Table 2. *The molecular conformation: selected torsion angles* (°)

Furan ring (*A*)	
O(1)–C(2)–C(3)–C(9)	+16·0
C(2)–C(3)–C(9)–C(8)	−29·2
C(3)–C(9)–C(8)–O(1)	+35·6
C(9)–C(8)–O(1)–C(2)	−26·4
C(8)–O(1)–C(2)–C(3)	+5·6
Benzo ring (*B*)	
C(4)–C(5)–C(6)–C(7)	−5·3
C(5)–C(6)–C(7)–C(8)	+4·0
C(6)–C(7)–C(8)–C(9)	+6·8
C(7)–C(8)–C(9)–C(4)	−15·0
C(8)–C(9)–C(4)–C(5)	+13·5
C(9)–C(4)–C(5)–C(6)	−4·2
Phenyl ring (*C*)	
C(15)–C(16)–C(17)–C(18)	−1·4
C(16)–C(17)–C(18)–C(19)	+2·9
C(17)–C(18)–C(19)–C(20)	−2·7
C(18)–C(19)–C(20)–C(15)	+1·1
C(19)–C(20)–C(15)–C(16)	+0·4
C(20)–C(15)–C(16)–C(17)	−0·2
Exocyclic torsion angles	
O(1)–C(2)–C(15)–C(16)	−59·0
C(4)–C(5)–C(12)–C(13)	−92·7
C(5)–C(12)–C(13)–C(14)	+2·0
C(4)–C(9)–O(2)–C(11)	+66·7
C(16)–C(17)–O(4)–C(21)	−4·4
C(17)–C(18)–O(5)–C(22)	+85·8
C(18)–C(19)–O(6)–C(23)	−173·5
Asymmetric centers	
C(8)–O(1)–$\underline{\mathrm{C(2)}}$–C(15)	+135·2
O(1)–C(2)–$\underline{\mathrm{C(3)}}$–C(10)	−105·1
C(2)–C(3)–$\underline{\mathrm{C(9)}}$–O(2)	+84·7

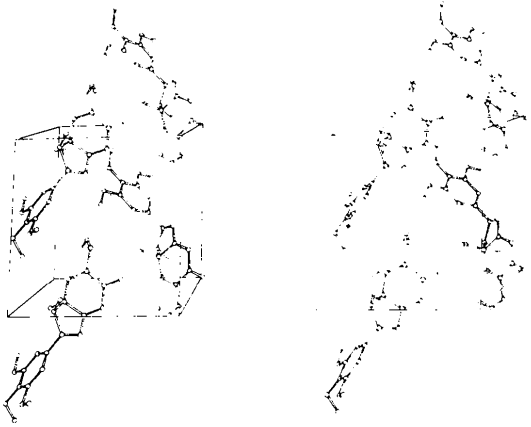

Fig. 3. Unit-cell contents and molecular packing, viewed in the direction of **c** with **b** horizontal.

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Rubidium Neodymium Metaphosphate

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Abstract. $RbNdP_4O_{12}$, monoclinic, $C2/c$ (C_{2h}^6), a = 7·845 (2), b = 12·691 (3), c = 10·688 (3) Å, β = 112·34 (1)°, Z = 4, U = 984·23 Å^3, D_x = 3·681 g cm^{-3}, μ(Mo $K\alpha$) = 112·2 cm^{-1}. The tetrametaphosphate $(P_4O_{12})^{4-}$ rings, located on symmetry centres, are connected by isolated NdO_8 dodecahedra and irregularly shaped Rb polyhedra to form a layer structure parallel to (001). The refinement converged to $R = 0·054$ for 1054 independent reflexions.

Introduction. Following the development of a new efficient phosphate laser material with high Nd concentration, $LiNdP_4O_{12}$ (Yamada, Otsuka & Nakano, 1974), the other alkaline Nd metaphosphate crystals, $KNdP_4O_{12}$ and $NaNdP_4O_{12}$, were synthesized and their structures determined (Hong, 1975*b*; Nakano, Otsuka & Yamada, 1976; Koizumi, 1976*b*). The common feature of these structures is helical chains of PO_4 tetrahedra linked by $-Nd^{3+}-M^+-$ chains (M^+ stands for Li^+, Na^+ and K^+).

Although these crystal structures are quite similar, they belong to different space groups and the axial relations between them are not straightforward (Koizumi, 1976*b*).

Single crystals were grown by the top-seeding Kyropoulos method from a melt composed of $35Rb_2O$, $5Nd_2O_3$ and $60P_2O_5$ (mol%). Transparent crystals, of the largest size 1 × 0·5 × 0·5 mm, were obtained from a polycrystalline block. A crystal was ground to a sphere of radius 0·23 mm using an air grinder with emery paper. Precession and Weissenberg photographs exhibited $2/m$ Laue symmetry with the following systematic absences: hkl when $h + k = 2n + 1$, $h0l$ when $l = 2n + 1$.

The spherical specimen was mounted so that its a axis was along the φ axis of the Rigaku Denki automatic four circle X-ray diffractometer. Monochromated Mo $K\alpha$ radiation was used with the ω–2θ scan technique. Intensity data were collected for 1054 independent reflexions up to $2\theta = 65°$, with $|F| > 3\sigma_F$. Standard reflexions were measured every 60 reflexions. The intensities were corrected for Lorentz–polarization, absorption and extinction effects.

A Howells, Phillips & Rogers (1950) plot of intensities indicated a centrosymmetric structure; therefore the space group $C2/c$ was assumed. In this space group, with $Z = 4$, Nd and Rb atoms should occupy the special positions $4(a) \sim 4(e)$. From a three-dimensional Patterson synthesis the heavy atoms, Nd and Rb, were found to be located on the twofold axis [4(*e*)]. Minimum-function procedures on the Harker peaks of the four Nd atoms yielded positions for the P atoms. The structure factors calculated from the coordinates of Nd, Rb and P atoms gave an R value of 0·304.

Table 1. *The final positional and thermal parameters*

Estimated standard deviations are given in parentheses.

	x	y	z	B_{eq} (Å^2)
Nd	0	0·1281 (1)	$\frac{1}{4}$	0·57 (2)
Rb	0	0·4365 (1)	$\frac{1}{4}$	2·12 (2)
P(1)	0·2034 (3)	0·0837 (2)	0·9925 (2)	0·76 (2)
P(2)	0·0253 (3)	0·7273 (2)	0·0589 (2)	0·73 (2)
O(1)	0·2945 (9)	0·4973 (5)	0·1077 (7)	1·07 (2)
O(2)	0·1489 (9)	0·0554 (5)	0·1059 (6)	0·92 (2)
O(3)	0·4108 (11)	0·1266 (5)	0·0616 (9)	1·47 (3)
O(4)	0·0904 (9)	0·8198 (5)	0·4108 (7)	1·00 (2)
O(5)	0·2983 (10)	0·2183 (5)	0·3259 (8)	1·18 (3)
O(6)	0·0173 (11)	0·2580 (6)	0·4184 (7)	1·28 (3)

O positions were indicated on successive Fourier syntheses along the b axis and the vector maps yielded possible parameters, indicating tetrahedral coordination around each P atom.

The structure was refined by *ORFLS* (Busing, Martin & Levy, 1962) with isotropic thermal factors, to give $R = 0·136$. All the parameters were then refined by two further cycles of least squares with anisotropic

Table 2. *Bond distances and angles in* $RbNdP_4O_{12}$ *with standard deviations in parentheses*

Dodecahedron around Nd

Nd–O(1)	2·409 (6) Å	O(1)–O(2)	2·884 (10) Å
Nd–O(2)	2·440 (8)	O(1)–O(2)	3·016 (9)
Nd–O(5)	2·450 (7)	O(1)–O(5)	3·048 (9)
Nd–O(6)	2·406 (8)	O(2)–O(5)	3·013 (9)
Nd–Nd	6·129 (2)	O(2)–O(6)	2·850 (10)
	6·253 (2)	O(5)–O(6)	2·878 (9)

Polyhedron around Rb

Rb–O(1)	3·304 (8) Å	O(1)–O(2)	2·884 (10) Å
Rb–O(2)	3·002 (6)	O(1)–O(3)	3·297 (10)
Rb–O(3)	3·048 (8)	O(1)–O(6)	3·888 (9)
Rb–O(5)	3·516 (7)	O(2)–O(3)	2·450 (11)
Rb–O(6)	2·864 (8)	O(2)–O(3)	4·005 (9)

Tetrahedron around P(1)

P(1)–O(1)	1·488 (8) Å	O(1)–P(1)–O(2)	119·8 (4)°
P(1)–O(2)	1·474 (8)	O(1)–P(1)–O(3)	106·2 (5)
P(1)–O(3)	1·605 (8)	O(1)–P(1)–O(4)	107·0 (4)
P(1)–O(4)	1·568 (7)	O(2)–P(1)–O(3)	105·5 (4)
O(1)–O(2)	2·573 (10)	O(2)–P(1)–O(4)	112·7 (5)
O(1)–O(3)	2·475 (9)	O(3)–P(1)–O(4)	102·3 (6)
O(1)–O(4)	2·463 (9)		
O(2)–O(3)	2·450 (12)		
O(2)–O(4)	2·517 (9)		
O(3)–O(4)	2·510 (9)		

Tetrahedron around P(2)

P(2)–O(3)	1·571 (8) Å	O(3)–P(2)–O(4)	104·4 (4)°
P(2)–O(4)	1·599 (8)	O(3)–P(2)–O(5)	107·2 (5)
P(2)–O(5)	1·466 (7)	O(3)–P(2)–O(6)	108·9 (6)
P(2)–O(6)	1·484 (7)	O(4)–P(2)–O(5)	109·6 (5)
O(3)–O(4)	2·469 (9)	O(4)–P(2)–O(6)	108·8 (4)
O(3)–O(5)	2·433 (9)	O(5)–P(2)–O(6)	118·8 (6)
O(3)–O(6)	2·481 (12)		
O(4)–O(5)	2·481 (9)		
O(4)–O(6)	2·488 (12)		
O(5)–O(6)	2·577 (9)		

Inter-tetrahedral angle

P(1)–O(3)–P(2)	134·9 (3)°
P(1)–O(4)–P(2)	133·4 (4)

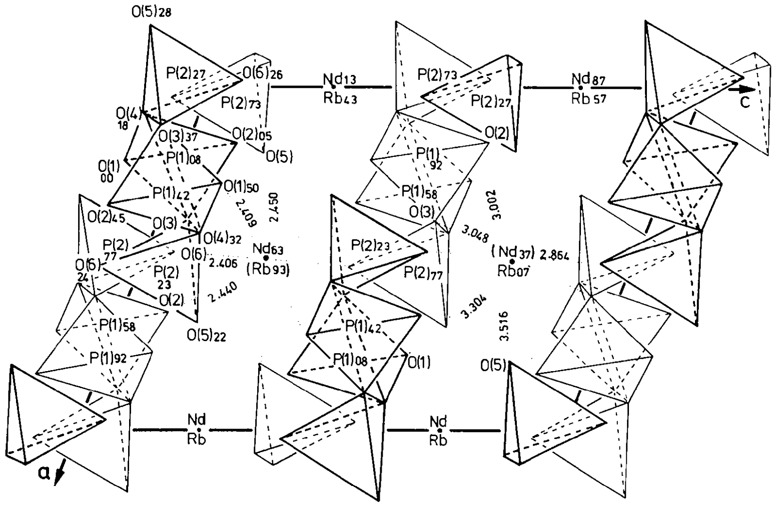

Fig. 1. Atomic arrangement projected along the b axis. For clarity the PO_4 tetrahedra lying at the higher level have been drawn with thicker lines.

thermal factors. The final R and R_w values are 0·054 and 0·069 respectively. The final atomic positional parameters are listed in Table 1.*

The atomic scattering factors for Nd^{3+}, Rb^+, P^0 and O^0 listed in *International Tables for X-ray Crystallography* (1962) were used. The weighting scheme used during the final stages of the refinement was $w = (5{\cdot}8 + |F_o| + 0{\cdot}038|F_o|^2)^{-1}$.

Discussion. Bond distances and angles calculated from the final atomic coordinates are given in Table 2. Views of the structure projected along the b and c axes are shown in Figs. 1 and 2.

The basic structure unit is the tetrametaphosphate ring $(P_4O_{12})^{4-}$ consisting of PO_4 tetrahedra each of which shares two corners with others. The $(P_4O_{12})^{4-}$ ring has a centre of symmetry located on the mean plane (defined in Table 3), which is nearly perpendicular to (100) and (010). This type of ring was also found in $Al(PO_3)_3$ (Pauling & Sherman, 1937), $(NH_4)_4P_4O_{12}$ (Romers, Ketelaar & MacGillavry, 1951), $Na_4P_4O_{12}.4H_2O$ (Ondik, Block & MacGillavry, 1961), $Ca(NH_4)_2P_4O_{12}.2H_2O$ (Tordjman, Masse & Guitel, 1976), *etc.*

In the $(PO_3)_\infty$ chain structures of the alkaline Nd metaphosphates reported, the average inter-tetrahedral angle between adjacent PO_4 groups increases with the

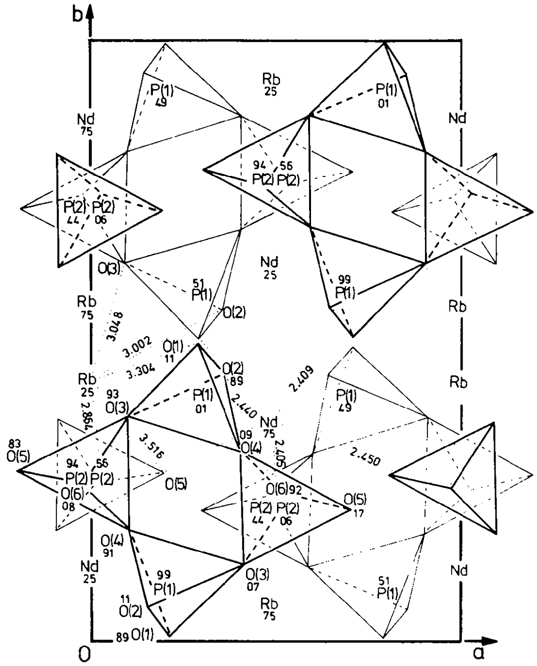

Fig. 2. Atomic arrangement projected along the c axis. For clarity the PO_4 tetrahedra lying at the higher level have been drawn with thicker lines.

Table 3. *Mean plane and atom deviations* (Å) *of the* $(P_4O_{12})^{4-}$ *ring in* $RbNdP_4O_{12}$

The mean plane was calculated through the four P atoms belonging to the ring. The plane constants are referred to crystallographic axes.

$$-0{\cdot}2688X + 0{\cdot}0112Y + 0{\cdot}9313Z + 0{\cdot}4916 = 0.$$

O(1)	O(2)	O(3)	O(4)	O(5)	O(6)
1·045	1·279	0·265	0·591	0·801	1·421

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32641 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

ionic radius and coordination number of M^+; therefore a large P—O—P angle (~140°) is expected if $RbNdP_4O_{12}$ is isostructural. The P—O—P angles in the present structure are 133·4 and 134·9° (Table 4).

Within the $(P_4O_{12})^{4-}$ ring, the P—O bonds of the ring O atoms O(3) and O(4) (mean value 1·586 Å) are much longer than those of the terminal oxygens O(1), O(2), O(5) and O(6) (mean value 1·478 Å). Furthermore, the tetrahedral angles between terminal P—O bonds (mean value 119·3°) are much longer than the others (mean value 107·3°) [Fig. 3(*a*)]. It is possible to explain these differences on the basis of the valence-bond model suggested for the structure of $(NH_4)_4P_4O_{12}$ (Romers *et al.*, 1951). In this model the P—O bonds are considered to be formed mainly by the electrostatic force between the P^{5+} and O^{2-} ions, and the most probable charge distribution around the bonding is illustrated in Fig. 3(*b*). The distinct deviations of the P—O bond length and O—P—O angles from the average values (1·532 Å, 109·3°) would be caused by the electrostatic attraction and repulsion between these ionic charges (P^+ and O^-) [Fig. 3(*b*)]. The longer and shorter P—O bonds seem to correspond to the single and double bonds respectively in the resonance structure (Pauling, 1945).

Table 4. *The relation between the ionic radius* (*r*) *and the average inter-tetrahedral angle* (*θ*) *for adjacent* PO_4 *groups in the* $(PO_3)_\infty$ *chain of* $MNdP_4O_{12}$

M^+	Li^+	Na^+	K^+	Rb^+
r(Å)	0·60	0·95	1·33	1·49
θ(°)	132·5	136·3	138·0	(139·7)*
Coordination number (*n*)	4	6 + 1	7	8 + 2

* The value for $RbNdP_4O_{12}$ was calculated from extrapolation of the values for the other ions, assuming a chain structure.

The negative layer consisting of the $(P_4O_{12})^{4-}$ ring and the positive layer of Nd^{3+} and Rb^+ ions are arranged alternately to form a sandwich structure along the *c* axis. As shown in Fig. 2, the cations form zigzag $-Nd^{3+}-Rb^{+}-$ chains of amplitude 1·251 Å along the *a* axis. The chain resembles those of the other alkaline Nd metaphosphates (Koizumi, 1976*b*). These chains are connected to each other by four kinds of bonds including the relatively short Nd—O(6) (2·406 Å) and Rb—O(6) (2·864 Å), each of which is the shortest bond in each cation coordination.

On the twofold axes, Nd^{3+} and Rb^+ ions are arranged alternately at quite different spacings d_1 (3·914 Å) and d_2 (8·777 Å), compared with the almost equal spacing of Li^+ and Nd^{3+} in the $LiNdP_4O_{12}$ crystal (Koizumi, 1976*a*). The ratio d_2/d_1 (2·24) is similar to the ratio of the diameter of the $(P_4O_{12})^{4-}$ ring to the edge length of the PO_4 tetrahedron in the [010] direction (2·57) (Fig. 3).

Each NdO_8 dodecahedron in $RbNdP_4O_{12}$ is surrounded by four others, with Nd—Nd distances of 6·129 and 6·253 Å, but these dodecahedra are isolated from each other in the sense that they do not share a common O atom. This type of isolation is a common structural feature of all the Nd compounds exhibiting reduced fluorescence quenching despite their high Nd^{3+} concentration (Hong, 1975*a*). The shortest Nd—Nd distance (6·129 Å) is longer than that in $LiNdP_4O_{12}$ (5·644 Å), but a greater interaction between Nd^{3+} and the alkaline ion (Rb^+) is predicted. The symmetry of the O coordination of Nd^{3+} is lower than those of $NdNa_5(WO_4)_4$ (Hong & Dwight, 1974) and $LiNdP_4O_{12}$ which have respectively rigorous and approximate $\bar{4}$ symmetry.

The shape of the Rb coordination in this crystal is quite irregular, as can be seen frequently in many other Rb double oxides, and similar to that of the Na coordination in $Na_4P_4O_{12}.4H_2O$ but involves an additional weak interaction [Rb—O(5), 3·516 Å].

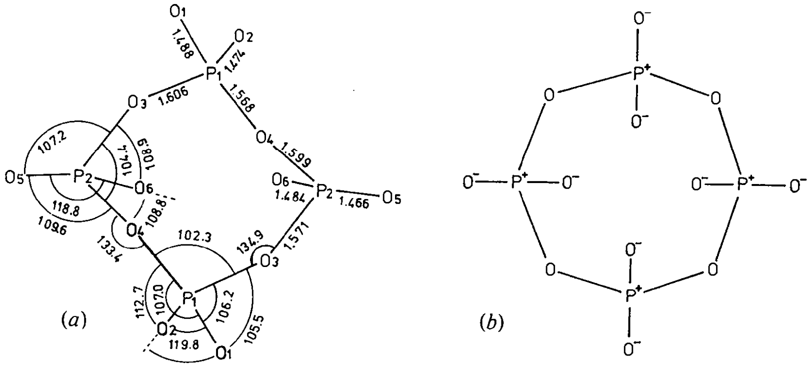

Fig. 3. (*a*) Bond system and (*b*) most probable electronic structure of the tetrametaphosphate ion $(P_4O_{12})^{4-}$.

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Sodium Dideuteriumarsenate Monodeuterate

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Abstract. $NaD_2AsO_4.D_2O$, monoclinic, $P2_1/m$, a = 5·865 (6), b = 7·123 (6), c = 5·619 (5) Å, β = 92·58 (6)°, Z = 2, D_x = 2·63 g cm^{-3}, Mo radiation, R = 0·049 for 801 reflexions. The structure contains $AsO_2(OD)_2^-$ ions linked into (001) sheets by O–D···O hydrogen bonds, directly by pairs of bonds along **b** and *via* D_2O molecules along **a**. The sheets are joined by $NaO_4(OD_2)_2$ coordination octahedra which share edges along **b**. As–OD = 1·725 (3), As–O = 1·647, 1·689 (4), Na–OD_2 = 2·414, Na–O = 2·379, 2·534, O–D···O = 2·621, 2·781, 3·104 Å.

Introduction. Unit-cell and intensity data were measured on a Datex-automated GE XRD-6 diffractometer with Mo $K\alpha$ radiation, a θ–2θ scan at a scan speed of 2° min^{-1} in 2θ over a 2θ range of (1·80 + 0·86 tan θ), a background count for 20 s at the beginning and end of each scan, and measurement of a check reflexion, whose intensity gradually dropped by 5% during the data collection. Of 911 reflexions with $2\theta < 65°$, 807 had intensities greater than 3σ above background [$\sigma^2(I) = S + B + (0{\cdot}08\ S)^2$, where S = scan and B = background count]. Lorentz and polarization corrections were applied, but no absorption corrections were made (μ = 76 cm^{-1}).

The E statistics corresponded closely to a noncentrosymmetric distribution (mean $|E|$ = 0·88, mean $|E^2 - 1|$ = 0·68, no reflexions with $|E| > 2{\cdot}0$), and the structure was determined in space group $P2_1$ by Patterson and electron-density methods. Refinement of As, Na, and O parameters proceeded smoothly by full-matrix least-squares techniques; however, the refined structure corresponded closely to space group $P2_1/m$, there were many large correlation coefficients between parameters (as large as 0·94 between positional parameters of the two O atoms related by a mirror plane in $P2_1/m$), and some thermal parameters were non-positive-definite. Refinement was therefore continued and completed satisfactorily in the centrosymmetric space group (largest correlation 0·6 between overall scale and As thermal parameters). A difference synthesis computed at R = 0·052 contained density fluctuations as high as ±2 e Å^{-3} near the As positions, the only other significant features being three peaks of about 1 e Å^{-3} in plausible deuterium positions. Final refinement with anisotropic thermal parameters for non-deuterium atoms and isotropic parameters for

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