Crystal structure of hexaaquanickel(II) hydrogenphosphate monohydrate, $[Ni(H_2O)_6][HPO_4] \cdot H_2O$

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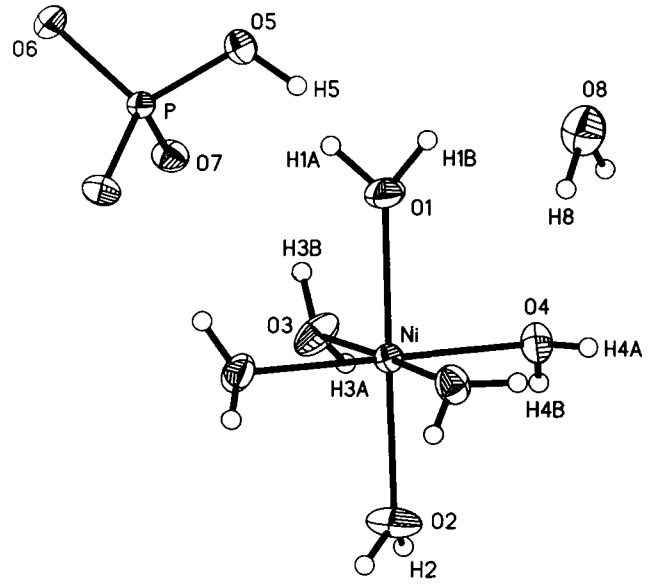

Abstract

$H_{15}NiO_{11}P$, orthorhombic, $Pmn2_1$ (no. 31), $a = 6.9160(3)$ Å, $b = 6.1032(3)$ Å, $c = 11.1679(6)$ Å, $V = 471.4$ Å^3, $Z = 2$, $R_{gt}(F) = 0.018$, $wR_{ref}(F^2) = 0.047$, $T = 293$ K.

Source of material

$Ni(ClO_4)_2 \cdot H_2O$ (0.365 g, 1.000 mmol) was added to an aqueous solution of *o*-phospho-L-serine (0.185 g, 1.000 mmol) in 20 ml H_2O. The mixture was stirred for one hour and then filtered out. Green crystals were grown by slow evaporation of the filtrate at room temperature for two weeks.

Experimental details

All hydrogen atoms were located from difference Fourier maps. During refinement, those H atom parameter which did not converge were fixed on the initial values. The correct absolute structure was confirmed by a Flack parameter of x = 0.00(1).

Discussion

The title compound consists of the $[Ni(H_2O)_6]^{2+}$ cations, $[HPO_4]^{2-}$ anions and hydrogen bonded lattice H_2O molecules. The Ni atoms are each coordinated by six aqua oxygen atoms to form a slightly distorted octahedron with d(Ni—O) = 2.037(2) Å – 2.095(2) Å, *cis*-∠O–Ni–O = 88.1(1)° – 95.3(1)° and *cis*-∠O–Ni–O = 176.6(1)° – 179.9(1)°. The PO_4 tetrahedron in the $[HPO_4]^{2-}$ anion exhibits a nearly ideal geometry with d(P—O) = 1.534(2) Å – 1.541(2) Å and ∠O–P–O = 108.9(1)° – 110.1(1)° and, in particular, the P—O bond to the hydroxyl oxygen O5 shows no difference in length from the others. Both cation and anion are crystallographically imposed by *m* symmetry. In addition, the mirror plane passes through the O1–Ni–O2 axis and bisects both O3–Ni–O3$^{\#1}$ and O4–Ni–O4$^{\#1}$ angles (#1: $-x,y,z$), and in the latter the H5, O5, P and O6 define the mirror plane to bisect the O7–Ni–O7$^{\#2}$ angle (#2: $1-x,y,z$). Each $[Ni(H_2O)]^{2+}$ complex cation is coordinated by five $[HPO_4]^{2-}$ anions, two lattice H_2O molecules and one cationic neighbor. Around each $[HPO_4]^{2-}$ anion, six complex cations build up a trigonal prism with one prismatic face capped by one lattice H_2O molecule to which the hydroxyl group forms a hydrogen bond. Extensive O–H···O hydrogen bonds (d(O–H···O) = 2.616 Å – 2.990 Å and ∠(O–H···O) = 154° – 177°) between the aqua ligands and the hydrogen phosphate oxygen atoms assemble the cations and anions to generate a 3D framework with the lattice water molecules located in cavities. Each lattice water molecule functions as H-bond acceptor and donor from the hydroxyl group and to an aqua oxygen O4 with d(O–H···O) = 2.795 Å, 2.974 Å, respectively. The bonding values of the complex cation in the title compound are comparable with those of corresponding ions in $(C_2H_{10}N_2)[Ni(H_2O)_6][HPO_4]_2$, where, however, the tetrahedral PO_4 groups exhibit considerable distortion with the P—O bond to hydroxyl oxygen substantially longer than the others [1].

Table 1. Data collection and handling.

Crystal:	green block, size 0.242 × 0.254 × 0.540 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	22.69 cm^{-1}
Diffractometer, scan mode:	Bruker P4, $\theta/2\theta$
$2\theta_{max}$:	56.16°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	2664, 970
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 958
$N(param)_{refined}$:	97
Programs:	SHELXS-97 [2], SHELXL-97 [3]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(1A)	2*a*	0	0.1848	0.5458	0.059
H(1B)	2*a*	0	0.2601	0.4395	0.039
H(2)	4*b*	0.102(4)	0.987(4)	0.707(3)	0.028(6)
H(3A)	4*b*	0.301(6)	0.600(5)	0.722(4)	0.04(1)
H(3B)	4*b*	0.261(6)	0.392(6)	0.710(4)	0.05(1)
H(4A)	4*b*	0.187(4)	0.785(5)	0.425(4)	0.035(7)
H(4B)	4*b*	0.278(5)	0.807(6)	0.520(4)	0.06(1)
H(5)	2*a*	½	0.091(6)	0.551(4)	0.034
H(8)	4*b*	0.394(4)	0.457(5)	0.479(3)	0.037(7)

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Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ni	2*a*	0	0.62723(5)	0.59653(2)	0.0183(2)	0.0155(2)	0.0145(2)	0	0	0.0001(1)
O(1)	2*a*	0	0.3196(4)	0.5133(2)	0.077(2)	0.0164(9)	0.022(1)	0	0	–0.0036(9)
O(2)	2*a*	0	0.9347(4)	0.6790(2)	0.019(1)	0.027(1)	0.049(2)	0	0	–0.019(1)
O(3)	4*b*	0.2056(2)	0.5207(3)	0.7135(2)	0.0296(8)	0.0210(7)	0.0383(9)	–0.0032(6)	–0.0154(8)	0.0089(6)
O(4)	4*b*	0.2198(2)	0.7317(2)	0.4864(1)	0.0246(7)	0.0294(7)	0.0191(8)	–0.0047(6)	0.0008(6)	0.0028(6)
P	2*a*	½	–0.0057(1)	0.72479(6)	0.0161(3)	0.0127(3)	0.0136(3)	0	0	–0.0007(2)
O(5)	2*a*	½	–0.0234(3)	0.5878(2)	0.029(1)	0.0232(9)	0.0157(9)	0	0	0.0002(9)
O(6)	2*a*	½	–0.2381(3)	0.7786(2)	0.025(1)	0.0160(9)	0.0226(9)	0	0	0.0034(7)
O(7)	4*b*	0.6823(2)	0.1151(2)	0.7668(1)	0.0190(7)	0.0207(7)	0.0225(7)	–0.0031(5)	–0.0006(6)	–0.0045(5)
O(8)	2*a*	½	0.3663(5)	0.4562(3)	0.046(2)	0.042(2)	0.040(2)	0	0	0.007(1)

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