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

Ru(1)—N(11)	2.102 (4)	Ru(3)—N(32)	2.097 (3)
Ru(1)—N(12)	2.088 (4)	Ru(3)—N(33)	2.097 (3)
Ru(1)—N(13)	2.089 (5)	Ru(4)—N(41)	2.082 (3)
Ru(2)—N(21)	2.092 (4)	Ru(4)—N(42)	2.081 (4)
Ru(2)—N(22)	2.093 (3)	Ru(4)—N(43)	2.092 (3)
Ru(3)—N(31)	2.087 (3)		
N(11)—Ru(1)—N(12)	88.9 (2)	N(32)—Ru(3)—N(33^{ii})	91.0 (1)
N(21)—Ru(2)—N(22)	90.8 (1)	N(41)—Ru(4)—N(42)	88.6 (2)
N(22)—Ru(2)—N(22^{i})	87.8 (2)	N(41)—Ru(4)—N(43)	89.2 (2)
N(31)—Ru(3)—N(32)	90.5 (2)	N(42)—Ru(4)—N(43)	89.7 (2)
N(31)—Ru(3)—N(33)	89.7 (1)	N(41)—Ru(4)—N(41^{iii})	91.0 (2)
N(32)—Ru(3)—N(33)	90.3 (1)	N(42)—Ru(4)—N(41^{iii})	90.9 (2)
N(31)—Ru(3)—N(31^{ii})	89.9 (2)	N(42)—Ru(4)—N(42^{iii})	179.3 (3)
N(33)—Ru(3)—N(31^{ii})	89.0 (1)	N(43)—Ru(4)—N(41^{iii})	179.4 (2)
N(33)—Ru(3)—N(33^{ii})	178.1 (2)	N(43)—Ru(4)—N(42^{iii})	90.8 (2)
N(32)—Ru(3)—N(31^{ii})	179.2 (1)		

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

Data collection, reduction and cell refinement programs: *SHELXS*86 (Robinson & Sheldrick, 1988) was used by direct methods for crystal structure solution and *SHELXL*93 (Sheldrick, 1993) for structure refinement. Molecular graphics: *SHELXTL* (Sheldrick, 1991).

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Nickel Ultraphosphate, NiP4O11

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Abstract

The structure of NiP_4O_{11} is built of layers of cations and layers of corner-sharing PO_4 tetrahedra. These crystals display a new connectivity scheme. Layers of rings containing 6 or 14 PO_4 tetrahedra were observed.

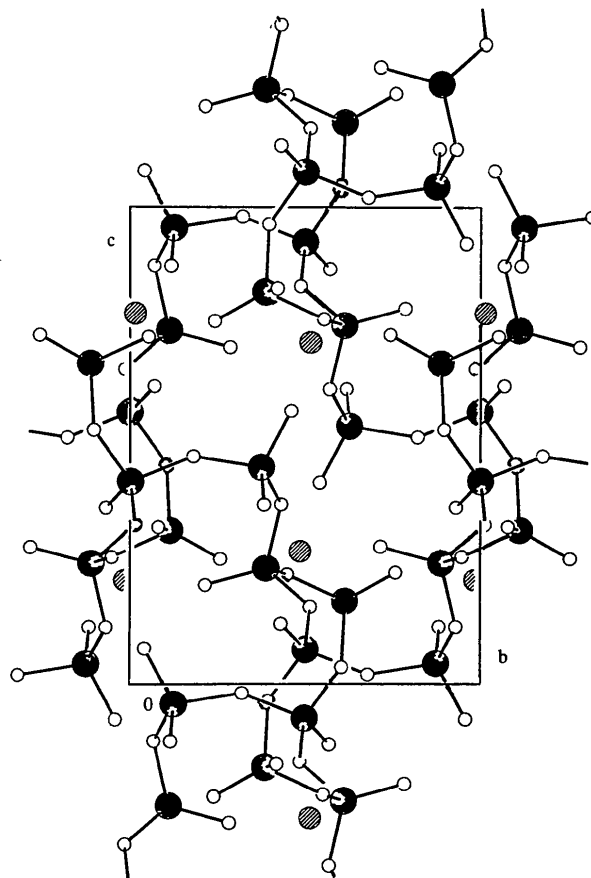
Fig. 1. *PLUTON*93 (Spek, 1993) view along the [100] direction. All atoms are drawn as circles of arbitrary radii: Ni hatched, P filled and O open.

Comment

This structure is not isostructural with the known ultra-phosphates and has a new type of network consisting of 6- and 14-membered rings. The NiP$_4$O$_{11}$ single crystals were synthesized from an acidic melt of metal oxide and an excess of P$_2$O$_5$ and H$_3$PO$_4$. They were prepared in a tightly closed gold crucible at 605 K over a period of one week. The needle-like crystals were extracted from the glassy melt by solvents such as water, methanol and acetone in different proportions.

Experimental

A mixture of phosphorous acid, phosphorous pentoxide and nickel oxide was heated to 605 K. The melt was kept at that temperature for several days. Light-green crystals were formed.

Crystal data

NiP$_4$O$_{11}$
$M_r = 358.59$
Monoclinic
$P2_1/n$
$a = 9.3750\,(10)$ Å
$b = 8.0190\,(10)$ Å
$c = 11.135\,(2)$ Å
$\beta = 100.730\,(10)°$
$V = 822.5\,(2)$ Å^3
$Z = 4$
$D_x = 2.896$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 2.61–18.41°$
$\mu = 3.189$ mm^{-1}
$T = 299\,(2)$ K
Needle
$0.20 \times 0.08 \times 0.03$ mm
Light green

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction:
 ψ scan (North, Phillips & Mathews, 1968)
 $T_{min} = 0.729$, $T_{max} = 0.806$
6490 measured reflections
3602 independent reflections

2571 observed reflections
 $[I > 2\sigma(I)]$
$R_{int} = 0.0373$
$\theta_{max} = 34.96°$
$h = -15 \rightarrow 9$
$k = 0 \rightarrow 12$
$l = -17 \rightarrow 17$
3 standard reflections
 frequency: 120 min
 intensity decay: 2.9%

Refinement

Refinement on F^2
$R(F) = 0.0265$
$wR(F^2) = 0.0683$
$S = 1.026$
3602 reflections
145 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0330P)^2 + 0.0299P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = -0.002$
$\Delta\rho_{max} = 0.683$ e Å^{-3}
$\Delta\rho_{min} = -0.636$ e Å^{-3}
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

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

	x	y	z	U_{eq}
Ni1	0.03312 (3)	1.01493 (3)	0.78053 (2)	0.00858 (6)
P2	−0.28727 (5)	0.62572 (6)	0.54285 (4)	0.00806 (8)
P3	0.31224 (5)	0.88687 (6)	0.67510 (4)	0.00734 (8)
P4	−0.05998 (5)	0.61181 (6)	0.75521 (4)	0.00736 (8)
P5	0.25814 (5)	1.00091 (6)	0.42755 (4)	0.00742 (8)
O6	0.15712 (15)	0.9198 (2)	0.66799 (13)	0.0119 (3)
O7	0.34376 (15)	0.8961 (2)	0.53562 (12)	0.0098 (2)
O8	0.1132 (2)	1.2420 (2)	0.76443 (13)	0.0138 (3)
O9	−0.0753 (2)	0.7855 (2)	0.79050 (14)	0.0134 (3)
O10	−0.1187 (2)	1.0695 (2)	0.62728 (13)	0.0135 (3)
O11	0.40104 (15)	1.0525 (2)	0.73149 (13)	0.0108 (2)
O12	−0.1300 (2)	0.5691 (2)	0.62058 (12)	0.0123 (3)
O13	−0.1043 (2)	1.1173 (2)	0.87894 (14)	0.0166 (3)
O14	−0.2550 (2)	0.8205 (2)	0.51975 (13)	0.0127 (3)
O15	−0.1302 (2)	0.4859 (2)	0.83688 (13)	0.0110 (2)
O16	0.1973 (2)	0.9592 (2)	0.92468 (13)	0.0137 (3)

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

Ni1—O8	1.9903 (15)	P3—O11	1.6302 (15)
Ni1—O6	2.0115 (14)	P3—O7	1.6358 (14)
Ni1—O13	2.015 (2)	P4—O9	1.4612 (15)
Ni1—O10	2.0552 (15)	P4—O11^{iii}	1.5447 (14)
Ni1—O16	2.0554 (15)	P4—O12	1.5586 (15)
P2—O13^i	1.458 (2)	P4—O15	1.5819 (14)
P2—O16^{ii}	1.4645 (15)	P5—O10^{iv}	1.4504 (15)
P2—O14	1.6204 (15)	P5—O14^{iv}	1.5501 (15)
P2—O12	1.6289 (15)	P5—O7	1.5618 (14)
P3—O8^{iii}	1.4548 (15)	P5—O15^v	1.5878 (15)
P3—O6	1.4656 (14)		
O8—Ni1—O6	91.11 (6)	O8^{iii}—P3—O11	107.79 (8)
O8—Ni1—O13	88.07 (6)	O6—P3—O11	107.72 (8)
O6—Ni1—O13	174.56 (6)	O8^{iii}—P3—O7	108.62 (8)
O8—Ni1—O10	86.85 (6)	O6—P3—O7	107.06 (8)
O6—Ni1—O10	87.39 (6)	O11—P3—O7	99.17 (7)
O13—Ni1—O10	87.19 (7)	O9—P4—O11^{iii}	114.13 (9)
O8—Ni1—O16	91.67 (6)	O9—P4—O12	115.03 (8)
O6—Ni1—O16	88.20 (6)	O11^{iii}—P4—O12	104.53 (8)
O13—Ni1—O16	97.20 (6)	O9—P4—O15	112.43 (8)
O10—Ni1—O16	175.32 (6)	O11^{iii}—P4—O15	104.21 (8)
O13^i—P2—O16^{ii}	123.48 (9)	O12—P4—O15	105.48 (8)
O13^i—P2—O14	108.10 (8)	O10^{iv}—P5—O14^{iv}	116.10 (9)
O16^{ii}—P2—O14	107.20 (8)	O10^{iv}—P5—O7	114.12 (8)
O13^i—P2—O12	109.42 (9)	O14^{iv}—P5—O7	104.41 (8)
O16^{ii}—P2—O12	106.04 (8)	O10^{iv}—P5—O15^v	114.07 (8)
O14—P2—O12	100.13 (8)	O14^{iv}—P5—O15^v	103.89 (8)
O8^{iii}—P3—O6	123.74 (9)	O7—P5—O15^v	102.75 (8)

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

Data collection: *CAD-4 Diffractometer Control Software* (Enraf–Nonius, 1993). Cell refinement: *Enraf–Nonius Structure Determination Package* (Frenz, 1993). Data reduction: *REDU4* (Stoe & Cie, 1988). 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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Fig. 1. The structure of a sheet of o'-$(P_2O_5)_\infty$.

Phosphorus Pentoxide at 233 K

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Fig. 2. The stacking of the sheets in P_2O_5.

Abstract

The structure of the thermodynamically most stable form of phosphorus pentoxide, o'-$(P_2O_5)_\infty$, consists of infinite layers built from six-membered rings of three-corner linked PO_4^- tetrahedra, as described in 1964 by Cruickshank [*Acta Cryst.* (1964), 17, 679–680]. The P—O bond distances and P—O—P bond angles reported here differ from Cruickshank's values and show a better agreement with the average ranges of known crystalline phosphate structures.

Comment

The o'-$(P_2O_5)_\infty$ single crystals were prepared from the melt in a tightly covered gold crucible at 635 K over two to three weeks in an electrically heated furnace. The needle-like crystals were extracted from the glassy melt by means of acetone at room temperature over several days. X-ray measurements on the single crystal were performed at 233 (2) K and without any contact with air or water vapour (by immersion of the crystal in paraffin within a glass capillary).

The average bond lengths are 1.570 (4) Å for P—O linked bonds and 1.440 (10) Å for unlinked double bonds.
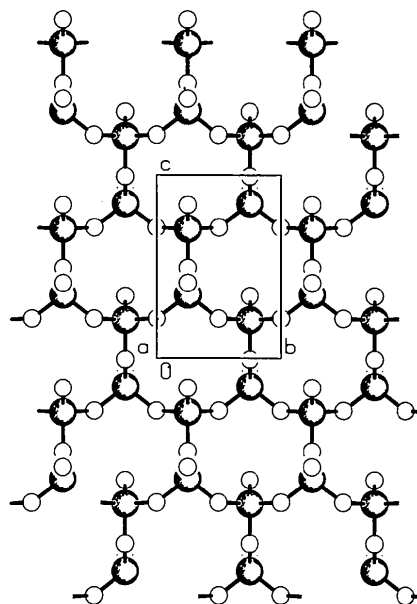
Experimental

Crystal data

P_2O_5	Mo $K\alpha$ radiation
$M_r = 141.94$	$\lambda = 0.71069$ Å
Orthorhombic	Cell parameters from 25
Pnma	reflections
$a = 9.193$ (9) Å	$\theta = 3.60$–$16.89°$
$b = 4.890$ (4) Å	$\mu = 1.081$ mm^{-1}
$c = 7.162$ (7) Å	$T = 233$ (2) K
$V = 322.0$ (5) Å^3	Needle
$Z = 4$	$0.18 \times 0.08 \times 0.05$ mm
$D_x = 2.928$ Mg m^{-3}	Colourless