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A Mixed Zinc–Nickel *cyclo*-Tetraphosphate, ZnNiP₄O₁₂

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Abstract

Zinc nickel *cyclo*-tetraphosphate is composed of cyclic [P₄O₁₂] groups forming sheets parallel to the crystallographic (100) plane. These sheets are separated by zigzag chains of alternating NiO₆ or ZnO₆ octahedra that share a common edge, the cations being statistically disordered. The chains are extended along the *c*

axis and link two consecutive sheets, thus ensuring the cohesion of the structure.

Comment

The structures of the tetrametaphosphates of bivalent ions, M₂P₄O₁₂ (M = Mg, Mn, Fe, Co, Ni, Zn and Cd), are well known (Beucher & Grenier, 1968; Shchegrov *et al.*, 1989; Nord, 1982; Nord *et al.*, 1990; Averbuch-Pouchot & Durif, 1983). They crystallize in the monoclinic system with the same space group, C2/c. However, only the structures of Cu₂P₄O₁₂ and Mg₂P₄O₁₂ are based on single-crystal measurements (Nord & Lindberg, 1975*a,b*; Läggt *et al.*, 1972; Genkina *et al.*, 1985). In these structures, the metal ions occupy two octahedral sites with different symmetries: 1̄ for M^I and 2 for M^{II}. Moreover, the M^IO₆ site is generally slightly smaller than the M^{II}O₆ site. The frameworks of all the M₂P₄O₁₂ structures show a succession of planes formed by the cyclic P₄O₁₂ groups, linked by chains of alternating edge-sharing M^IO₆ and M^{II}O₆ octahedra.

The magnetic study of the phosphates M₂P₄O₁₂ (M = Mn, Co, Ni and Cu) reveals the existence of chains of paramagnetic ions that confer monodimensional magnetic behaviour (Gunsser *et al.*, 1989). Exceptionally, Cd₂P₄O₁₂ presents a high-pressure phase in which the structure is composed of long chains of polyphosphates instead of P₄O₁₂ *cyclo*-tetraphosphates (Averbuch-Pouchot & Durif, 1983).

Unlike the aforementioned monometallic phosphates, the tetrametaphosphates of mixed bivalent ions have been scarcely studied. NiCoP₄O₁₂ and NiZnP₄O₁₂ have been studied by neutron powder diffraction (Nord, 1983). They belong to the same family as the monometallic phosphates M₂P₄O₁₂, with monoclinic symmetry C2/c. They show two mixed cationic sites, M^IO₆ and M^{II}O₆, unequally occupied. The smaller ions, Ni²⁺, prefer to lodge in the M^I sites, while the Zn²⁺ or Co²⁺ ions have a tendency to occupy the larger M^{II} sites. We must point out that the NiCoP₄O₁₂ and NiZnP₄O₁₂ samples prepared by Nord (1983) were quenched in liquid nitrogen. Consequently, the Zn²⁺, Co²⁺ and Ni²⁺ ions are partially disordered over both kinds of sites. We thus thought it useful to prepare single crystals of the mixed tetrametaphosphate NiZnP₄O₁₂ in order to establish whether a cationic structural order was achieved.

During the crystal structure solution and refinement it was not possible to distinguish the Zn²⁺ and Ni²⁺ cations and mixed-atom sites were therefore considered with *x*Zn + *y*Ni on site I, denoted M^I, and ($\frac{1}{2} - x$)Zn + ($\frac{1}{2} - y$)Ni on site II, denoted M^{II}, where $x + y = \frac{1}{2}$. Best refinement results were obtained for $x = y = \frac{1}{4}$, indicating that the Zn²⁺ and Ni²⁺ cations are fully disordered on the M^I and M^{II} sites. This partition can be related to the thermodynamic conditions necessary for the preparation of the single crystals, which were obtained by a slow decrease of the temperature, allowing

a total equilibrium partition between the two cations. In contrast, the powder material prepared by Nord (1983) was obtained by a rapid annealing in liquid nitrogen, leading to a different occupation of the M^I and M^{II} sites (70/30 for Zn²⁺ and 30/70 for Ni²⁺).

Sheets of [P₄O₁₂]⁴⁻ *cyclo-tetraphosphate* groups lie parallel to the crystallographic (010) plane and are separated by zigzag chains of NiO₆ or ZnO₆ octahedra (Fig. 1). These octahedra share a common edge formed by the O3 and O5 atoms and the chains are extended along the *c* axis. A zigzag chain of alternating Zn/NiO₆ octahedra is shown in Fig. 2.

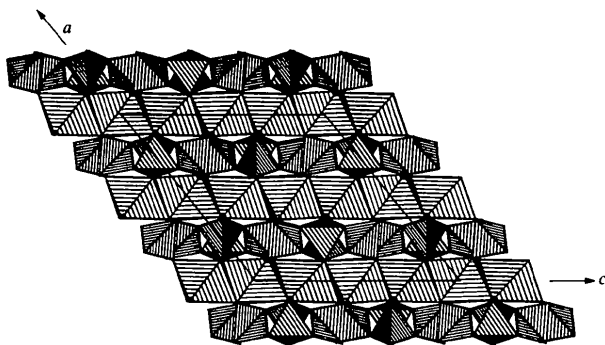


Fig. 1. Projection of the structure on the (010) plane.

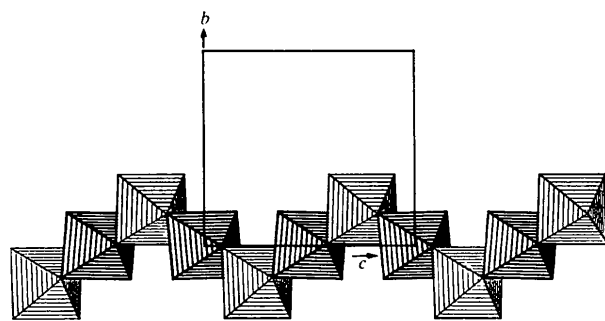


Fig. 2. View of a zigzag chain of NiO₆ or ZnO₆ octahedra projected on the (100) plane.

The centrosymmetric [P₄O₁₂]⁴⁻ *cyclo-tetraphosphate* entity is illustrated in Fig. 3. The P—O distances range from 1.457 (2) to 1.509 (2) Å for the terminal bonds and from 1.585 (2) to 1.592 (2) Å for the O—P—O bridges. These values agree with those given in the literature (Cruickshank, 1972), where the bridge bonds are always longer than the terminal bonds. The P1—O4—P2 and P1—O6—P2 angles are 138.78 (8) and 134.6 (1)°, respectively; they are close to those found in Mg₂P₄O₁₂. The O—P1—O angles vary between

105.0 (1) and 118.1 (1)°, and the O—P2—O angles vary between 101.2 (1) and 119.62 (9)°, indicating that both tetrahedra are distorted.

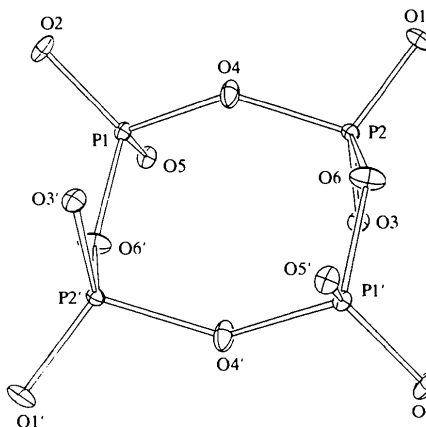


Fig. 3. An ORTEPII (Johnson, 1976) drawing of the [P₄O₁₂]⁴⁻ entity. Displacement ellipsoids are shown at the 50% probability level.

Experimental

Crystals were prepared from NiO, ZnO and (NH₄)₂HPO₄ in suitable proportions heated progressively to 773 K. After decomposition of the phosphate and elimination of water and ammonia, the mixture was melted at 1273 K for 2 h. It was then cooled to 873 K at a rate of 2 K h⁻¹ and then to 573 K at a rate of 10 K h⁻¹. Below this temperature the furnace was turned off.

Crystal data

ZnNiP₄O₁₂
M_r = 439.97
 Monoclinic
*C*2/*c*
a = 11.636 (2) Å
b = 8.232 (1) Å
c = 11.086 (2) Å
 β = 128.71 (1)°
V = 828.7 (5) Å³
Z = 4
D_x = 3.53 Mg m⁻³
D_m not measured

Mo *K*α radiation
 λ = 0.71073 Å
 Cell parameters from 25 reflections
 θ = 9–20°
 μ = 6.087 mm⁻¹
T = 294 K
 Spherical
 0.2 × 0.2 × 0.2 mm
 Yellow

Data collection

Enraf–Nonius CAD-4 diffractometer
 $\theta/2\theta$ scans
 Absorption correction: empirical, ψ scans (Enraf–Nonius, 1989)
 T_{\min} = 0.232, T_{\max} = 0.296
 3984 measured reflections
 2554 independent reflections

1856 reflections with $I > 3\sigma(I)$
 R_{int} = 0.048
 θ_{max} = 40°
 h = -20 → 16
 k = 0 → 14
 l = 0 → 20
 2 standard reflections
 frequency: 120 min
 intensity decay: 1.41%

Refinement

Refinement on F
 $R = 0.031$
 $wR = 0.041$
 $S = 1.227$
 1856 reflections
 85 parameters
 $w = 4F_o^2/[\sigma^2(F_o^2) + 0.0016F_o^4]$
 $(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.851 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.581 \text{ e } \text{\AA}^{-3}$
 Extinction correction:
 isotropic (Zachariasen, 1963)
 Extinction coefficient:
 $8.9(1) \times 10^{-7}$
 Scattering factors from
International Tables for Crystallography (Vol. C)

Table 1. Selected geometric parameters (\AA , $^\circ$)

M^I-O1	1.998 (1)	$P1-O4$	1.589 (2)
M^I-O3^I	2.134 (1)	$P1-O5$	1.502 (2)
M^I-O5^{II}	2.103 (1)	$P1-O6^V$	1.588 (2)
$M^{II}-O2^{III}$	2.000 (1)	$P2-O1$	1.457 (2)
$M^{II}-O3^{IV}$	2.079 (1)	$P2-O3$	1.509 (1)
$M^{II}-O5^{IV}$	2.070 (1)	$P2-O4$	1.592 (2)
$P1-O2$	1.459 (1)	$P2-O6$	1.585 (2)
$O1-M^I-O3^{VI}$	176.40 (8)	$O3^{IV}-M^{II}-O3^{VI}$	180
$O1^{VII}-M^I-O3^I$	176.40 (7)	$O5^{IV}-M^{II}-O5^{VI}$	180
$O5^{II}-M^I-O5^{IV}$	166.37 (7)	$P1-O4-P2$	138.78 (8)
$O2^{III}-M^{II}-O2^{VIII}$	180	$P1^V-O6-P2$	134.57 (12)

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

Refinements with distinct Zn and Ni sites gave worse results in terms of R values, residual electron density and S .

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *BEGIN in SDP* (Frenz, 1985). Program(s) used to solve structure: Patterson and Fourier methods (*MolEN*; Fair, 1990). Program(s) used to refine structure: *LSFM in SDP*. Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *CIF VAX in MolEN*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1265). Services for accessing these data are described at the back of the journal.

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End Member of the Rhodium-Based Quaternary Borocarbides, $\text{ErRh}_2\text{B}_2\text{C}$

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Abstract

Erbium dirhodium diboron carbide, the end member of the rhodium-based quaternary borocarbides, was synthesized by the flux method. Structure analyses revealed that the compound crystallizes as a derivative structure of the ThCr_2Si_2 type, which can be viewed as a layered structure of tetrahedrally coordinated Rh_2B_2 thick layers and ErC NaCl -type layers. A comparison of the structural parameters of the $\text{RRh}_2\text{B}_2\text{C}$ (R is a rare earth metal) compounds showed that the atomic distance between transition metal atoms contracts significantly with decreasing rare earth size, resulting in increasing instability of compounds with smaller R .

Comment

A series of newly discovered quaternary borocarbides $\text{RT}_2\text{B}_2\text{C}$ (R is a rare earth and T is a transition metal) are reported to crystallize in a modified ThCr_2Si_2 -type structure (Ban & Sikirica, 1965) by an insertion of a C atom in the rare earth layer. The ThCr_2Si_2 -type structure seems to selectively accept rare earth atoms depending on the type of transition metals in the structure. For $T = \text{Ni}$, all lanthanides ranging from the large lanthanum down to the small lutetium ion are reported to form $\text{RNi}_2\text{B}_2\text{C}$ compounds (Siegrist, Cava *et al.*, 1994). For larger transition metals such as Rh, Ir, Pd and Pt, however, only larger lanthanides are found to form the stable $\text{RT}_2\text{B}_2\text{C}$ phase. No quaternary compound has