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Sodium Nickel Polyphosphate

FATIMA ERRAGH,[a,b] ALI BOUKHARI,[b] ABDERAHIM SADEL[a] AND ELIZABETH M. HOLT[c]

[a]*Laboratoire de Physico-chimie des Materiaux, Département de Chimie, Faculté des Sciences, Université Chouaib Doukkali, BP 20, El Jadida, Morocco,* [b]*Laboratoire de Chimie de Solide Appliqué, Laboratoire Associé Francophone n° 501, Faculté des Sciences de Rabat, Université Mohammed V, Avenue Ibn Batouta, Rabat, Morocco, and* [c]*Department of Chemistry, Oklahoma State University, Stillwater, Oklahoma 74078, USA. E-mail: chememh@mvs.okstate.edu*

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Abstract

Sodium nickel tris(phosphate), $NaNi(PO_3)_3$, has been shown to be isotypic with $AgM(PO_3)_3$ (M = Zn, Co, Ni or Mg), but not with other known compounds of the form $A^IB^{II}(PO_3)_3$ (A = Li, Na or K; B is a divalent cation). Na^+ and Ni^{2+} ions alternate in forming columns, and are bridged in pairs by three O atoms [Na···Ni 3.190 (2) Å].

Comment

Polyphosphate compounds containing alkali metals (A = Li, Na or K) and divalent cations (B) may be found in one of three stoichiometries, *i.e.* $A^IB^{II}(PO_3)_3$, $A^I_2B^{II}(PO_3)_4$ or $A^IB^{II}_2(PO_3)_5$. Most known compounds are of the first type, however, examples of the second class are well documented and there are crystallographic studies of compounds of the third type (Durif, 1995).

In a few cases, more than one form has been observed for the same combination of A and B: $LiPb(PO_3)_3$ (Guitel & Brunel-Laugt, 1977) and $LiPb_2(PO_3)_5$ (El-Horr & Bagieu-Beucher, 1986); $NaMg(PO_3)_3$ (Shepelev *et al.*, 1983) and $Na_2Mg(PO_3)_4$ (Thonnérieux *et al.*, 1968); $KCo(PO_3)_3$ (Durif *et al.*, 1966) and $K_2Co(PO_3)_4$ (Thonnérieux *et al.*, 1968; Laugt *et al.*, 1974).

Many compounds of type $A^IB^{II}(PO_3)_3$ are isotypic with $LiPb(PO_3)_3$, in which columns of alternating Li and Pb atoms are bridged successively by two and three O atoms, and there are additional O atoms bridging Pb atoms of adjacent columns.

We have prepared crystals of $NaNi(PO_3)_3$ as a result of an attempt to synthesize $NaNi_2P_3O_{10}$ and we find them to be of stoichiometry $A^IB^{II}(PO_3)_3$, but not to be isotypic with $LiPb(PO_3)_3$.

The structure of $NaNi(PO_3)_3$ is, however, isotypic with compounds of the series $AgM(PO_3)_3$ (M = Zn, Co, Ni or Mg; Averbuch-Pouchot & Durif, 1983), with Ni in the M site and sodium replacing silver.

In $NaNi(PO_3)_3$, columns of alternating and pseudo-octahedral Na^+ and Ni^{2+} ions [N···Ni 3.190 (2) Å] show three bridging O atoms between each adjacent pair of atoms [average Na—O 2.467 (2), Ni1—O 2.043 (2) and Ni2—O 2.054 (2) Å]. Columns are widely separated with no intercolumn bridging O atoms and lie on the 210 and $\overline{2}10$ planes.

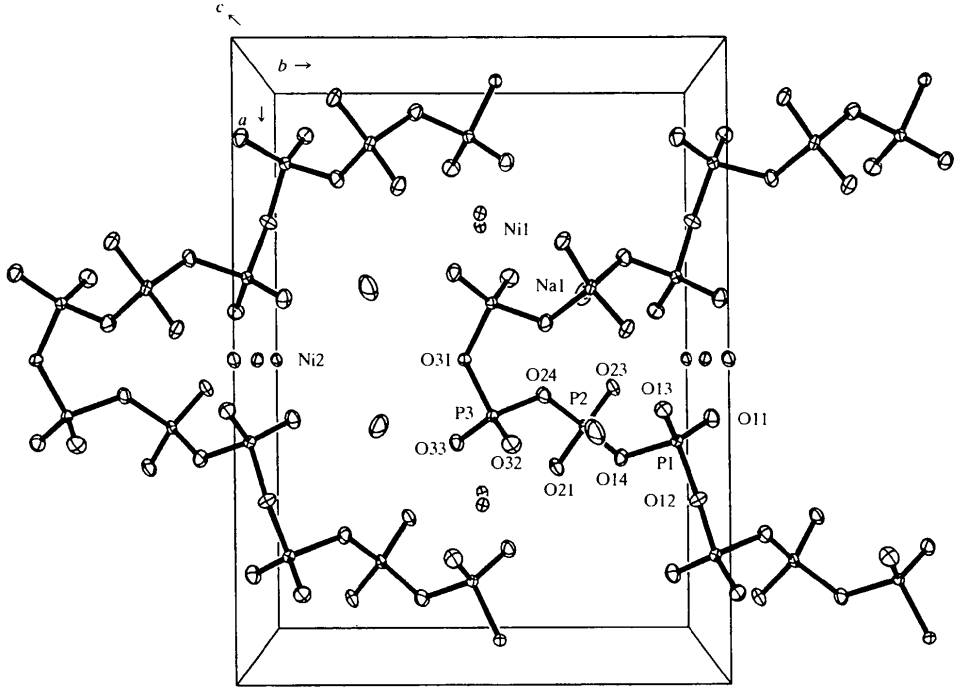

Fig. 1. Projection view of $NaNi(PO_3)_3$. Displacement ellipsoids are drawn at the 50% probability level.

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The polyphosphate chain is observed with a wide 'zigzag' conformation and six PO_3 units between turns. Atoms O12 and O31 lie on twofold axes, one at the turn of the chain and the other in the middle of the section between turns. Phosphorous–oxygen bond angles and distances are normal.

There is no other sodium nickel polyphosphate compound reported in the literature.

Experimental

The slow cooling (6 K h^{-1}) of a mixture of $NaCO_3$, NiO and $(NH_4)_2HPO_4$ in an excess of P_2O_5 heated to fusion led to the formation of yellow–green crystals corresponding to $NaNi(PO_3)_3$ and yellow forms which were shown to be σ-$Ni_2P_2O_7$.

Crystal data

$NaNi(PO_3)_3$	Mo $K\alpha$ radiation
M_r = 318.6	λ = 0.71073 Å
Orthorhombic	Cell parameters from 38 reflections
Pcca	θ = 6.40–12.49°
a = 13.734 (2) Å	μ = 3.489 mm^{-1}
b = 10.543 (2) Å	T = 298 K
c = 9.830 (2) Å	Chunk
V = 1423.5 (4) $Å^3$	0.2 × 0.2 × 0.1 mm
Z = 8	Yellow–green
D_x = 2.973 Mg m^{-3}	
D_m not measured	

Data collection

Syntex *P*4 four-circle diffractometer	1750 reflections with $F > 4\sigma(F)$
$\theta/2\theta$ scans	R_{int} = 0.028
Absorption correction: ψ scan (*XEMP*; Sheldrick, 1990)	θ_{max} = 30°
	$h = -19 \rightarrow 1$
T_{min} = 0.33, T_{max} = 0.45	$k = -14 \rightarrow 1$
2696 measured reflections	$l = -1 \rightarrow 13$
2082 independent reflections	3 standard reflections every 97 reflections intensity decay: none%

Refinement

Refinement on F	$\Delta\rho_{max}$ = 0.67 e $Å^{-3}$
R = 0.030	$\Delta\rho_{min}$ = −0.77 e $Å^{-3}$
wR = 0.043	Extinction correction: *SHELXS*86
S = 1.06	Extinction coefficient: 0.00099 (9)
1750 reflections	Scattering factors from *International Tables for Crystallography* (Vol. C)
133 parameters	
$w = 1/[\sigma^2(F) + 0.0008F^2]$	
$(\Delta/\sigma)_{max}$ = 0.06	

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	1/4	1/2	0.0285 (1)	0.009 (1)
Ni2	1/2	0	0	0.009 (1)
Na1	0.3755 (1)	0.7517 (1)	−0.0129 (1)	0.025 (1)
P1	0.6478 (1)	0.9554 (1)	0.2370 (1)	0.009 (1)
O11	0.6085 (1)	1.0481 (2)	0.1383 (2)	0.014 (1)
O12	3/4	1	0.2949 (3)	0.012 (1)
O13	0.5893 (1)	0.9167 (2)	0.3563 (2)	0.013 (1)
O14	0.6800 (1)	0.8300 (2)	0.1578 (2)	0.013 (1)
P2	0.6254 (1)	0.7476 (1)	0.0460 (1)	0.009 (1)
O21	0.7027 (1)	0.6822 (2)	−0.0310 (2)	0.013 (1)
O23	0.5526 (1)	0.8234 (2)	−0.0285 (2)	0.013 (1)
O24	0.5651 (1)	0.6479 (2)	0.1329 (2)	0.013 (1)
P3	0.6016 (1)	0.5255 (1)	0.2146 (1)	0.009 (1)
O31	1/2	0.4616 (2)	1/4	0.012 (1)
O32	0.6499 (1)	0.5682 (2)	0.3400 (2)	0.016 (1)
O33	0.6529 (1)	0.4390 (2)	0.1204 (2)	0.013 (1)

Table 2. *Selected bond distances (Å)*

Ni1—O21^{i}	2.028 (2)	Ni2—O13^{vii}	2.067 (2)
Ni1—O21^{ii}	2.028 (2)	Ni2—O23^{v}	2.016 (2)
Ni1—O32^{iii}	2.019 (2)	Ni2—O23^{i}	2.016 (2)
Ni1—O32^{iv}	2.019 (2)	Na1—O23	2.552 (2)
Ni1—O33^{i}	2.083 (2)	Na1—O11^{viii}	2.454 (2)
Ni1—O33^{ii}	2.083 (2)	Na1—O13^{iii}	2.373 (2)
Ni2—O11^{v}	2.080 (2)	Na1—O21^{ii}	2.520 (2)
Ni2—O11^{i}	2.080 (2)	Na1—O32^{iii}	2.599 (2)
Ni2—O13^{vi}	2.067 (2)	Na1—O33^{i}	2.304 (2)

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

A variable scan rate was used, with a $\theta/2\theta$ scan mode and a scan width of 0.6° below $K\alpha_1$ and 0.6° above $K\alpha_2$ to a maximum 2θ value of 60°. Refinement was completed using full-matrix least-squares methods.

Data collection: *XSCANS* (Siemens, 1991). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXS*86. Molecular graphics: *XP* (Siemens, 1990). Software used to prepare material for publication: *SHELXS*86.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1195). Services for accessing these data are described at the back of the journal.

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