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Structure of Tetraammonium Monosodium Triphosphate Tetrahydrate

BY M. T. AVERBUCH-POUCHOT AND A. DURIF

Laboratoire de Cristallographie, Centre National de la Recherche Scientifique, Laboratoire associé à l'USMG, 166 X, 38042 Grenoble CEDEX, France

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Abstract. $(NH_4)_4NaP_3O_{10}.4H_2O$, $M_r = 420{\cdot}12$, monoclinic, $C2/c$, $a = 11{\cdot}813\,(8)$, $b = 7{\cdot}292\,(3)$, $c = 20{\cdot}20\,(8)$ Å, $\beta = 105{\cdot}19\,(5)°$, $V = 1679{\cdot}2$ Å^3, $Z = 4$, $D_x = 1{\cdot}661$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}7107$ Å, $\mu = 4{\cdot}60$ cm^{-1}, $F(000) = 880$, $T = 293$ K, $R = 0{\cdot}026$ for 1598 independent reflexions. Alternating P_3O_{10} groups and NaO_6 octahedra form chains running along the c axis. NH_4O_4 tetrahedra are grouped together to form either finite centrosymmetric $(NH_4)_2O_6$ groups (two tetrahedra sharing an edge) or infinite NH_4O_3 chains around a 2_1 axis. The hydrogen-bond scheme is described.

Introduction. Structural investigations dealing with alkali or mixed alkali triphosphates are very rare. The crystal structures of the two forms of $Na_5P_3O_{10}$ (Corbridge, 1960; Davies & Corbridge. 1958) and that of its hexahydrate determined first by Dyroff (1965) and later reinvestigated by Wiench, Jansen & Hoppe (1982) have been reported. In the present work we describe the crystal structure of $Na(NH_4)_4P_3O_{10}.4H_2O$.

The thermal behavior of this salt has been studied by Prodan, Galogadja, Petrovskaia & Kordjev (1981). These authors proposed the following scheme of thermal evolution for this salt:

$$Na(NH_4)_4P_3O_{10}.4H_2O \xrightarrow{308K} Na(NH_4)_4P_3O_{10}.H_2O \xrightarrow{323K} Na(NH_4)_3HP_3O_{10}.H_2O.$$

Experimental. $Na(NH_4)_4P_3O_{10}.4H_2O$ is easily prepared by a process using ion-exchange resins. An aqueous solution of pentasodium triphosphate is passed through a column of Amberlite IR 120. The triphosphoric acid so obtained is immediately neutralized by a stoichiometric mixture of the corresponding carbonates. To avoid any hydrolytic cleavage of the anion this reaction must be run at a temperature close to 273 K. To the resulting solution is then added a large excess of ethyl alcohol to precipitate $Na(NH_4)_4P_3O_{10}.4H_2O$. The salt is well crystallized. Larger crystals can be grown by slow and careful evaporation of aqueous solution; they appear as diamond-like thick platelets. Crystal size: $0{\cdot}32 \times 0{\cdot}32 \times 0{\cdot}24$ mm; apparatus: Enraf–Nonius CAD-4; graphite monochromator; θ range 3–30°; scan type: ω; scan width: 1·20°; scan speed: 0·01 to 0·04° s^{-1}; 2 standard reflexions, no variation in intensity; unit-cell refinement with 22 reflexions ($11 < \theta < 15°$); 2691 reflexions collected ($\bar{h}kl$, hkl); $h_{max} = 16$, $k_{max} = 10$, $l_{max} = 28$; systematic absences: $h0l$ ($h = 2n$, $l = 2n$), hkl ($h + k = 2n$); Lorentz–polarization correction, no absorption correction; structure solved by direct methods: *MULTAN*77 (Main, Lessinger, Woolfson, Germain & Declercq, 1977); H atoms from difference Fourier map; final refinements with 1598 reflexions ($F_o > 3\sigma_F$); full-matrix refinements on F with anisotropic thermal parameters for non-hydrogen atoms, isotropic for hydrogen atoms; unitary weighting scheme; max. Δ/σ: 0·01; max. density on final difference-Fourier map: 0·16 e Å^{-3}; final $R = 0{\cdot}026$, $wR = 0{\cdot}035$, $S = 0{\cdot}765$. Scattering factors for neutral atoms and f', f'' from *International Tables for X-ray Crystallography* (1974). Enraf–Nonius (1977) *SDP* used for all calculations.*

Discussion. Table 1 reports the final atomic coordinates. As shown by Fig. 1, which represents a projection along the b axis, the atomic arrangement may be described as a succession of chains, built up by sodium octahedra and P_3O_{10} groups and parallel to the c axis. Ammonium polyhedra are located between these chains so as to ensure the three-dimensional cohesion. The centrosymmetric sodium octahedron is made of two oxygen atoms and four water molecules. Table 2 reports the main geometrical features of this polyhedron. The two oxygen atoms of this octahedron are shared with two adjacent P_3O_{10} groups. The triphosphate groups P_3O_{10} have twofold symmetry, the central phosphorus atom being located on the twofold axis. Table 2 gives the main interatomic distances and bond angles in this group.

All N—O distances lie within a range of 3 Å, and the coordination polyhedra of the two crystallographically independent NH_4 groups are distorted tetrahedra whose main characteristics are reported in Table 2. More interesting is the method of linkage of these ammonium

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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 42386 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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groups. The N(1)H_4 groups are located close to a 2_1 axis. They form infinite $(NH_4)O_3$ chains running along the 2_1 axes, the oxygen atom O(*E*1) being shared between two adjacent $(NH_4)O_4$ tetrahedra. The second type of $(NH_4)O_4$ tetrahedron corresponding to the N(2) nitrogen atoms has a very different linkage. Located close to a center of inversion, two of these tetrahedra have a common edge and so form a finite unit $(NH_4)_2O_2(H_2O)_4$.

Table 1. *Final atomic coordinates for* $Na(NH_4)_4P_3O_{10}.4H_2O$, B_{eq} *for non-hydrogen atoms,* B_{iso} *for hydrogen atoms*

$$B_{eq} = \tfrac{4}{3}\textstyle\sum_i\sum_j \beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}/B_{iso}(Å^2)
P(1)	0	0·0763 (1)	$\frac{3}{4}$	1·16 (1)
P(2)	0·96403 (5)	0·32500 (8)	0·63149 (3)	1·205 (8)
Na	0	0	$\frac{1}{2}$	1·88 (2)
N(1)	0·1799 (2)	0·3916 (3)	0·2559 (1)	1·86 (4)
N(2)	0·1994 (2)	0·4519 (3)	0·0448 (1)	2·34 (4)
O(*L*)	0·4259 (1)	0·2894 (2)	0·19256 (8)	1·83 (3)
O(*E*1)	0·4131 (1)	0·5295 (2)	0·27708 (8)	1·81 (3)
O(*E*21)	0·4174 (1)	0·2845 (3)	0·06652 (8)	2·04 (3)
O(*E*22)	0·3996 (2)	−0·0062 (2)	0·13044 (9)	2·12 (3)
O(*E*23)	0·4042 (1)	0·1554 (2)	0·34785 (8)	1·81 (3)
O(*W*1)	0·3165 (2)	0·3576 (3)	0·43842 (9)	2·54 (4)
O(*W*2)	0·0329 (2)	0·2112 (3)	0·09500 (9)	2·88 (4)
H(*W*11)	0·341 (3)	0·307 (5)	0·401 (2)	3·7 (7)
H(*W*12)	0·251 (3)	0·407 (5)	0·418 (2)	4·4 (8)
H(*W*21)	0·025 (3)	0·273 (5)	0·402 (2)	3·9 (8)
H(*W*22)	0·044 (3)	0·132 (5)	0·136 (2)	3·9 (8)
H(N11)	0·163 (3)	0·421 (5)	0·299 (2)	3·8 (8)
H(N12)	0·151 (3)	0·279 (5)	0·238 (2)	4·5 (9)
H(N13)	0·148 (3)	0·466 (5)	0·219 (2)	5·1 (9)
H(N14)	0·259 (3)	0·395 (5)	0·264 (2)	3·7 (8)
H(N21)	0·347 (3)	0·108 (5)	0·002 (2)	4·8 (9)
H(N22)	0·281 (3)	0·416 (5)	0·059 (2)	4·1 (8)
H(N23)	0·305 (4)	0·062 (6)	0·464 (2)	7 (1)
H(N24)	0·162 (3)	0·417 (5)	0·076 (2)	5 (1)

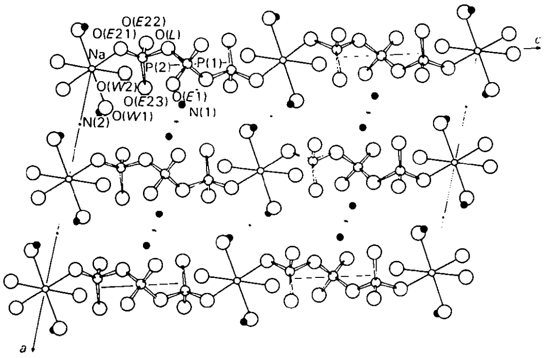

Fig. 1. Projection of the atomic arrangement of $Na(NH_4)_4P_3O_{10}$.-$4H_2O$ along the *b* axis. Hydrogen atoms are not represented.

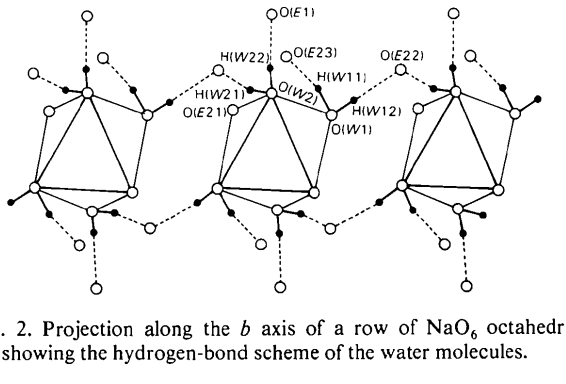

Fig. 2. Projection along the *b* axis of a row of NaO_6 octahedra showing the hydrogen-bond scheme of the water molecules.

Table 2. *Main interatomic distances* (Å) *and bond angles* (°) *in the atomic arrangement of* $Na(NH_4)_4P_3O_{10}.4H_2O$

$P(1)O_4$ tetrahedron

P(1)–O(*L*)	1·594 (2) (×2)	P(1)–O(*E*)	1·497 (2) (×2)
O(*L*)–P(1)–O(*L*)	104·1 (2)	O(*L*)–O(*L*)	2·514 (4)
O(*L*)–P(1)–O(*E*1)	106·5 (1)	O(*L*)–O(*E*1)	2·478 (3)
O(*L*)–P(1)–O(*E*1)	110·4 (1)	O(*L*)–O(*E*1)	2·539 (3)
O(*E*1)–P(1)–O(*E*1)	118·0 (2)	O(*E*1)–O(*E*1)	2·567 (4)

$P(2)O_4$ tetrahedron

P(2)	O(*L*)	O(*E*21)	O(*E*22)	O(*E*23)
O(*L*)	1·647 (2)	2·522 (3)	2·472 (3)	2·557 (3)
O(*E*21)	105·9 (1)	1·511 (2)	2·520 (3)	2·532 (3)
O(*E*22)	102·5 (1)	112·3 (1)	1·522 (2)	2·534 (3)
O(*E*23)	107·8 (1)	113·9 (1)	113·4 (1)	1·509 (2)

P(1)–P(2)	2·944 (1)	P(1)–O(*L*)–P(2)	130·6 (1)
P(2)–P(2)	4·638 (1)		

NaO_6 octahedron

O(*E*21)–Na–O(*W*1)	97·22 (7)	Na–O(*E*21)	2·432 (2) (×2)
O(*E*21)–Na–O(*W*2)	88·71 (8)	Na–O(*W*1)	2·431 (2) (×2)
O(*W*1)–Na–O(*W*2)	95·95 (9)	Na–O(*W*2)	2·412 (2) (×2)

N(1)O_4 tetrahedron

N(1)–O(*E*1)	2·858 (3)	N(1)–O(*E*1)	2·870 (3)
N(1)–O(*E*23)	2·826 (3)	N(1)–O(*E*22)	2·800 (3)

N(2)O_4 tetrahedron

N(2)–O(*E*21)	2·883 (4)	N(2)–O(*E*21)	2·778 (4)
N(2)–O(*W*1)	2·989 (4)	N(2)–O(*W*2)	3·004 (4)

N(1)H_4 tetrahedron

N(1)	H(N11)	H(N12)	H(N13)	H(N14)
H(N11)	0·97 (4)	1·58 (6)	1·61 (6)	1·50 (5)
H(N12)	113 (3)	0·92 (5)	1·41 (6)	1·51 (6)
H(N13)	117 (4)	101 (4)	0·91 (5)	1·48 (6)
H(N14)	106 (3)	111 (4)	109 (4)	0·91 (4)

N(2)H_4 tetrahedron

N(2)	H(N21)	H(N22)	H(N23)	H(N24)
H(N21)	1·06 (5)	1·70 (6)	1·48 (7)	1·56 (6)
H(N22)	113 (3)	0·97 (4)	1·46 (7)	1·53 (6)
H(N23)	102 (4)	109 (4)	0·82 (6)	1·45 (7)
H(N24)	106 (4)	111 (4)	115 (5)	0·89 (5)

Hydrogen bonds

		N–H···O	H···O
N(1)	H(N11)···O(*E*22)	168 (4)	1·84 (5)
	H(N12)···O(*E*1)	167 (4)	1·96 (5)
	H(N13)···O(*E*23)	170 (4)	1·92 (5)
	H(N14)···O(*E*1)	152 (4)	2·02 (4)
N(2)	H(N21)···O(*E*21)	160 (4)	1·86 (5)
	H(N22)···O(*E*21)	161 (4)	1·85 (5)
	H(N23)···O(*W*1)	153 (5)	2·23 (6)
	H(N24)···O(*W*2)	143 (4)	2·24 (5)

		O(*W*)–H	H–O(*W*) –H	O(*W*)–H ···O	H···O	O(*W*)–O
O(*W*1)	H(*W*11)···O(*E*23)	0·96 (4)	102 (4)	163 (4)	1·83 (4)	2·755 (3)
	H(*W*12)···O(*E*22)	0·85 (5)		175 (5)	1·90 (5)	2·753 (3)
O(*W*2)	H(*W*21)···O(*E*22)	0·83 (4)	101 (4)	153 (4)	2·03 (4)	2·798 (3)
	H(*W*22)···O(*E*1)	0·99 (4)		166 (4)	1·86 (4)	2·824 (3)

Table 2 reports the main characteristics of the NH_4 groups and details of the hydrogen bonds involving hydrogen atoms of these groups.

Details of the hydrogen-bond scheme involving water molecules are given in Fig. 2, which shows a projection along the *b* axis of a row of NaO_6 octahedra. Numerical data corresponding to these hydrogen bridges are given in Table 2. It should be noticed that one oxygen atom [O(*E*22)] acts as an acceptor for three bonds.

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Structure of Pentarubidium Heptahydrogentetrakis(phosphate)

By M. T. Averbuch-Pouchot and A. Durif

Laboratoire de Cristallographie, Centre National de la Recherche Scientifique, Laboratoire associé à l'USMG, 166X, 38042 Grenoble CEDEX, France

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Abstract. $Rb_5H_7(PO_4)_4$, $M_r = 814{\cdot}29$, orthorhombic, *Pnma*, $a = 28{\cdot}57\ (6)$, $b = 10{\cdot}277\ (5)$, $c = 6{\cdot}090\ (3)$ Å, $V = 1788{\cdot}3$ Å^3, $Z = 4$, $D_x = 3{\cdot}024$ Mg m^{-3}, $\lambda(\text{Ag } K\alpha) = 0{\cdot}5608$ Å, $\mu = 8{\cdot}017$ mm^{-1}, $F(000) = 1520$, $T = 293$ K, final $R = 0{\cdot}056$ for 1060 unique reflexions. Isolated PO_4 tetrahedra intercalate in a three-dimensional network of RbO_{10}, RbO_9 and RbO_8 polyhedra. Both P and Rb atoms are located in mirror planes. This compound is the first example of an alkali monophosphate with such a chemical formula.

Introduction. During experiments aimed at preparing the high-temperature form of RbH_2PO_4 a new type of alkali monophosphate has been characterized: $Rb_5H_7(PO_4)_4$. Schematically, the chemical reaction leading to this salt corresponds to the departure of one mole of H_3PO_4 for five moles of RbH_2PO_4:

$$5RbH_2PO_4 \rightarrow H_3PO_4 + Rb_5H_7(PO_4)_4.$$

Experimental. Rubidium dihydrogenmonophosphate is normally prepared by evaporation at room temperature of a solution containing stoichiometric amounts of H_3PO_4 and Rb_2CO_3. If a small excess of H_3PO_4 is added and the resulting solution kept at 353 K for 1 d, large orthorhombic prisms form, which were originally thought to be crystals of the high-temperature form of RbH_2PO_4. The present crystal structure study shows the correct chemical formula to be $Rb_5H_7(PO_4)_4$. D_m not measured. Prismatic crystal ($0{\cdot}20 \times 0{\cdot}20 \times 0{\cdot}20$ mm). Philips PW 1100 diffractometer. Systematic absences: $h0l$, $h = 2n$; $0kl$, $k + l = 2n$. 25 reflexions ($10 < \theta < 13°$) used for refining the unit cell. ω scan. 2235 reflexions measured ($3 < \theta < 30°$). $H_{\max} = 50$, $K_{\max} = 18$, $L_{\max} = 9$. Scan width 1·20°, scan speed 0·02° s^{-1}, total background-measuring time 20 s. Lorentz–polarization correction; no absorption correction. Classical methods for structure determination: Patterson function and successive Fourier syntheses. Anisotropic full-matrix least-squares refinement on *F*. Unit weights. Total number of unique reflexions 2203. Final refinement cycles with 1060 reflexions ($F_o > 3\sigma_F$). Final $R = 0{\cdot}056$ ($wR = 0{\cdot}064$). For the complete set of unique reflexions (2203 *HKL*) $R = 0{\cdot}080$, $S = 5{\cdot}811$. Max. $\Delta/\sigma = 0{\cdot}38$ (extinction coefficient). Extinction coefficient refined, $g = 0{\cdot}586 \times 10^{-7}$ (Stout & Jensen, 1968). Max. peak height in difference Fourier map 0·46 e Å^{-3}. Scattering factors for neutral atoms and f', f'' from *International Tables for X-ray Crystallography* (1974). Enraf–Nonius (1977) *SDP* used for all calculations.

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