Redetermination of the crystal structures of nickel cyclotetraphosphate, $Ni_2P_4O_{12}$ and of cobalt cyclotetraphosphate, $Co_2P_4O_{12}$

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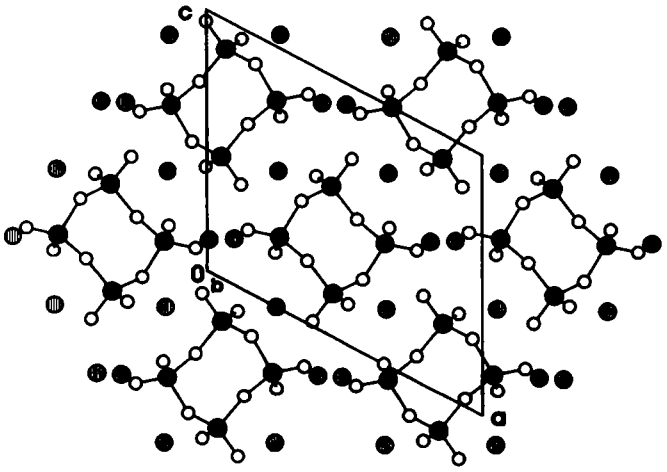
1. Nickel cyclotetraphosphate, $Ni_2P_4O_{12}$



Source of material: A mixture of phosphorus acid, phosphorus pentoxide and nickel oxide was heated to 605 K. The melt was kept at that temperature for about 7 days. Green and prism-shaped crystals were formed.

The title compound has been reported by Anders G. Nord in 1983 (see ref. 1) based on powder diffraction data. The structure of $Ni_2P_4O_{12}$ is isomorphous to Zn-, Co-, Fe-, Mg-, Cu-, Mn- and Cd-cyclotetraphosphates.

$Ni_2O_{12}P_4$, monoclinic, $C12/c1$ (No. 15), a =11.611(2) Å, b =8.218(2) Å, c =9.826(2) Å, β =118.41(2)°, V =824.7 Å^3, Z =4, $R(F)$ =0.029, $R_w(F^2)$ =0.088.

Table 1. Parameters used for the X-ray data collection

Crystal:	green prism, size 0.06 x 0.15 x 0.25 mm
Wavelength:	Mo K_α radiation (0.71093 Å)
μ:	54.29 cm^{-1}
Diffractometer:	Nonius CAD4
Scan mode:	ω/2θ
$T_{measurement}$:	304 K
$2\theta_{max}$:	69.9°
N(hkl)$_{unique}$:	1816
Criterion for I_o:	$I_o > 2\,\sigma(I_o)$
N($param$)$_{refined}$:	85
Programs:	SHELXS-96, SHELXL-93, COSMOS

Table 2. Final atomic coordinates and displacement parameters (in Å^2)

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ni(1)	4*d*	1/4	1/4	1/2	0.0065(2)	0.0063(2)	0.0064(2)	–0.0000(1)	0.0040(1)	–0.0001(1)
Ni(2)	4*e*	0	0.44430(5)	1/4	0.0066(2)	0.0061(2)	0.0074(2)	0	0.0042(1)	0
P(1)	8*f*	0.30292(6)	0.50720(7)	0.30227(7)	0.0055(2)	0.0058(2)	0.0065(2)	–0.0002(2)	0.0033(2)	0.0009(2)
P(2)	8*f*	0.48963(6)	0.73852(7)	0.52371(7)	0.0059(2)	0.0053(2)	0.0067(2)	–0.0001(2)	0.0039(2)	–0.0003(2)
O(1)	8*f*	0.4230(2)	0.3884(2)	0.3446(2)	0.0119(7)	0.0142(8)	0.0130(8)	0.0065(6)	0.0086(6)	0.0062(6)
O(2)	8*f*	0.3560(2)	0.6414(2)	0.4348(2)	0.0088(7)	0.0142(8)	0.0134(8)	–0.0054(6)	0.0068(6)	–0.0060(6)
O(3)	8*f*	0.2660(2)	0.5770(2)	0.1502(2)	0.0132(8)	0.0113(7)	0.0102(7)	0.0006(6)	0.0052(6)	0.0042(6)
O(4)	8*f*	0.1998(2)	0.4159(2)	0.3228(2)	0.0068(7)	0.0083(7)	0.0113(7)	–0.0014(5)	0.0047(6)	0.0017(6)
O(5)	8*f*	0.0487(2)	0.2578(2)	0.4169(2)	0.0079(7)	0.0098(7)	0.0088(7)	–0.0001(5)	0.0053(6)	0.0012(5)
O(6)	8*f*	0.0352(2)	0.6183(2)	0.4064(2)	0.0151(8)	0.0085(7)	0.0136(8)	0.0007(6)	0.0080(7)	–0.0035(6)

2. Cobalt cyclotetraphosphate, $Co_2P_4O_{12}$

Source of material: A mixture of phosphorus acid, phosphorus pentoxide and $Co_2(OH)_2CO_3$ was heated to 673 K. The melt was kept at that temperature for about 4 days. Pink and prism-shaped crystals were formed.
The title compound has been reported by Anders G. Nord in 1982 (see ref. 2) based on powder diffraction data. The structure of $Co_2P_4O_{12}$ is isomorphous to Zn-, Ni-, Fe-, Mg-, Cu-, Mn-, and Cd-cyclotetraphosphates.

$Co_2O_{12}P_4$, monoclinic, $C12/c1$ (No. 15), a =11.782(2) Å, b =8.279(2) Å, c =9.884(2) Å, β =118.38(1)°, V =848.3 Å^3, Z =4, $R(F)$ =0.021, $R_w(F^2)$ =0.053.

Table 3. Parameters used for the X-ray data collection

Crystal:	pink, prism, size 0.05 x 0.20 x 0.25 mm
Wavelength:	Mo K_α radiation (0.71093 Å)
μ:	47.21 cm^{-1}
Diffractometer:	Nonius CAD4
Scan mode:	ω/2θ
$T_{measurement}$:	300 K
$2\theta_{max}$:	70.1°
$N(hkl)_{unique}$:	1863
Criterion for I_o:	$I_o > 2\ \sigma(I_o)$
$N(param)_{refined}$:	85
Programs:	SHELXS-86, SHELXL-93, COSMOS

Table 4. Final atomic coordinates and displacement parameters (in Å^2)

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Co(1)	4*d*	1/4	1/4	1/2	0.0079(1)	0.00796(9)	0.00636(9)	–0.00009(6)	0.00411(7)	–0.00027(6)
Co(2)	4*e*	0	0.44789(2)	1/4	0.0084(1)	0.00743(9)	0.00777(9)	0	0.00456(7)	0
P(1)	8*f*	0.30460(3)	0.50632(3)	0.30287(3)	0.0068(1)	0.0076(1)	0.0066(1)	–0.00027(8)	0.00327(9)	0.00126(8)
P(2)	8*f*	0.48989(3)	0.73697(3)	0.52339(3)	0.0074(1)	0.0067(1)	0.0069(1)	–0.00017(8)	0.00415(9)	–0.00050(8)
O(1)	8*f*	0.42196(9)	0.3864(1)	0.3441(1)	0.0135(4)	0.0168(4)	0.0149(4)	0.0078(3)	0.0098(3)	0.0080(3)
O(2)	8*f*	0.35922(9)	0.6377(1)	0.4362(1)	0.0117(3)	0.0171(4)	0.0144(4)	–0.0069(3)	0.0079(3)	–0.0071(3)
O(3)	8*f*	0.26956(9)	0.5775(1)	0.1527(1)	0.0156(4)	0.0141(3)	0.0094(3)	0.0000(3)	0.0050(3)	0.0051(3)
O(4)	8*f*	0.20177(8)	0.4180(1)	0.3217(1)	0.0080(3)	0.0102(3)	0.0109(3)	–0.0018(2)	0.0048(3)	0.0016(3)
O(5)	8*f*	0.04750(8)	0.2592(1)	0.4177(1)	0.0091(3)	0.0118(3)	0.0089(3)	0.0001(2)	0.0056(3)	0.0013(2)
O(6)	8*f*	0.03665(9)	0.6213(1)	0.4084(1)	0.0174(4)	0.0098(3)	0.0134(4)	0.0011(3)	0.0084(3)	–0.0035(3)

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