Table 2. *Main interatomic distances* (Å) *and bond angles* (°) *in the atomic arrangement of* $Ag_3(NH_4)_3P_6O_{18}.H_2O$

E.s.d.'s are given in parentheses.

The $P(1)_6O_{18}$ ring anion

P(1)	O(*L*1)	O(*L*1)	O(*E*11)	O(*E*21)
O(*L*1)	1·609 (3)	2·477 (4)	2·487 (4)	2·528 (3)
O(*L*1)	101·2 (1)	1·596 (3)	2·523 (4)	2·473 (3)
O(*E*11)	107·1 (1)	110·1 (1)	1·481 (3)	2·573 (4)
O(*E*21)	109·6 (1)	106·7 (2)	120·4 (2)	1·485 (3)

P(1)—P(1) 2·916 (1)

P(1)—O(*L*1)—P(1) 131·0 (2) P(1)—P(1)—P(1) 110·36 (3)

The $P(2)_6O_{18}$ ring anion

P(2)	O(*L*2)	O(*L*2)	O(*E*12)	O(*E*22)
O(*L*2)	1·596 (2)	2·473 (3)	2·538 (3)	2·471 (3)
O(*L*2)	101·5 (2)	1·599 (2)	2·496 (3)	2·522 (3)
O(*E*12)	111·0 (2)	108·2 (2)	1·482 (2)	2·553 (4)
O(*E*22)	106·5 (2)	109·6 (1)	118·7 (2)	1·486 (2)

P(2)—P(2) 2·907 (1)

P(2)—O(*L*2)—P(2) 131·0 (2) P(2)—P(2)—P(2) 110·32 (3)

AgO_5 polyhedron

Ag—O(*E*11)	2·428 (2)	Ag—O(*E*21)	2·362 (2)
Ag—O(*E*12)	2·360 (3)	Ag—O(*E*22)	2·370 (2)
Ag—O(*E*22)	2·652 (3)		

$(NH_4)O_9$ polyhedron

N—O(*L*1)	3·158 (4)	N—O(*E*11)	2·823 (4)
N—O(*E*11)	3·334 (4)	N—O(*E*21)	2·853 (4)
N—O(*E*21)	3·298 (5)	N—O(*L*2)	3·431 (4)
N—O(*E*12)	2·934 (4)	N—O(*E*22)	2·884 (3)
N—O(*W*)	3·154 (4)		

The hydrogen bonds

N—H···O	N—H	H···O	N—O	N—H—O
N—H(1N)···O(*E*21)	0·98 (8)	1·93 (8)	2·853 (4)	155 (5)
N—H(2N)···O(*E*22)	0·85 (6)	2·09 (6)	2·884 (3)	156 (9)
N—H(3N)···O(*E*11)	1·02 (8)	1·83 (9)	2·823 (4)	165 (5)
N—H(4N)···O(*E*12)	0·94 (9)	2·08 (9)	2·934 (4)	150 (5)

drawing was prepared using the *STRUPLO* program (Fischer, 1985).

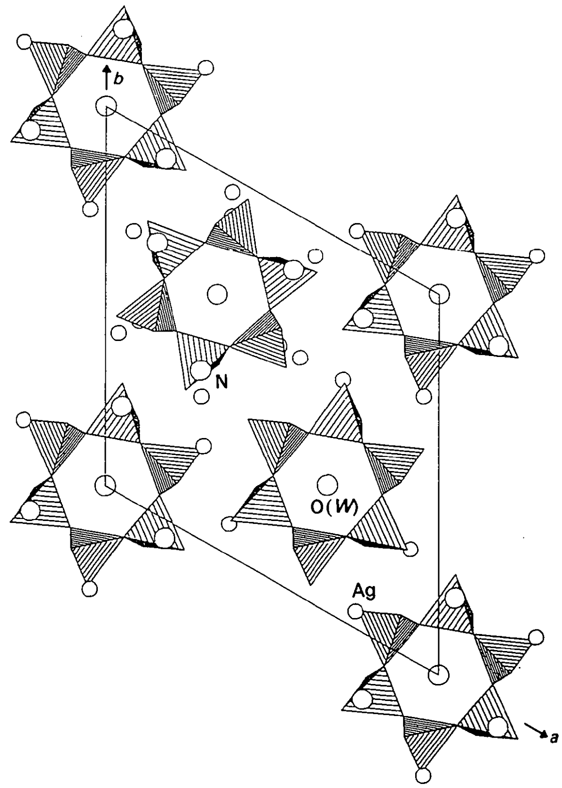

Fig. 1. Projection of the atomic arrangement of $Ag_3(NH_4)_3P_6O_{18}.H_2O$ along the *c* axis. The H atoms have been omitted and the projection is restricted to $-0·10 < z < 0·50$.

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Crystal Chemistry of *cyclo*-Hexaphosphates. XV. Structures of Sodium Ammonium *cyclo*-Hexaphosphate Dihydrate and Sodium Rubidium *cyclo*-Hexaphosphate Hexahydrate

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Abstract. $Na_2(NH_4)_4P_6O_{18}.2H_2O$, $M_r = 627·992$, monoclinic, $P2_1/n$, $a = 13·363$ (7), $b = 11·580$ (12), $c = 6·809$ (5) Å, $\beta = 101·87$ (5)°, $V = 1031$ (2) Å^3, $Z = 2$, $D_x = 2·022$ Mg m^{-3}, λ(Ag $K\alpha$) = 0·5608 Å, $\mu = 0·353$ mm^{-1}, $F(000) = 640$, room temperature, final $R = 0·023$ for 3892 independent reflections.

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$Na_4Rb_2P_6O_{18}.6H_2O$, $M_r = 844{\cdot}16$, triclinic, $P\bar{1}$, $a = 7{\cdot}532\,(3)$, $b = 9{\cdot}752\,(3)$, $c = 8{\cdot}730\,(3)$ Å, $\alpha = 113{\cdot}92\,(4)$, $\beta = 102{\cdot}29\,(4)$, $\gamma = 85{\cdot}00\,(4)°$, $V = 572{\cdot}7\,(9)$ Å^3, $Z = 1$, $D_x = 2{\cdot}449$ Mg m^{-3}, λ(Ag $K\alpha$) $= 0{\cdot}5608$ Å, $\mu = 2{\cdot}768$ mm^{-1}, $F(000) = 412$, room temperature, final $R = 0{\cdot}040$ for 3352 independent reflections. In both compounds the P_6O_{18} ring anions are centrosymmetric and very significantly distorted with P—P—P angles varying from 95·33 to 141·71° as is commonly observed for such rings with $\bar{1}$ internal symmetry. The three-dimensional cohesion between the rings involves interconnection of NaO_6, NO_7 and NO_8 polyhedra in the case of the sodium ammonium salt and of NaO_6 and RbO_7 polyhedra for the sodium rubidium salt. Hydrogen atoms have been located and refined. Detailed hydrogen-bond schemes are reported. In addition, chemical preparations and unit-cell dimensions of $Na_4Cs_2P_6O_{18}.6H_2O$ and $Na_2Tl_4P_6O_{18}.2H_2O$ are given. The former compound is isotypic with the sodium rubidium salt, the latter with the sodium ammonium compound.

Introduction. Some mixed-alkali or mixed-alkali–monovalent cation *cyclo*-hexaphosphates have been previously reported by the authors. They correspond to two different types of stoichiometries for the associated cations: a 1/1 order is observed for $Li_3Na_3P_6O_{18}.12H_2O$ (Averbuch-Pouchot, 1989), $Li_3K_3P_6O_{18}.H_2O$ (Averbuch-Pouchot, 1989) and $Ag_3(NH_4)_3P_6O_{18}.H_2O$ (Averbuch-Pouchot, 1991); a 1/2 order is observed for $Ag_2Li_4P_6O_{18}.2H_2O$ (Averbuch-Pouchot & Durif, 1991).

In the present work we report two new structure types corresponding to this second type of order: $Na_2(NH_4)_4P_6O_{18}.2H_2O$ and $Na_4Rb_2P_6O_{18}.6H_2O$. Two other compounds belonging to these structure types have been characterized: $Na_4Cs_2P_6O_{18}.6H_2O$, isotypic with the sodium rubidium salt, and $Na_2Tl_4P_6O_{18}.2H_2O$, isotypic with the sodium ammonium salt. Their unit-cell dimensions are $a = 7{\cdot}653\,(4)$, $b = 9{\cdot}959\,(4)$, $c = 8{\cdot}740\,(4)$ Å, $\alpha = 114{\cdot}64\,(4)$, $\beta = 102{\cdot}47\,(4)$, $\gamma = 84{\cdot}94\,(4)°$ for the sodium caesium salt and $a = 13{\cdot}215\,(8)$, $b = 11{\cdot}583\,(18)$, $c = 6{\cdot}874\,(8)$ Å, $\beta = 101{\cdot}43\,(5)°$ for the sodium thallium salt.

Experimental. Crystals of the title compounds have been prepared by slow evaporation at room temperature of aqueous solutions of the alkali *cyclo*-hexaphosphates in the proper ratios. Crystals of $Na_4Rb_2P_6O_{18}.6H_2O$ appear as stout triclinic prisms while those of $Na_2(NH_4)_4P_6O_{18}.2H_2O$ are elongated monoclinic prisms. The sodium caesium salt, reported in the *Introduction*, was prepared by the same process while the sodium thallium compound was synthesized by evaporation at room temperature of an aqueous solution of sodium *cyclo*-hexaphosphate and thallium nitrate with a starting stoichiometry Na/Tl = 3/2.

$Na_2(NH_4)_4P_6O_{18}.2H_2O$. Crystal size: 0·48 × 0·40 × 0·32 mm. Density not measured. Nonius CAD-4 diffractometer, graphite monochromator. 25 reflections ($11{\cdot}0 < \theta < 15{\cdot}0°$) for refining unit-cell dimensions. ω scan, scan width 1·20°, variable scan speed 0·02–0·06° s^{-1}, total background measuring time between 30 and 10 s. 3892 reflections collected ($2 < \theta < 30°$), $\pm h$, k, l, $h_{max} = 23$, $k_{max} = 20$, $l_{max} = 12$. Two orientation ($\bar{5}7\bar{3}$ and $\overline{10},\bar{5},1$) and two intensity ($57\bar{3}$ and $\bar{5}73$) control reflections, measured every 2 h without any significant variation. Lorentz and polarization corrections, no absorption correction.

$Na_4Rb_2P_6O_{18}.6H_2O$. Crystal size: 0·18 × 0·30 × 0·40 mm. Density not measured. Philips PW1100 diffractometer, graphite monochromator. 20 reflections ($10{\cdot}0 < \theta < 15{\cdot}0°$) for refining unit-cell dimensions. $\omega/2\theta$ scan, scan width 1·20°, scan speed 0·03° s^{-1}, total background measuring time 6 s. 4967 reflections collected ($3 < \theta < 30°$), $\pm h$, $\pm k$, l, $h_{max} = 13$, $k_{max} = 16$, $l_{max} = 14$. 4685 independent reflections after averaging Friedel pairs ($R_{int} = 0{\cdot}019$). Two orientation and intensity reference reflections ($\bar{4}40$ and $4\bar{7}0$) measured every 2 h without any significant variation. Lorentz and polarization corrections, no absorption correction.

The two crystal structures were solved using the same strategy: heavy atoms located by direct methods (*MULTAN*77; Main, Lessinger, Woolfson, Germain & Declercq, 1977) and successive Fourier syntheses. H atoms located by difference Fourier syntheses. Anisotropic full-matrix least-squares refinement (on F), isotropic for H atoms. Unit weights. Scattering factors for neutral atoms and f', f'' from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B). Enraf–Nonius (1977) *SDP* used for all calculations. Computer used: MicroVAX II. In both cases no secondary-extinction correction. Final refinement cycles for $Na_2(NH_4)_4P_6O_{18}.2H_2O$ with 3892 reflections (no rejection). Final $R = 0{\cdot}023$ ($wR = 0{\cdot}031$), $S = 0{\cdot}613$, max. $\Delta/\sigma = 0{\cdot}05$, max. peak height in the final difference Fourier synthesis = 0·462 e Å^{-3}. Final refinement cycles for $Na_4Rb_2P_6O_{18}.6H_2O$ with 3352 reflections [$I > 3\sigma(I)$]. Final $R = 0{\cdot}040$ ($wR = 0{\cdot}044$), $S = 1{\cdot}063$, max. $\Delta/\sigma = 0{\cdot}01$, max. peak height in the final difference Fourier synthesis = 0·895 e Å^{-3}.

Tables 1 and 2 list the final atomic coordinates for these two structures.*

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53686 (62 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Final atomic coordinates and* B_{eq}/B_{iso} *values for* $Na_2(NH_4)_4P_6O_{18}.2H_2O$

H atoms were refined isotropically. E.s.d.'s are given in parentheses.

$$B_{eq} = (4/3)\sum_i\sum_j \beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}/B_{iso} (Å²)
P(1)	0·34893 (2)	0·46059 (3)	0·17916 (5)	1·227 (4)
P(2)	0·64252 (2)	0·33170 (3)	0·04981 (5)	1·284 (4)
P(3)	0·48112 (2)	0·25573 (3)	0·25302 (5)	1·279 (4)
Na	0·21742 (4)	0·20204 (5)	0·07810 (8)	1·543 (8)
N(1)	0·3615 (1)	0·3627 (1)	0·6722 (2)	2·55 (2)
N(2)	0·4228 (1)	0·9419 (1)	0·2449 (2)	2·45 (2)
O(E11)	0·19563 (8)	0·01024 (9)	0·1591 (2)	2·07 (2)
O(E12)	0·21796 (8)	0·89388 (9)	0·4819 (2)	1·89 (2)
O(L12)	0·40730 (7)	0·55918 (8)	0·0805 (2)	1·67 (1)
O(L13)	0·05342 (7)	0·88645 (8)	0·2186 (2)	1·81 (2)
O(E21)	0·30563 (8)	0·74226 (9)	0·0757 (2)	1·97 (2)
O(E22)	0·30041 (8)	0·6299 (1)	0·7528 (2)	2·32 (2)
O(L23)	0·03826 (7)	0·23126 (9)	0·5683 (2)	1·73 (1)
O(E31)	0·44628 (8)	0·7746 (1)	0·5604 (2)	2·25 (2)
O(E32)	0·39182 (7)	0·18145 (8)	0·1808 (2)	2·09 (2)
O(W)	0·3760 (1)	−0·0035 (1)	0·7902 (2)	3·65 (3)
H(N11)	0·338 (2)	0·365 (3)	0·807 (5)	3·8 (7)
H(N12)	0·428 (2)	0·343 (3)	0·685 (5)	3·4 (7)
H(N13)	0·319 (2)	0·313 (3)	0·593 (5)	3·6 (7)
H(N14)	0·154 (3)	0·924 (3)	0·898 (5)	4·6 (8)
H(N21)	0·069 (2)	0·399 (3)	0·139 (5)	3·4 (7)
H(N22)	0·479 (2)	0·953 (3)	0·225 (5)	4·0 (7)
H(N23)	0·113 (2)	0·501 (3)	0·237 (5)	3·8 (7)
H(N24)	0·384 (2)	0·897 (3)	0·175 (5)	3·7 (7)
H(1W)	0·178 (3)	0·553 (3)	0·718 (5)	4·5 (8)
H(2W)	0·157 (3)	0·452 (3)	0·812 (5)	4·6 (8)

Table 2. *Final atomic coordinates and* B_{eq}/B_{iso} *values for* $Na_4Rb_2P_6O_{18}.6H_2O$

H atoms were refined isotropically. E.s.d.'s are given in parentheses.

$$B_{eq} = (4/3)\sum_i\sum_j \beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}/B_{iso} (Å²)
Rb	0·24345 (5)	0·37992 (4)	0·84913 (4)	2·153 (6)
P(1)	0·0750 (1)	0·24108 (8)	0·13752 (9)	1·03 (1)
P(2)	0·7412 (1)	0·88303 (8)	0·61883 (9)	1·15 (1)
P(3)	0·2429 (1)	0·80028 (8)	0·12834 (9)	1·04 (1)
Na(1)	0·5352 (2)	0·2863 (2)	0·2214 (2)	1·81 (3)
Na(2)	0·1511 (2)	0·8597 (2)	0·5250 (2)	2·21 (3)
O(E11)	0·7600 (3)	0·7884 (3)	0·9380 (3)	1·67 (4)
O(E12)	−0·0182 (4)	0·6013 (3)	0·7729 (3)	1·71 (4)
O(L12)	0·0860 (3)	0·1553 (2)	0·2615 (3)	1·40 (4)
O(L13)	0·0911 (3)	0·8521 (3)	0·0036 (3)	1·50 (4)
O(L23)	0·3316 (3)	0·9614 (2)	0·2529 (3)	1·34 (4)
O(E21)	0·8168 (4)	0·9068 (3)	0·4883 (3)	1·81 (4)
O(E22)	0·5937 (4)	0·7737 (3)	0·5698 (3)	1·99 (5)
O(E31)	0·1556 (4)	0·7386 (3)	0·2239 (3)	1·80 (4)
O(E32)	0·6150 (3)	0·2883 (3)	0·9660 (3)	1·91 (5)
O(W1)	0·3327 (4)	0·9537 (3)	0·8047 (3)	2·02 (5)
O(W2)	0·5511 (4)	0·4669 (3)	0·7129 (4)	2·47 (6)
O(W3)	0·1936 (4)	0·6218 (3)	0·5519 (3)	2·23 (5)
H(1W1)	0·31 (1)	0·017 (8)	0·886 (9)	3 (2)
H(2W1)	0·41 (1)	0·017 (9)	0·81 (1)	5 (2)
H(1W2)	0·490 (9)	0·604 (7)	0·370 (8)	2 (1)
H(2W2)	0·37 (1)	0·609 (8)	0·286 (9)	3 (2)
H(1W3)	0·188 (9)	0·545 (7)	0·453 (8)	3 (2)
H(2W3)	0·14 (1)	0·586 (8)	0·616 (9)	4 (2)

Table 3. *Main interatomic distances* (Å) *and bond angles* (°) *in the atomic arrangement of* $Na_2(NH_4)_4P_6O_{18}.2H_2O$

E.s.d.'s are given in parentheses.

The P_6O_{18} ring anion

$P(1)O_4$ tetrahedron

P(1)	O(E11)	O(E12)	O(L12)	O(L13)
O(E11)	1·472 (1)	2·543 (1)	2·522 (2)	2·479 (1)
O(E12)	118·83 (6)	1·482 (1)	2·521 (1)	2·537 (1)
O(L12)	109·95 (6)	109·38 (6)	1·606 (1)	2·420 (1)
O(L13)	107·69 (6)	110·89 (6)	98·11 (5)	1·597 (1)

$P(2)O_4$ tetrahedron

P(2)	O(L12)	O(L23)	O(E21)	O(E22)
O(L12)	1·608 (1)	2·415 (1)	2·515 (1)	2·525 (1)
O(L23)	97·66 (5)	1·600 (1)	2·484 (1)	2·536 (1)
O(E21)	109·06 (6)	107·49 (6)	1·479 (1)	2·544 (2)
O(E22)	110·15 (6)	111·21 (6)	119·11 (6)	1·471 (1)

$P(3)O_4$ tetrahedron

P(3)	O(L13)	O(L23)	O(E31)	O(E32)
O(L13)	1·606 (1)	2·489 (2)	2·460 (1)	2·537 (1)
O(L23)	101·56 (6)	1·607 (1)	2·544 (2)	2·461 (2)
O(E31)	105·98 (6)	111·25 (6)	1·473 (1)	2·545 (2)
O(E32)	110·98 (5)	106·06 (6)	119·58 (7)	1·471 (1)

P(1)—P(2)	2·8820 (5)	P(1)—O(L12)—P(2)	127·46 (6)
P(1)—P(3)	2·9393 (4)	P(1)—O(L13)—P(3)	133·12 (6)
P(2)—P(3)	2·9272 (5)	P(2)—O(L23)—P(3)	131·75 (6)
P(2)—P(1)—P(3)	132·63 (2)		
P(1)—P(2)—P(3)	128·45 (1)	P(1)—P(3)—P(2)	98·73 (1)

NaO_6 polyhedron

Na—O(E11)	2·322 (1)	Na—O(E31)	2·352 (1)
Na—O(E12)	2·449 (1)	Na—O(E32)	2·304 (1)
Na—O(E21)	2·483 (1)	Na—O(E22)	2·368 (1)

$N(1)O_7$ polyhedron

N(1)—O(E11)	2·808 (2)	N(1)—O(E12)	2·799 (2)
N(1)—O(E22)	3·276 (2)	N(1)—O(L12)	3·325 (2)
N(1)—O(L23)	3·379 (2)	N(1)—O(L13)	3·113 (2)
N(1)—O(E21)	2·870 (2)		

$N(2)O_8$ polyhedron

N(2)—O(W)	2·839 (2)	N(2)—O(E31)	2·863 (2)
N(2)—O(W)	3·095 (2)	N(2)—O(L23)	3·351 (2)
N(2)—O(E21)	2·895 (2)	N(2)—O(E32)	2·826 (2)
N(2)—O(E12)	3·496 (2)	N(2)—O(E11)	3·074 (2)

The hydrogen bonds

O(N)—H···O	O(N)—H	H···O	O(N)—O	O(N)—H···O
N(1)—H(N11)···O(E12)	1·03 (3)	1·78 (3)	2·779 (2)	168 (3)
N(1)—H(N12)···O(L12)	0·90 (3)	2·69 (3)	3·325 (2)	128 (2)
N(1)—H(N13)···O(E21)	0·91 (3)	1·99 (3)	2·870 (2)	163 (3)
N(1)—H(N14)···O(E11)	0·86 (3)	2·01 (3)	2·808 (2)	154 (3)
N(2)—H(N21)···O(E31)	0·93 (3)	1·96 (3)	2·863 (2)	166 (3)
N(2)—H(N22)···O(W)	0·80 (3)	2·05 (3)	2·839 (2)	170 (3)
N(2)—H(N23)···O(E32)	0·86 (3)	2·17 (3)	2·826 (2)	133 (3)
N(2)—H(N24)···O(E21)	0·82 (3)	2·11 (3)	2·895 (2)	160 (3)
O(W)—H(1W)···O(E22)	0·97 (3)	1·84 (3)	2·784 (2)	166 (3)
O(W)—H(2W)···O(E12)	0·90 (3)	2·06 (3)	2·908 (2)	155 (3)

Discussion. The main interest of these two atomic arrangements is the geometry of the common cyclic phosphoric group, P_6O_{18}. Up to now, only 28 accurate structure determinations of *cyclo*-hexaphosphates have been performed. In these arrangements, the phosphoric ring anion can adopt various internal symmetries (3, $\bar{3}$, *m*, 2/*m*), but in more than 50% of cases (18) the internal symmetry is $\bar{1}$. The centrosymmetric P_6O_{18} groups are always very distorted, with P—P—P angles varying from 88 to 143°, while for the other internal symmetries they do not depart significantly from an average value of 109°. In the two atomic arrangements described in the present work the P_6O_{18} ring anions are also centrosymmetric and again very distorted: 98·73 < P—P—P < 132·63° for the sodium ammonium salt and 95·33 < P—P—P < 141·71° for the sodium rubidium salt.

The great flexibility of the P_6O_{18} ring can probably partly explain the very good stability of *cyclo*-hexaphosphates. Tables 3 and 4 report the main interatomic distances and bond angles in the two P_6O_{18}

Table 4. *Main interatomic distances* (Å) *and bond angles* (°) *in the atomic arrangement of* $Na_4Rb_2P_6O_{18}.6H_2O$

E.s.d.'s are given in parentheses.

The P_6O_{18} ring anion

$P(1)O_4$ tetrahedron

P(1)	O(*E*11)	O(*E*12)	O(*L*12)	O(*L*13)
O(*E*11)	1·482 (3)	2·562 (3)	2·536 (4)	2·512 (3)
O(*E*12)	119·2 (2)	1·487 (2)	2·508 (4)	2·523 (3)
O(*L*12)	110·6 (2)	108·5 (1)	1·601 (3)	2·389 (3)
O(*L*13)	109·4 (1)	109·9 (1)	96·8 (1)	1·594 (2)

$P(2)O_4$ tetrahedron

P(2)	O(*L*12)	O(*L*23)	O(*E*21)	O(*E*22)
O(*L*12)	1·605 (2)	2·517 (3)	2·447 (4)	2·533 (3)
O(*L*23)	103·0 (1)	1·611 (2)	2·544 (3)	2·455 (3)
O(*E*21)	104·9 (1)	110·8 (1)	1·480 (3)	2·579 (4)
O(*E*22)	110·4 (2)	105·1 (1)	121·3 (1)	1·479 (3)

$P(3)O_4$ tetrahedron

P(3)	O(*L*13)	O(*L*23)	O(*E*31)	O(*E*32)
O(*L*13)	1·602 (3)	2·437 (5)	2·529 (4)	2·460 (4)
O(*L*23)	98·7 (2)	1·608 (2)	2·543 (5)	2·478 (4)
O(*E*31)	110·1 (1)	110·5 (1)	1·484 (3)	2·522 (3)
O(*E*32)	109·5 (1)	106·2 (1)	119·7 (2)	1·485 (3)

P(1)—P(2)	2·907 (1)	P(1)—O(*L*12)—P(2)	130·1 (1)
P(1)—P(3)	2·885 (1)	P(1)—O(*L*13)—P(3)	129·1 (2)
P(2)—P(3)	2·975 (1)	P(2)—O(*L*23)—P(3)	135·1 (2)
P(2)—P(1)—P(3)	141·71 (4)		
P(1)—P(2)—P(3)	95·33 (3)	P(1)—P(3)—P(2)	109·41 (3)

RbO_7 polyhedron

Rb—O(*E*11)	2·941 (3)	Rb—O(*E*31)	3·157 (3)
Rb—O(*E*12)	2·975 (3)	Rb—O(*E*32)	2·959 (2)
Rb—O(*E*21)	3·110 (2)	Rb—O(*E*32)	3·137 (2)
Rb—O(*W*2)	3·136 (4)		

$Na(1)O_6$ polyhedron

Na(1)—O(*E*11)	2·356 (3)	Na(1)—O(*W*1)	2·404 (3)
Na(1)—O(*E*22)	2·515 (3)	Na(1)—O(*W*2)	2·304 (3)
Na(1)—O(*E*32)	2·438 (4)	Na(1)—O(*W*3)	2·460 (3)

$Na(2)O_6$ polyhedron

Na(2)—O(*L*12)	2·892 (3)	Na(2)—O(*E*31)	2·413 (3)
Na(2)—O(*E*21)	2·495 (3)	Na(2)—O(*W*1)	2·378 (3)
Na(2)—O(*E*21)	2·363 (3)	Na(2)—O(*W*3)	2·412 (4)

The hydrogen bonds

O—H···O	O—H	H···O	O—O	O—H···O
O(*W*1)—H(1*W*1)···O(*E*11)	0·78 (6)	2·00 (6)	2·764 (3)	166 (9)
O(*W*1)—H(2*W*1)···O(*L*23)	0·87 (9)	2·17 (9)	2·929 (4)	145 (6)
O(*W*2)—H(1*W*2)···O(*E*22)	0·80 (5)	1·92 (5)	2·719 (3)	179 (6)
O(*W*2)—H(2*W*2)···O(*E*31)	0·89 (7)	2·11 (8)	2·968 (4)	163 (6)
O(*W*3)—H(1*W*3)···O(*E*12)	0·88 (5)	2·13 (6)	2·902 (3)	147 (6)
O(*W*3)—H(2*W*3)···O(*E*12)	0·95 (9)	1·94 (9)	2·826 (5)	155 (6)

ring anions observed in the title compounds. Apart from the distortion of the rings, the other geometrical features measured here are those commonly observed in all condensed phosphoric anions.

In the case of the sodium ammonium salt the phosphoric rings are interconnected in a three-dimensional way by distorted NaO_6 octahedra and NO_7 and NO_8 polyhedra while for the sodium rubidium compound this cohesion involves interconnection of RbO_7 polyhedra and distorted NaO_6 octahedra.

In the first of these compounds the Na—O distances vary from 2·304 to 2·483 Å and the NaO_6 polyhedron does not include any O(*L*) bonding oxygen atom. Within 3·5 Å the first ammonium group has seven neighbors with N(1)—O distances ranging from 2·799 to 3·379 Å while the second ammonium group has an eightfold coordination involving six oxygen atoms and two water molecules with N(2)—O distances varying from 2·826 to 3·496 Å.

For the sodium rubidium salt the two sodium atoms are coordinated by six oxygen atoms building distorted octahedra, with Na—O distances ranging from 2·304 to 2·515 Å for Na(1) and from 2·363 to 2·495 Å for Na(2). Within 3·5 Å the rubidium atom has seven neighbors with $2·941 < Rb—O < 3·157$ Å.

It is to be noticed that in both compounds some bonding oxygens [O(*L*)] take part in the coordination polyhedra of the associated cations, a feature not

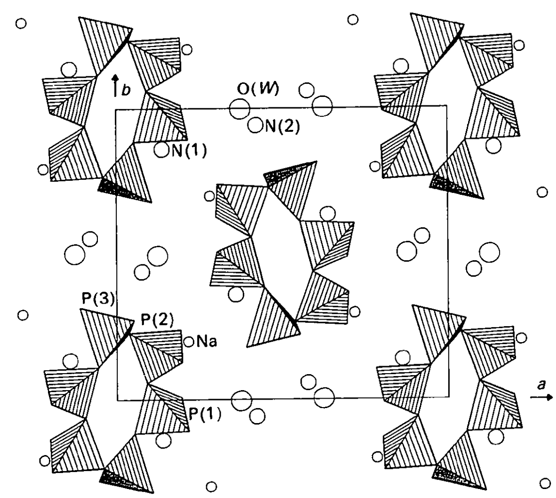

Fig. 1. Projection of the atomic arrangement of $Na_2(NH_4)_4P_6O_{18}.2H_2O$ along the *c* axis.

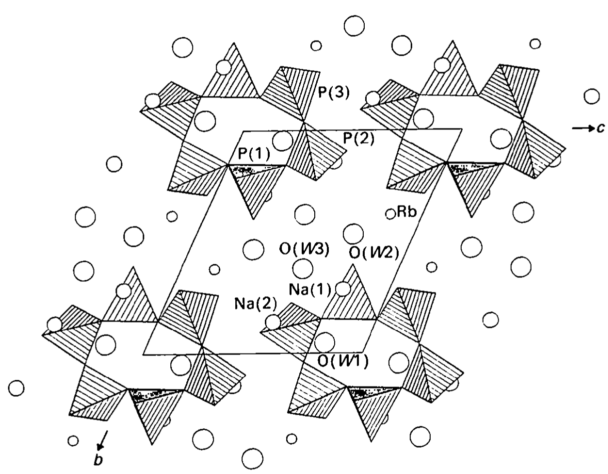

Fig. 2. Projection of the atomic arrangement of $Na_4Rb_2P_6O_{18}.6H_2O$ along the *a* axis.

frequently observed in condensed phosphate chemistry.

Main interatomic distances in these various polyhedra are given in Tables 3 and 4 which also report the main geometrical features of the two three-dimensional hydrogen-bond schemes.

Fig. 1 is a projection along the *c* axis of the sodium ammonium salt and Fig. 2 a projection along the *a* axis of the sodium rubidium compound. In both figures, the hydrogen atoms have been omitted. The drawings were prepared using the *STRUPLO* program (Fischer, 1985).

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Structure of Mixed-Valent Titanium Silicophosphates, $KTi_3P_6Si_2O_{25}$ and $CsTi_3P_6Si_2O_{25}$

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Abstract. $KTi_3P_6Si_2O_{25}$, $M_r = 824{\cdot}80$, trigonal, $P\bar{3}1c$, $a = 8{\cdot}2648\,(9)$, $c = 17{\cdot}038\,(1)$ Å, $V = 1007{\cdot}9\,(3)$ Å^3, $Z = 2$, $D_x = 2{\cdot}72$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 2{\cdot}07$ mm^{-1}, $F(000) = 403$, $T = 294$ K, $R = 0{\cdot}036$, $wR = 0{\cdot}043$ for 1438 reflections with $I > 3\sigma(I)$ out of 4577 unique reflections measured. $CsTi_3P_6Si_2O_{25}$, $M_r = 918{\cdot}60$, trigonal, $P\bar{3}1c$, $a = 8{\cdot}2145\,(6)$, $c = 17{\cdot}249\,(1)$ Å, $V = 1008{\cdot}0\,(2)$ Å^3, $Z = 2$, $D_x = 3{\cdot}03$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 3{\cdot}63$ mm^{-1}, $F(000) = 439$, $T = 294$ K, $R = 0{\cdot}034$, $wR = 0{\cdot}039$ for 1655 reflections with $I > 3\sigma(I)$ out of 4547 unique reflections measured. The '$Ti_3P_6Si_2O_{25}$' host lattice is built up from corner-sharing TiO_6 octahedra and PO_4 and SiO_4 tetrahedra, which form wide tunnels in which the K or Cs ions are located. In the titanium and molybdenum silicophosphates, the thermal motion of the *A* ion in the tunnel increases rapidly as the difference between the *A*—O length and the sum of the ionic radii increases.

Introduction. During the investigation of the system *A*–Mo–P–Si–O, the silicomolybdenophosphates $AMo_3P_6Si_2O_{25}$ (*A* = K, Rb, Tl, Cs) (Leclaire, Borel, Grandin & Raveau, 1985; Leclaire, Monier & Raveau, 1984, 1985), MoP_3SiO_{11} (Leclaire & Raveau, 1987), $Mo_4P_6Si_2O_{25}$ (Leclaire, Lamire & Raveau, 1988) and $Mo_2P_4Si_4O_{23}$ (Leclaire, Borel, Grandin & Raveau, 1989) were isolated. The oxides $AMo_3P_6Si_2O_{25}$ exhibit a particular behaviour with respect to the valency of molybdenum. This latter element is characterized here by mixed valency (Mo^{III}–Mo^{IV}) which cannot lead to electronic delocalization since the MoO_6 octahedra are isolated, *i.e.* are linked to each other through PO_4 tetrahedra. From the crystal structure, it appears that two sites are available for molybdenum, Mo(1) located within the layers and Mo(2) bridging the layers. The number of sites suggests that they are occupied in an ordered way by Mo^{IV} and Mo^{III} respectively, according to the formula $AMo_2^{IV}Mo^{III}P_6Si_2O_{25}$. However, an examination of the Mo—O bond lengths shows clearly that this type of ordering of Mo^{IV} and Mo^{III} does not exist. Thus, although the Mo(1)—O distances are longer than the Mo(2)—O distances, indicating that the valency of Mo(2) is greater than that of Mo(1), the mean length of the Mo(1)—O bonds is intermediate between that of the Mo(2)—O bonds and the mean values of the Mo^{III}—O bonds observed for MoP_3SiO_{11} and $Mo_4P_6Si_2O_{25}$. This leads to the conclusion that molybdenum exhibits a mixed valency, Mo^{III}–Mo^{IV}, within the $Mo_2P_6Si_2O_{25}$ layers whereas it is tetravalent between these layers. In order to determine whether this phenomenon could be generalized to the other $AM_3P_6Si_2O_{25}$ members of the series, the crystal growth of silicophosphates of titanium was undertaken. We report here

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