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# Hexaaquanickel(II) bis(hypophosphite)

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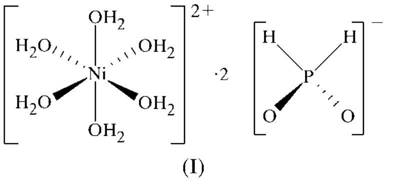
The structure of hexaaquanickel(II) bis(hypophosphite), $[Ni(H_2O)_6](H_2PO_2)_2$, has been determined. The crystals are prismatic. The packing of the Ni and P atoms (not the entire hypophosphite anions) is the same as in the structures of $[Co(H_2O)_6](H_2PO_2)_2$ and $[Co_{0.5}Ni_{0.5}(H_2O)_6](H_2PO_2)_2$. The $Ni^{II}$ cations have a pseudo-face-centered cubic cell, with cell parameter $a \simeq 10.216$ Å and tetrahedral cavities occupied by P atoms. The $Ni^{II}$ cation has crystallographically imposed twofold symmetry and has an octahedral coordination sphere consisting of six water O atoms, two of which also lie on the twofold axis. The planes of oppositely coordinated water molecules are in a cross conformation. The geometry of the hypophosphite anion is close to point symmetry *mm*2. The hypophosphite anions are hydrogen bonded to the coordinated water molecules.

## Comment

Studies of hexaaquametal(II) bis(hypophosphite)s have been reported previously by Ferrari & Colla (1937), Pédrazuela *et al.* (1953), Galigné & Dumas (1973) and Kuratieva *et al.* (2002). This paper presents the results of the single-crystal X-ray diffraction analysis of hexaaquanickel(II) bis(hypophosphite), $[Ni(H_2O)_6](H_2PO_2)_2$. The calculated powder pattern of this compound, (I), is in good agreement with the experimental powder pattern, but is different from those of hexaaquacobalt(II) bis(hypophosphite) and hexaaquacobalt(II)/nickel(II) bis(hypophosphite) (Kuratieva *et al.*, 2002).



(I)

The packing of the $Ni^{II}$ cations and P atoms (not the entire hypophosphite anions) is the same as in the structures of $[Co(H_2O)_6](H_2PO_2)_2$ and $[Co_{0.5}Ni_{0.5}(H_2O)_6](H_2PO_2)_2$. The nickel cations form a pseudo-face-centered cubic cell, with cell parameter $a \simeq 10.216$ Å and tetrahedral cavities occupied by P atoms. The powder pattern for this compound was reported previously by Ferrari & Colla (1937) and the compound was indexed as a cubic system with an *a* cell parameter of 10.30 Å. This mismatch has been discussed by Kuratieva *et al.* (2002).

The first coordination sphere of the $Ni^{II}$ cation consists of six water molecules, which form a slightly distorted octahedron. The hypophosphite anions do not coordinate to the $Ni^{II}$ cation. According to previously reported data, the average *M*—O distance for hexahydrated bivalent metal hypophosphites is 2.05 (1) Å for magnesium(II) (Galigné & Dumas, 1973), 2.074 (3) Å for cobalt(II) and 2.055 (2) Å for cobalt(II)/nickel(II) (Kuratieva *et al.*, 2002). The average Ni—O distance in the present study is 2.045 (7) Å.

There is only one orientation of the coordinated water molecules. The planes of oppositely coordinated water molecules are in a cross conformation. The first coordination sphere differs from those in $[Co(H_2O)_6](H_2PO_2)_2$ and $[Co_{0.5}Ni_{0.5}(H_2O)_6](H_2PO_2)_2$, which have one pair of oppositely coordinated water molecules with their planes in an eclipsed conformation.

The oppositely coordinated water molecules can be classified into three logical groups. The first group consists of molecules O1*W* and O2*W* [Ni—O distances of 2.038 (3) and 2.054 (2) Å, respectively]. The planes of these water molecules (*i.e.* consisting of the O and two H atoms of each molecule) are perpendicular to the plane formed by the O atoms of the other four coordinated water molecules and the $Ni^{II}$ atom (basal plane). The angle between the normal to the planes of these water molecules is 86.5 (19)°. The second group consists of molecules O3*W* and O3*W*$^{i}$ [Ni—O distances of 2.0403 (17) Å; symmetry code: (i) $-x, y, \frac{1}{2} - z$]; the angle between the normal to the plane of the O3*W* water molecule and the normal to the basal plane is 59.9 (18)°. The third group consists of molecules O4*W* and O4*W*$^{i}$ [Ni—O distances of 2.0469 (18) Å]; the angle

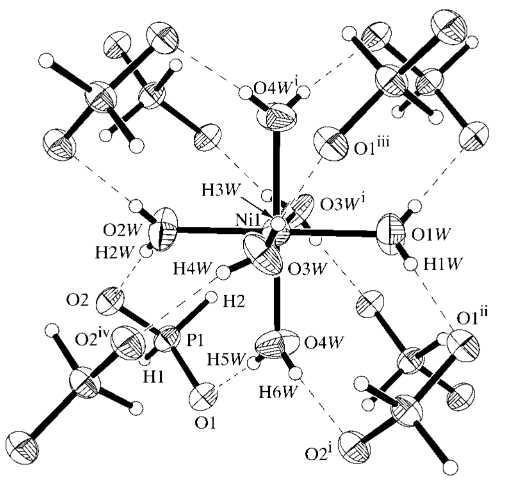


**Figure 1**
The environment of the hexaaquanickel(II) cation in relation to the hypophosphite anions. Displacement ellipsoids are plotted at the 50% probability level and H atoms are drawn as small spheres of arbitrary radii [symmetry codes: (i) $-x, y, \frac{1}{2} - z$; (ii) $\frac{1}{2} - y, \frac{1}{2} + y, \frac{1}{2} - z$; (iii) $x, -y, \frac{1}{2} + z$; (iv) $x - \frac{1}{2}, \frac{1}{2} - y, \frac{1}{2} + z$].

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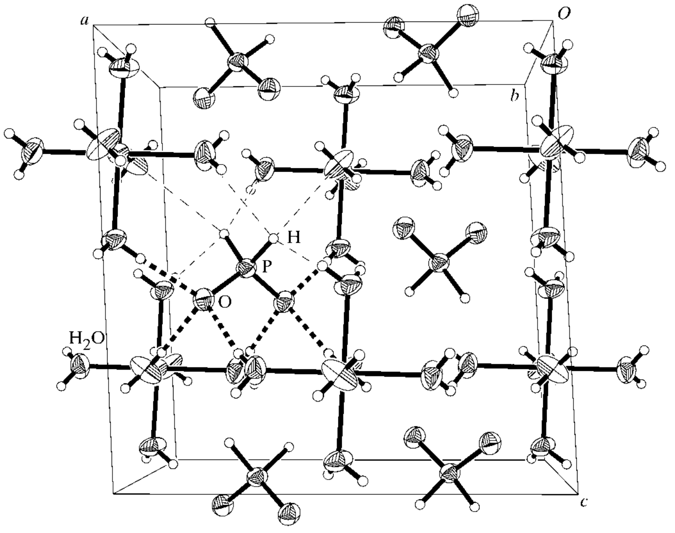

**Figure 2**
The environment of the hypophosphite anion of $[Ni(H_2O)_6](H_2PO_2)_2$ in relation to the hexaaquanickel(II) cations, viewed along *b*. Thick dashed lines indicate O—H···O—P hydrogen bonds and thin dashed lines indicate O*W*···H—P contacts. Displacement ellipsoids are plotted at the 50% probability level and H atoms are drawn as small spheres of arbitrary radii.

between the normal to the plane of the O4*W* water molecule and the normal to the basal plane is 76.5 (19)° (Fig. 1 and Table 1). The planes of all the coordinated water molecules in $[Co(H_2O)_6](H_2PO_2)_2$ and $[Co_{0.5}Ni_{0.5}(H_2O)_6](H_2PO_2)_2$ are perpendicular to the basal plane.

The second coordination sphere of the $Ni^{II}$ cation consists of eight hypophosphite anions, which are hydrogen bonded to water molecules coordinated to the $Ni^{II}$ cation (Fig. 1). In spite of the similarities in the packing of the $Ni^{II}$ cations and P atoms (Fig. 2), the orientation of the hypophosphite anions differs from that in the structures of $[Co(H_2O)_6](H_2PO_2)_2$ and $[Co_{0.5}Ni_{0.5}(H_2O)_6](H_2PO_2)_2$ due to distinctions in the first coordination spheres.

The geometry of the hypophosphite anion remains practically the same, with point symmetry *mm*2 (Naumov *et al.*, 2001, 2002; Kuratieva *et al.*, 2002), to the previously reported structures, with respective P—O distances and O—P—O angles of 1.507 (3) Å and 116.2 (3)° in $[Mg(H_2O)_6](H_2PO_2)_2$ (Galigné & Dumas, 1973), 1.527 (1)/1.516 (1) Å and 115.3° in $Co(H_2PO_2)Cl(H_2O)$ (Marcos *et al.*, 1991), 1.541 (2)/ 1.480 (2) Å and 118.7 (3)° in $Ni(H_2PO_2)Cl(H_2O)$ (Marcos *et al.*, 1993), 1.5076 (13) Å and 115.74 (13)° in $[Co(H_2O)_6](H_2PO_2)_2$, and 1.5092 (12) Å and 115.90 (11)° in $[Co_{0.5}Ni_{0.5}(H_2O)_6](H_2PO_2)_2$ (Kuratieva *et al.*, 2002) (Table 1).

Each hypophosphite O atom is hydrogen bonded to three water molecules from different complex cations (Table 2; thick dashed lines in Fig. 2), while each hypophosphite H atom is surrounded by three water molecules from other (different) complex cations, and these H atoms are situated directly above the centers of the triangles formed by the O atoms of these three water molecules (thin dashed lines in Fig. 2). The distances between hypophosphite atom H1 and water atoms O1$W^{ii}$, O3$W^{iii}$ and O4$W^{iv}$ [symmetry codes: (ii) $\frac{1}{2}-x, \frac{1}{2}-y, -z$; (iii) $\frac{1}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z$; (iv) $x, -y, z-\frac{1}{2}$] are 2.94 (2), 2.91 (2) and 2.97 (2) Å, respectively, and between hypophosphite atom H2 and water atoms O2$W^{v}$, O3$W^{i}$ and O4$W^{ii}$ [symmetry code: (v) $-x, -y, -z$] are 2.92 (2), 2.90 (2) and 2.83 (2) Å [the average P—H···O bond length is 2.91 (2) Å]. This environment of the hypophosphite anion is similar to that in the structures of the hexaaquamagnesium(II), hexaaquacobalt(II) and hexaaquacobalt(II)/nickel(II) bis(hypophosphite)s.

## Experimental

The title compound was synthesized by slow evaporation of an aqueous solution of nickel(II) hypophosphite, prepared by adding a solution of hypophosphorous acid, $H_3PO_2$, to the nickel(II) carbonate hydroxide $NiCO_3{\cdot}n Ni(OH)_2{\cdot}m H_2O$. The reaction mixture was evacuated in a vacuum to separate the carbon dioxide. Crystals were grown at 293 K in air.

*Crystal data*

$[Ni(H_2O)_6](H_2PO_2)_2$
$M_r = 296.78$
Monoclinic, *C*2/*c*
$a = 10.1453$ (3) Å
$b = 10.1467$ (4) Å
$c = 10.3571$ (3) Å
$\beta = 92.632$ (3)°
$V = 1065.05$ (6) Å$^3$
$Z = 4$
$D_x = 1.851$ Mg m$^{-3}$
Mo *Kα* radiation
Cell parameters from 20 reflections
$\theta = 12.5$–13.0°
$\mu = 2.15$ mm$^{-1}$
$T = 293$ (2) K
Prism, green
0.20 × 0.10 × 0.05 mm

*Data collection*

Enraf–Nonius CAD-4 diffractometer
2θ/θ scans
Absorption correction: empirical (*CADDAT*; Enraf–Nonius, 1989)
$T_{min} = 0.636$, $T_{max} = 0.898$
1401 measured reflections
1331 independent reflections
1243 reflections with $I > 2\sigma(I)$
$R_{int} = 0.024$
$\theta_{max} = 28.3°$
$h = 0 \rightarrow 13$
$k = 0 \rightarrow 13$
$l = -13 \rightarrow 13$
3 standard reflections
frequency: 60 min
intensity decay: none

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.028$
$wR(F^2) = 0.081$
$S = 1.06$
1331 reflections
94 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0402P)^2 + 1.2793P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.47$ e Å$^{-3}$
$\Delta\rho_{min} = -0.42$ e Å$^{-3}$
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0116 (9)

**Table 1**
Selected geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| Ni1—O1*W* | 2.038 (3) | P1—O1 | 1.5102 (14) |
| Ni1—O2*W* | 2.054 (2) | P1—O2 | 1.5122 (14) |
| Ni1—O3*W* | 2.0403 (17) | P1—H1 | 1.27 (3) |
| Ni1—O4*W* | 2.0469 (18) | P1—H2 | 1.26 (2) |
| | | | |
| O1*W*—Ni1—O3*W* | 87.83 (5) | O4$W^{i}$—Ni1—O4*W* | 179.17 (12) |
| O3*W*—Ni1—O3$W^{i}$ | 175.66 (11) | O1—P1—O2 | 115.90 (8) |
| O1*W*—Ni1—O4*W* | 89.59 (6) | H1—P1—H2 | 102.2 (16) |
| O3*W*—Ni1—O4*W* | 88.42 (8) | | |

Symmetry code: (i) $-x, y, \frac{1}{2}-z$.

i2 Natalia V. Kuratieva et al. • $[Ni(H_2O)_6](H_2PO_2)_2$ Acta Cryst. (2003). C59, i1–i3

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

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O1*W*—H1*W*···O1$^{\rm i}$ | 0.74 (3) | 2.00 (3) | 2.7412 (19) | 176 (3) |
| O2*W*—H2*W*···O2 | 0.74 (3) | 2.03 (3) | 2.7628 (19) | 174 (4) |
| O3*W*—H3*W*···O1$^{\rm ii}$ | 0.79 (4) | 1.96 (4) | 2.743 (2) | 173 (4) |
| O3*W*—H4*W*···O2$^{\rm iii}$ | 0.75 (3) | 2.02 (3) | 2.754 (2) | 168 (3) |
| O4*W*—H5*W*···O1 | 0.76 (4) | 2.01 (4) | 2.761 (2) | 169 (4) |
| O4*W*—H6*W*···O2$^{\rm i}$ | 0.77 (3) | 1.98 (4) | 2.751 (2) | 174 (3) |

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

The H atoms were located from a difference electron-density map and refined without constraints (see Tables 1 and 2 for distances).

Data collection: *CD*4*CA*0 (Enraf–Nonius, 1989); cell refinement: *CD*4*CA*0; data reduction: *CADDAT* (Enraf–Nonius, 1989); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*III (Burnett & Johnson, 1996); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1594). Services for accessing these data are described at the back of the journal.

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