

# Hexaaquanickel(II) dihydrogen hypodiphosphate

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 Key indicators: single-crystal X-ray study;  $T = 223$  K; mean  $\sigma(\text{Ni}-\text{O}) = 0.001$  Å;  $R$  factor = 0.029;  $wR$  factor = 0.074; data-to-parameter ratio = 16.3.

The asymmetric unit of the title compound,  $[\text{Ni}(\text{H}_2\text{O})_6] \cdot (\text{H}_2\text{P}_2\text{O}_6)$ , contains one-half of the hexaaquanickel(II) cation and one-half of the dihydrogen hypodiphosphate anion. In the complex cation, the  $\text{Ni}^{2+}$  atom is located on an inversion center and has an octahedral coordination sphere. The P—P distance in the centrosymmetric anion is 2.1853 (7) Å. In the crystal, discrete  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$  cations and  $(\text{H}_2\text{P}_2\text{O}_6)^{2-}$  anions are stacked in columns parallel to the  $c$  axis and are linked into a three-dimensional network by medium-strength O—H...O hydrogen bonds.

## Related literature

For the synthesis of hypodiphosphates, see: Leininger & Chulski (1953). For applications of hypodiphosphates, see: Bloss & Henzel (1967); Ruffin *et al.* (2007); Szklarz *et al.* (2011). For the crystal structures of transition metal hypodiphosphate 12-hydrates, see: Hagen & Jansen (1995); Haag *et al.* (2005). For the crystal structures of hydrogen hypodiphosphate compounds, see: Collin & Willis (1971); Szafranowska *et al.* (2012); Wu *et al.* (2012).

## Experimental

### Crystal data

$[\text{Ni}(\text{H}_2\text{O})_6](\text{H}_2\text{P}_2\text{O}_6)$   
 $M_r = 326.76$   
 Monoclinic,  $P2_1/n$   
 $a = 9.3031$  (14) Å  
 $b = 5.8892$  (8) Å  
 $c = 9.7620$  (12) Å  
 $\beta = 96.111$  (11)°

$V = 531.80$  (13) Å<sup>3</sup>  
 $Z = 2$   
 Mo  $K\alpha$  radiation  
 $\mu = 2.18$  mm<sup>-1</sup>  
 $T = 223$  K  
 $0.29 \times 0.25 \times 0.22$  mm

### Data collection

Stoe IPDS-II diffractometer  
 Absorption correction: numerical  
 ( $X$ -SHAPE and  $X$ -RED; Stoe & Cie, 1999, 2001)  
 $T_{\min} = 0.537$ ,  $T_{\max} = 0.619$   
 8061 measured reflections  
 1601 independent reflections  
 1546 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.056$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.029$   
 $wR(F^2) = 0.074$   
 $S = 1.16$   
 1601 reflections  
 98 parameters  
 All H-atom parameters refined  
 $\Delta\rho_{\max} = 0.44$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -1.08$  e Å<sup>-3</sup>

**Table 1**

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O3—H3...O2 <sup>i</sup>	0.92 (3)	1.68 (3)	2.5919 (15)	168 (3)
O4—H4A...O3 <sup>ii</sup>	0.82 (3)	1.93 (3)	2.7293 (16)	165 (3)
O4—H4B...O2 <sup>iii</sup>	0.82 (3)	1.89 (3)	2.6822 (14)	162 (3)
O5—H5A...O1	0.81 (3)	1.98 (3)	2.7770 (15)	171 (3)
O5—H5B...O2 <sup>iv</sup>	0.84 (3)	2.04 (3)	2.8722 (16)	171 (3)
O6—H6A...O1 <sup>v</sup>	0.81 (2)	2.05 (2)	2.8163 (16)	159 (2)
O6—H6B...O1 <sup>ii</sup>	0.84 (3)	2.08 (3)	2.9132 (17)	168 (3)

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

Data collection:  $X$ -AREA (Stoe & Cie, 2002); cell refinement:  $X$ -AREA; data reduction:  $X$ -AREA; program(s) used to solve structure:  $SHELXS97$  (Sheldrick, 2008); program(s) used to refine structure:  $SHELXL97$  (Sheldrick, 2008); molecular graphics:  $DIAMOND$  (Brandenburg, 2012); software used to prepare material for publication:  $SHELXL97$ ,  $PLATON$  (Spek, 2009) and  $pubCIF$  (Westrip, 2010).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: WM2784).

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## supporting information

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## Hexaaquanickel(II) dihydrogen hypodiphosphate

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### S1. Comment

Although main group hypodiphosphates have rather academic interest, the dihydrogen sodium and ammonium derivatives, ( $M_2H_2P_2O_6$  with  $M = Na^+$  and  $NH_4^+$ ) (Collin & Willis, 1971), respective their hydrates, have certain practical use. Ammonium dihydrogen hypodiphosphate-based powder material is applied as a green flame retardant and as a multipurpose extinguishing agent suitable for all classes of fire (Ruffin *et al.*, 2007). Acidic  $Na_2H_2P_2O_6$  solutions are applied for gravimetric precipitation and immobilization of uranium(IV) (Bloss & Henzel, 1967). The ferroelectricity of diammonium hypodiphosphate was discovered recently (Szklarz *et al.*, 2011).

The crystal structures of transition metal hypodiphosphate 12-hydrates  $M_2P_2O_6 \cdot 12H_2O$  ( $M = Co$  und  $Ni$ ) were determined by Hagen & Jansen (1995) and Haag *et al.* (2005). However, the crystal structures of transition metal dihydrogen hypodiphosphate hydrates have not been reported up to now.

The structure of the title compound,  $[Ni(H_2O)_6](H_2P_2O_6)$  is characterized by discrete  $[Ni(H_2O)_6]^{2+}$  cations and  $(H_2P_2O_6)^{2-}$  anions (Fig. 1). The  $Ni^{2+}$  ion is located on an inversion centre and is octahedrally coordinated by water molecules. In the  $(H_2P_2O_6)^{2-}$  anion, which is located about an inversion centre, the tetravalent phosphorus atom is surrounded by three oxygen atoms and one additional phosphorus atom with a P–P distance of 2.1854 (7) Å. The P–O bond lengths are ranging from 1.5050 (11) to 1.5816 (11) Å. All bond lengths and angles are well within the expected ranges (Wu *et al.*, 2012) and are comparable to those found for  $Ni_2P_2O_6 \cdot 12H_2O$  (2.1700 (13) Å for the P–P bond; Haag *et al.*, 2005), however with a characteristically longer P–OH distance in comparison with the P–O distance.

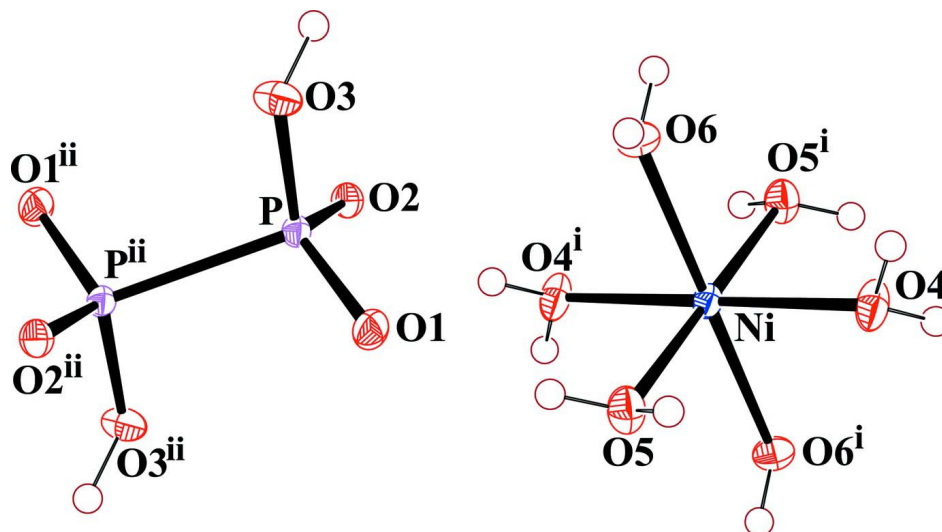
The  $(H_2P_2O_6)^{2-}$  anions are joined to ribbons parallel to [010] by rather strong hydrogen bonds ( $O \cdots O$  2.5919 (15) Å). Anions and complex cations are stacked alternately in columns parallel to [001], held together by medium-strength  $O \cdots H \cdots O$  hydrogen bonds (Fig. 2). The  $O \cdots O$  distances between water molecules and  $(H_2P_2O_6)^{2-}$  ions range from 2.6822 (14) to 2.9132 (17) Å (Table 1). All hydrogen bonding interactions considered, a three-dimensional network structure is established in the crystal.

### S2. Experimental

Disodium dihydrogen hypodiphosphate was prepared using the procedure reported by Leininger & Chulski (1953). An aqueous solution of hypodiphosphoric acid was obtained by passing a saturated solution of disodium dihydrogen hypodiphosphate through a cation exchange resin (Dowex 50WX2 50-100). Single crystals of hexaaquanickel(II) dihydrogenhypodiphosphate were prepared by adding nickel hydroxide (148 mg) to a solution of hypodiphosphoric acid (40 mL).

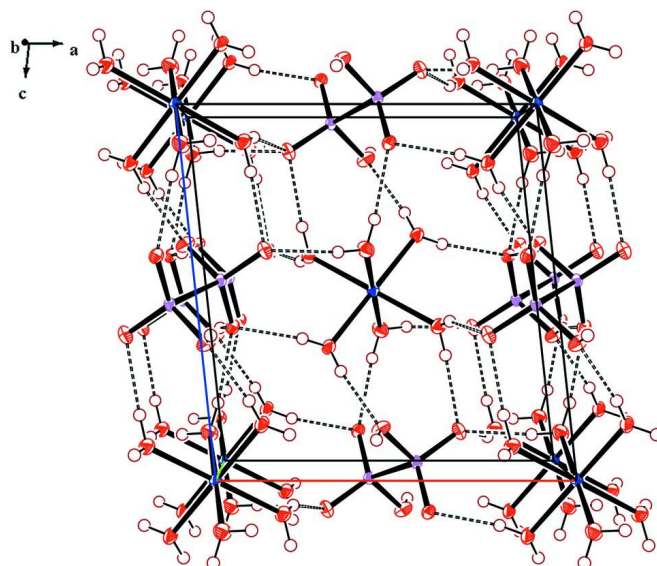
#### S2.1. Refinement

All hydrogen atoms were located in a difference Fourier map and were refined isotropically with no restraints.



**Figure 1**

The molecular entities in the title compound with atom labels and displacement ellipsoids drawn at the 50% probability level. [Symmetry codes: (i)  $-x + 1, -y + 1, -z + 1$ ; (ii)  $-x, -y, -z + 1$ .]



**Figure 2**

The crystal structure of the title compound viewed along the  $b$  axis. Displacement ellipsoids are drawn at the 50% probability level. O—H $\cdots$ O hydrogen bonds are shown as dashed lines.

### Hexaaquanickel(II) dihydrogen hypodiphosphate

#### Crystal data

$[\text{Ni}(\text{H}_2\text{O})_6](\text{H}_2\text{P}_2\text{O}_6)$   
 $M_r = 326.76$

Monoclinic,  $P2_1/n$   
Hall symbol:  $-P 2_1n$

$a = 9.3031$  (14) Å  
 $b = 5.8892$  (8) Å  
 $c = 9.7620$  (12) Å  
 $\beta = 96.111$  (11)°  
 $V = 531.80$  (13) Å<sup>3</sup>  
 $Z = 2$   
 $F(000) = 336$   
 block, green

$D_x = 2.041$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å  
 Cell parameters from 8465 reflections  
 $\theta = 2.9$ – $30.5$ °  
 $\mu = 2.18$  mm<sup>-1</sup>  
 $T = 223$  K  
 Block, green  
 $0.29 \times 0.25 \times 0.22$  mm

*Data collection*

Stoe IPDS-II  
 diffractometer  
 Radiation source: fine-focus sealed tube  
 Graphite monochromator  
 $\omega$ -scans  
 Absorption correction: numerical  
 (*X-SHAPE* and *X-RED*; Stoe & Cie, 1999, 2001)  
 $T_{\min} = 0.537$ ,  $T_{\max} = 0.619$

8061 measured reflections  
 1601 independent reflections  
 1546 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.056$   
 $\theta_{\max} = 30.5$ °,  $\theta_{\min} = 2.9$ °  
 $h = -13 \rightarrow 13$   
 $k = -8 \rightarrow 8$   
 $l = -13 \rightarrow 13$

*Refinement*

Refinement on  $F^2$   
 Least-squares matrix: full  
 $R[F^2 > 2\sigma(F^2)] = 0.029$   
 $wR(F^2) = 0.074$   
 $S = 1.16$   
 1601 reflections  
 98 parameters  
 0 restraints  
 Primary atom site location: structure-invariant  
 direct methods

Secondary atom site location: difference Fourier  
 map  
 Hydrogen site location: inferred from  
 neighbouring sites  
 All H-atom parameters refined  
 $w = 1/[\sigma^2(F_o^2) + (0.0423P)^2 + 0.1511P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.001$   
 $\Delta\rho_{\max} = 0.44$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -1.08$  e Å<sup>-3</sup>

*Special details*

**Geometry.** All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

**Refinement.** Refinement of  $F^2$  against ALL reflections. The weighted  $R$ -factor  $wR$  and goodness of fit  $S$  are based on  $F^2$ , conventional  $R$ -factors  $R$  are based on  $F$ , with  $F$  set to zero for negative  $F^2$ . The threshold expression of  $F^2 > \sigma(F^2)$  is used only for calculating  $R$ -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement.  $R$ -factors based on  $F^2$  are statistically about twice as large as those based on  $F$ , and  $R$ -factors based on ALL data will be even larger.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å<sup>2</sup>)*

	$x$	$y$	$z$	$U_{\text{iso}}^*/U_{\text{eq}}$
Ni	0.5000	0.5000	0.5000	0.01306 (10)
P	0.06859 (3)	0.14612 (5)	0.53007 (3)	0.01116 (10)
O1	0.20361 (11)	0.05887 (19)	0.61176 (12)	0.0177 (2)
O2	0.08555 (10)	0.28724 (17)	0.40289 (10)	0.01404 (19)
O3	-0.02399 (12)	0.28534 (18)	0.62787 (11)	0.0185 (2)
O4	0.64678 (11)	0.6071 (2)	0.65421 (12)	0.0211 (2)
O5	0.48685 (12)	0.20885 (19)	0.61392 (12)	0.0204 (2)
O6	0.32539 (11)	0.62296 (19)	0.59655 (12)	0.0180 (2)
H3	-0.042 (3)	0.436 (5)	0.605 (3)	0.037 (7)*

H4A	0.620 (3)	0.681 (5)	0.719 (3)	0.037 (7)*
H4B	0.720 (3)	0.664 (5)	0.630 (3)	0.042 (7)*
H5A	0.407 (4)	0.154 (5)	0.607 (3)	0.045 (8)*
H5B	0.521 (3)	0.223 (5)	0.696 (3)	0.039 (7)*
H6A	0.296 (2)	0.750 (4)	0.581 (2)	0.019 (5)*
H6B	0.313 (3)	0.584 (5)	0.678 (3)	0.036 (7)*

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Ni	0.01080 (13)	0.01511 (15)	0.01334 (15)	-0.00152 (7)	0.00159 (9)	-0.00086 (8)
P	0.00991 (15)	0.01073 (17)	0.01287 (17)	-0.00066 (9)	0.00128 (11)	0.00094 (10)
O1	0.0130 (4)	0.0173 (4)	0.0219 (5)	-0.0003 (4)	-0.0026 (4)	0.0023 (4)
O2	0.0140 (4)	0.0134 (4)	0.0151 (5)	-0.0015 (3)	0.0037 (3)	0.0017 (3)
O3	0.0251 (5)	0.0138 (4)	0.0179 (5)	0.0040 (4)	0.0086 (4)	0.0022 (4)
O4	0.0138 (4)	0.0332 (6)	0.0169 (5)	-0.0071 (4)	0.0043 (4)	-0.0090 (4)
O5	0.0194 (5)	0.0207 (5)	0.0204 (5)	-0.0044 (4)	-0.0005 (4)	0.0028 (4)
O6	0.0180 (5)	0.0194 (5)	0.0172 (5)	0.0040 (4)	0.0041 (4)	-0.0003 (4)

*Geometric parameters (Å, °)*

Ni—O4	2.0226 (11)	P—O3	1.5814 (11)
Ni—O4 <sup>i</sup>	2.0227 (11)	P—P <sup>ii</sup>	2.1853 (7)
Ni—O5 <sup>i</sup>	2.0544 (11)	O3—H3	0.92 (3)
Ni—O5	2.0544 (11)	O4—H4A	0.82 (3)
Ni—O6	2.0922 (11)	O4—H4B	0.82 (3)
Ni—O6 <sup>i</sup>	2.0922 (11)	O5—H5A	0.81 (3)
P—O1	1.5048 (10)	O5—H5B	0.84 (3)
P—O1	1.5048 (10)	O6—H6A	0.81 (2)
P—O2	1.5161 (10)	O6—H6B	0.84 (3)
O4—Ni—O4 <sup>i</sup>	180.0	O1—P—O3	109.55 (6)
O4—Ni—O5 <sup>i</sup>	93.91 (5)	O1—P—O3	109.55 (6)
O4 <sup>i</sup> —Ni—O5 <sup>i</sup>	86.09 (5)	O2—P—O3	108.73 (6)
O4—Ni—O5	86.09 (5)	O1—P—P <sup>ii</sup>	107.70 (5)
O4 <sup>i</sup> —Ni—O5	93.91 (5)	O1—P—P <sup>ii</sup>	107.70 (5)
O5 <sup>i</sup> —Ni—O5	179.999 (1)	O2—P—P <sup>ii</sup>	108.69 (5)
O4—Ni—O6	92.97 (5)	O3—P—P <sup>ii</sup>	103.32 (5)
O4 <sup>i</sup> —Ni—O6	87.03 (5)	O1—O1—P	0 (10)
O5 <sup>i</sup> —Ni—O6	92.80 (5)	P—O3—H3	116.7 (19)
O5—Ni—O6	87.20 (5)	Ni—O4—H4A	119.9 (19)
O4—Ni—O6 <sup>i</sup>	87.03 (5)	Ni—O4—H4B	115 (2)
O4 <sup>i</sup> —Ni—O6 <sup>i</sup>	92.97 (5)	H4A—O4—H4B	109 (3)
O5 <sup>i</sup> —Ni—O6 <sup>i</sup>	87.20 (5)	Ni—O5—H5A	114 (2)
O5—Ni—O6 <sup>i</sup>	92.80 (5)	Ni—O5—H5B	113 (2)
O6—Ni—O6 <sup>i</sup>	180.0	H5A—O5—H5B	112 (3)
O1—P—O1	0.00 (11)	Ni—O6—H6A	119.9 (16)

O1—P—O2	117.86 (6)	Ni—O6—H6B	121.2 (19)
O1—P—O2	117.86 (6)	H6A—O6—H6B	111 (2)

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

*Hydrogen-bond geometry (Å, °)*

<i>D—H...A</i>	<i>D—H</i>	<i>H...A</i>	<i>D...A</i>	<i>D—H...A</i>
O3—H3...O2 <sup>iii</sup>	0.92 (3)	1.68 (3)	2.5919 (15)	168 (3)
O4—H4A...O3 <sup>iv</sup>	0.82 (3)	1.93 (3)	2.7293 (16)	165 (3)
O4—H4B...O2 <sup>i</sup>	0.82 (3)	1.89 (3)	2.6822 (14)	162 (3)
O5—H5A...O1	0.81 (3)	1.98 (3)	2.7770 (15)	171 (3)
O5—H5B...O2 <sup>v</sup>	0.84 (3)	2.04 (3)	2.8722 (16)	171 (3)
O6—H6A...O1 <sup>vi</sup>	0.81 (2)	2.05 (2)	2.8163 (16)	159 (2)
O6—H6B...O1 <sup>iv</sup>	0.84 (3)	2.08 (3)	2.9132 (17)	168 (3)

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