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The Crystal Structure of $Na_4Ni_7(PO_4)_6$

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$Na_4Ni_7(PO_4)_6$ crystallizes in the space group *Cm* with $a = 10.550(2)$, $b = 13.985(5)$, and $c = 6.398(2)$ Å; $\beta = 104.87(2)°$. For $Z = 2$ the calculated density is 3.906 g/cm³ ($V = 912.4$ Å³). Structure determination and refinement ($R = 0.041$, $R_W = 0.045$) were carried out on flux (NaF) grown crystals. The structure consists of layers of nickel-containing octahedra and phosphorus-containing tetrahedra interconnected to form a pseudocentrosymmetric framework. A layer consisting of parallel tunnels which run along the *a* direction contains the sodium ions in a noncentrosymmetric arrangement. © 1986 Academic Press, Inc.

Introduction

Very little single-crystal structural work has been reported for orthophosphates containing both sodium and nickel. Kolsi (*1*) reported a phase diagram for the Na_3PO_4–$Ni_3(PO_4)_2$ system, claiming identification of the compounds $Na_4Ni(PO_4)_2$, $NaNiPO_4$, $Na_6Ni_6(PO_4)_8$, and $Na_3Ni_9(PO_4)_7$.

The crystal structure of $NaNi_4(PO_4)_3$ has recently been determined by Anderson and co-workers (*2*). It is structurally related to $NaMg_4(PO_4)_3$ (*3*). We have grown single crystals of $Na_4Ni_7(PO_4)_6$ and would like to report the determination and refinement of its structure.

Experimental

Crystals of $Na_4Ni_7(PO_4)_6$ were grown from NaF flux using a method adapted from Wanklyn *et al.* (*4*). A mixture of 9.0 g NiO, 5.8 g NaF, and 6.9 g $NH_4H_2PO_4$ was placed in a crimped platinum crucible and soaked at 1150°C for 1 hr in air in a resistance-heated furnace. The mixture was then cooled slowly (10°C/hr to 600°C). The crystals recovered were irregularly shaped and pleochroic, appearing golden brown when viewed along the *c* direction and medium green when viewed along the *a* or *b* direction.

A crystal ground to an approximately spherical shape (diameter 0.020 cm) was selected for data collection. Systematic extinctions in precession photographs indicated possible space groups *C2/m*, *C2*, or *Cm*.

Lattice parameters were determined in a least-squares refinement using 23 reflections within the angular range $40° < 2\theta < 53°$, each automatically centered on a Picker FACS-I four-circle diffractometer using Mo$K\alpha$ radiation ($\lambda = 0.70930$ Å). At 25°C the lattice parameters were found to be $a = 10.550(2)$, $b = 13.986(5)$, and $c = 6.398(2)$ Å; $\beta = 104.87(2)°$ where the figures in parentheses represent the standard

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deviations in the last reported figure. The calculated volume is 912.4 Å^3, giving a calculated density, with $Z = 2$, of 3.906 g/cm^3.

Diffraction intensities were measured using Zr-filtered Mo$K\alpha$ radiation at a take-off angle of 0.5° with the diffractometer operating in the ω-scan mode. Ten-second background counts were taken at the both ends of a 1.4° scan (1°/min) corrected for dispersion. Of the 3014 independent data investigated in the angular range $2\theta < 60°$, 1268 were considered observable according to the criterion $F_0 > 3.0\sigma$, where σ is defined as $0.2|F_0| + [C + k^2B]^{1/2}/2|F_0|Lp$; the total scan count is C, k is the ratio of scanning time to the total background time, and B is the total background count. Three reflections were systematically monitored; the maximum variation in intensity observed was never greater than ±6% over the data collection period.

Intensity data were corrected for Lorentz and polarization effects, and spherical absorption corrections ($\mu = 78.0$ cm^{-1}, Mo$K\alpha$) were made. The maximum relative absorption correction was less than 2% of $|F_0|$.

The structure was solved by assuming the space group $C2/m$ and the formula $NaNiPO_4$ ($Z = 12$) as input to the direct methods crystallographic program MULTAN (5). Isotropic refinement in $C2/m$ using the positions produced by MULTAN and other positions located by means of Fourier difference maps produced a residual $R = 0.083$ ($R_W = 0.117$). Varying the occupancies of the Na sites reduced the residual to $R = 0.068$ ($R_W = 0.086$) and indicated that the Na positions were only half-occupied. Because the residual was still larger than was consistent with the quality of the data, the space group was changed to Cm, removing the center of symmetry and splitting each of the Na positions in $C2/m$ into two positions. Only one of each set of two Na positions turned out to be occupied, and the residual was reduced to $R = 0.044$ ($R_W = 0.047$).

A full-matrix least-squares refinement (6) in Cm using a $1/\sigma^2$ weighting scheme, zerovalent scattering factors (7) for Na, Ni, P, and O, corrections for secondary extinction and anomalous dispersion, and anisotropic temperature factors for only the Na atoms yielded a residual $R = 0.041$ ($R_W = 0.045$). The data : parameter ratio was 12.7 for 102 independently varied parameters. The maximum extinction correction (8) was 23% of $|F_0|$ for the 001 reflection.[1] An attempt at a full anisotropic refinement resulted in negative temperature factors for some of the P atoms because of high correlations due to the pseudocentrosymmetric nature of the framework. Subsequent isotropic refinement of the unit cell of opposite handedness produced $R = 0.045$ ($R_W = 0.049$).

Results and Discussion

The final atomic coordinates and isotropic (anisotropic for Na) thermal parameters are presented in Table I.

The structure of $Na_4Ni_7(PO_4)_6$ consists of layers composed of Ni octahedra and P tetrahedra lying parallel to the *ab* plane. These layers (hereafter called the "Ni layers") are connected to each other by corner sharing between the P(1) tetrahedron and the Ni(3) octahedron and between the P(2) tetrahedron and the Ni(4) octahedron to form a section of parallel tunnels in which the Na atoms reside. The tunnels run parallel to the *a* direction and have side cavities which

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[1] See NAPS document No. 04359 for 11 pages of supplementary material. Order from ASIS/NAPS % Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, New York 10017. Remit in advance for each NAPS Accession number. Institutions and organizations may use purchase orders when ordering; however, there is a billing charge for this service. Make checks payable to Microfiche Publications. Photocopies are $5.00. Microfiche are $3.00. Outside of the U.S. and Canada, postage is $3.00 for a photocopy or $1.50 for a fiche.

TABLE I

POSITIONAL AND THERMAL PARAMETERS FOR $Na_4Ni_7(PO_4)_6$

Atom	10^4x	10^4y	10^4z	B^a
Ni(1)	0	0	0	0.51(2)
Ni(2)	2(4)	3735(1)	−1(7)	0.73(2)
Ni(3)	3302(4)	6935(1)	1821(7)	0.48(3)
Ni(4)	6710(4)	6874(1)	8187(7)	0.55(3)
P(1)	9073(6)	1919(2)	7162(11)	0.67(7)
P(2)	940(6)	1888(2)	2800(10)	0.30(7)
P(3)	3146(7)	0	437(12)	0.60(8)
P(4)	6927(7)	0	9655(12)	0.48(8)
Na(1)	6133(7)	1237(3)	5356(12)	1.77(10)
Na(2)	7811(10)	5000	5371(15)	2.88(27)
Na(3)	4326(9)	5000	4786(13)	1.61(18)
O(1)	38(11)	2785(8)	2454(18)	0.78(17)
O(2)	0(10)	2811(7)	7445(16)	0.51(16)
O(3)	−79(10)	1081(7)	2044(18)	0.47(16)
O(4)	39(11)	1057(7)	7846(18)	0.60(17)
O(5)	1929(12)	2040(8)	1474(21)	0.84(18)
O(6)	8135(11)	2063(8)	8647(19)	0.52(16)
O(7)	1676(11)	1720(8)	5127(20)	0.83(17)
O(8)	8293(11)	1682(8)	4922(19)	0.73(17)
O(9)	1944(12)	4103(8)	1109(20)	1.21(20)
O(10)	8131(11)	4114(7)	8963(18)	0.41(16)
O(11)	2006(16)	0	1419(27)	0.87(26)
O(12)	7961(15)	0	8438(26)	0.61(23)
O(13)	4493(18)	0	1954(29)	1.10(28)
O(14)	5535(18)	0	7962(29)	0.97(26)

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Na(1)	2.30(21)	1.63(21)	2.18(21)	0.58(16)	0.84(17)	0.83(16)
Na(2)	4.27(44)	3.64(40)	1.69(32)	0	0.78(31)	0
Na(3)	4.14(37)	1.13(25)	0.99(26)	0	0.63(27)	0

Note. Numbers in parentheses are estimated standard deviations in the last significant figures. The B's are defined by the general temperature factor $\exp[-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)$.

[a] Isotropic thermal parameters for the sodium atoms are calculated from the anisotropic B's.

contain Na(1). Na(2) and Na(3) are centrally located on the mirror plane in the tunnels. All of the Na ions have a z coordinate of approximately $\frac{1}{2}$. Figure 1, a view down a tunnel, shows the locations of the Na ions. The framework formed by the interconnected nickel layers is pseudocentrosymmetric; no atom in the framework moved more than 0.06 Å from its position in the centrosymmetric structure when the center of symmetry was removed. The arrangement of Na ions within the framework is noncentrosymmetric.

Figure 2 shows the Ni layer projected onto the ab plane. The layer can be considered to be composed of parallel ribbons containing Ni(1), Ni(2), P(3), and P(4) polyhedra. These ribbons are interconnected by means of pairs of edge-sharing Ni(3) and Ni(4) octahedra. Each Ni(3) octahedra shares an edge with a P(2) tetrahedron, and each Ni(4) shares an edge with a P(1) tetra-

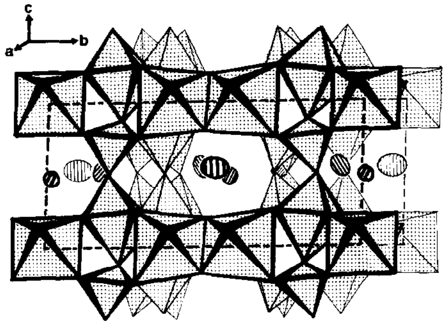

FIG. The unit cell of $Na_4Ni_7(PO_4)_6$ projected onto the *bc* plane and rotated 10° about *c* to clarify the interlayer connections. The heavy dashed line outlines the front of the unit cell; the lighter dashed line outlines the side. The area within the Ni layers behind the front row of octahedra has been left unshaded for clarity, although actually it is filled.

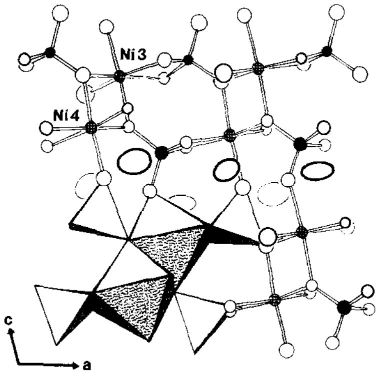

FIG. 3. The sheet of Ni(3) and Ni(4) octahedra and P(1) and P(2) tetrahedra projected onto the *ac* plane and rotated (for clarity) 10° about *a*. The Na ions in the tunnels in front of and behind the sheet are included.

hedron. Corner sharing between the Ni(3) and P(1) polyhedra at O(8) and between the Ni(4) and P(2) polyhedra at O(7) constitutes the only connections between the Ni layers. Figure 3 illustrates a sheet of Ni(3) and Ni(4) octahedra with their connecting P(1) and P(2) tetrahedra projected onto the *ac* plane. The Na ions in the tunnels in front of and behind the sheet are also included.

The most unusual feature of this structure is the unit shown in Fig. 4: a portion of the Ni layer comprising two Ni(2) octahedra and one P(3) and one P(4) tetrahedron. Each of the P tetrahedra shares an edge with each Ni octahedron; the Ni octahedra also share an edge. The P atoms and the shared Ni–Ni octahedral edge lie on the mirror plane.

All Ni ions in $Na_4Ni_7(PO_4)_6$ are octahedrally coordinated; the average Ni–O distance is 2.071 Å. The P atoms are tetrahedrally coordinated with an average P–O distance of 1.539 Å. The phosphate tetrahedra are somewhat distorted, with each P tetrahedron sharing one of its shorter edges with a Ni octahedron. The nickel octahedra, with the exception of Ni(1), are highly distorted; this distortion is due to the exten-

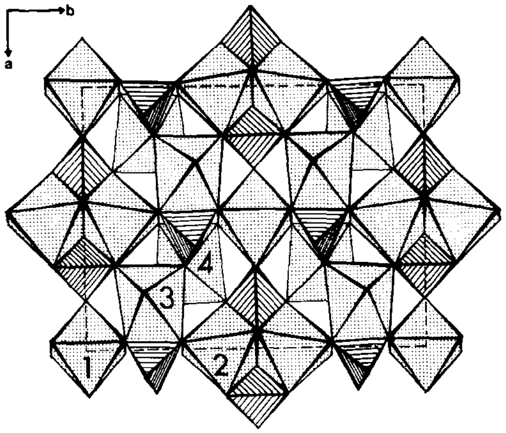

FIG. 2. A Ni layer projected onto the *ab* plane. Each octahedron in the lower left portion is labeled with the number of the Ni atom it contains. The P(1) tetrahedra, which share edges with the Ni(4) octahedra, have been omitted for clarity.

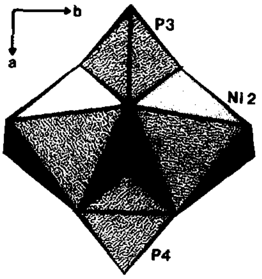

FIG. 4. The Ni(2)–P(3)–P(4) unit projected onto the *ab* plane. P(3) and P(4) lie in the mirror plane.

sive edge sharing with P tetrahedra. Each Ni octahedron except Ni(1) shares its shortest edge (two shortest edges in the case of Ni(2)) with a P tetrahedron; only the Ni(1) octahedron shares only corners and not edges. Tables II and III present the relevant distances and angles for the nickel and phosphorus polyhedra, respectively.

The coordination of the Na ions is ill-defined; Na–O distances are given in Table IV. The coordination can be best summarized in terms of Na–O bond distances. Na(1) has four distances which are short (less than 2.7 Å) and five more which are longer (2.8–3.1 Å). Na(2) has five short and two long. Na(3) has six short distances and one long distance with two oxygens at 3.22 Å and two more at 3.42 Å. These are too far away to be considered bonded to Na(3); any Na–O distances greater than 3.0 Å are considered to be very long. Bond length–bond strength calculations (*9*) including all oxygen atoms out to 3.3 Å give sums of Na–O bond strengths equal to 1.0 v.u. for Na(1) and Na(3), but the sum of the Na(2)–

TABLE II

INTERATOMIC DISTANCES (Å), BOND ANGLES (°), AND POLYHEDRAL EDGE LENGTHS (Å) FOR THE NICKEL OCTAHEDRA

		Distance	Angle	Edge
Ni(1) octahedron				
Ni(1) –O(3)	2×	2.014(10)		
Ni(1) –O(4)	2×	2.028(11)		
Ni(1) –O(11)		2.078(16)		
Ni(1) –O(12)		2.126(15)		
O(3) –Ni(1) –O(3)			97.2(6)	3.023(19)
O(3) –Ni(1) –O(11)	2×		85.6(4)	2.782(15)
O(3) –Ni(1) –O(12)	2×		95.7(4)	3.071(16)
O(3) –Ni(1) –O(4)	2×		84.6(2)	2.720(8)
O(4) –Ni(1) –O(4)			93.6(6)	2.956(20)
O(4) –Ni(1) –O(11)	2×		95.8(4)	3.047(17)
O(4) –Ni(1) –O(12)	2×		82.8(4)	2.749(15)
O(11)–Ni(1) –O(12)			178.0(8)	4.204(11)
O(3) –Ni(1) –O(4)	2×		177.8(5)	4.042(7)
Ni(2) octahedron				
Ni(2) –O(10)		1.987(10)		
Ni(2) –O(1)		2.050(11)		
Ni(2) –O(9)		2.054(12)		
Ni(2) –O(2)		2.083(10)		
Ni(2) –O(13)		2.308(12)		
Ni(2) –O(14)		2.349(12)		
O(10)–Ni(2) –O(1)			104.5(4)	3.191(15)
O(10)–Ni(2) –O(2)			95.9(4)	3.022(14)
O(10)–Ni(2) –O(13)			68.1(5)	2.419(16)
O(10)–Ni(2) –O(14)			88.5(5)	3.036(19)
O(1) –Ni(2) –O(9)			94.4(4)	3.011(15)
O(1) –Ni(2) –O(2)			101.2(2)	3.195(9)
O(1) –Ni(2) –O(13)			92.4(5)	3.152(11)
O(9) –Ni(2) –O(2)			103.1(4)	3.239(15)
O(9) –Ni(2) –O(13)			88.4(5)	3.045(19)
O(9) –Ni(2) –O(14)			69.1(5)	2.510(17)
O(2) –Ni(2) –O(14)			89.1(4)	3.115(10)
O(13)–Ni(2) –O(14)			81.1(2)	3.029(13)
O(10)–Ni(2) –O(9)			150.0(2)	3.903(8)
O(1) –Ni(2) –O(14)			162.3(5)	4.348(17)
O(2) –Ni(2) –O(13)			161.3(5)	4.333(16)
Ni(3) octahedron				
Ni(3) –O(6)		2.001(12)		
Ni(3) –O(9)		2.008(12)		
Ni(3) –O(5)		2.009(12)		
Ni(3) –O(8)		2.017(11)		
Ni(3) –O(3)		2.059(10)		
Ni(3) –O(1)		2.134(11)		
O(6) –Ni(3) –O(5)			87.2(5)	2.765(7)
O(6) –Ni(3) –O(9)			87.8(5)	2.781(16)
O(6) –Ni(3) –O(3)			88.7(4)	2.839(15)
O(6) –Ni(3) –O(1)			89.4(5)	2.910(16)
O(5) –Ni(3) –O(9)			92.2(5)	2.895(18)
O(5) –Ni(3) –O(8)			92.7(5)	2.915(16)
O(5) –Ni(3) –O(1)			100.3(5)	3.187(17)
O(9) –Ni(3) –O(8)			85.0(5)	2.720(16)
O(9) –Ni(3) –O(3)			97.3(4)	3.053(15)
O(8) –Ni(3) –O(3)			92.5(4)	2.945(14)
O(8) –Ni(3) –O(3)			97.6(4)	3.124(15)
O(3) –Ni(3) –O(1)			69.8(4)	2.398(16)
O(6) –Ni(3) –O(8)			172.9(4)	4.010(6)
O(5) –Ni(3) –O(3)			169.5(5)	4.051(16)
O(9) –Ni(3) –O(1)			166.8(5)	4.115(16)
Ni(4) octahedron				
Ni(4) –O(7)		1.961(11)		
Ni(4) –O(10)		2.005(10)		
Ni(4) –O(4)		2.065(10)		
Ni(4) –O(5)		2.069(13)		
Ni(4) –O(6)		2.081(11)		
Ni(4) –O(2)		2.181(10)		
O(7) –Ni(4) –O(10)			89.6(5)	2.793(15)
O(7) –Ni(4) –O(4)			92.2(4)	2.901(15)
O(7) –Ni(4) –O(6)			92.7(5)	2.925(15)
O(7) –Ni(4) –O(2)			92.7(4)	3.000(14)
O(10)–Ni(4) –O(4)			102.1(4)	3.164(14)
O(10)–Ni(4) –O(5)			86.8(4)	2.800(15)
O(10)–Ni(4) –O(6)			89.4(5)	2.875(16)
O(4) –Ni(4) –O(5)			92.2(5)	2.980(16)
O(4) –Ni(4) –O(2)			71.0(4)	2.467(16)
O(5) –Ni(4) –O(6)			83.5(4)	2.765(7)
O(5) –Ni(4) –O(2)			91.4(4)	3.042(16)
O(6) –Ni(4) –O(2)			97.4(4)	3.202(15)
O(7) –Ni(4) –O(5)			174.8(5)	4.025(17)
O(10)–Ni(4) –O(2)			172.7(4)	4.178(14)
O(4) –Ni(4) –O(6)			167.6(4)	4.122(15)

Note. In this and in the following tables the numbers in parentheses are estimated standard deviations in the last significant figures.

TABLE III

INTERATOMIC DISTANCES (Å), BOND ANGLES (°), AND POLYHEDRAL EDGE LENGTHS (Å) FOR THE PHOSPHATE TETRAHEDRA

		Distance	Angle	Edge
P(1) tetrahedron				
P(1)–O(8)		1.495(11)		
P(1)–O(6)		1.551(13)		
P(1)–O(2)		1.568(11)		
P(1)–O(4)		1.567(11)		
O(8) –P(1)–O(6)			109.6(6)	2.489(16)
O(8) –P(1)–O(2)			117.4(6)	2.617(15)
O(8) –P(1)–O(4)			104.8(6)	2.427(14)
O(6) –P(1)–O(2)			107.6(6)	2.517(14)
O(6) –P(1)–O(4)			113.6(7)	2.069(15)
O(2) –P(1)–O(4)			103.8(6)	2.467(16)
P(2) tetrahedron				
P(2)–O(7)		1.511(12)		
P(2)–O(5)		1.520(14)		
P(2)–O(3)		1.548(10)		
P(2)–O(1)		1.556(11)		
O(7) –P(2)–O(5)			108.6(6)	2.461(17)
O(7) –P(2)–O(3)			109.5(6)	2.499(14)
O(7) –P(2)–O(1)			114.0(6)	2.571(15)
O(5) –P(2)–O(3)			116.7(7)	2.612(15)
O(5) –P(2)–O(1)			106.9(6)	2.470(16)
O(3) –P(2)–O(1)			101.2(6)	2.398(16)
P(3) tetrahedron				
P(3)–O(11)		1.493(17)		
P(3)–O(13)		1.500(18)		
P(3)–O(10)	2×	1.555(11)		
O(11)–P(3)–O(13)			117.3(10)	2.557(21)
O(11)–P(3)–O(10)	2×		111.8(5)	2.524(17)
O(13)–P(3)–O(10)	2×		104.7(6)	2.419(16)
O(10)–P(3)–O(10)			105.7(8)	2.479(19)
P(4) tetrahedron				
P(4)–O(12)		1.495(15)		
P(4)–O(9)	2×	1.559(13)		
P(4)–O(14)		1.585(18)		
O(12)–P(4)–O(9)	2×		114.4(6)	2.567(18)
O(12)–P(4)–O(14)			108.4(9)	2.499(20)
O(9) –P(4)–O(9)			107.2(10)	2.509(23)
O(9) –P(4)–O(14)	2×		105.9(6)	2.510(17)

O bond strengths never approaches 1.0 v.u., even when all oxygens out to 3.8 Å have been included. For this reason, and because the Na ions are located in tunnels, their coordination must be decided arbitrarily on the basis of breaks in the continuum of Na–O bond lengths. The environments about the oxygen atoms are detailed in Table V, which has been deposited (see NAPS footnote).

A Fourier difference map of the Na plane showed no significant electron density in the empty Na sites from *C2/m* or anywhere else on the Na plane; therefore there is no Na disorder, and the empty Na sites are indeed empty.

The *d* spacings and intensities found for the powder X-ray diffraction pattern of $Na_4Ni_7(PO_4)_6$ are a close match for those reported by Kolsi (*1*) for the phase he identifies as $NaNiPO_4$, although some lines exist in each pattern which do not appear in the other. A table of *d* spacing for $Na_4Ni_7(PO_4)_6$ is not reported here because several lines in the powder pattern could not be indexed on the $Na_4Ni_7(PO_4)_6$ unit cell. Our sample was visibly contaminated with other phases from the flux mixture. Because we have only a small amount of $Na_4Ni_7(PO_4)_6$, we were not able to obtain a pure powder sample. The pattern reported by Kolsi must be regarded with suspicion.

TABLE IV

SODIUM–OXYGEN INTERATOMIC DISTANCES (SEE TEXT)

		Distance (Å)
Na(1) polyhedron		
Na(1)–O(1)		2.356(11)
Na(1)–O(2)		2.409(11)
Na(1)–O(8)		2.446(11)
Na(1)–O(14)		2.591(14)
Na(1)–O(6)		2.819(13)
Na(1)–O(7)		2.925(12)
Na(1)–O(12)		2.941(13)
Na(1)–O(13)		2.965(15)
Na(1)–O(9)		3.089(14)
Na(2) polyhedron		
Na(2)–O(11)		2.451(19)
Na(2)–O(10)	2×	2.556(12)
Na(2)–O(7)	2×	2.674(12)
Na(2)–O(14)		2.926(19)
Na(2)–O(13)		3.149(20)
Na(3) polyhedron		
Na(3)–O(4)	2×	2.414(12)
Na(3)–O(3)	2×	2.514(12)
Na(3)–O(8)	2×	2.604(11)
Na(3)–O(12)		3.043(17)
Na(3)–O(9)	2×	3.223(14)

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