O21—Zn11—O42	109.0 (3)	O22—P22—O42^{iv}	107.5 (6)
O32—Zn11—O42	117.3 (2)	O41—P22—O42^{iv}	108.7 (4)
O12—Zn12—O22	105.2 (2)	O12^{iii}—P31—O21	110.5 (6)
O12—Zn12—O31^{i}	108.2 (3)	O12^{iii}—P31—O31^{v}	108.6 (5)
O12—Zn12—O41^{ii}	108.4 (4)	O12^{iii}—P31—O32^{v}	110.4 (3)
O22—Zn12—O31^{i}	112.2 (2)	O21—P31—O31^{v}	107.6 (4)
O22—Zn12—O41^{ii}	106.1 (3)	O21—P31—O32^{v}	110.0 (5)
O31^{i}—Zn12—O41^{ii}	116.0 (5)	O31^{v}—P31—O32^{v}	109.7 (6)
O12—Li21—O21	107.9 (18)	O11—Li32—O22^{ii}	106.8 (15)
O12—Li21—O41^{iii}	110.2 (16)	O11—Li32—O31	118.3 (8)
O12—Li21—O42^{iii}	117.5 (9)	O11—Li32—O32^{iv}	111.6 (14)
O21—Li21—O41^{iii}	102.2 (9)	O22^{ii}—Li32—O31	104.2 (14)
O21—Li21—O42^{iii}	111.3 (17)	O22^{ii}—Li32—O32^{iv}	112.6 (9)
O41^{iii}—Li21—O42^{iii}	106.6 (18)	O31—Li32—O32^{iv}	103.3 (15)

Symmetry codes: (i) $\frac{2}{3}-y, x-y-\frac{2}{3}, z-\frac{2}{3}$; (ii) $\frac{2}{3}-y, x-y-\frac{2}{3}, \frac{1}{3}+z$; (iii) $\frac{2}{3}-x+y, \frac{1}{3}-x, \frac{1}{3}+z$; (iv) $1-y, x-y, z$; (v) $\frac{1}{3}-y, x-y-\frac{1}{3}, z-\frac{1}{3}$.

A measurement of the second harmonic generation gave a value 0.9 times that of quartz, confirming the non-centrosymmetric nature of the space group.

The structure refinement was based on the model for α-LiGaSiO$_4$. Only the Zn and P atoms were refined anisotropically, as the loss of centrosymmetry led to an unfavorable reflection-to-parameter ratio. The chirality parameter was not refined as the structure deviates only slightly from centrosymmetry.

Data collection: *UCLA CCP* (Strouse, 1991). Cell refinement: *UCLA CCP*. Data reduction: *UCLA CCP*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *NRCVAX* (Gabe, Le Page, Charland, Lee & White, 1989). Molecular graphics: *ATOMS* (Dowty, 1994). Software used to prepare material for publication: *NRCVAX*.

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NiHP$_5$O$_{14}$ Ultraphosphate

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Abstract

The structure of the title compound, NiHP$_5$O$_{14}$, is built of two parallel chains interconnected to form a ribbon. The polyphosphate ribbons are coupled by hydrogen bonds.

Comment

The ratio between tetrahedra that are bridged *via* two O atoms (Q^2) and three O atoms (Q^3) is 2:3. These types of double chains and ribbons, respectively, are similar to those in ultraphophates with trivalent cations. Within the ribbons unusual distances are observed for P1—O11 and P5—O14. These bond lengths are long compared with typical values for unbridged O atoms. This can be explained by an additional H atom situated between the O atoms O11 and O14, belonging to Q^2 tetrahedra, and not coordinated to Ni. This assumption was confirmed by a difference Fourier map, which revealed an H atom covalently bonded to O11 and forming a hydrogen bond with O14. The O11$\cdots$O14 and O14$\cdots$H11 distance are 2.412 (1) and 1.402 (1) Å, respectively. The Ni—O distances are in the range 2.031 (2) to 2.080 (2) Å and
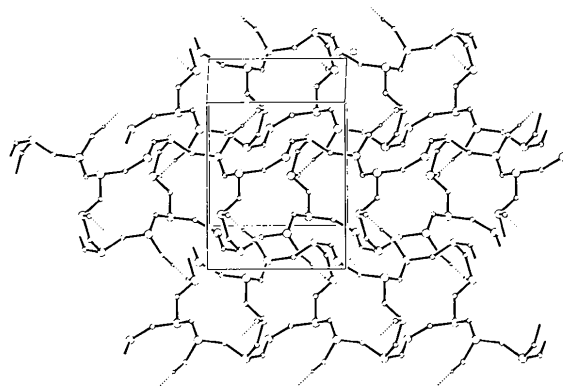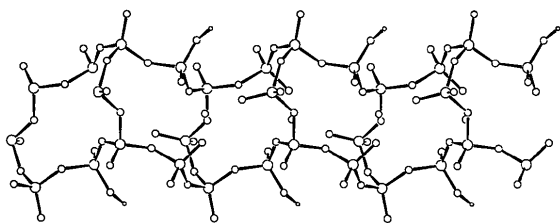

Fig. 1. The structure of NiHP$_5$O$_{14}$ as viewed along [010]. The atoms are drawn as circles of arbitrary radii: P large, O medium and H small. Only the bonding O, P and H atoms are shown.

Fig. 2. Ribbons of eight-membered rings of [PO₄] tetrahedra.

the O—Ni—O angles range from 86.13 (7) to 95.28 (7)° and from 175.08 (6) to 177.93 (6)°, resulting in slightly distorted isolated octahedra.

Experimental

The synthesis of $NiHP_5O_{14}$ was performed by tempering NiO with an excess of P_2O_5 and H_3PO_4 in a closed system at 665 K for several days. The reaction product consists of a glassy matrix containing crystals of different modifications of ultraphosphates and metaphosphates. Pale-green needle-shaped crystals of the title compound were extracted from the soluble glassy matrix using water and subsequently washed with methanol and acetone.

Crystal data

$NiHP_5O_{14}$	Mo $K\alpha$ radiation
$M_r = 438.57$	$\lambda = 0.7107$ Å
Monoclinic	Cell parameters from 25
$P2_1/n$	reflections
$a = 9.666\,(1)$ Å	$\theta = 3.30\text{--}11.15°$
$b = 8.062\,(1)$ Å	$\mu = 2.817$ mm^{-1}
$c = 12.996\,(1)$ Å	$T = 299\,(2)$ K
$\beta = 97.262\,(9)°$	Prism
$V = 1004.6\,(2)$ Å^3	$0.10 \times 0.08 \times 0.05$ mm
$Z = 4$	Pale green
$D_x = 2.90$ Mg m^{-3}	

Data collection

Enraf–Nonius CAD-4	3151 observed reflections
diffractometer	$[I > 2\sigma(I)]$
$\omega/2\theta$ scans	$R_{int} = 0.0269$
Absorption correction:	$\theta_{max} = 34.96°$
ψ scan (North, Phillips	$h = -15 \rightarrow 3$
& Mathews, 1968)	$k = 0 \rightarrow 12$
$T_{min} = 0.754$, $T_{max} = 0.821$	$l = -20 \rightarrow 20$
5521 measured reflections	3 standard reflections
4415 independent reflections	frequency: 120 min
	intensity decay: 0.6%

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} = -0.005$
$R[F^2 > 2\sigma(F^2)] = 0.0302$	$\Delta\rho_{max} = 0.662$ e Å^{-3}
$wR(F^2) = 0.0729$	$\Delta\rho_{min} = -0.631$ e Å^{-3}
$S = 1.023$	Extinction correction: none
4415 reflections	Atomic scattering factors
185 parameters	from *International Tables*
$w = 1/[\sigma^2(F_o^2) + (0.0288P)^2$	*for Crystallography* (1992,
$+ 0.7054P]$	Vol. C, Tables 4.2.6.8 and
where $P = (F_o^2 + 2F_c^2)/3$	6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Ni1	0.80057 (3)	0.21038 (3)	0.00173 (2)	0.00787 (6)
P1	0.45945 (6)	−0.06925 (6)	0.16090 (4)	0.00833 (9)
P2	0.56827 (6)	0.27257 (6)	0.16260 (4)	0.00721 (9)
P3	0.99373 (6)	−0.06185 (6)	0.14203 (4)	0.00717 (9)
P4	1.09090 (6)	0.27879 (7)	0.14675 (4)	0.00781 (9)
P5	1.31132 (6)	0.40437 (7)	0.03340 (4)	0.00851 (9)
O1	0.8819 (2)	−0.0086 (2)	0.0617 (1)	0.0116 (3)
O2	1.0828 (2)	0.0980 (2)	0.1877 (1)	0.0130 (3)
O3	0.9712 (2)	0.3374 (2)	0.0774 (1)	0.0127 (3)
O4	0.9063 (2)	0.1930 (2)	−0.1237 (1)	0.0115 (3)
O5	0.4898 (2)	0.1187 (2)	0.1974 (1)	0.0125 (3)
O6	1.2318 (2)	0.2771 (2)	0.1001 (1)	0.0121 (3)
O7	0.7048 (2)	0.2406 (2)	0.1309 (1)	0.0121 (3)
O8	0.6322 (2)	0.0721 (2)	−0.0620 (1)	0.0142 (3)
O9	0.3705 (2)	−0.1175 (2)	0.2524 (1)	0.0115 (3)
O10	0.5761 (2)	0.3936 (2)	0.2555 (1)	0.0147 (3)
O11	0.5924 (2)	−0.1620 (2)	0.1756 (1)	0.0187 (3)
O12	0.7157 (2)	0.4244 (2)	−0.0626 (1)	0.0137 (3)
O13	0.4687 (2)	0.3544 (2)	0.0724 (1)	0.0157 (3)
O14	1.2867 (2)	0.3570 (2)	−0.0781 (1)	0.0176 (3)

Table 2. *Selected geometric parameters (Å, °)*

Ni1—O7	2.0314 (15)	P3—O2	1.620 (2)
Ni1—O4	2.0353 (15)	P4—O3	1.453 (2)
Ni1—O12	2.044 (2)	P4—O2	1.557 (2)
Ni1—O1	2.046 (2)	P4—O9^{iv}	1.559 (2)
Ni1—O8	2.058 (2)	P4—O6	1.559 (2)
Ni1—O3	2.080 (2)	P5—O12^v	1.464 (2)
P1—O8^i	1.466 (2)	P5—O14	1.489 (2)
P1—O11	1.479 (2)	P5—O13^{vi}	1.593 (2)
P1—O9	1.602 (2)	P5—O6	1.601 (2)
P1—O5	1.604 (2)	O4—P3^{ii}	1.472 (2)
P2—O7	1.454 (2)	O8—P1^i	1.466 (2)
P2—O10	1.547 (2)	O9—P4^{iii}	1.559 (2)
P2—O5	1.551 (2)	O10—P3^{iv}	1.608 (2)
P2—O13	1.565 (2)	O11—H11	1.02 (4)
P3—O1	1.469 (2)	O12—P5^v	1.464 (2)
P3—O4^{ii}	1.472 (2)	O13—P5^{vii}	1.593 (2)
P3—O10^{iii}	1.608 (2)		
O7—Ni1—O4	175.92 (7)	O4^{ii}—P3—O10^{iii}	109.06 (9)
O7—Ni1—O12	92.04 (7)	O1—P3—O2	109.69 (9)
O4—Ni1—O12	86.94 (6)	O4^{ii}—P3—O2	107.5 (1)
O7—Ni1—O1	88.97 (6)	O10^{iii}—P3—O2	97.67 (9)
O4—Ni1—O1	92.18 (6)	O3—P4—O2	116.48 (9)
O12—Ni1—O1	177.93 (6)	O3—P4—O9^{iv}	115.75 (9)
O7—Ni1—O8	88.70 (7)	O2—P4—O9^{iv}	103.40 (9)
O4—Ni1—O8	95.28 (7)	O3—P4—O6	115.36 (9)
O12—Ni1—O8	92.09 (7)	O2—P4—O6	102.04 (9)
O1—Ni1—O8	86.13 (7)	O9^{iv}—P4—O6	101.71 (9)
O7—Ni1—O3	88.13 (7)	O12^v—P5—O14	118.9 (1)
O4—Ni1—O3	87.95 (7)	O12^v—P5—O13^{vi}	110.5 (1)
O12—Ni1—O3	91.78 (7)	O14—P5—O13^{vi}	105.9 (1)
O1—Ni1—O3	90.06 (6)	O12^v—P5—O6	110.49 (9)
O8—Ni1—O3	175.08 (6)	O14—P5—O6	109.5 (1)
O8^i—P1—O11	121.6 (1)	O13^{vi}—P5—O6	99.77 (9)
O8^i—P1—O9	109.02 (9)	P3—O1—Ni1	137.4 (1)
O11—P1—O9	108.7 (1)	P4—O2—P3	131.8 (1)
O8^i—P1—O5	110.01 (9)	P4—O3—Ni1	130.9 (1)
O11—P1—O5	108.4 (1)	P3^{ii}—O4—Ni1	125.85 (9)
O9—P1—O5	96.02 (9)	P2—O5—P1	138.3 (1)
O7—P2—O10	112.1 (1)	P4—O6—P5	135.0 (1)
O7—P2—O5	115.85 (1)	P2—O7—Ni1	141.3 (1)
O10—P2—O5	104.72 (9)	P1^i—O8—Ni1	136.1 (1)
O7—P2—O13	110.87 (9)	P4^{iii}—O9—P1	131.3 (1)
O10—P2—O13	106.5 (1)	P2—O10—P3^{iv}	143.4 (1)
O5—P2—O13	106.16 (9)	P1—O11—H11	131. (2)
O1—P3—O4^{ii}	122.30 (9)	P5^v—O12—Ni1	139.9 (1)
O1—P3—O10^{iii}	107.8 (1)	P2—O13—P5^{vii}	144.7 (1)

Symmetry codes: (i) $1 - x, -y, -z$; (ii) $2 - x, -y, -z$; (iii) $\frac{3}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$; (iv) $\frac{3}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; (v) $2 - x, 1 - y, -z$; (vi) $1 + x, y, z$; (vii) $x - 1, y, z$.

Data collection: *Diffractometer Control Software* (Enraf–Nonius, 1993). Cell refinement: *Diffractometer Control Software*. Data reduction: *REDU4* (Stoe & Cie, 1992). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *PLUTON93* (Spek, 1993). Software used to prepare material for publication: *SHELXL93*.

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Hexaaquagallium Hexahydrogenhexamolybdocobaltate(III) Decahydrate†

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Abstract

The structure of hexaaquagallium(III) hexahydrogentetracosaoxocobalt(III)hexamolybdate decahydrate, [Ga(H$_2$O)$_6$][Co(OH)$_6$Mo$_6$O$_{18}$].10H$_2$O, includes a polyanion with the so-called Anderson structure, of general formula H$_6$[X^{n+}Mo$_6$O$_{24}$]$^{(6-n)-}$ (X is a heteroatom), where

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all the O atoms in the central XO$_6$ octahedron are protonated. The Ga^{3+} ion is coordinated by six water molecules and the Co^{3+} ion by six O atoms. Both ions are located at inversion centers.

Comment

The title compound was investigated as part of structural studies on polymolybdate salts. *B*-type Anderson structure heteropolyanions (Anderson, 1937), *i.e.* containing a heteroatom X of low oxidation state within a protonated polyanion such as H$_6$[X^{n+}Mo$_6$O$_{24}$]$^{(6-n)-}$, have been reported for heteroatoms Cr^{3+} (Perloff, 1970), Cu^{2+} (Ito, Ozeki, Ichida & Sasaki, 1989) and Co^{3+} (Nagano, Lee, Ichida & Sasaki, 1990).

The present polyanion, [Co(OH)$_6$Mo$_6$O$_{18}$]$^{3-}$, containing Co^{3+} as the heteroatom but Ga^{3+} as the counter ion, is close to having $D_{3d}(\bar{3}m)$ symmetry. It consists of a ring of six distorted MoO$_6$ octahedra surrounding one Co atom; the six Mo atoms form an almost planar (r.m.s. deviation 0.003 Å) hexagon with an edge of approximately 3.36 Å. The O atoms in the anion can be divided into three groups, O*c*, O*b* and O*t*, where O*t* represents a terminal O atom bound to one Mo atom, O*b* represents a bridging O atom bound to two Mo atoms and O*c* represents a central O atom coordinated to both the Co atom and an Mo atom. The Mo—O distances are Mo—O*c* 2.282 (4)–2.352 (4), Mo—O*b* 1.944 (4)–1.971 (4) and Mo—O*t* 1.715 (5)–1.749 (4) Å. A similar trend has been found in Ba$_3$[Co(OH)$_6$Mo$_6$O$_{18}$]$_2$.20H$_2$O (Soriano-García, Panneerselvam & Holguín-Quiñones, 1996), (C$_{12}$H$_{24}$O$_6$K)$_2$K[Co(OH)$_6$Mo$_6$O$_{18}$].12H$_2$O (Nagano, Lee, Ichida & Sasaki, 1990) and Na$_3$[Cr(OH)$_6$Mo$_6$O$_{18}$].-8H$_2$O (Perloff, 1970).

The Co^{3+} and Ga^{3+} ions both have coordination number six. The Co^{3+} ion is coordinated to six O*c* atoms at an average distance of 1.967 (4) Å. Of the 16
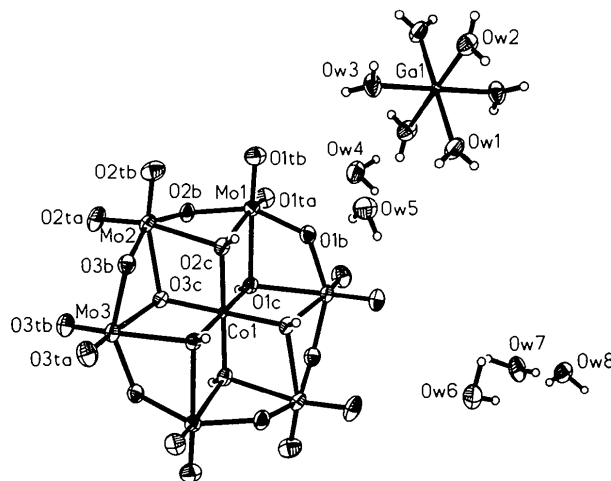

Fig. 1. The molecular structure of the title compound showing the atom-labeling scheme. Displacement ellipsoids are shown at the 50% probability level.