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Structure of $Na_2MZr(P_2O_7)_2$ (M = Ni and Co)

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Abstract. $Na_2NiZr(P_2O_7)_2$, M_r = 543·8, triclinic, $P1$, a = 6·461 (3), b = 7·257 (4), c = 6·501 (3) Å, α = 123·24 (1), β = 91·95 (1), γ = 93·79 (1)°, V = 253·5 (1) Å^3, Z = 1, D_x = 3·564 g cm^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, μ = 34·41 cm^{-1}, $F(000)$ = 262, T = 293 K, R = 0·041 for 1121 independent observed reflexions. $Na_2CoZr(P_2O_7)_2$, M_r = 544·0, triclinic, $P1$, a = 6·535 (3), b = 7·266 (4), c = 6·496 (3) Å, α = 122·96 (2), β = 92·28 (2), γ = 93·75 (2)°, V = 257·2 (1) Å^3, Z = 1, D_x = 3·512 g cm^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, μ = 31·77 cm^{-1}, $F(000)$ = 261, T = 293 K, R = 0·046 for 1244 independent observed reflexions. In both structures the Zr atom is surrounded by a distorted octahedron of pyrophosphate O atoms so that a framework of ZrO_6 octahedra is formed. The MO_6 (M = Ni,Co) octahedra are edge bridged to the ZrO_6 octahedra. The two independent Na^+ ions, which are responsible for the unusual electrical conductivity of the solids, are located in irregular cavities formed by O atoms.

Introduction. Crystals of the title compounds were synthesized and grown by the hydrothermal method in a Morey-type autoclave at 473 to 573 K and 1 to 10 GPa. The starting materials were oxides of the transition metals, orthophosphoric acid and 2·5M NaOH solution which acts as a mineralizer. Details of the synthesis will be published elsewhere.

The crystals are interesting as ionic conductors: powdered samples pressed into pellets gave conductivities of 5×10^{-4} to $2{\cdot}2 \times 10^{-1}\,\Omega^{-1}\,cm^{-1}$ and activation-energy values of 0·27 to 0·62 eV at 1 kHz and 298–673 K.

As in other ionic conductors (see, for example, Goodenough, Hong & Kafalas, 1976; Subramanian, Rudolf & Clearfield, 1985; Kohler & Schulz, 1985), conductivity is attributed to diffusion of Na^+ through a network of tunnels in a rigid structure made of pyrophosphate anions sharing corners with ZrO_6/MO_6 octahedra.

Experimental. Both crystals displayed the forms (010), $(0\bar{1}0)$, $(01\bar{1})$, $(0\bar{1}1)$, $(1\bar{1}1)$ and $(\bar{1}1\bar{1})$. Distances between parallel faces 0·15, 0·20, 0·25 and 0·15, 0·25, 0·20 mm respectively. Philips 1100 diffractometer, graphite monochromator. Cell dimensions from setting angles of 18 reflexions with $6 < \theta < 14°$ for M = Ni and from 22 reflexions with $4 < \theta < 12°$ for M = Co. Intensities from $\omega/2\theta$ scans at a rate 0·03° s^{-1}, width 0·9° in θ. 1223 and 1297 intensities with $2 < \theta < 25°$ collected, of which 102 and 53 were considered unobserved under the condition $I < 5\sigma(I)$. For both complexes $-9 \le h \le 9$, $0 \le k \le 10$, $0 \le l \le 9$. Standard reflexions, $2\bar{1}1$, $0\bar{2}2$ and $0\bar{3}2$, every 2 h, no variation. Structure was solved by direct methods using the *MULTAN*80 system of programs (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). E maps generated with 276 independent structure factors gave all but a few O atoms which were located by difference Fourier synthesis.

Refinements were carried out by the program *SHELX*76 (Sheldrick, 1976). Scattering factors for neutral atoms and f', f'' from *International Tables for X-ray Crystallography* (1974). O atoms were refined isotropically, and the remainder anisotropically. Final R values: R = 0·041 (wR = 0·047) and R = 0·046 (wR = 0·051) respectively. For the enantiomers the final values were R = 0·051 (wR = 0·056) and R = 0·056 (wR = 0·065). The function minimized was $\sum w||F_o| - |F_c||^2$ where $w^{-1} = \sigma^2(F_o) + 0{\cdot}03|F_o|$. Max. Δ/σ 0·78 and 0·81. Max. and min. peak height in final difference Fourier synthesis 1·6, 1·7 and −1·2, −1·7 e Å^{-3}. Since the occupancies of the metals refined to very near unity, they were fixed at this value in the final calculations. Final atomic coordinates and B_{eq} are reported in Table 1.*

Discussion. The cobalt and nickel complexes are isostructural and the discussion will focus on the nickel complex. The atomic arrangement of $Na_2NiZr(P_2O_7)_2$ projected along the c axis is shown in Fig. 1. Distorted O_6 octahedra about Zr and Ni

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52029 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Atomic coordinates and* B_{eq}

$B_{eq} = (8\pi^2/3)(U_{11} + U_{22} + U_{33})$ for the orthogonalized U_{ij} tensor.

	x	y	z	B_{eq}(Å^2)
$Na_2NiZr(P_2O_7)_2$				
Zr	0·0	0·0	0·0	1·6 (1)
Ni	0·7147 (2)	0·2169 (2)	0·7899 (2)	0·39 (9)
P(1)	0·500 (1)	−0·113 (1)	−0·083 (1)	0·55 (7)
P(2)	0·7388 (9)	0·7425 (9)	0·197 (1)	0·28 (7)
P(3)	−0·024 (1)	0·470 (1)	0·593 (1)	0·5 (1)
P(4)	0·217 (1)	0·325 (1)	0·866 (1)	0·42 (7)
O(1)	0·022 (2)	0·153 (2)	−0·207 (2)	0·3 (2)
O(2)	−0·057 (2)	−0·156 (2)	0·180 (2)	0·4 (2)
O(3)	−0·319 (2)	0·051 (2)	−0·035 (2)	0·4 (2)
O(4)	0·324 (2)	0·010 (2)	0·060 (2)	0·8 (2)
O(5)	−0·025 (2)	−0·298 (2)	−0·348 (2)	0·6 (2)
O(6)	0·059 (2)	0·331 (2)	0·333 (2)	0·1 (2)
O(7)	0·445 (2)	−0·261 (2)	−0·356 (3)	0·6 (2)
O(8)	0·563 (2)	−0·261 (2)	0·012 (2)	0·6 (2)
O(9)	0·747 (2)	0·508 (2)	0·116 (2)	0·6 (2)
O(10)	0·649 (3)	0·895 (3)	0·447 (3)	1·5 (3)
O(11)	0·148 (2)	0·490 (2)	0·786 (2)	0·6 (2)
O(12)	0·784 (2)	0·342 (2)	0·588 (2)	0·5 (2)
O(13)	0·262 (2)	0·488 (2)	0·150 (3)	0·6 (2)
O(14)	0·403 (2)	0·221 (2)	0·730 (2)	0·5 (2)
Na(1)	0·225 (2)	0·861 (2)	0·398 (3)	4·9 (7)
Na(2)	0·516 (2)	0·371 (2)	0·350 (2)	1·8 (3)
$Na_2CoZr(P_2O_7)_2$				
Zr	0·0	0·0	0·0	1·6 (1)
Co	0·7088 (2)	0·2209 (2)	0·7854 (2)	0·32 (8)
P(1)	0·5005 (8)	−0·1104 (8)	−0·0823 (9)	0·21 (4)
P(2)	0·7305 (8)	0·7492 (8)	0·2000 (9)	0·21 (6)
P(3)	−0·0279 (8)	0·4772 (9)	0·5921 (9)	0·34 (6)
P(4)	0·2142 (8)	0·3299 (8)	0·8637 (9)	0·25 (5)
O(1)	0·028 (2)	0·159 (2)	−0·201 (2)	0·3 (2)
O(2)	−0·067 (2)	−0·147 (2)	0·184 (2)	0·3 (2)
O(3)	−0·317 (2)	0·052 (2)	−0·036 (2)	0·3 (2)
O(4)	0·323 (2)	0·005 (2)	0·072 (2)	0·5 (2)
O(5)	−0·033 (2)	−0·292 (2)	−0·346 (2)	0·7 (2)
O(6)	0·057 (2)	0·328 (2)	0·330 (2)	0·4 (2)
O(7)	0·447 (2)	−0·265 (2)	−0·366 (2)	0·4 (2)
O(8)	0·560 (2)	−0·265 (2)	0·007 (2)	0·1 (2)
O(9)	0·739 (2)	0·517 (2)	0·126 (2)	0·4 (2)
O(10)	0·636 (2)	0·888 (2)	0·442 (2)	0·6 (2)
O(11)	0·136 (2)	0·495 (2)	0·794 (2)	0·8 (3)
O(12)	0·780 (2)	0·350 (2)	0·582 (2)	0·5 (2)
O(13)	0·270 (2)	0·479 (2)	0·137 (2)	0·5 (2)
O(14)	0·394 (2)	0·221 (2)	0·733 (2)	0.7 (2)
Na(1)	0·223 (2)	0·868 (1)	0·399 (2)	3·8 (5)
Na(2)	0·510 (2)	0·377 (2)	0·354 (2)	2·1 (3)

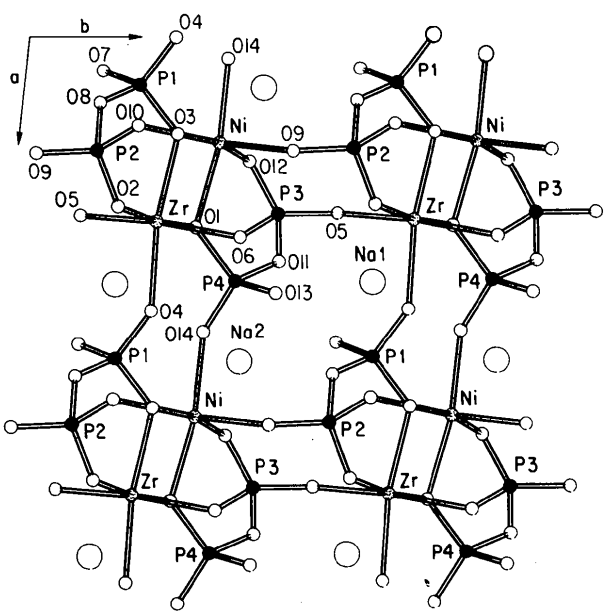

Fig. 1. Projection of the atomic arrangement of $Na_2NiZr(P_2O_7)_2$ along the c axis.

Table 2. *Main interatomic distances* (Å) *and bond angles* (°) *of* $Na_2NiZr(P_2O_7)_2$

Zr octahedron

Zr	O(1)	O(2)	O(3)	O(4)	O(5)	O(6)
O(1)	2·17 (1)	173·3 (5)	79·1 (4)	94·8 (5)	84·5 (4)	87·4 (4)
O(2)	4·21 (3)	2·05 (1)	94·8 (4)	91·6 (5)	93·3 (5)	95·3 (4)
O(3)	2·74 (2)	3·09 (2)	2·14 (1)	169·9 (5)	92·7 (4)	90·8 (4)
O(4)	3·14 (2)	2·98 (2)	4·22 (3)	2·10 (1)	94·7 (5)	80·8 (5)
O(5)	2·87 (2)	3·74 (3)	3·07 (2)	3·09 (2)	2·09 (1)	170·4 (5)
O(6)	3·00 (2)	3.12 (2)	3·07 (2)	2·78 (2)	4·25 (3)	2·17 (1)

Ni octahedron

Ni	O(1)	O(3)	O(9)	O(10)	O(12)	O(14)
O(1)	2·07 (1)	82·9 (4)	95·8 (5)	88·8 (5)	88·8 (4)	169·3 (5)
O(3)	2·74 (2)	2·07 (1)	90·6 (5)	86·7 (5)	170·0 (4)	95·5 (5)
O(9)	3·02 (2)	2·89 (2)	2·00 (1)	174·1 (6)	85·8 (5)	94·8 (5)
O(10)	2·97 (2)	2·90 (2)	4·17 (3)	2·17 (2)	87·9 (5)	80·5 (5)
O(12)	2·86 (2)	4·07 (3)	2·73 (2)	2·91 (2)	2·01 (1)	91·6 (5)
O(14)	4·09 (3)	3·04 (2)	2·97 (2)	2·72 (2)	2·90 (2)	2·04 (1)

P_2O_7 anions

P(1)	O(3)	O(4)	O(7)	O(8)
O(3)	1·51 (1)	109·4 (8)	108·5 (8)	109·7 (8)
O(4)	2·45 (2)	1·50 (1)	113·7 (9)	107·4 (8)
O(7)	2·44 (2)	2·52 (2)	1·50 (1)	108·0 (8)
O(8)	2·52 (2)	2·48 (2)	2·49 (2)	1·58 (1)

P(2)	O(2)	O(8)	O(9)	O(10)
O(2)	1·51 (1)	109·2 (7)	112·3 (7)	111·8 (8)
O(8)	2·54 (2)	1·61 (1)	105·9 (8)	100·4 (8)
O(9)	2·49 (2)	2·47 (2)	1·49 (1)	116·1 (8)
O(10)	2·53 (2)	2·42 (2)	2·57 (2)	1·54 (2)

P(1)—P(2) 2·983 (8) P(1)—O(8)—P(2) 139 (1)

P(3)	O(5)	O(6)	O(11)	O(12)
O(5)	1·51 (1)	106·0 (7)	104·8 (8)	122·1 (8)
O(6)	2·45 (2)	1·56 (1)	107·2 (7)	106·7 (7)
O(11)	2·45 (2)	2·53 (2)	1·59 (2)	109·2 (7)
O(12)	2·62 (2)	2·44 (2)	2·51 (2)	1·49 (1)

P(4)	O(1)	O(11)	O(13)	O(14)
O(1)	1·57 (1)	105·7 (8)	112·5 (7)	113·4 (7)
O(11)	2·55 (2)	1·62 (1)	101·5 (8)	107·4 (8)
O(13)	2·60 (2)	2·46 (2)	1·55 (1)	115·0 (8)
O(14)	2·57 (2)	2·52 (2)	2·58 (2)	1·50 (1)

P(3)—P(4) 2·960 (8) P(3)—O(11)—P(4) 135 (1)

Na polyhedra (distances shorter than 3 Å)

Na(1)		Na(2)	
O(1)	2·73 (2)	O(3)	2·64 (1)
O(2)	2·22 (2)	O(4)	2·44 (2)
O(4)	3·00 (2)	O(6)	2·94 (2)
O(5)	2·95 (2)	O(7)	2·37 (2)
O(7)	2·63 (2)	O(9)	2·67 (2)
O(10)	2·73 (2)	O(12)	2·38 (2)
O(13)	2·31 (2)	O(13)	2·51 (2)
O(14)	2·46 (2)		
Mean	2·628	Mean	2·564

share an edge [O(1)–O(3)] forming isolated groups oriented roughly along [$1\bar{1}1$]. These groups are linked together by the two pyrophosphate anions. One anion connects two Zr octahedra in the direction [100] through P(1), and two Ni octahedra in the direction [010] through P(2). The other links Zr octahedra in the direction [011] and Zr–Ni octahedra in the direction [100].

Table 2 reports the main interatomic distances and bond angles for the nickel compound. The two independent pyrophosphate anions show the expected features, with average P—O bonds 1·530 and 1·549 Å, and P—O—P angles 139–135°. The average Zr—O distance is slightly longer than that encountered in similar compounds (Rudolf, Subramanian, Clearfield & Jorgensen, 1985; de la Rochère, Kahn, d'Yvoire & Bretey, 1985), on account of our unit occupancy factor.

The Na^+ ions lie in cavities with coordination numbers that depend on the interatomic distances considered [*i.e.* CN = 8 for Na(1)—O distances less than 3 Å]. O(7) and O(13) play a particular role in the structure since they coordinate only Na atoms, and thus participate in the shorter Na—O distances.

Close examination of the structure shows the most apparent diffusion path of Na^+ to be along the [001] direction. Average Na(1)—O (2·628 Å) and Na(2)—O (2·564 Å) distances are comparable to the values encountered in other ionic sodium conductors.

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Structure of Trigonal Thorium Molybdate

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Abstract. $Th(MoO_4)_2$, $M_r = 551{\cdot}92$, trigonal, $P\bar{3}$, $a = 17{\cdot}593\,(7)$, $c = 6{\cdot}238\,(7)$ Å, $V = 1672{\cdot}2$ Å^3, $Z = 9$, $D_x = 4{\cdot}933$ g cm^{-3}, $\lambda(\text{Mo } K\alpha_1) = 0{\cdot}70930$ Å, $\mu(\text{Mo } K\alpha) = 239{\cdot}2$ cm^{-1}, $F(000) = 2142$, $T = 298$ K. $R = 0{\cdot}024$ and $wR = 0{\cdot}030$ for 990 reflections with $I \geq 3\sigma(I)$. The structure contains MoO_4 tetrahedra which bridge three-dimensionally to both six- and nine-coordinate thorium atoms. The Mo—O distances range from 1·733–1·800 Å. The octahedral Th—O distances are 2·292–2·305 Å, while the nine-coordinate Th—O bond lengths range from 2·416 to 2·488 Å.

Introduction. Recovery of plutonium from spent nuclear fuel solutions may be complicated by the undesired formation of insoluble actinide molybdate residues (Penneman, Haire & Lloyd, 1980; Cremers, Eller, Penneman & Herrick, 1983). In a previous publication we described the structure determination of the orthorhombic (low-temperature) form of thorium(IV) molybdate which contains thorium in square antiprismatic coordination and tetrahedral molybdate ligands (Cremers, Eller & Penneman, 1983). In the present paper we describe the structure of the trigonal high-temperature form of $Th(MoO_4)_2$, which has totally different thorium coordination.

Trigonal $Th(MoO_4)_2$ has been investigated previously by others but there seemed ample reason for a reinvestigation of its structure. On the basis of X-ray diffraction data from layer photographs, Thoret (1974) proposed the space group $P\bar{6}$, and that one of the thorium atoms, located at the origin, was situated in the center of a planar ring of six oxygen atoms. In our view this is an unlikely coordination for thorium. Above and below and parallel to this six-membered ring were equilateral triangles of three O atoms making the total coordination of thorium

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