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Contribution to the Crystal Chemistry of Tetrametaphosphates (I)

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Crystal structures of $K_4P_4O_{12} \cdot 2H_2O$ and of two polymorphs of $Na_2K_2P_4O_{12} \cdot 2H_2O$ are reported. $K_4P_4O_{12} \cdot 2H_2O$ is triclinic $P1$ with $a = 8.153(4)$, $b = 8.222(4)$, $c = 11.154(8)$ Å, $\alpha = 97.33(5)$, $\beta = 95.46(5)$, $\gamma = 88.92(5)°$, and $Z = 2$. $R = 0.021$ for 2898 reflections. $Na_2K_2P_4O_{12} \cdot 2H_2O$ has two crystalline forms: a triclinic one ($P\bar{1}$) with $a = 11.366(8)$, $b = 7.908(5)$, $c = 7.929(5)$ Å, $\alpha = 90.07(5)$, $\beta = 106.85(5)$, $\gamma = 95.66(5)°$, and $Z = 2$, and a tetragonal one ($P4_1$) with $a = 7.928(5)$, $c = 21.66(2)$, and $Z = 4$. The crystal structures of the first and second crystalline forms have been solved with final R values of 0.022 for 2505 reflections and 0.036 for 1347 reflections, respectively. Crystal data and chemical preparations are given for $Na_2(NH_4)_2P_4O_{12} \cdot 2H_2O$ and $Na_2Rb_2P_4O_{12} \cdot 2H_2O$, both isotypic with the triclinic form of $Na_2K_2P_4O_{12} \cdot 2H_2O$. Unit-cell dimensions are, respectively, $a = 11.547(8)$, $b = 8.012(5)$, $c = 8.044(5)$ Å, $\alpha = 89.76(5)$, $\beta = 106.22(5)$, and $\gamma = 94.78(5)°$, for the ammonium salt, and $a = 11.577(8)$, $b = 8.006(5)$, $c = 8.032(5)$ Å, $\alpha = 89.79(5)$, $\beta = 106.58(5)$, and $\gamma = 95.19(5)°$ for the rubidium salt. In addition the crystal structures of the two crystalline forms of $Na_4P_4O_{12} \cdot 4H_2O$ were reexamined in order to localize the hydrogen atoms and refine their positions.

Introduction

The crystal chemistry of monovalent cation tetrametaphosphates is comparatively poorly developed in comparison with the great number of studies dealing with other types of tetrametaphosphates, mainly represented by $M^{II}_2P_4O_{12} \cdot xH_2O$, $M^{I}_2M^{II}P_4O_{12} \cdot$

TABLE I

MAIN CRYSTALLOGRAPHIC DATA FOR THE ALREADY KNOWN $M^{I}_4P_4O_{12} \cdot xH_2O$

Formula	a (Å) α (°)	b (Å) β (°)	c (Å) γ (°)	Structure	System	Space group	Z	Ref.
$(NH_4)_4P_4O_{12}$	10.433	10.871	12.588	Known	Orthorhombic	*Cmca*	4	(1–4)
$Tl_4P_4O_{12}$	7.635		11.087	Known	Tetragonal	$P\bar{r}2_1/c$	2	(5)
$Na_4P_4O_{12}$	13.65	13.63	6.027	Known	Orthorhombic	$P2_12_12_1$	4	(12)
$Na_2H_2P_4O_{12}$	18.74	14.79	7.03	Known	Orthorhombic	*Pbnm*	8	(6)
$(NH_4)_3HP_4O_{12} \cdot H_2O$	11.144	11.322	10.514	Unknown	Monoclinic	$P2_1/n$	4	(7)
		90.67						
$Na_4P_4O_{12} \cdot H_2O$	13.65	13.47	6.291	Known	Orthorhombic	$P2_12_12_1$	4	(12)
$Na_4P_4O_{12} \cdot 4H_2O$ (I)	6.652	9.579	6.320	Known	Triclinic	$P\bar{1}$	1	(8)
	103.40	106.98	93.28					
$Na_4P_4O_{12} \cdot 4H_2O$ (II)	9.667	12.358	6.170	Known	Monoclinic	$P2_1/a$	2	(9)

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TABLE II

MAIN CRYSTALLOGRAPHIC DATA FOR THE TITLE COMPOUNDS

	a (Å) α (°)	b (Å) β (°)	c (Å) γ (°)	Z	M (g)	dx	V (Å^3)
$K_4P_4O_{12} \cdot 2H_2O$ ($P\bar{1}$)	8.165(4) 97.37(3)	8.228(4) 95.43(3)	11.154(6) 88.84(4)	2	508.32	2.282	739.8
$Na_2K_2P_4O_{12} \cdot 2H_2O$ ($P4_1$)	7.922(3)	7.922(3)	21.72(2)	4	476.10	2.320	1363.1
$Na_2K_2P_4O_{12} \cdot 2H_2O$ ($P\bar{1}$)	11.341(17) 89.94(9)	7.907(12) 106.95(8)	7.918(14) 95.61(7)	2	476.10	2.340	675.6
$Na_2(NH_4)_2P_4O_{12} \cdot 2H_2O$ ($P\bar{1}$)	11.547(8) 89.76(4)	8.012(6) 106.22(3)	8.044(5) 94.78(3)	2	433.97	2.024	711.9
$Na_2Rb_2P_4O_{12} \cdot 2H_2O$ ($P\bar{1}$)	11.577(9) 89.79(5)	8.006(6) 106.58(4)	8.032(7) 95.19(4)	2	568.83	2.659	710.4

xH_2O, $M^{I}_4M^{II}_4(P_4O_{12})_3$, $M^{III}_4(P_4O_{12})_3$, and $M^{III}M^{I}P_4O_{12}$ series, corresponding to several dozen accurately characterized compounds.

In Table I we report what is the present state of the known crystal chemistry of monovalent cation tetrametaphosphates. In addition, several authors claim the existence of two crysalline forms of $K_4P_4O_{12} \cdot 4H_2O$ and two crystalline forms of the anhydrous salt (*10*). Griffith (*11*) described the preparation of $Na_2M^{I}_2P_4O_{12}$ using $Na_2H_2P_4O_{12}$ as starting material. A decahydrate of sodium tetrametaphosphate, $Na_4P_4O_{12} \cdot 10H_2O$, is said to crystallize at low temperature (t < 15°C) (*10*). In the present work, we describe chemical preparations and crystal structures of $K_4P_4O_{12} \cdot 2H_2O$, $Na_2K_2P_4O_{12} \cdot 2H_2O$ (triclinic), and $Na_2K_2P_4O_{12} \cdot 2H_2O$ (tetragonal). Chemical preparations and crystal data are reported for $Na_2(NH_4)_2P_4O_{12} \cdot 2H_2O$ and $Na_2Rb_2P_4O_{12} \cdot 2H_2O$, both isotypic with the triclinic form of $Na_2K_2P_4O_{12} \cdot 2H_2O$.

We also reexamine the crystal structures of the two forms of $Na_4P_4O_{12} \cdot 4H_2O$ in or-

TABLE III

PARAMETERS USED FOR THE X-RAY DIFFRACTION DATA COLLECTION

	$K_4P_4O_{12} \cdot 2H_2O$	$Na_2K_2P_4O_{12} \cdot 2H_2O$ (triclinic)	$Na_2K_2P_4O_{12} \cdot 2H_2O$ (tetragonal)	$Na_4P_4O_{12} \cdot 4H_2O$ (monoclinic)	$Na_4P_4O_{12} \cdot 4H_2O$ (triclinic)
Apparatus	Philips PW 1100	Philips PW 1100	Nonius CAD 4	Philips PW 1100	Nonius CAD 4
Monochromator	Graphite plate	Graphite plate	Graphite plate	Graphite plate	Graphite plate
Wavelength (Å)	Mo$K\alpha$ (0.7107)	Mo$K\alpha$ (0.7107)	Ag$K\alpha$ (0.5608)	Mo$K\alpha$ (0.7107)	Mo$K\alpha$ (0.7107)
Scan mode	ω	$\omega/2\theta$	ω	ω	ω
Scan speed (°/sec)	0.02	0.02	from 0.015 to 0.06	0.03	from 0.01 to 0.033
Total background measurement (sec)	20	20	from 10 to 40	10	from 20 to 60
Scan width (°)	1.20	1.40	1.20	1.10	1.20
Theta range (°)	3–30	3–30	3–25	3–30	3–35
Intensity reference reflections	$404; \bar{4}0\bar{4}$	$800; \bar{8}00$	$0016; 00\overline{16}$	$204; \bar{2}0\bar{4}$	$11\bar{5}; \bar{1}4\bar{4}$
Number of collected reflections	7942($\pm h, \pm k, \pm l$)	3468($\pm h, \pm k, l$)	2783(h, k, l)	1929($\pm h, k, l$)	3256($\pm h, \pm k, l$)
Crystal size (mm)	0.30 × 0.30 × 0.16	0.40 × 0.40 × 0.30	0.14 × 0.14 × 0.14	0.30 × 0.24 × 0.24	0.24 × 0.20 × 0.24
μ (cm^{-1})	16.78	12.97	6.66	7.27	7.21
F(000)	252	236	236	240	240

TABLE IV

FINAL ATOMIC COORDINATES AND $B_{eq.}$ OR $B_{iso.}$ FOR $K_4P_4O_{12} \cdot 2H_2O$

Atom	$x(\sigma)$	$y(\sigma)$	$z(\sigma)$	$B_{eq.}(\sigma)$
K(1)	0.24600(7)	0.70492(7)	0.05166(5)	1.92(1)
K(2)	0.71314(7)	0.88032(7)	0.07416(5)	1.91(1)
K(3)	0.60796(8)	0.70057(7)	0.42953(5)	2.02(1)
K(4)	0.82115(8)	0.22230(8)	0.45222(5)	2.07(1)
P(1)	0.37233(8)	−0.00357(7)	0.29608(5)	1.17(1)
P(2)	0.05761(7)	0.13909(8)	0.19794(6)	1.22(1)
P(3)	0.21499(8)	0.45424(7)	0.28555(5)	1.17(1)
P(4)	0.51787(7)	0.28620(7)	0.21755(5)	1.10(1)
O(L12)	0.2258(2)	0.0314(2)	0.1940(2)	1.40(3)
O(E11)	0.3109(2)	−0.0165(2)	0.4146(2)	2.06(4)
O(E12)	0.4725(2)	0.8629(2)	0.2371(2)	1.81(4)
O(E21)	0.9316(2)	0.0510(2)	0.2515(2)	1.87(4)
O(E22)	0.0225(2)	0.1897(2)	0.0759(2)	2.03(4)
O(L23)	0.1137(2)	0.2923(2)	0.2986(1)	1.41(4)
O(E31)	0.2966(2)	0.5115(2)	0.4074(2)	1.76(4)
O(E32)	0.1073(2)	0.5695(2)	0.2214(2)	1.78(4)
O(E41)	0.6440(2)	0.4007(2)	0.2832(2)	1.69(4)
O(E42)	0.5485(2)	0.1907(2)	0.1000(2)	1.56(4)
O(L14)	0.4735(2)	0.1680(2)	0.3143(1)	1.31(3)
O(L34)	0.3470(2)	0.3839(2)	0.1929(1)	1.41(4)
O(W1)	0.7846(3)	0.5651(3)	0.1158(2)	2.51(5)
O(W2)	0.9181(3)	0.7819(3)	0.3737(2)	2.82(5)
				$B_{iso.}$
H(11)	0.726(5)	0.528(5)	0.167(3)	3.6(8)
H(12)	0.888(5)	0.555(4)	0.134(3)	3.6(8)
H(21)	0.941(4)	0.887(4)	0.350(3)	3.4(8)
H(22)	0.969(5)	0.695(5)	0.330(4)	4.3(9)

TABLE V

ATOMIC PARAMETERS AND $B_{eq.}$ OR $B_{iso.}$ FOR THE TRICLINIC FORM OF $Na_2K_2P_4O_{12} \cdot 2H_2O$

Atom	$x(\sigma)$	$y(\sigma)$	$z(\sigma)$	$B_{eq.}(\sigma)$
K(1)	0.43767(5)	0.22608(8)	0.64107(8)	2.03(1)
K(2)	0.06139(5)	0.34210(8)	0.76355(8)	2.03(1)
Na(1)	0.42060(9)	0.6667(1)	0.8525(1)	1.65(1)
Na(2)	0.07762(9)	0.1235(1)	0.2097(1)	1.69(1)
P(1)	0.29076(5)	0.44672(8)	0.15962(8)	1.09(1)
P(2)	0.21053(5)	0.78151(8)	0.06786(8)	1.09(1)
P(3)	0.28748(5)	0.85313(8)	0.44719(8)	1.16(1)
P(4)	0.20919(5)	0.49185(8)	0.47291(8)	1.17(1)
O(L12)	0.1982(1)	0.5770(2)	0.0796(2)	1.32(2)
O(L23)	0.3107(1)	0.8323(2)	0.2554(2)	1.26(3)
O(L34)	0.1885(1)	0.6911(2)	0.4431(2)	1.32(2)
O(L14)	0.3103(1)	0.4668(2)	0.3690(2)	1.37(2)
O(E11)	0.2290(2)	0.2754(2)	0.0927(2)	1.58(3)
O(E12)	0.4110(1)	0.5071(2)	0.1310(2)	1.51(3)
O(E21)	0.0905(1)	0.8459(2)	0.0575(1)	1.50(3)
O(E22)	0.2727(2)	0.8238(2)	0.9305(2)	1.57(3)
O(E31)	0.4075(2)	0.8348(2)	0.5797(2)	1.77(3)
O(E32)	0.2240(2)	0.0078(2)	0.4494(2)	1.68(3)
O(E41)	0.2719(2)	0.4642(2)	0.6608(2)	1.66(3)
O(E42)	0.0889(2)	0.3951(2)	0.3824(2)	1.73(3)
O(W1)	0.4123(2)	0.1433(2)	0.9646(3)	2.36(3)
O(W2)	0.0907(2)	0.0121(3)	0.6962(3)	2.40(3)
				$B_{iso.}$
H(11)	0.350(3)	0.175(4)	0.001(5)	3.3
H(12)	0.404(3)	0.049(5)	−0.014(5)	3.7
H(21)	0.116(3)	0.017(4)	0.610(5)	2.9
H(22)	0.149(3)	0.966(4)	0.770(4)	3.2

TABLE VI

ATOMIC PARAMETERS AND $B_{eq.}$ FOR THE TETRAGONAL FORM OF $Na_2K_2P_4O_{12} \cdot 2H_2O$

Atom	$x(\sigma)$	$y(\sigma)$	$z(\sigma)$	$B_{eq.}(\sigma)$
K(1)	0.3486(2)	0.1546(2)	0.57318(9)	1.99(4)
K(2)	−0.0160(3)	0.3723(2)	0.13493(9)	1.98(4)
P(1)	0.0719(2)	0.0876(2)	0.00000(0)	1.02(4)
P(2)	0.1442(2)	0.2756(2)	0.70911(9)	1.10(4)
P(3)	0.7831(2)	0.4939(2)	0.99844(9)	1.10(4)
P(4)	0.1303(2)	0.4334(2)	0.95992(9)	1.01(4)
Na(1)	0.7945(4)	0.0664(4)	0.6439(2)	1.64(8)
Na(2)	0.4330(4)	0.2900(4)	0.656(1)	1.54(8)
O(E11)	0.1507(6)	0.1305(7)	0.0603(2)	1.34(13)
O(E12)	0.0748(7)	0.1137(7)	0.2192(3)	1.52(14)
O(L12)	0.1053(7)	0.1297(6)	0.7600(3)	1.40(14)
O(E21)	0.7644(8)	0.0654(7)	0.8987(3)	1.94(16)
O(E22)	0.5609(7)	0.1062(7)	0.9904(3)	1.51(14)
O(L23)	0.7456(7)	0.3449(6)	0.9487(2)	1.25(13)
O(E31)	0.6570(7)	0.2455(7)	0.7165(3)	1.60(14)
O(E32)	0.4562(7)	0.3004(7)	0.8082(2)	1.53(14)
O(L34)	0.0154(6)	0.5300(6)	0.5098(2)	1.11(12)
O(E41)	0.7062(6)	0.5324(7)	0.4910(3)	1.53(14)
O(E42)	0.4867(7)	0.0915(7)	0.1496(2)	1.68(15)
O(L14)	0.7681(7)	0.1107(7)	0.1992(2)	1.47(14)
O(W1)	0.6826(8)	0.2330(8)	0.5605(3)	2.31(18)
O(W2)	0.3185(8)	0.4531(8)	0.1505(3)	2.22(17)

der to localize the hydrogen atoms and refine the atomic arrangements of these two fundamental starting materials.

Chemical Preparations

All the title compounds have been prepared by using the following process: a water solution of the alkali carbonate(s) is kept at a temperature close to 0°C and a stoichiometric amount of P_4O_{10} is then slowly added. The resulting solution is kept at room temperature for one day and then a large excess of ethanol is added. If the resulting precipitates of tetrametaphosphates are left some days in this liquid one observes in most cases a large increase of the crystal size. The two crystalline forms observed for $Na_2K_2P_4O_{12} \cdot 2H_2O$ always occur simultaneously during the precipitation.

TABLE VII

ATOMIC PARAMETERS AND $B_{eq.}$ OR $B_{iso.}$ FOR THE TRICLINIC FORM OF $Na_4P_4O_{12} \cdot 4H_2O$

Atom	$x(\sigma)$	$y(\sigma)$	$z(\sigma)$	$B_{eq.}(\sigma)$
P(1)	0.26653(5)	0.08995(3)	0.24381(5)	0.97(1)
P(2)	0.89850(5)	0.21206(3)	0.98661(5)	0.99(1)
Na(1)	0.82110(9)	0.12600(0)	0.42149(9)	1.64(1)
Na(2)	0.55608(9)	0.40321(6)	0.23963(10)	1.74(1)
O(L1)	0.1207(1)	0.1505(1)	0.0431(2)	1.37(1)
O(E11)	0.1579(1)	0.0795(1)	0.4148(2)	1.61(1)
O(E12)	0.4806(1)	0.1711(1)	0.3179(2)	1.71(1)
O(E21)	0.8916(2)	0.2747(1)	0.7915(2)	1.71(1)
O(E22)	0.8695(1)	0.3008(1)	0.1987(2)	1.50(1)
O(L2)	0.7270(1)	0.0698(1)	0.9047(2)	1.55(1)
O(W1)	0.3493(2)	0.3582(1)	0.8208(2)	2.93(2)
O(W2)	0.2613(2)	0.4951(1)	0.3559(2)	1.89(1)
				$B_{iso.}$
H(11)	0.342(4)	0.275(3)	0.727(4)	4.4(6)
H(12)	0.219(4)	0.334(3)	0.833(4)	5.0(6)
H(21)	0.778(4)	0.431(3)	0.692(4)	3.5(5)
H(22)	0.143(4)	0.437(3)	0.331(4)	3.6(5)

$K_4P_4O_{12} \cdot 2H_2O$ crystals are multifaceted, almost isometric polyhedra.

$Na_2(NH_4)_2P_4O_{12} \cdot 2H_2O$, $Na_2Rb_2P_4O_{12} \cdot 2H_2O$, and the triclinic form of $Na_2K_2P_4O_{12} \cdot 2H_2O$ occur as slightly distorted octahedra while the tetragonal form of $Na_2K_2P_4O_{12} \cdot 2H_2O$ mostly crystallizes as regular octahedra.

TABLE VIII

ATOMIC COORDINATES AND $B_{eq.}$ OR $B_{iso.}$ FOR THE MONOCLINIC FORM OF $Na_4P_4O_{12} \cdot 4H_2O$

Atom	$x(\sigma)$	$y(\sigma)$	$z(\sigma)$	$B_{eq.}(\sigma)$
P(1)	0.18699(5)	−0.00348(4)	0.40241(8)	1.07(2)
P(2)	0.4904(5)	0.32181(4)	0.45642(7)	1.16(2)
Na(1)	0.07184(9)	0.12550(7)	0.9391(1)	1.74(3)
Na(2)	0.47394(9)	0.06384(7)	0.7368(1)	1.66(3)
O(L1)	0.1190(1)	0.0993(1)	0.5173(2)	1.63(5)
O(L2)	0.3618(1)	0.4031(1)	0.4365(2)	1.69(5)
O(E11)	0.1622(1)	0.5073(1)	0.5666(2)	1.70(5)
O(E12)	0.3785(1)	0.4800(1)	0.8178(2)	1.46(5)
O(E21)	0.4801(2)	0.2521(1)	0.6498(2)	1.75(5)
O(E22)	0.5041(2)	0.2743(1)	0.2384(2)	1.79(5)
O(W1)	0.1187(2)	0.4160(1)	0.0593(3)	2.15(6)
O(W2)	0.2957(2)	0.1835(2)	0.9492(3)	2.92(7)
				$B_{iso.}$
H(11)	0.201(3)	0.417(2)	0.002(5)	3.1(6)
H(12)	0.117(3)	0.360(2)	0.137(5)	3.6(7)
H(21)	0.337(3)	0.195(3)	0.052(5)	3.8(7)
H(22)	0.336(3)	0.221(2)	0.856(5)	3.7(7)

TABLE IXa

METAL–OXYGEN INTERATOMIC DISTANCES IN THE POTASSIUM POLYHEDRA

K(1)–O(L12)	2.949(2) Å	K(2)–O(E12)	2.816(2)
–O(E12)	2.837(2)	–O(E21)	2.787(2)
–O(E22)	2.686(2)	–O(E22)	2.859(2)
–O(E32)	2.663(2)	–O(E42)	2.856(2)
–O(E42)	2.715(2)	–O(E42)	2.763(2)
–O(W1)	2.712(3)	–O(W1)	2.733(3)
–O(L34)	3.295(2)	–O(L12)	3.252(2)
K(3)–O(E11)	2.983(2)	K(4)–O(E11)	2.691(2)
–O(E12)	2.799(2)	–O(E21)	2.709(2)
–O(E31)	2.975(2)	–O(E31)	2.738(2)
–O(E31)	2.728(2)	–O(L23)	3.168(2)
–O(E41)	2.805(2)	–O(E41)	2.811(2)
–O(L14)	3.053(2)	–O(L14)	3.105(2)
–O(W2)	2.775(3)	–O(W2)	2.742(3)

Crystal Chemistry

For most of the title compounds approximate unit cells and possible space groups have been determined by single crystal film techniques. Unit-cell dimensions were refined by using the angular data obtained from low-scan-speed powder diffractograms. These refined values are reported in Table II with some other crystal chemical data. It should be noted that unit-cell dimensions reported in this table for $K_4P_4O_{12} \cdot 2H_2O$ and $Na_2K_2P_4O_{12} \cdot 2H_2O$ (I) and (II) are slightly different from these obtained during the four-circle diffractometer data collection. These latter values are given in the abstract and have been used throughout the crystal structure determination, including the final calculations of interatomic distances and bond angles. For the triclinic compounds, crystal structure determinations confirmed their common space group to be $P\bar{1}$.

For the tetragonal form of $Na_2K_2P_4O_{12} \cdot 2H_2O$ the only extinction condition is $00l$ with $l = 4n$. This condition combined with the observation that $I(kkl) \neq I(khl)$ leads unambiguously to the $P4_1$ space group.

TABLE IXb

MAIN INTERATOMIC DISTANCES AND BOND ANGLES IN THE P_4O_{12} RING ANION OF $K_4P_4O_{12} \cdot 2H_2O$

P(1)O$_4$ tetrahedron				
P(1)	O(L12)	O(E11)	O(E12)	O(L14)
O(L12)	1.618(2)	2.570(3)	2.465(3)	2.514(3)
O(E11)	112.3(1)	1.475(2)	2.567(3)	2.470(3)
O(E12)	105.4(1)	120.6(1)	1.480(2)	2.546(3)
O(L14)	101.6(1)	105.4(1)	110.0(1)	1.628(2)
P(2)O$_4$ tetrahedron				
P(2)	O(L23)	O(E21)	O(E22)	O(L12)
O(L23)	1.619(2)	2.473(3)	2.564(3)	2.508(3)
O(E21)	105.8(1)	1.481(2)	2.562(3)	2.539(3)
O(E22)	111.9(1)	120.2(1)	1.474(2)	2.474(3)
O(L12)	101.5(1)	109.8(1)	106.1(1)	1.619(2)
P(3)O$_4$ tetrahedron				
P(3)	O(L34)	O(E31)	O(E32)	O(L23)
O(L34)	1.611(2)	2.554(3)	2.476(3)	2.507(3)
O(E31)	111.4(1)	1.479(2)	2.555(3)	2.478(3)
O(E32)	106.1(1)	119.1(1)	1.485(2)	2.535(3)
O(L23)	102.2(1)	106.7(1)	110.0(1)	1.609(2)
P(4)O$_4$ tetrahedron				
P(4)	O(L14)	O(E41)	O(E42)	O(L34)
O(L14)	1.611(2)	2.465(3)	2.553(3)	2.516(3)
O(E41)	105.6(1)	1.482(2)	2.571(3)	2.532(3)
O(E42)	111.3(1)	120.4(1)	1.479(2)	2.470(3)
O(L34)	102.5(1)	109.7(1)	105.9(1)	1.613(2)

P(1)–P(2)	2.973(1) Å	P(1)–O(L12)–P(2)	133.4(1)°
P(2)–P(3)	2.925(1)	P(2)–O(L23)–P(3)	130.0(1)°
P(3)–P(4)	2.923(1)	P(3)–O(L34)–P(4)	130.0(1)°
P(4)–P(1)	2.948(1)	P(4)–O(L14)–P(1)	131.0(1)°

P(1)–P(2)–P(3)	84.51(3)°
P(2)–P(3)–P(4)	84.77(3)
P(3)–P(4)–P(1)	85.00(3)
P(4)–P(1)–P(2)	83.49(3)

Crystal Structure Determination

Experimental

Parameters used for the five X-ray diffraction data collections are reported in Table III. In all cases, Lorentz and polarization corrections have been made, but in view of the short wavelengths used, no absorption correction has been applied. The three new crystal structures were solved by direct methods, using the MULTAN program (*13*). Throughout the least-squares refinements (*14*), a unitary weighting scheme was used. In the last refinement cycles, reflections which are too weak, i.e., badly measured, or overly strong (attenuator) i.e., badly corrected, are rejected.

(*a*) $K_4P_4O_{12} \cdot 2H_2O$. From the original data collection (7942: $\pm h$, $\pm k$, $\pm l$) a set of 3743 ($\pm h$, $\pm k$, l) independent reflections is conserved and used for the crystal structure determination. The final R value for this complete set is 0.030. This same factor decreases to 0.021 for 2898 reflections corresponding to the elimination of 836 reflections such that $F < 4\sigma_F$ and 9 reflections such that $\|F_{\text{obs}}| - |F_{\text{cal}}\| > 35$ in a scale ranging from 0 to 1334. Final atomic coordinates, $B_{\text{eq.}}$ or $B_{\text{iso.}}$ (hydrogen atoms), are given in Table IV.

(*b*) $Na_2K_2P_4O_{12} \cdot 2H_2O$ (*triclinic form*). In this case, the final R value for the complete set of the 3468 measured reflections is 0.033. After rejection of 963 reflections according to the criterion $F_{\text{obs}} < 4\sigma_F$, the R factor decreases to 0.022 for the 2505 re-

TABLE IXc

MAIN GEOMETRICAL FEATURES OF THE HYDROGEN-BOND SCHEME IN $K_4P_4O_{12} \cdot 2H_2O$

	O(W)–H	H . . . O	O(W)–O	$\widehat{\text{O(W)–H . . . O}}$	$\widehat{\text{H–O(W)–H}}$
O(W1)–H(11) . . . O(E41)	0.86(5)	1.94(5)	2.781(3)	164(4)	114(4)
O(W1)–H(12) . . . O(E32)	0.85(5)	1.95(5)	2.777(3)	162(2)	
O(W2)–H(21) . . . O(E21)	0.96(4)	1.84(5)	2.752(4)	157(3)	114(4)
O(W2)–H(22) . . . O(E32)	0.92(5)	1.93(5)	2.820(3)	162(2)	

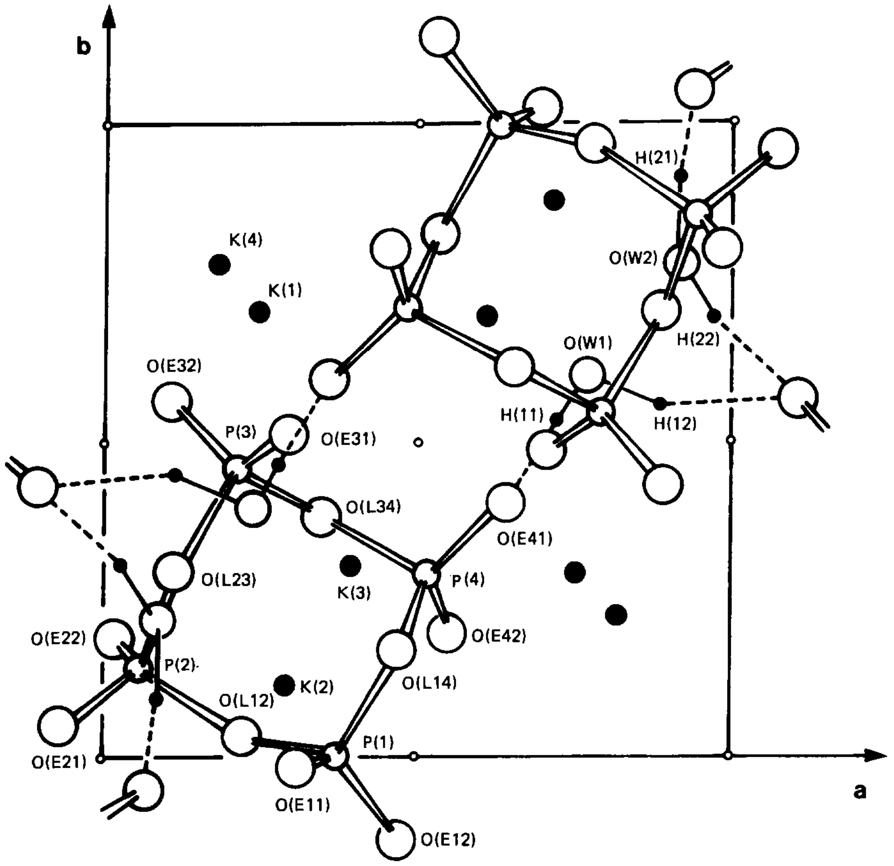

FIG. 1. Projection along the c axis of the atomic arrangement of $K_4P_4O_{12} \cdot 2H_2O$.

maining observations. Final atomic parameters, $B_{eq.}$ or $B_{iso.}$ (hydrogen atoms) are reported in Table V.

(*c*) *$Na_2K_2P_4O_{12} \cdot 2H_2O$ (tetragonal form).* After the elimination of the non-independent and very weak reflections ($F_o < \sqrt{3}\sigma_F$) 1347 observations remained from the 2783 measured intensity reflections. For this set, the R factor is 0.036. Final atomic parameters ($B_{eq.}$) are given in Table VI.

(*d*) *$Na_4P_4O_{12} \cdot 4H_2O$ (triclinic form).* For the complete set of data collection, (3256 reflections) the R factor is 0.034; while this same factor takes the value of 0.021 for 2568 observations corresponding to the rejections of 668 reflections for which $F_{obs} < 4\sigma_F$ and 20 reflections such that $||F_{obs}| - |F_{cal}|| > 28$ in a scale of $|F_{obs}|$ varying from 0 to 549. Atomic parameters, $b_{eq.}$ or $B_{iso.}$ (hydrogen atoms), are reported in Table VII.

(*e*) *$Na_4P_4O_{12} \cdot 4H_2O$ (monoclinic form).* For the complete set of 1929 measured reflections the R value is 0.030. After elimination of 414 reflections such that $F_{obs} < 3\sigma_F$ and 4 reflections for which $||F_{obs}| - |F_{cal}|| > 71$ ($|F_{obs}|$ varying from 0 to 1026), the R factor decreases to 0.021 for the 1511 remaining observations. Table VIII reports the final values of the atomic coordinates and $B_{eq.}$ ($B_{iso.}$ for hydrogen atoms).

Structure Descriptions

(*a*) *$K_4P_4O_{12} \cdot 2H_2O$.* Figure 1 is a projection of the atomic arrangement along the **c** axis. P_4O_{12} ring anions are located in planes $z \sim 0.25$ and 0.75 while potassium atoms are in planes $z \sim 0.0$ and 0.5. These two planes of potassium polyhedra have nevertheless some common oxygen atoms (O(E12) for instance) and thus form a three-dimensional network. The four independent potassium atoms have a sevenfold coordination. Potassium–oxygen distances in these polyhedra are reported in Table IXa.

Main interatomic distances and bond angles in the P_4O_{12} ring are given in Table IXb. In spite of the absence of any symmetry element this ring is quite regular:

$$2.923 < \text{P–P} < 2.973 \text{ Å}$$

$$83.49 < \text{P–P–P} < 85.00°$$

$$130.0 < \text{P–O–P} < 133.4°.$$

Water molecules are located halfway between the K and P_4O_{12} planes i.e., approximately at $z = \pm 0.125$ and ± 0.375. The set of hydrogen bridges is indicated in Fig. 1. It must be noticed that these hydrogen bridges spread in a two-dimensional way connecting all P_4O_{12} located at the same z value. Geometrical features of the hydrogen bond scheme are reported in Table IXc.

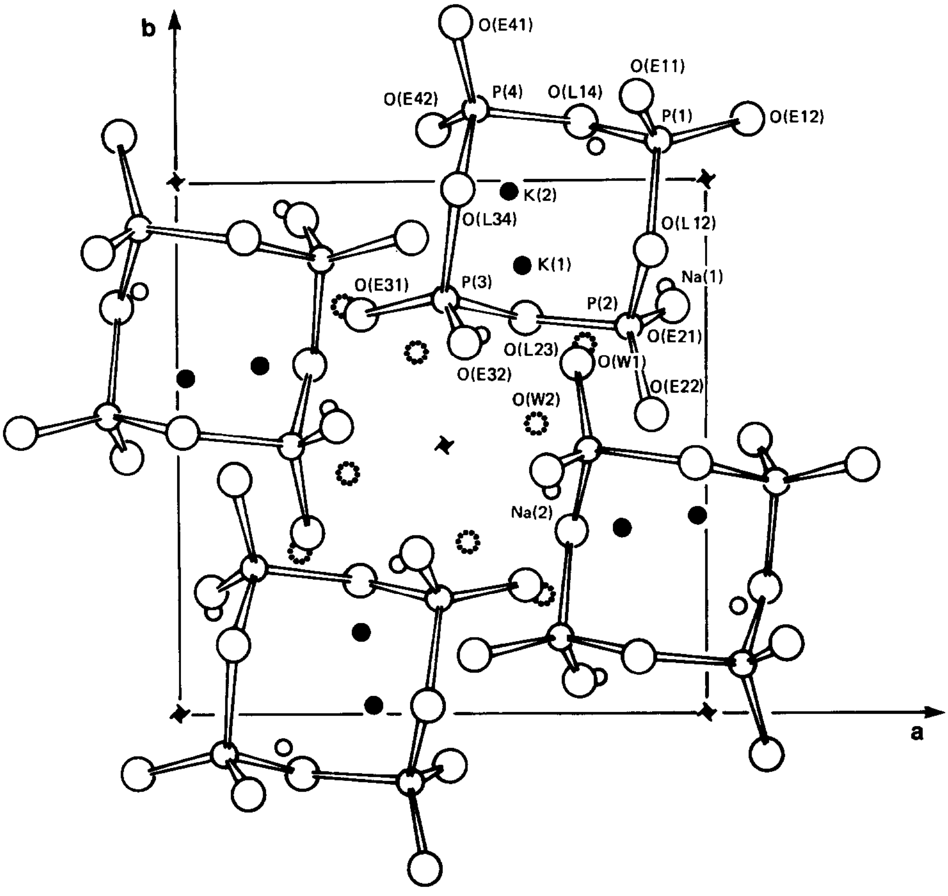

FIG. 2. Projection along the **c** axis of the atomic arrangement of the tetragonal form of $Na_2K_2P_4O_{12} \cdot 2H_2O$.

TABLE Xa

MAIN GEOMETRICAL FEATURES OF THE P_4O_{12} ANION IN THE TETRAGONAL FORM OF $Na_2K_2P_4O_{12} \cdot 2H_2O$

$P(1)O_4$ tetrahedron

P(1)	O(E11)	O(E12)	O(L12)	O(L14)
O(E11)	1.487(5)	119.9(3)	106.1(3)	110.9(3)
O(E12)	2.574(7)	1.487(5)	110.8(3)	105.4(3)
O(L12)	2.484(6)	2.557(6)	1.619(5)	102.6(2)
O(L14)	2.556(7)	2.470(7)	2.524(6)	1.616(5)

$P(2)O_4$ tetrahedron

P(2)	O(E21)	O(E22)	O(L12)	O(L23)
O(E21)	1.483(6)	120.0(3)	111.4(3)	105.6(3)
O(E22)	2.578(8)	1.494(5)	105.7(3)	110.6(3)
O(L12)	2.571(8)	2.489(6)	1.627(5)	102.0(2)
O(L23)	2.471(7)	2.558(7)	2.520(6)	1.616(5)

$P(3)O_4$ tetrahedron

P(3)	O(L23)	O(E31)	O(E32)	O(L34)
O(L23)	1.625(5)	107.2(3)	110.5(3)	101.3(2)
O(E31)	2.505(7)	1.484(5)	120.9(3)	108.8(3)
O(E32)	2.557(7)	2.582(6)	1.484(6)	106.4(3)
O(L34)	2.515(6)	2.531(7)	2.494(6)	1.627(5)

$P(4)O_4$ tetrahedron

P(4)	O(L34)	O(E41)	O(E42)	O(L14)
O(L34)	1.607(5)	106.9(3)	111.4(3)	101.8(2)
O(E41)	2.485(6)	1.486(5)	120.1(3)	109.2(3)
O(E42)	2.556(7)	2.574(7)	1.485(5)	106.0(3)
O(L14)	2.506(6)	2.533(7)	2.482(7)	1.622(5)

P(1)–P(2)	2.928(2)	P(2)–P(3)	2.937(2)
P(1)–P(4)	2.912(2)	P(3)–P(4)	2.916(2)
P(2)–P(1)–P(4)	85.14(8)	P(2)–P(3)–P(4)	84.91(8)
P(1)–P(2)–P(3)	84.71(8)	P(1)–P(4)–P(3)	85.38(8)
P(1)–O(L12)–P(2)	128.9(3)	P(3)–O(L34)–P(4)	128.7(3)
P(2)–O(L23)–P(3)	129.9(3)	P(1)–O(L14)–P(4)	128.2(3)

TABLE Xb

MAIN INTERATOMIC DISTANCES IN THE Na AND K POLYHEDRA OF $Na_2K_2P_4O_{12} \cdot 2H_2O$ (TETRAGONAL FORM)

Na(1)–O(E11)	2.429(6)	Na(1)–O(E31)	2.384(6)
–O(E12)	2.403(6)	–O(E42)	2.559(6)
–O(E21)	2.531(6)	–O(W1)	2.407(6)
Na(2)–O(E11)	2.573(5)	Na(2)–O(E41)	2.410(6)
–O(E22)	2.409(6)	–O(E42)	2.443(6)
–O(E32)	2.496(6)	–O(W2)	2.425(6)
K(1)–O(L12)	3.022(5)	K(1)–O(E31)	2.870(6)
–O(E21)	2.852(6)	–O(E32)	3.126(6)
–O(E22)	2.829(5)	–O(E42)	2.872(6)
–O(L23)	2.832(5)	–O(W1)	2.734(6)
K(2)–O(E11)	2.835(5)	K(2)–O(E32)	2.879(6)
–O(E12)	2.838(5)	–O(L34)	2.819(5)
–O(E21)	3.147(6)	–O(L14)	3.028(5)
–O(E22)	2.823(5)	–O(W2)	2.749(6)

One of the oxygen atoms, O(E32), is twice an acceptor.

(*b*) *$Na_2K_2P_4O_{12} \cdot 2H_2O$ (tetragonal).* Figure 2 presents a projection along the **c** axis of the atomic arrangement showing that the mean plane of the P_4O_{12} ring anion is almost perpendicular to the 4_1 axis. Associated cation polyhedra link to form bidimensional arrays of KO_8 and NaO_6 groups spreading in plane $z \sim 0.10$ and 0.35, therefore located almost halfway between planes containing P_4O_{12} rings (0.0, 0.25, 0.50, 0.75). Water molecules are also all located halfway between the P_4O_{12} planes. Detailed geometrical features of the ring anions are reported in Table Xa while associated cation polyhedra are described in Table Xb.

As in the other structures described in this paper the ring anion is quite regular:

$$2.912 < \text{P–P} < 2.937 \text{ Å}$$

$$84.71 < \text{P–P–P} < 85.38°$$

$$128.2 < \text{P–O–P} < 129.9°.$$

Due to the relatively poor quality of the crystal, hydrogen atoms have not been localized in this particular case.

TABLE XIa

MAIN INTERATOMIC DISTANCES IN THE Na AND K POLYHEDRA OF $Na_2K_2P_4O_{12} \cdot 2H_2O$ (TRICLINIC FORM)

K(1)–O(L23)	2.823(2) Å	K(2)–O(L12)	3.031(2) Å
–O(L14)	3.019(2)	–O(L34)	2.824(2)
–O(E12)	2.854(2)	–O(E11)	2.835(2)
–O(E31)	3.102(2)	–O(E21)	2.850(2)
–O(E31)	2.888(2)	–O(E41)	2.827(2)
–O(E32)	2.866(2)	–O(E42)	3.152(2)
–O(E41)	2.827(2)	–O(E42)	2.853(2)
–O(W1)	2.737(3)	–O(W2)	2.734(3)
Na(1)–O(E12)	2.569(2)	Na(2)–O(E11)	2.405(2)
–O(E12)	2.437(2)	–O(E21)	2.541(2)
–O(E22)	2.400(2)	–O(E21)	2.438(2)
–O(E31)	2.515(2)	–O(E32)	2.385(2)
–O(E41)	2.388(2)	–O(E42)	2.518(2)
–O(W1)	2.409(3)	–O(W2)	2.407(3)

(c) $Na_2K_2P_4O_{12} \cdot 2H_2O$ (triclinic). Figure 3 represents the projection of the atomic arrangement along the *a* axis. There is no apparent structure relation between this form and the tetragonal one, the P_4O_{12} an-

TABLE XIb

MAIN INTERATOMIC DISTANCES AND BOND ANGLES IN THE P_4O_{12} RING OF $Na_2K_2P_4O_{12} \cdot 2H_2O$ (TRICLINIC FORM)

		$P(1)O_4$ tetrahedron		
P(1)	O(L12)	O(E11)	O(E12)	O(L14)
O(L12)	1.615(2)	2.468(3)	2.551(3)	2.517(3)
O(E11)	105.5(1)	1.485(2)	2.572(3)	2.547(3)
O(E12)	110.8(1)	120.1(1)	1.483(2)	2.481(3)
O(L14)	102.3(1)	110.4(1)	106.3(1)	1.615(2)
		$P(2)O_4$ tetrahedron		
P(2)	O(L12)	O(E21)	O(E22)	O(L23)
O(L12)	1.618(2)	2.483(3)	2.529(3)	2.500(3)
O(E21)	106.3(1)	1.483(2)	2.572(3)	2.552(3)
O(E22)	109.2(1)	120.3(1)	1.483(2)	2.486(3)
O(L23)	101.5(1)	111.1(1)	106.8(1)	1.611(2)
		$P(3)O_4$ tetrahedron		
P(3)	O(L23)	O(E31)	O(E32)	O(L34)
O(L23)	1.627(2)	2.486(3)	2.530(3)	2.507(3)
O(E31)	106.1(1)	1.482(2)	2.571(3)	2.557(3)
O(E32)	108.8(1)	120.3(1)	1.482(2)	2.495(3)
O(L34)	101.3(1)	111.3(1)	107.3(1)	1.613(2)
		$P(4)O_4$ tetrahedron		
P(4)	O(L34)	O(E41)	O(E42)	O(L14)
O(L34)	1.624(2)	2.548(3)	2.480(3)	2.522(3)
O(E41)	110.3(1)	1.480(2)	2.571(3)	2.476(3)
O(E42)	105.9(1)	120.5(1)	1.481(2)	2.557(3)
O(L14)	102.0(1)	105.8(1)	110.9(1)	1.622(2)

P(1)–P(2)	2.910(1) Å	P(1)–O(L12)–P(2)	128.3(1)°
P(2)–P(3)	2.916(1)	P(2)–O(L23)–P(3)	128.5(1)
P(3)–P(4)	2.933(1)	P(3)–O(L34)–P(4)	129.9(1)
P(4)–P(1)	2.925(1)	P(4)–O(L14)–P(1)	129.2(1)

P(1)–P(2)–P(3)	85.31(3)
P(3)–P(4)–P(1)	84.74(3)
P(4)–P(1)–P(2)	85.22(3)
P(2)–P(3)–P(4)	84.96(3)

TABLE XIIa

MAIN GEOMETRICAL FEATURES OF THE P_4O_{12} RING IN THE MONOCLINIC FORM OF $Na_4P_4O_{12} \cdot 4H_2O$

		$P(1)O_2$ tetrahedron		
P(1)	O(L1)	O(l2)	O(E11)	O(E12)
O(L1)	1.608(2)	2.442(3)	2.478(2)	2.540(2)
O(L2)	98.9(1)	1.607(2)	2.484(3)	2.537(2)
O(E11)	107.2(1)	107.6(1)	1.470(2)	2.571(2)
O(E12)	110.2(1)	110.1(1)	120.7(1)	1.488(2)
		$P(2)O_4$ tetrahedron		
P(2)	O(L1)	O(L2)	O(E21)	O(E22)
O(L1)	1.606(2)	2.516(2)	2.435(2)	2.541(3)
O(L2)	103.3(1)	1.602(2)	2.526(3)	2.463(3)
O(E21)	104.2(1)	110.0(1)	1.479(2)	2.576(3)
O(E22)	110.8(1)	106.0(1)	121.1(1)	1.479(2)

P(1)–P(2)	2.915(1)	P(2)–P(1)–P(2)	97.76(2)
P(1)–P(2)	2.964(1)	P(1)–P(2)–P(1)	82.24(2)

P(1)–O(L1)–P(2)	134.5(1)
P(1)–O(L2)–P(2)	130.6(1)

TABLE XIIb

SODIUM-OXYGEN DISTANCES IN THE TWO NaO_6 OCTAHEDRA OF THE MONOCLINIC $Na_4P_4O_{12} \cdot 4H_2O$

	$Na(1)O_6$ octahedron		
Na(1)–O(L1)	2.684(2)	Na(1)–O(E21)	2.473(2)
Na(1)–O(E12)	2.375(2)	Na(1)–O(E22)	2.341(2)
Na(1)–O(E12)	2.373(2)	Na(1)–O(W2)	2.280(2)
	$Na(2)O_6$ octahedron		
Na(2)–O(E11)	2.347(2)	Na(2)–O(W1)	2.411(2)
Na(2)–O(E11)	2.316(2)	Na(2)–O(W1)	2.396(2)
Na(2)–O(E21)	2.383(2)	Na(2)–O(W2)	2.660(3)

TABLE XIc

MAIN CHARACTERISTICS OF THE HYDROGEN-BOND BRIDGES IN $Na_2K_2P_4O_{12} \cdot 2H_2O$ (TRICLINIC FORM)

	O(W)–H	H . . . O	O(W)–O	$\widehat{\text{O(W)–H . . . O}}$	$\widehat{\text{H–O(W)–H}}$
O(W1)–H(11) . . . O(E11)	0.90(5)	1.96(5)	2.848(3)	171(4)	96(4)
O(W1)–H(12) . . . O(E22)	0.77(5)	2.16(5)	2.817(3)	143(5)	
O(W2)–H(21) . . . O(E32)	0.81(5)	2.02(5)	2.803(5)	163(4)	99(3)
O(W2)–H(22) . . . O(E22)	0.86(5)	2.03(5)	2.887(3)	172(4)	

TABLE XIIc

MAIN GEOMETRICAL FEATURES OF THE HYDROGEN-BOND SCHEME IN THE MONOCLINIC $Na_2P_4O_{12} \cdot 4H_2O$

	O(W)–H	H . . . O	O(W)–O	$\widehat{\text{O(W)–H . . . O}}$	$\widehat{\text{H–O(W)–H}}$
O(W1)–H(11) . . . O(E12)	0.89(4)	2.24(4)	3.083(2)	158(3)	
O(W1)–H(12) . . . O(E22)	0.85(4)	2.09(4)	2.841(3)	147(3)	106(3)
O(W2)–H(21) . . . O(E22)	0.75(4)	2.17(4)	2.861(3)	152(4)	
O(W2)–H(22) . . . O(E21)	0.84(4)	1.97(4)	2.760(3)	155(4)	103(4)

ion stacking in the space being completely different. The only common points are that the P_4O_{12} anion planes are quite parallel to a basis plane, here (**b**, **c**) at $x \simeq 0.25$ and 0.75 and that all the associated cations are in planes, located between the P_4O_{12} rings in $x \simeq 0$ and 0.5.

As usually, the Na(1) and Na(2) coordinations are octahedral, while the K(1) and K(2) atoms are surrounded by eight oxygen

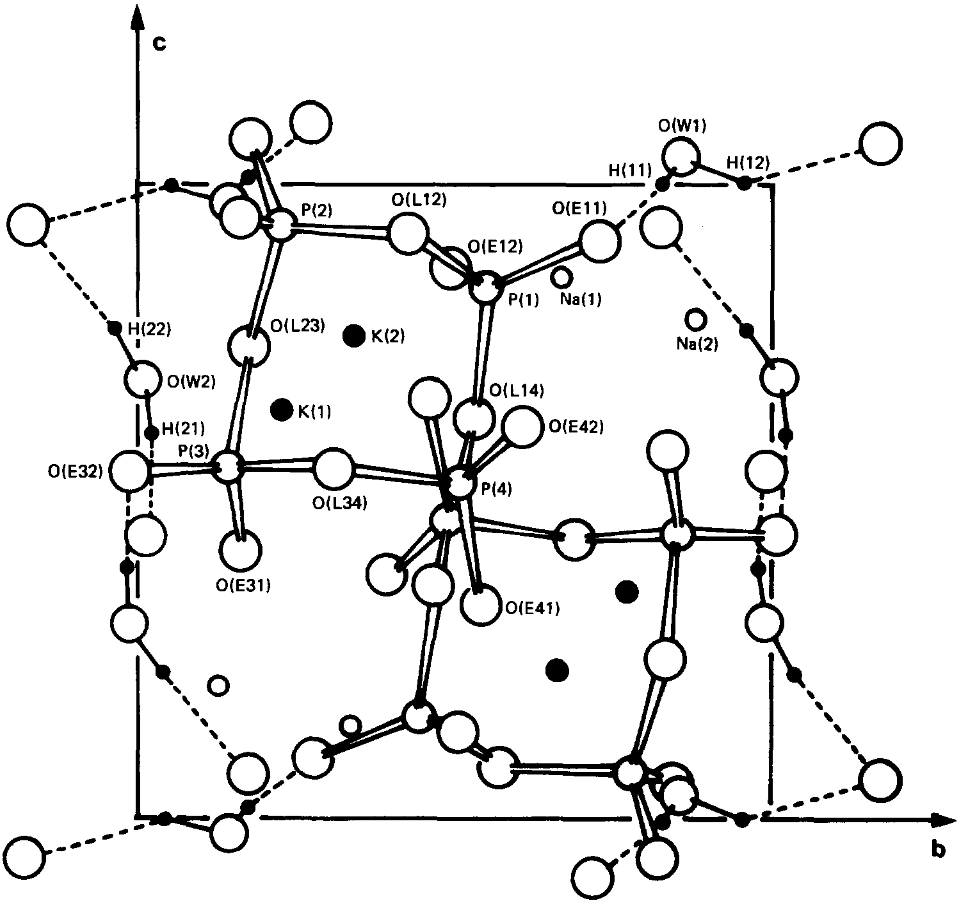

FIG. 3. Projection along the **a** axis of the atomic arrangement of the triclinic form of $Na_2K_2P_4O_{12} \cdot 2H_2O$.

atoms within a distance of 3.2 Å. These coordination polyhedra build up a tridimensional network. Table XIa gives the sodium–oxygen and potassium–oxygen distances and Table XIb gives the main interatomic distances and bond angles in the P_4O_{12} anion.

TABLE XIIIa

MAIN INTERATOMIC DISTANCES AND BOND ANGLES IN THE P_4O_{12} ANION OF TRICLINIC $Na_4P_4O_{12} \cdot 4H_2O$

P(1)O$_4$ tetrahedron

P(1)	O(L1)	O(E11)	O(E12)	O(L2)
O(L1)	1.604(2)	2.541(2)	2.478(2)	2.441(2)
O(E11)	110.82(9)	1.482(2)	2.559(2)	2.530(2)
O(E12)	107.32(9)	120.1(1)	1.471(2)	2.491(2)
O(L2)	98.89(9)	109.8(1)	107.81(9)	1.610(2)

P(2)O$_4$ tetrahedron

P(2)	O(E21)	O(E22)	O(L1)	O(L2)
O(E21)	1.481(2)	2.576(2)	2.435(2)	2.534(2)
O(E22)	120.7(1)	1.483(2)	2.533(2)	2.464(2)
O(L1)	104.54(9)	110.60(9)	1.597(2)	2.518(2)
O(L2)	110.3(1)	105.81(9)	103.71(9)	1.605(2)

P(1)–P(2)	2.981(1)	P(2)–P(1)–P(2)	96.09(2)
P(1)–P(2)	2.905(1)	P(1)–P(2)–P(1)	83.91(2)
	P(1)–O(L1)–P(2)	137.3(1)	
	P(1)–O(L2)–P(2)	129.4(1)	

TABLE XIIIb

SODIUM-OXYGEN DISTANCES IN THE TWO NaO_6 OCTAHEDRA OF THE TRICLINIC $Na_4P_4O_{12} \cdot 4H_2O$

Na(1)–O(E21)	2.335(2)	Na(1)–O(E11)	2.419(2)
Na(1)–O(E22)	2.486(2)	Na(1)–O(E12)	2.263(2)
Na(1)–O(E11)	2.320(2)	Na(1)–O(L2)	3.049(2)
Na(2)–O(E22)	2.410(2)	Na(2)–O(W1)	2.478(2)
Na(2)–O(E12)	2.442(2)	Na(2)–O(W2)	2.429(2)
Na(2)–O(W1)	2.521(2)	Na(2)–O(W2)	2.420(2)

TABLE XIV

AVERAGE VALUES OF P–P DISTANCES, P–P–P AND P–O–P ANGLES IN THE THREE NEW RINGS

Formula	P–P(Å)	P–P–P(°)	P–O–P(°)
$K_4P_4O_{12} \cdot 2H_2O$	2.942	84.44	131.1
$Na_2K_2P_4O_{12} \cdot 2H_2O$ ($P\bar{1}$)	2.921	85.06	129.0
$Na_2K_2P_4O_{12} \cdot 2H_2O$ ($P4_1$)	2.923	85.04	128.9

One can also see here the great regularity of the ring:

$$2.910 < \text{P–P} < 2.933\ \text{Å}$$

$$84.75 < \text{P–P–P} < 85.22°$$

$$128.3 < \text{P–O–P} < 129.9°.$$

The water molecule W(1) is located in the same plane (**b**, **c**) as K(1) and Na(1) ($x \simeq 0$) while W(2) is in the same plane as K(2) and Na(2) ($x \simeq 0.5$). The hydrogen bonds, drawn in the Figure 3, form a bidimensional network connecting parallel to b and c directions the P_4O_{12} rings located at the same x values (0.025 0 ~ 0.75). This hydrogen bond scheme is very similar to that described in $K_4P_4O_{12} \cdot 2H_2O$ structure. Its main characteristics are reported in Table XIc.

(*d*) *$Na_4P_4O_{12} \cdot 4H_2O$ (monoclinic and triclinic)*. The crystal structures of these two fundamental starting materials have been reexamined mainly to determine their hydrogen bond schemes. Tables XIIa, XIIb, XIIIa, and XIIIb report the main inter-

TABLE XIIIc

MAIN GEOMETRICAL FEATURES OF THE HYDROGEN-BOND SCHEME IN THE TRICLINIC $Na_2P_4O_{12} \cdot 4H_2O$

	O(W)–H	H . . . O	O(W)–O	$\widehat{\text{O(W)–H . . . O}}$	$\widehat{\text{H–O(W)–H}}$
O(W1)–H(11) . . . O(E11)	0.86(5)	2.35(5)	3.140(3)	152(4)	92(4)
O(W1)–H(12) . . . O(E21)	0.91(5)	2.15(5)	3.044(3)	169(4)	
O(W2)–H(21) . . . O(E21)	0.86(4)	1.87(4)	2.723(2)	173(4)	106(4)
O(W2)–H(22) . . . O(E22)	0.89(4)	2.01(4)	2.884(3)	167(4)	

atomic bond lengths and angles as observed after these new examinations, while Figs. 4 and 5 show the atomic arrangements including the hydrogen bridges whose detailed features are reported in Tables XIIc and XIIIc. It must be noticed that the hydrogen bond schemes suggested by early authors (*8, 9*) are fully verified. As shown in Figs. 4 and 5 hydrogen bridges form a monodimensional array along the *a* axis in the case of the triclinic form while they spread in a bidimensional way in the monoclinic form.

Discussion

It is worth noticing that for these three new compounds the unit cells have, with more or less large distortions, some analogies with the tetragonal unit cells observed in the $M^{I}_{2}M^{II}P_4O_{12}$ (M^{I} = K, NH_4, Tl; M^{II} = Sr, Pb, Ca) tetrametaphosphate series (*15, 16*):

$a_0 \sim 7.5$, $c_0 \sim 10.5$ Å,
$a \sim a_0$, $c \sim 2c_0$ for the tetragonal $Na_2K_2P_4O_{12} \cdot 2H_2O$,

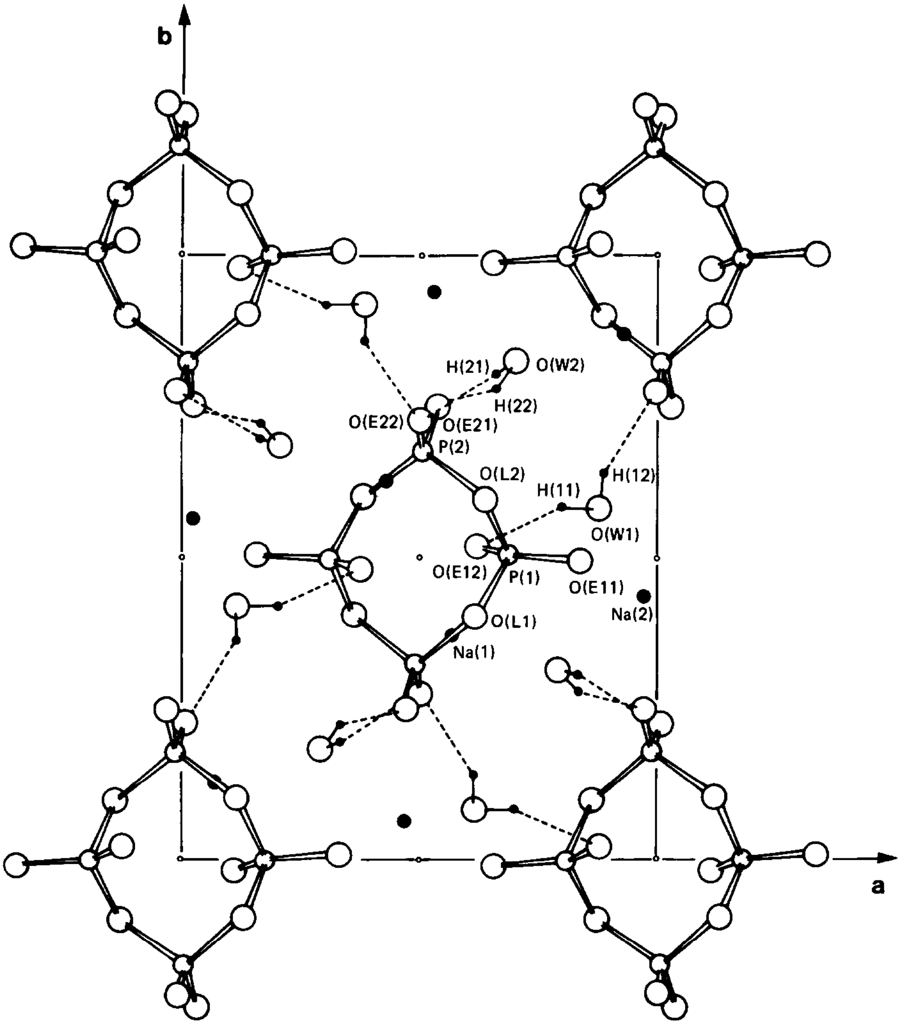

FIG. 4. Projection along the c axis of the atomic arrangement of the monoclinic $Na_4P_4O_{12} \cdot 4H_2O$.

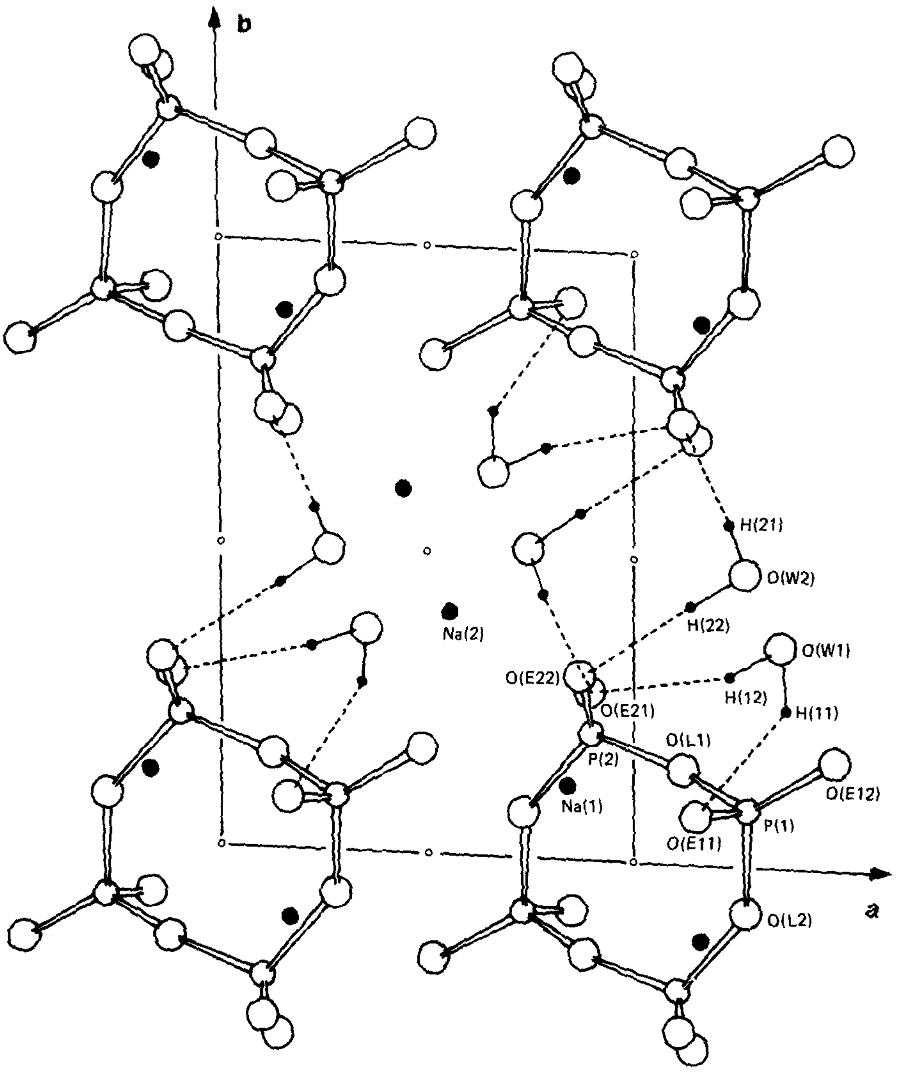

FIG. 5. Projection along the c axis of the atomic arrangement of the triclinic $Na_4P_4O_{12} \cdot 4H_2O$.

$a \sim c_0$, $b \sim a_0$, $c \sim a_0$ for the triclinic form,

$a \sim a_0$, $b \sim a_0$, $c \sim c_0$ for the $K_4P_4O_{12} \cdot 2H_2O$.

The same analogies appear for most of the tetrametaphosphates listed in Table I, for instance,

$a \sim a_0$, $c \sim c_0$ for $Tl_4P_4O_{12}$,

$a \sim a_0\sqrt{2}$, $b \sim a_0\sqrt{2}$, $c \sim c_0$ for $(NH_4)_3HP_4O_{12} \cdot H_2O$.

In spite of these metric similarities no analogies could be found in the atomic arrangements of these three new structure types.

The most striking feature observed during this investigation is the remarkable geometrical similarity of the P_4O_{12} rings. Tables IXb, Xa, and XIb report the detailed geometry of these rings but it seems useful to gather in Table XIV the average values of the P–P distances and the P–P–P and P–O–

P angles as observed in these three rings.[1]

P–O–P angles as large as 137.4 and 138.3° have been observed in $Zn_2P_4O_{12} \cdot 8H_2O$ (*17*) and $SrNa_2P_4O_{12} \cdot 6H_2O$ (*18*), respectively, while in the same compounds values of the P–P distances are as large as 2.981 and 2.994 Å.

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[1] Tables of anistropic thermal parameters and lists of structure factors are available on request to the authors.