c^2)/3$
140 parameters	$(\Delta/\sigma)_{max} = 0.010$
	$\Delta\rho_{max} = 0.53$ e Å^{-3}
	$\Delta\rho_{min} = -0.72$ e Å^{-3}

Table 1
Selected bond lengths (Å).

Ni1—O3	2.0389 (17)	P2—O3	1.5248 (18)
Ni1—O1	2.0780 (17)	P2—O2	1.6230 (18)
Ni1—O8	2.1070 (18)	O8—H8A	0.848 (10)
P1—O5	1.4901 (19)	O8—H8B	0.851 (10)
P1—O1	1.5144 (19)	N1—C2	1.502 (4)
P1—O4	1.5632 (19)	N4—C3	1.472 (3)
P1—O2	1.6141 (19)	C2—C2^{ii}	1.515 (5)
P2—O7	1.5134 (19)	C3—C3^{iii}	1.503 (5)
P2—O6	1.5163 (19)		

Symmetry codes: (ii) $-x + 2, -y + 2, -z + 1$; (iii) $-x + 1, -y + 1, -z + 1$.

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O7—H7$\cdots$O4^{iv}	0.82	1.73	2.501 (3)	156
O8—H8A$\cdots$O7^{v}	0.848 (10)	1.918 (12)	2.756 (3)	169 (3)
O8—H8B$\cdots$O5^{vi}	0.851 (10)	1.947 (11)	2.795 (3)	174 (3)
N1—H1A$\cdots$O1^{i}	0.89	1.96	2.846 (3)	175
N1—H1C$\cdots$O6^{vii}	0.89	1.84	2.718 (3)	170
N1—H1B$\cdots$O4^{iv}	0.89	2.10	2.888 (3)	147
N4—H4A$\cdots$O3^{ii}	0.89	2.04	2.816 (3)	145
N4—H4B$\cdots$O5^{viii}	0.89	1.89	2.779 (3)	172
N4—H4C$\cdots$O6^{vii}	0.89	1.96	2.748 (3)	146

Symmetry codes: (i) $-x + 2, -y + 2, -z$; (ii) $-x + 2, -y + 2, -z + 1$; (iv) $-x + 2, -y + 1, -z$; (v) $x, y + 1, z$; (vi) $-x + 3, -y + 2, -z$; (vii) $x - 1, y, z$; (viii) $x - 1, y, z + 1$.

H atoms bonded to C and N atoms were positioned with idealized geometry, with C—H = 0.97 and N—H = 0.89 Å, and refined using a riding model with fixed individual displacement parameters of U_{iso}(H) = $1.2U_{eq}$(C) or $1.5U_{eq}$(N). The O—H H atoms of the anion were positioned with idealized geometry, with O—H = 0.82 Å, and refined using a riding model with torsional freedom of the O—H group and with fixed isotropic displacement parameters of U_{iso}(H) = $1.2U_{eq}$(O). The H atoms of the water molecules were located in a difference map and were refined with restraints for the O—H (0.85 Å) and H$\cdots$H (1.365 Å) distances.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2002); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2002); 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*.
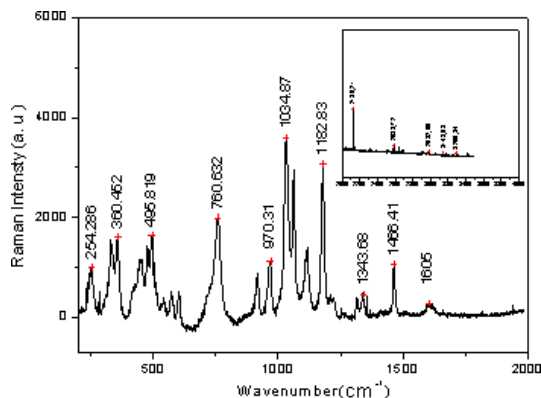
Figure 3
Raman spectrum of the title compound.

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