Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Hexaaquacobalt(II) bis(hypophosphite) and hexaaquacobalt(II)/nickel(II) bis(hypophosphite)

Natalia V. Kuratieva,* Marina I. Naumova and Dmitry Yu. Naumov

Institute of Inorganic Chemistry, SB Russian Academy of Sciences, Academition Lavrentiev Avenue 3, Novosibirsk 90, 630090 Russia
Correspondence e-mail: n.v.kuratieva@mill.solid.nsc.ru

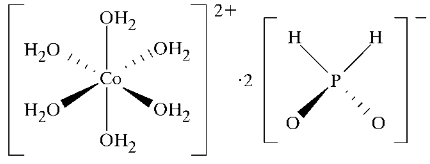
Received 28 May 2002
Accepted 19 July 2002
Online 31 August 2002

The title compounds, hexaaquacobalt(II) bis(hypophosphite), $[Co(H_2O)_6](H_2PO_2)_2$, and hexaaquacobalt(II)/nickel(II) bis(hypophosphite), $[Co_{0.5}Ni_{0.5}(H_2O)_6](H_2PO_2)_2$, are shown to adopt the same structure as hexaaquamagnesium(II) bis(hypophosphite). The packing of the Co(Ni) and P atoms is the same as in the structure of CaF_2. The $Co^{II}(Ni^{II})$ atoms have a pseudo-face-centred cubic cell, with $a = b \sim 10.3$ Å, and the P atoms occupy the tetrahedral cavities. The central metal cation has a slightly distorted octahedral coordination sphere. The geometry of the hypophosphite anion in the structure is very close to ideal, with point symmetry *mm*2. Each O atom of the hypophosphite anion is hydrogen bonded to three water molecules from different cation complexes, and each H atom of the hypophosphite anion is surrounded by three water molecules from further different cation complexes.

Comment

Investigations of hexahydrated bivalent metal hypophosphites have been reported by Ferrari & Colla (1937), Pédrazuela *et al.* (1953) and Galigné & Dumas (1973). Here, we report the results of the single-crystal X-ray diffraction analysis of hexaaquacobalt(II) bis(hypophosphite), $[Co(H_2O)_6](H_2PO_2)_2$, (I), and hexaaquacobalt(II)/nickel(II) bis(hypophosphite), $[Co_{0.5}Ni_{0.5}(H_2O)_6](H_2PO_2)_2$, (II), the structures of which are very similar to that of hexaaquamagnesium(II) bis(hypophosphite) (Galigné & Dumas, 1973). The crystals of (II) are a solid solution of the Co^{II} and Ni^{II} hypophosphites. The calculated powder pattern of (II) is in good agreement with the experimental powder pattern.

The packing of the $Co^{II}(Ni^{II})$ and P atoms (not the hypophosphite anion) is the same as in the structure of CaF_2. The $Co^{II}(Ni^{II})$ atoms have a pseudo-face-centred cubic cell, with $a = b \sim 10.3$ Å, and the P atoms occupy the tetrahedral cavities. The powder pattern for (I) was reported earlier by Ferrari & Colla (1937), and it was indexed as a cubic system with a cell parameter of 10.22 Å. Some differences between the work of Ferrari & Colla and our studies are evident, in that reflections at high angles could be indexed as a Cu $K\alpha_1$—Cu $K\alpha_2$ relation; indeed, this is the complex result of an unclear ratio for $c = 2a$, because of an incomplete range for the powder data (only from $d = 3.090$ Å) and a real Cu $K\alpha_1$—Cu $K\alpha_2$ relation. The experimental powder patterns are in good agreement with the known powder pattern at high angles, but the reflections responsible for the *c* parameter at small angles were missed under the conditions used by Ferrari & Colla (1937).



(I)

The coordination number of six for bivalent metals (Mg, Co, Ni) is achieved by water molecules; the hypophosphite anion does not coordinate to the metal cation. The metal cation has a slightly distorted octahedral coordination sphere. The average *M*—O distances are 2.05 (1) Å in magnesium(II) bis(hypophosphite) (Galigné & Dumas, 1973), 2.074 (3) Å in (I) and 2.055 (2) Å in (II). There are two types of orientation for the water molecules relative to the oppositely coordinated water molecule. The dihedral angles between the two planes, consisting of one O atom and two H atoms of oppositely coordinated water molecules, are: type 1 [two pairs, O2*W* and O2*W*^{i} with their opposite symmetry equivalents; symmetry code: (i) $\frac{1}{4} - y, \frac{1}{4} - x, \frac{1}{4} - z$] 65.1 (1)° in magnesium(II) bis(hypophosphite) (Galigné & Dumas, 1973), 78.0 (1)° in (I) and 69.8 (1)° in (II); type 2 (one pair, O1*W* with its opposite symmetry equivalent) 3.0 (1)° in magnesium(II) bis(hypophosphite) (Galigné & Dumas, 1973), 2.8 (1)° in (I) and 1.6 (1)° in (II) (Fig. 1).

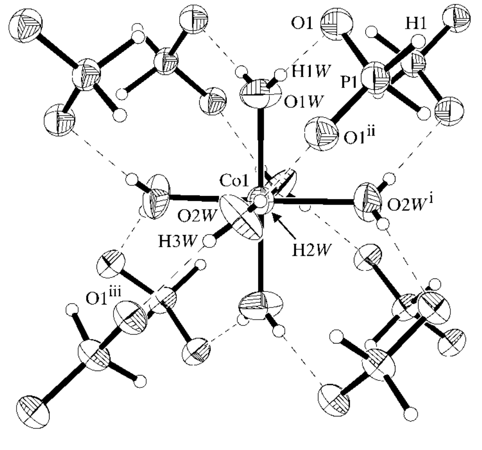


Figure 1
The environment of the hexaaquacobalt(II) cation of (I) in relation to the hypophosphite anions; the environment of the Co^{II}/Ni^{II} cation in (II) is equivalent. Displacement ellipsoids are plotted at the 50% probability level and H atoms are drawn as small spheres of arbitrary radii [symmetry codes: (i) $\frac{1}{4} - y, \frac{1}{4} - x, \frac{1}{4} - z$; (ii) $x, -y, \frac{1}{2} - z$; (iii) $y - \frac{1}{4}, x - \frac{1}{4}, z - \frac{1}{4}$].

DOI: 10.1107/S0108270102013094

The second coordination sphere of the metal atom consists of eight hypophosphite anions, which are hydrogen bonded to the water molecules coordinated to the $[Co(H_2O)_6]^{2+}$ ($[Ni(H_2O)_6]^{2+}$) cation (Fig. 1). This rigid construction is three-dimensional, similar to the structure of CaF_2.

The geometry of the hypophosphite anion in the structures of (I) and (II) is very close to ideal, with point symmetry *mm*2 (Naumov *et al.*, 2001, 2002). The geometric parameters for the anion (Tables 1 and 3) are comparable with earlier reported data, with P—O distances and O—P—O angles, respectively, 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 (3)° in $Co(H_2PO_2)Cl(H_2O)$ (Marcos *et al.*, 1991) and 1.541 (2)/ 1.480 (2) Å and 118.7 (3)° in $Ni(H_2PO_2)Cl(H_2O)$ (Marcos *et al.*, 1993).

Each O atom of the hypophosphite anion is hydrogen bonded to three water molecules from different cation complexes (Tables 2 and 4; thick dashed lines in Fig. 2), while each H atom of the hypophosphite anion is surrounded by three water molecules from further different cation complexes, and these H atoms are situated directly above the centres of the triangles formed by the O atom and two H atoms of the water molecules (thin dashed lines in Fig. 2). The distances between atom H1 of the hypophosphite and the O atoms [O2*W*^{i}, O1*W*^{ii} and O2*W*^{iii}; symmetry codes: (i) $\frac{1}{4} - y, x - \frac{1}{4}, \frac{1}{4} + z$; (ii) $\frac{1}{2} + x, -y, z$; (iii) $\frac{1}{2} + x, y, \frac{1}{2} - z$] of the water molecules are 2.93 (2), 2.94 (2) and 2.95 (2) Å (average 2.94 Å) for (I), and 2.865 (16), 2.912 (17) and 2.850 (16) Å (average 2.88 Å) for (II). This environment can be found in all three structures of hexaaquamagnesium(II), -cobalt(II) and -cobalt(II)/nickel(II) bis(hypophosphite).

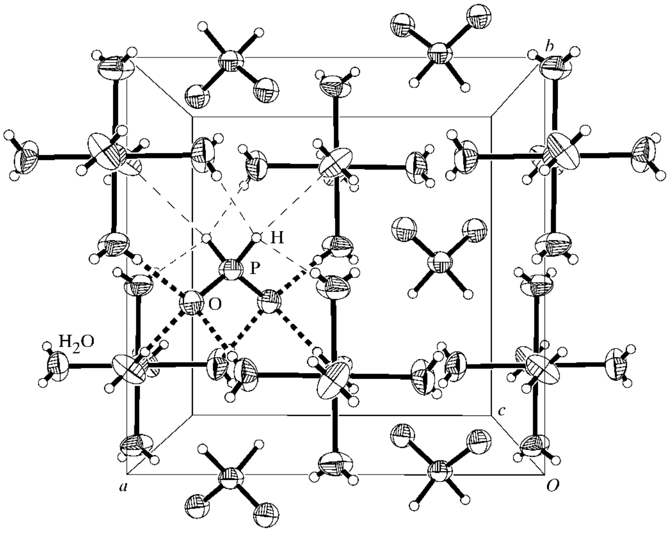


Figure 2
The environment of the hypophosphite anion of (I) in relation to the hexaaquacobalt(II) cations, viewed along [001]; the corresponding diagram in relation to the Co^{II}/Ni^{II} cations in (II) is equivalent. The thick dashed lines indicate the O—H···O—P hydrogen bonds and the thin dashed lines indicate the O*W*···H—P contacts.

Experimental

Compound (I) was synthesized by slow evaporation of an aqueous solution of cobalt(II) hypophosphite, which was prepared by adding a solution of calcium hypophosphite, $Ca(H_2PO_2)_2$, to cobalt(II) sulfate, $CoSO_4$, in an equimolar ratio. The reaction mixture was filtered and crystals of (I) were grown at 293 K in air. Compound (II) was synthesized by mixing aqueous solutions of cobalt(II) and nickel(II) bis(hypophosphite) in an equimolar ratio. Light-green crystals of (II) were grown at 293 K in air and their chemical composition was determined by UV spectroscopy. The UV spectrum of the hexaaquacobalt(II) cation had no overlap with that for the hexaaquanickel(II) cation (maximum absorption 317 and 288 nm, respectively). The quantities of each cation in the crystals were calculated using calibration solutions of pure cobalt(II) and nickel(II) bis(hypophosphite). The actual ratio of metals in the crystals was found to be the same as that calculated based on the preparation experiment.

Compound (I)

Crystal data

$[Co(H_2O)_6](H_2PO_2)_2$
$M_r = 297.00$
Tetragonal, $I4_1/acd$
$a = 10.3406$ (15) Å
$c = 20.402$ (3) Å
$V = 2181.6$ (6) Å^3
$Z = 8$
$D_x = 1.809$ Mg m^{-3}

Mo *K*α radiation
Cell parameters from 24 reflections
$\theta = 9.7$–12.0°
$\mu = 1.89$ mm^{-1}
$T = 293$ (2) K
Prism, purple
0.64 × 0.36 × 0.36 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$2\theta/\theta$ scans
Absorption correction: empirical (*CADDAT*; Enraf–Nonius, 1989)
$T_{min} = 0.477$, $T_{max} = 0.506$
1315 measured reflections
686 independent reflections
419 reflections with $I > 2\sigma(I)$

$R_{int} = 0.030$
$\theta_{max} = 28.3°$
$h = 0 \rightarrow 13$
$k = 0 \rightarrow 13$
$l = 0 \rightarrow 27$
3 standard reflections
frequency: 60 min
intensity decay: none

Table 1
Selected geometric parameters (Å, °) for (I).

Co1—O1*W*	2.070 (3)	P1—O1	1.5076 (13)
Co1—O2*W*	2.0765 (18)	P1—H1	1.21 (2)
O1*W*—Co1—O2*W*	90.68 (7)	O2*W*—Co1—O2*W*^{i}	88.50 (14)
O1*W*—Co1—O2*W*^{i}	89.32 (7)	O1^{ii}—P1—O1	115.74 (13)

Symmetry codes: (i) $\frac{1}{4} - y, \frac{1}{4} - x, \frac{1}{4} - z$; (ii) $x, -y, \frac{1}{2} - z$.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*W*—H1*W*···O1	0.75 (2)	2.01 (2)	2.7524 (18)	177 (3)
O2*W*—H2*W*···O1^{i}	0.64 (2)	2.11 (3)	2.752 (3)	174 (3)
O2*W*—H3*W*···O1^{ii}	0.74 (3)	2.01 (3)	2.744 (3)	173 (3)

Symmetry codes: (i) $x, -y, \frac{1}{2} - z$; (ii) $y - \frac{1}{4}, x - \frac{1}{4}, z - \frac{1}{4}$.

i130 Natalia V. Kuratieva et al. • $[Co(H_2O)_6](H_2PO_2)_2$ and $[Co_{0.5}Ni_{0.5}(H_2O)_6](H_2PO_2)_2$ Acta Cryst. (2002). C58, i129–i131

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.037$
$wR(F^2) = 0.093$
$S = 0.92$
686 reflections
49 parameters
All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0536P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.51$ e Å^{-3}
$\Delta\rho_{\min} = -0.41$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.0004 (1)

Compound (II)

Crystal data

$[Co_{0.5}Ni_{0.5}(H_2O)_6](H_2PO_2)_2$
$M_r = 296.89$
Tetragonal, $I4_1/acd$
$a = 10.3111$ (13) Å
$c = 20.346$ (3) Å
$V = 2163.2$ (5) Å^3
$Z = 8$
$D_x = 1.823$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 24 reflections
$\theta = 9.7$–$12.1°$
$\mu = 2.01$ mm^{-1}
$T = 293$ (2) K
Octahedron, light green
0.65 × 0.63 × 0.57 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$2\theta/\theta$ scans
Absorption correction: empirical (*CADDAT*; Enraf–Nonius, 1989)
$T_{\min} = 0.288$, $T_{\max} = 0.317$
1187 measured reflections
621 independent reflections
407 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.016$
$\theta_{\max} = 27.5°$
$h = 0 \rightarrow 13$
$k = 0 \rightarrow 13$
$l = 0 \rightarrow 26$
3 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.021$
$wR(F^2) = 0.073$
$S = 1.06$
621 reflections
49 parameters
All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0365P)^2 + 0.3503P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.23$ e Å^{-3}
$\Delta\rho_{\min} = -0.19$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.0030 (3)

Table 3
Selected geometric parameters (Å, °) for (II).

Co1—O1*W*	2.058 (2)	P1—O1	1.5092 (12)
Co1—O2*W*	2.0542 (16)	P1—H1	1.328 (15)
O1*W*—Co1—O2*W*	90.67 (5)	O2*W*—Co1—O2*W*$^{\rm i}$	88.83 (10)
O1*W*—Co1—O2*W*$^{\rm i}$	89.33 (5)	O1$^{\rm ii}$—P1—O1	115.90 (11)

Symmetry codes: (i) $\frac{1}{4} - y, \frac{1}{4} - x, \frac{1}{4} - z$; (ii) $x, -y, \frac{1}{2} - z$.

Table 4
Hydrogen-bonding geometry (Å, °) for (II).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O1*W*—H1*W*$\cdots$O1	0.86 (3)	1.90 (3)	2.7565 (16)	177 (3)
O2*W*—H2*W*$\cdots$O1$^{\rm i}$	0.70 (2)	2.06 (2)	2.750 (2)	170 (2)
O2*W*—H3*W*$\cdots$O1$^{\rm ii}$	0.77 (2)	1.98 (2)	2.735 (2)	168 (2)

Symmetry codes: (i) $x, -y, \frac{1}{2} - z$; (ii) $y - \frac{1}{4}, x - \frac{1}{4}, z - \frac{1}{4}$.

In both structures, the H atoms were located from a difference electron-density map and their positions were refined without any constraints.

For both compounds, 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.

The authors are grateful to Professor N. V. Podberezskaya for stimulating this study and for helpful comments.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV1112). Services for accessing these data are described at the back of the journal.

References

Burnett, M. N. & Johnson, C. K. (1996). *ORTEP*III. Report ORNL-6895. Oak Ridge National Laboratory, Tennessee, USA.

Enraf–Nonius (1989). *CAD*-4 *Software* (Version 5.0), incorporating *CD*4*CA*0 (Version 5.0) and *CADDAT* (Version 5.1). Enraf–Nonius, Delft, The Netherlands.

Ferrari, A. & Colla, C. (1937). *Gazz. Chim. Ital.* **67**, 294–301.

Galigné, J. L. & Dumas, Y. (1973). *Acta Cryst.* B**29**, 1115–1119.

Marcos, M. D., Amoros, P., Sapina, F., Porter, B. A., Manes, M. R. & Attfield, J. P. (1993). *Inorg. Chem.* **32**, 5044–5052.

Marcos, M. D., Ibáñez, R., Amorós, P. & Le Bail, A. (1991). *Acta Cryst.* C**47**, 1152–1155.

Naumov, D. Yu., Naumova, M. I., Kuratieva, N. V., Boldyreva, E. V. & Howard, J. A. K. (2002). *Acta Cryst.* C**58**, i55–i60.

Naumov, D. Yu., Yufit, D. S., Boldyreva, E. V. & Howard, J. A. K. (2001). *Acta Cryst.* C**57**, 790–792.

Pédrazuela, A. R., García-Blanco, S. & Rivoir, L. (1953). *An. Soc. Esp. Fis. Quim.* **49**, 255–262.

Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.