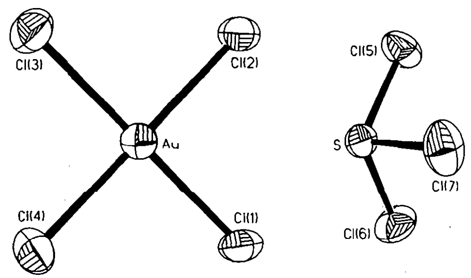

Fig. 1. Thermal-ellipsoid plot (50% level) of the asymmetric unit, showing the atom-numbering scheme.

Fig. 1). The average S—Cl bond length is 1·981 Å and the average Cl—S—Cl angle 101·5°, very similar to the values in $SCl_3^+.ICl_4^-$ (Edwards, 1978) of 1·988 Å, 101·3°. In the $SbCl_6^-$ salt (Christian *et al.*, 1986) the bonds are somewhat shorter (av. 1·956 Å) and the angles wider (av. 103·7°). The authors attribute these differences, and those between other SCl_3^+ salts in the literature, to secondary interactions (see below). The anions display considerable distortion from the ideal geometry, with a short Au—Cl(4) bond (2·265 Å, *cf.* 2·279, 2·282, 2·296 Å for the other Au—Cl bonds). This is also rationalized in terms of secondary interactions. The extent of the distortion is marginally less than in the Se analogue (Jones *et al.*, 1987).

Secondary interactions. Fig. 2 shows the formation of a centrosymmetric dimer by secondary S···Cl interactions of average length 3·08 Å (*cf.* 3·11 Å in $SCl_3^+.ICl_4^-$). These complete a distorted octahedral coordination at the S atom. The secondary interactions in the isostructural Se analogue are appreciably shorter (av. 2·94 Å). The one anionic chlorine that does not take part in secondary interactions, Cl(4), is the one with the shortest Au—Cl bond (see above).

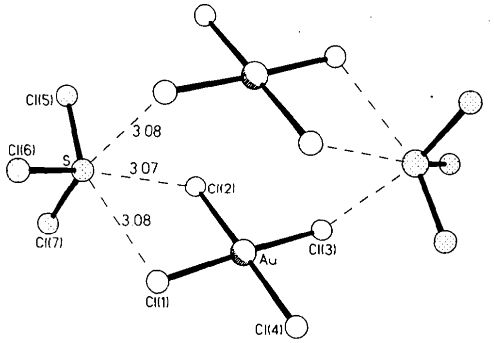

Fig. 2. The centrosymmetric dimer $[SCl_3.AuCl_4]_2$, showing the secondary interactions (dashed lines, distances in Å). The symmetry operator generating the second half of the dimer is $-x$, $1-y$, $1-z$.

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Crystal Structures of Two New Types of *cyclo*-Tetraphosphates: Tetracalcium Tetrapotassium Tris(*cyclo*-tetraphosphate) Octahydrate and Calcium Disodium *cyclo*-Tetraphosphate 5·5-Hydrate

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Abstract. $Ca_4K_4(P_4O_{12})_3.8H_2O$, $M_r = 1408·50$, monoclinic, $P2_1/a$, $a = 20·38\ (1)$, $b = 12·683\ (5)$, $c = 7·830\ (2)$ Å, $\beta = 89·31\ (5)°$, $V = 2024\ (5)$ Å^3, $Z = 2$, $D_x = 2·311$ Mg m^{-3}, $\lambda(\text{Mo}\ K\alpha) = 0·7107$ Å, $\mu = 1·520$ mm^{-1}, $F(000) = 1408$, $T = 295$ K, $R = 0·031$ for 2793 independent reflexions. $CaNa_2P_4O_{12}.5·5H_2O$, $M_r = 501·03$, orthorhombic, $Pma2$, $a = 27·88\ (10)$, $b = 7·536\ (5)$, $c = 7·378\ (5)$ Å, $V = 1550\ (3)$ Å^3, $\mu =$

0·956 mm^{-1}, $F(000) = 1012$, $T = 298$ K, $R = 0·066$ for 1787 independent reflexions. A common feature for the two compounds is the coexistence in their atomic arrangements of two crystallographically independent P_4O_{12} ring anions. One of the two anionic configurations (m) observed in the second title compound has never been described before. A complete hydrogen-bond scheme is given for the first compound.

Introduction. Very little is known concerning alkali–calcium *cyclo*-tetraphosphates. One can only report two salts: $CaK_2P_4O_{12}$ and $Ca(NH_4)_2P_4O_{12}.2H_2O$. $CaK_2P_4O_{12}$ (Cavero-Ghersi & Durif, 1975) is isotypic with the corresponding strontium salt $SrK_2P_4O_{12}$ (Durif, Martin, Tordjman & Tran Qui, 1966). The crystal structure of $Ca(NH_4)_2P_4O_{12}.2H_2O$ has been investigated by Tordjman, Masse & Guitel (1976).

In the present work we describe two new structure types of calcium–alkali *cyclo*-tetraphosphates: $Ca_4K_4(P_4O_{12})_3.8H_2O$ and $CaNa_2P_4O_{12}.5·5H_2O$.

Experimental. (I) $Ca_4K_4(P_4O_{12})_3.8H_2O$. Crystals are difficult to obtain. The most reproducible process is the following. To an aqueous solution of potassium *cyclo*-tetraphosphate one adds very slowly (a few drops a day) a concentrated aqueous solution of calcium chloride. After a few days the liquor becomes turbid; after a few weeks a crystalline crust is observed at the bottom of the solution. The addition of calcium chloride is then stopped and the system is kept at room temperature for a few more weeks. After filtration, well developed crystals of $Ca_4K_4(P_4O_{12})_3.8H_2O$ can be extracted from the solid crust; they appear as stout rectangular prisms. Density not measured. Prismatic crystal 0·13 × 0·24 × 16 mm. Nicolet diffractometer, graphite monochromator. Systematic absences: $h0l$: $h = 2n$, $0k0$: $k = 2n$. 16 reflexions ($7 < \theta < 11·5°$) for refining unit-cell dimensions. ω scan, scan width 1·20°, scan speed between 0·75 and 1·00° min^{-1}, background measuring time taken as 20% of the scan time. 4801 measured reflexions ($3 < \theta < 30°$), $\pm h, k, l$, $h_{\text{max}} = 28$, $k_{\text{max}} = 17$, $l_{\text{max}} = 10$. Two intensity and orientation reference reflexions ($4\bar{4}0$ and 440) every 200 scans, no variation. 4298 independent reflexions ($R_{\text{int}} = 0·013$). Lorentz and polarization corrections, no absorption correction. Unit weights. Direct methods (*MULTAN*77, Main, Lessinger, Germain, Declercq & Woolfson, 1977) used for structure determination. H atoms from difference-Fourier syntheses. Anisotropic full-matrix least-squares refinement (on F) for non-hydrogen atoms, isotropic for H atoms. Final refinement with 2793 reflexions ($I > 4\sigma_I$). Final $R = 0·031$ ($wR = 0·036$), $S = 1·977$. Max. $\Delta/\sigma = 0·09$. Max. peak height in final difference-Fourier synthesis 0·43 e $Å^{-3}$. No extinction correction. Scattering factors for neutral atoms and f', f'' from *International Tables for X-ray Crystallography* (1974). Enraf–Nonius (1977) *SDP* used for all calculations. Computer used: MICROVAX II.

(II) $CaNa_2P_4O_{12}.5·5H_2O$. Crystals are readily obtained by slow evaporation at room temperature of an aqueous solution of sodium *cyclo*-tetraphosphate and

Table 1. *Final atomic coordinates for* $Ca_4K_4(P_4O_{12})_3.8H_2O$

Starred atoms have been refined isotropically. $B_{eq} = \frac{4}{3}\sum_i\sum_j \mathbf{a}_i.\mathbf{a}_j\beta_{ij}$. E.s.d.'s are in parentheses.

	x	y	z	B_{eq}($Å^2$)
Ca(1)	0·12316 (4)	0·25512 (6)	0·4940 (1)	0·95 (1)
Ca(2)	0·08625 (4)	0·80389 (6)	0·0005 (1)	1·02 (1)
K(1)	0·16263 (5)	0·23065 (9)	0·0115 (1)	2·36 (2)
K(2)	0·33452 (5)	0·05043 (9)	0·2650 (2)	2·73 (2)
P(1)	0·28343 (5)	0·32829 (8)	0·3149 (1)	1·01 (2)
P(2)	0·38260 (5)	0·49243 (8)	0·3322 (1)	0·98 (2)
P(3)	0·13871 (5)	0·00394 (8)	0·2994 (1)	1·08 (2)
P(4)	0·28189 (5)	0·31449 (8)	0·6836 (1)	1·04 (2)
P(5)	0·52083 (5)	0·11376 (8)	0·1677 (1)	1·09 (2)
P(6)	0·51679 (5)	0·11080 (8)	−0·2094 (1)	1·10 (2)
O(E11)	0·3185 (1)	0·2670 (2)	0·1815 (4)	1·65 (5)
O(E12)	0·2105 (1)	0·3335 (2)	0·3141 (4)	1·51 (5)
O(L12)	0·3085 (1)	0·4487 (2)	0·3134 (4)	1·03 (5)
O(E21)	0·0715 (1)	0·9252 (2)	0·7691 (4)	1·49 (5)
O(E22)	0·1206 (2)	0·1076 (2)	0·7002 (4)	1·53 (5)
O(L23)	0·1021 (1)	0·9678 (2)	0·4721 (4)	1·02 (5)
O(E31)	0·0995 (2)	−0·0351 (2)	0·1545 (4)	1·61 (6)
O(E32)	0·1562 (2)	0·1170 (2)	0·3102 (4)	1·71 (6)
O(L34)	0·2927 (1)	0·4402 (2)	0·6908 (4)	1·23 (5)
O(E41)	0·3255 (1)	0·2619 (2)	0·8076 (4)	1·59 (6)
O(E42)	0·2904 (1)	0·7983 (3)	0·3058 (4)	1·77 (6)
O(L14)	0·1911 (1)	0·7856 (2)	0·5038 (4)	1·13 (5)
O(E51)	0·4528 (1)	0·1563 (2)	0·1619 (4)	1·66 (6)
O(E52)	0·4258 (1)	0·8306 (3)	0·7459 (4)	1·85 (6)
O(L56)	0·4790 (2)	0·0029 (2)	0·7562 (4)	1·90 (6)
O(E61)	0·4667 (2)	0·1960 (2)	0·7904 (4)	1·80 (6)
O(E62)	0·4257 (1)	0·8810 (3)	0·3269 (4)	1·97 (6)
O(L65)	0·4526 (1)	0·9079 (2)	0·0242 (4)	1·45 (5)
O(W1)	0·2311 (2)	0·5768 (3)	0·0405 (6)	3·85 (9)
O(W2)	0·4880 (2)	0·6839 (3)	0·5074 (5)	2·59 (7)
O(W3)	0·0291 (1)	0·1365 (3)	−0·0131 (4)	1·84 (6)
O(W4)	0·1572 (2)	0·5517 (4)	0·3928 (7)	4·7 (1)
H(1W1)	0·297 (4)	0·124 (7)	0·91 (1)	6 (2)*
H(2W1)	0·241 (4)	0·545 (6)	0·12 (1)	4 (2)*
H(1W2)	0·500 (4)	0·304 (6)	0·57 (1)	3 (2)*
H(2W2)	0·513 (4)	0·664 (7)	0·60 (1)	6 (2)*
H(1W3)	0·464 (3)	0·582 (6)	0·97 (1)	4 (2)*
H(2W3)	0·048 (4)	0·128 (6)	0·90 (1)	4 (2)*
H(1W4)	0·360 (4)	0·104 (7)	0·64 (1)	7 (3)*
H(2W4)	0·140 (4)	0·493 (7)	0·38 (1)	6 (3)*

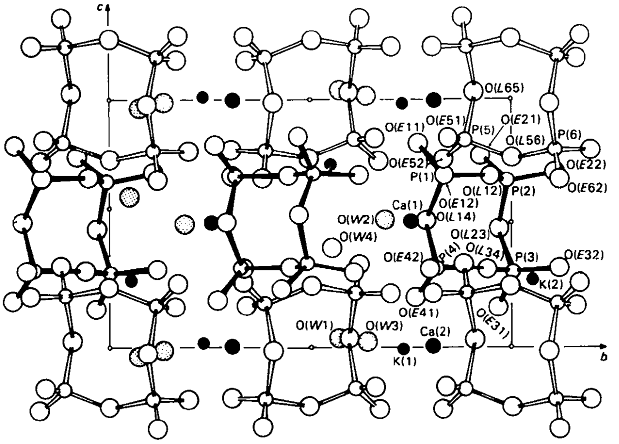

Fig. 1. Projection of the atomic arrangement of $Ca_4K_4(P_4O_{12})_3.8H_2O$ along the a axis. Atoms corresponding to $x > 0·50$ have been omitted.

calcium chloride in stoichiometric ratio; they appear as flat rectangular prisms. Density not measured. Prism fragment 0·08 × 0·12 × 0·20 mm. Philips PW 1100 diffractometer, graphite monochromator. Systematic absences: $h00$: $h = 2n$, $hk0$: $h = 2n$. 16 reflexions ($11 < \theta < 14°$) for refining unit-cell dimensions. $\omega/2\theta$ scan, scan width 1·20°, scan speed 0·02° s^{-1}, total background measuring time: 10 s. 2169 measured reflexions ($3 < \theta < 35°$), h, k, l, $h_{max} = 42$, $k_{max} = 11$, $l_{max} = 11$. Two intensity and orientation reference reflexions (033 and 033) every two hours, no significant variation. Lorentz and polarization corrections, no absorption correction. Unit weights. Conventional methods for structure resolution: Patterson and successive Fourier syntheses. H atoms not located. Anisotropic full-matrix least-squares refinement (on F). Final refinement with 1787 reflexions ($I > 4\sigma_I$). Final $R = 0{\cdot}066$ ($wR = 0{\cdot}070$), $S = 2{\cdot}433$. Max. $\Delta/\sigma =$

Table 2. *Main interatomic distances* (Å), *bond angles* (°) *and hydrogen-bond scheme in* $Ca_4K_4(P_4O_{12})_3.8H_2O$

The P_4O_{12} ring anions

(I) $P(1)O_4$ tetrahedron

P(1)	O(*E*11)	O(*E*12)	O(*L*12)	O(*L*14)
O(*E*11)	1·479 (2)	2·565 (3)	2·532 (3)	2·481 (3)
O(*E*12)	119·6 (1)	1·488 (2)	2·474 (3)	2·548 (3)
O(*L*12)	110·0 (1)	105·9 (1)	1·611 (2)	2·516 (3)
O(*L*14)	106·7 (1)	110·6 (1)	102·7 (1)	1·611 (2)

(I) $P(2)O_4$ tetrahedron

P(2)	O(*L*12)	O(*E*21)	O(*E*22)	O(*L*23)
O(*L*12)	1·617 (2)	2·540 (3)	2·481 (3)	2·504 (3)
O(*E*21)	109·7 (1)	1·488 (2)	2·576 (3)	2·461 (3)
O(*E*22)	106·2 (1)	120·1 (1)	1·484 (2)	2·548 (3)
O(*L*23)	102·3 (1)	105·7 (1)	111·4 (1)	1·598 (2)

(I) $P(3)O_4$ tetrahedron

P(3)	O(*L*23)	O(*E*31)	O(*E*32)	O(*L*34)
O(*L*23)	1·603 (2)	2·489 (3)	2·524 (3)	2·505 (3)
O(*E*31)	107·5 (1)	1·482 (2)	2·565 (3)	2·541 (3)
O(*E*32)	109·8 (1)	120·0 (1)	1·481 (2)	2·472 (3)
O(*L*34)	102·2 (1)	110·1 (1)	105·8 (1)	1·617 (2)

(I) $P(4)O_4$ tetrahedron

P(4)	O(*L*34)	O(*E*41)	O(*E*42)	O(*L*14)
O(*L*34	1·611 (2)	2·532 (3)	2·472 (3)	2·503 (3)
O(*E*41)	109·8 (1)	1·482 (2)	2·575 (3)	2·484 (3)
O(*E*42)	105·7 (1)	120·1 (1)	1·490 (2)	2·540 (3)
O(*L*14)	102·3 (1)	107·2 (1)	110·4 (1)	1·604 (2)

P(1)–P(2)	2·906 (1)	P(2)–P(1)–P(4)	89·78 (3)
P(1)–P(4)	2·892 (1)	P(1)–P(2)–P(3)	89·22 (3)
P(2)–P(3)	2·915 (1)	P(2)–P(3)–P(4)	89·42 (3)
P(3)–P(4)	2·901 (1)	P(1)–P(4)–P(3)	89·78 (3)

P(1)–O(*L*12)–P(2)	128·4 (1)
P(2)–O(*L*23)–P(3)	131·2 (1)
P(3)–O(*L*34)–P(4)	128·0 (1)
P(4)–O(*L*14)–P(1)	128·2 (1)

(II) $P(5)O_4$ tetrahedron

P(5)	O(*E*51)	O(*E*52)	O(*L*56)	O(*L*65)
O(*E*51)	1·489 (2)	2·592 (3)	2·539 (3)	2·538 (3)
O(*E*52)	122·3 (1)	1·469 (2)	2·443 (3)	2·457 (3)
O(*L*56)	110·7 (1)	105·6 (1)	1·596 (2)	2·474 (3)
O(*L*65)	109·6 (1)	105·6 (1)	100·8 (1)	1·615 (2)

(II) $P(6)O_4$ tetrahedron

P(6)	O(*L*56)	O(*E*61)	O(*E*62)	O(*L*65)
O(*L*56)	1·594 (2)	2·475 (3)	2·516 (3)	2·497 (3)
O(*E*61)	106·9 (1)	1·486 (2)	2·561 (3)	2·570 (3)
O(*E*62)	109·5 (1)	119·1 (1)	1·485 (2)	2·450 (3)
O(*L*65)	102·7 (1)	112·5 (1)	104·9 (1)	1·604 (2)

P(5)–P(6)	2·956 (1)	P(6)–P(5)–P(6)	95·02 (3)
P((6)–P(5)	2·966 (1)	P(5)–P(6)–P(5)	84·98 (3)

P(5)–O(*L*56)–P(6)	136·9 (2)
P(5)–O(*L*65)–P(6)	133·4 (1)

$Ca(1)O_7$ polyhedron

Ca(1)–O(*E*12)	2·466 (2)	Ca(1)–O(*E*52)	2·342 (2)
Ca(1)–O(*E*22)	2·471 (2)	Ca(1)–O(*E*62)	2·339 (2)
Ca(1)–O(*E*32)	2·360 (2)	Ca(1)–O(*W*2)	2·438 (3)
Ca(1)–O(*E*42)	2·434 (2)		

$Ca(2)O_7$ polyhedron

Ca(2)–O(*E*11)	2·435 (2)	Ca(2)–O(*E*51)	2·400 (2)
Ca(2)–O(*E*21)	2·393 (2)	Ca(2)–O(*E*61)	2·388 (2)
Ca(2)–O(*E*31)	2·392 (2)	Ca(2)–O(*W*3)	2·470 (2)
Ca(2)–O(*E*41)	2·422 (2)		

$K(1)O_7$ polyhedron

K(1)–O(*E*21)	2·885 (2)	K(1)–O(*E*52)	2·895 (2)
K(1)–O(*E*22)	3·027 (2)	K(1)–O(*W*1)	2·940 (4)
K(1)–O(*E*32)	2·749 (2)	K(1)–O(*W*3)	2·981 (3)
K(1)–O(*E*42)	2·787 (2)		

$K(2)O_6$ polyhedron

K(2)–O(*E*11)	2·844 (2)	K(2)–O(*W*1)	2·775 (4)
K(2)–O(*L*34)	2·963 (2)	K(2)–O(*W*4)	2·687 (4)
K(2)–O(*E*51)	2·867 (2)	K(2)–O(*E*62)	2·886 (2)

Hydrogen bonds

	O(*W*)–H···O	O(*W*)–H	H···O	O(*W*)–O	O(*W*)–H···O	H–O(*W*)–H
O(*W*1)	H(1*W*1)···O(*E*41)	0·91 (7)	2·01 (7)	2·867 (4)	156 (6)	101 (6)
	H(2*W*2)···O(*L*12)	0·74 (7)	2·42 (7)	3·127 (4)	161 (7)	
O(*W*2)	H(1*W*2)···O(*E*61)	0·67 (6)	2·30 (6)	2·926 (4)	157 (7)	125 (7)
	H(2*W*2)···O(*E*21)	0·96 (8)	2·09 (7)	3·016 (4)	161 (6)	
O(*W*3)	H(1*W*3)···O(*E*31)	0·78 (6)	2·20 (6)	2·926 (3)	154 (6)	99 (6)
	H(2*W*3)···O(*E*22)	0·79 (6)	2·15 (6)	2·925 (3)	166 (6)	
O(*W*4)	H(1*W*4)···O(*E*41)	0·79 (8)	2·51 (8)	3·112 (5)	135 (7)	123 (8)
	H(2*W*4)···O(*E*12)	0·82 (7)	2·54 (8)	3·034 (5)	120 (6)	

0·00. Max. peak height in the final difference-Fourier synthesis: 0·51 e Å^{-3}. No extinction correction. Scattering factors for neutral atoms and f', f'' from *International Tables for X-ray Crystallography* (1974). Enraf–Nonius (1977) *SDP* used for all calculations. Computer used: PDP 11.70.

Discussion. $Ca_4K_4(P_4O_{12})_3.8H_2O$. Table 1 reports the final atomic coordinates while Fig. 1 is a projection of the atomic arrangement along the *a* axis.*

The main feature of this atomic arrangement is the coexistence of two crystallographically independent P_4O_{12} ring anions. The first built up by P(1), P(2), P(3) and P(4) has no internal symmetry while the second built up by P(5) and P(6) is centrosymmetric.

Table 3. *Final atomic coordinates for* $CaNa_2P_4O_{12}.5{\cdot}5H_2O$

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

	x	y	z	B_{eq}(Å^2)
Ca(1)	0	0	0	1·20 (5)
Ca(2)	$\frac{1}{4}$	0·3718 (3)	0·6183 (4)	1·27 (5)
P(1)	0·04968 (7)	0·2925 (3)	0·3414 (4)	1·89 (4)
P(2)	0·05558 (7)	0·6884 (3)	0·3313 (3)	1·18 (5)
P(3)	0·19791 (8)	0·7170 (3)	0·9129 (3)	1·25 (5)
P(4)	0·19704 (8)	0·4374 (3)	0·1889 (3)	1·35 (5)
Na(1)	0·3765 (1)	0·0261 (6)	0·1048 (8)	2·50 (11)
Na(2)	0·1320 (1)	0·4781 (5)	0·6142 (6)	1·88 (9)
O(*E*11)	0·4178 (2)	0·2602 (10)	0·4954 (11)	2·06 (18)
O(*E*12)	0·4489 (2)	0·1711 (7)	0·1822 (10)	1·57 (15)
O(*L*12)	0·4449 (2)	0·4871 (8)	0·2597 (8)	1·35 (14)
O(*L*21)	0·0036 (2)	0·7030 (9)	0·4242 (8)	1·33 (13)
O(*E*21)	0·0907 (2)	0·7105 (10)	0·4772 (10)	1·86 (17)
O(*E*22)	0·4422 (2)	0·8007 (8)	0·1671 (10)	1·70 (16)
O(*E*31)	0·1986 (2)	0·5699 (9)	0·7773 (11)	1·93 (17)
O(*E*32)	0·3354 (2)	0·8656 (9)	0·8931 (10)	1·65 (16)
O(*E*41)	0·3369 (2)	0·3150 (9)	0·0967 (11)	2·01 (18)
O(*E*42)	0·1954 (2)	0·4532 (9)	0·3878 (8)	1·54 (15)
O(*L*44)	$\frac{1}{4}$	0·3916 (13)	0·1212 (13)	1·51 (21)
O(*L*33)	$\frac{1}{4}$	0·8017 (12)	0·9331 (15)	1·72 (24)
O(*L*43)	0·3103 (2)	0·6357 (9)	0·1112 (10)	1·72 (16)
O(*W*1)	0·4162 (3)	0·4865 (11)	0·8768 (10)	2·55 (21)
O(*W*2)	0·1853 (3)	0·2105 (11)	0·7521 (11)	2·51 (21)
O(*W*3)	0·0731 (2)	0·0095 (11)	0·8022 (11)	2·64 (20)
O(*W*4)	0·4995 (3)	0·2816 (10)	0·8279 (11)	2·51 (18)
O(*W*5)	0·1548 (3)	−0·0123 (13)	0·3991 (14)	3·50 (25)
O(*W*6)	$\frac{1}{4}$	0·0926 (15)	0·4593 (20)	3·65 (41)

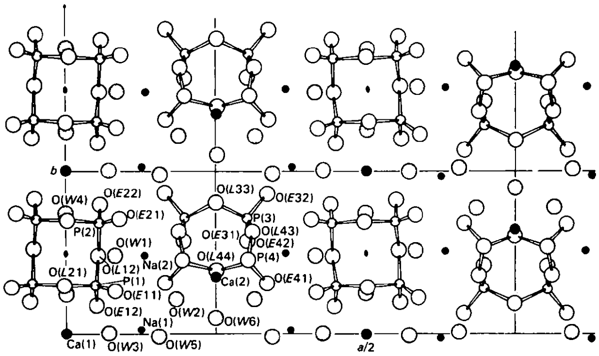

Fig. 2. Projection of the atomic arrangement of $CaNa_2P_4O_{12}.5{\cdot}5H_2O$ along the *c* axis.

Table 4. *Main interatomic distances* (Å) *and bond angles* (°) *in* $CaNa_2P_4O_{12}.5{\cdot}5H_2O$

The $P(1,2)_4O_{12}$ ring anion

$P(1)O_4$ tetrahedron

P(1)	O(*E*11)	O(*E*12)	O(*L*12)	O(*L*21)
O(*E*11)	1·474 (5)	2·557 (7)	2·553 (6)	2·464 (6)
O(*E*12)	119·3 (3)	1·490 (5)	2·452 (6)	2·533 (6)
O(*L*12)	112·7 (3)	105·3 (3)	1·592 (4)	2·489 (6)
O(*L*21)	106·2 (3)	109·8 (2)	102·2 (2)	1·606 (4)

$P(2)O_4$ tetrahedron

P(2)	O(*E*21)	O(*E*22)	O(*L*12)	O(*L*21)
O(*E*21)	1·465 (5)	2·557 (7)	2·530 (6)	2·461 (6)
O(*E*22)	120·6 (3)	1·479 (5)	2·462 (6)	2·536 (6)
O(*L*12)	110·8 (3)	105·8 (2)	1·607 (4)	2·486 (6)
O(*L*21)	106·3 (3)	110·4 (2)	101·3 (2)	1·608 (4)

P(1)–P(2)	2·989 (2)	P(2)–P(1)–P(2)	90·31 (6)
P(2)–P(1)	2·939 (2)	P(1)–P(2)–P(1)	89·62 (6)

P(1)–O(*L*12)–P(2)	138·3 (3)
P(1)–O(*L*21)–P(2)	132·3 (3)

The $P(3,4)O_{12}$ ring anion

$P(3)O_4$ tetrahedron

P(3)	O(*E*31)	O(*E*32)	O(*L*33)	O(*L*43)
O(*E*31)	1·493 (5)	2·568 (7)	2·536 (7)	2·525 (7)
O(*E*32)	120·6 (3)	1·463 (4)	2·448 (4)	2·466 (6)
O(*L*33)	110·4 (3)	106·4 (3)	1·593 (3)	2·473 (7)
O(*L*43)	109·3 (3)	107·0 (3)	101·4 (3)	1·602 (5)

$P(4)O_4$ tetrahedron

P(4)	O(*E*41)	O(*E*42)	O(*L*44)	O(*L*43)
O(*E*41)	1·487 (5)	2·552 (7)	2·498 (5)	2·531 (6)
O(*E*42)	119·1 (3)	1·473 (4)	2·530 (6)	2·466 (6)
O(*L*44)	108·2 (3)	111·0 (3)	1·596 (3)	2·493 (7)
O(*L*43)	109·4 (3)	106·0 (3)	101·9 (3)	1·614 (5)

P(3)–P(3)	2·904 (3)	P(3)–P(3)–P(4)	90·47 (4)
P(3)–P(4)	2·930 (2)	P(3)–P(4)–P(4)	89·53 (4)
P(4)–P(4)	2·953 (3)		

P(4)–O(*L*44)–P(4)	135·3 (4)
P(3)–O(*L*33)–P(3)	131·4 (4)
P(3)–O(*L*43)–P(4)	131·3 (3)

$Ca(1)O_8$ polyhedron

Ca(1)–O(*E*12)	2·345 (4) (×2)
Ca(1)–O(*E*22)	2·525 (5) (×2)
Ca(1)–O(*W*3)	2·507 (5) (×2)
Ca(1)–O(*W*4)	2·473 (5) (×2)

$Ca(2)O_8$ polyhedron

Ca(2)–O(*E*31)	2·379 (5) (×2)
Ca(2)–O(*E*42)	2·364 (4) (×2)
Ca(2)–O(*W*2)	2·388 (6) (×2)
Ca(2)–O(*W*6)	2·410 (8) (×2)

$Na(1)O_6$ octahedron

Na(1)–O(*E*12)	2·363 (5)	Na(1)–O(*E*41)	2·442 (5)
Na(1)–O(*E*22)	2·539 (5)	Na(1)–O(*W*3)	2·641 (7)
Na(1)–O(*E*32)	2·284 (6)	Na(1)–O(*W*5)	2·358 (7)

$Na(2)O_6$ octahedron

Na(2)–O(*E*11)	2·322 (5)	Na(2)–O(*E*42)	2·440 (5)
Na(2)–O(*E*21)	2·326 (6)	Na(2)–O(*W*1)	2·358 (6)
Na(2)–O(*E*31)	2·318 (5)	Na(2)–O(*W*2)	2·705 (6)

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* Lists of structure factors and anisotropic thermal parameters for both compounds have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44450 (39 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2 reports the main interatomic distances and bond angles in these two rings. The two Ca atoms have a sevenfold coordination involving six O atoms and one water molecule, with Ca—O distances ranging from 2·339 to 2·471 Å. Within a range of 3·5 Å the first K atom, K(1), has seven neighbours and the second, K(2), has six. Table 2 gives the main interatomic distances in the associated cation polyhedra.

The network of hydrogen bonds is also reported in Table 2.

$CaNa_2P_4O_{12}.5{\cdot}5H_2O$. Table 3 reports the final atomic coordinates. In this second salt one observes the same feature as in the first: two different configurations for the P_4O_{12} ring anions. More interesting is the fact that one of these two configurations (*m*) has, until now, never been observed for this kind of anion.

The first P_4O_{12} group built up by P(1) and P(2) has binary symmetry, the second built up by P(3) and P(4) has mirror symmetry (Fig. 2), the mirror plane containing the two bonding O atoms, O(*L*33) and O(*L*44), being perpendicular to the ring plane.

Table 4 reports the main interatomic distances and bond angles for these two ring anions. The two Ca atoms have an eightfold coordination involving four O atoms and four water molecules, while the two Na atoms have distorted octahedral coordinations.

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Aluminium Decavanadate 25-Hydrate

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Abstract. $Al_2V_{10}O_{28}.25H_2O$, $M_r = 1461{\cdot}46$, orthorhombic, *Cmma*, $a = 21{\cdot}618\,(2)$, $b = 18{\cdot}414\,(2)$, $c = 10{\cdot}533\,(1)$ Å, $V = 4193\,(1)$ Å^3, $Z = 4$, $D_m = 2{\cdot}35$, $D_x = 2{\cdot}32$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 2{\cdot}19$ mm^{-1}, $F(000) = 2920$, $T = 298\,(2)$ K, $R = 3{\cdot}31\%$, $wR = 3{\cdot}49\%$ for 1474 independent observed reflections $[I > 5\sigma(I)]$. The unit cell contains four $(V_{10}O_{28})^{6-}$ anions located on sites of point symmetry $2/m$, four $[Al(OH_2)_6]^{3+}$ cations on $2/m$ sites, four $[Al(OH_2)_6]^{3+}$ cations on 222 sites and 52 lattice water molecules, four of which show occupational disorder. The compound presents a packing characterized by successive layers parallel to (100); ionic forces and H bonds between the layers and within them stabilize the structure.

Introduction. This study was undertaken as part of a research programme on crystal chemistry and physicochemical properties of hydrated decavanadate salts (Rigotti, Lavat, Escobar & Baran, 1983; Rivero, Punte, Rigotti & Navaza, 1985, and references therein). The title compound had been previously described as a 22-hydrate on the basis of TGA/DTA measurements (Rigotti *et al.*, 1983).

Experimental. $Al_2V_{10}O_{28}.25H_2O$ was synthesized according to the method described by Rigotti *et al.* (1983). Bright orange hexagonal plates were grown and kindly supplied by Dr E. J. Baran and co-workers, Programa QUINOR, UNLP, Argentina. Density measured pycnometrically. Crystal used for data collection defined by the following planes: ±(100) (0·125), ±(010) (0·125), ±(001) (0·165) (numbers in parentheses are the distances in mm from the crystal faces to an arbitrary origin inside the crystal). Cell

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