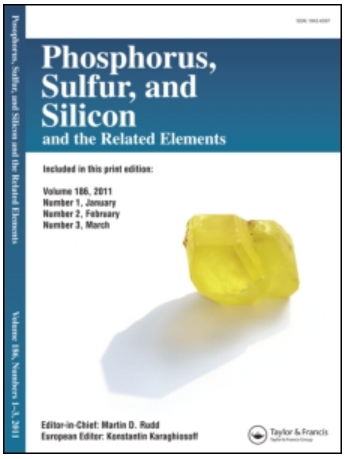

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Hydrothermal Synthesis, Crystal Structures and Characterization of Two Hydrogen Phosphates Templated by 4-Amino-2,2,6,6-tetramethylpiperidine

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*Chemical preparations, crystal structures, thermal analyses, and IR spectroscopic studies are given for two new hydrogen phosphates templated by 4-amino-2,2,6,6-tetramethylpiperidine: $(C_9H_{22}N_2)_2{\cdot}(H_2PO_4){\cdot}(HPO_4){\cdot}(F){\cdot}H_2O$ (**I**) and $(C_9H_{22}N_2){\cdot}(H_2PO_4)_2$(**II**). The structures are determined by single crystal X-ray diffraction. Both compounds crystallize in the $P2_1/c$ ($N^\circ 14$) monoclinic space group with the unit cell parameters: $a = 14.856$ (1) Å, $b = 14.092$ (2) Å, $c = 14.7166$ (9) Å, $\beta = 118.434$ (7)°, $V = 2709.2$ (4) Å^3, and $Z = 4$ for (**I**) and $a = 9.803$ (2) Å, $c = 0.466$ (2) Å, $c = 15.640$ (8) Å, $\beta = 94.990$ (4), $V = 1598.68$ (7) Å^3, and $Z = 4$ for (**II**).*

*The structure of **I**, refined to $R = 0.042$ and $R_w = 0.067$ for 6009 reflections ($I \geq 2\sigma(I)$), exhibits infinite inorganic chains $_\infty((H_2PO_4){\cdot}(HPO_4){\cdot}(F){\cdot}H_2O)^{4-}$ linked together through weak hydrogen bonds to form layers onto which the diprotonated $[C_9H_{22}N_2]^{2+}$ amine molecules are anchored.*

*The structure of **II**, refined to $R = 0.060$ and $R_w = 0.086$ for 1435 reflections ($I \geq 2\sigma(I)$), consists of $_\infty(H_2PO_4)^-$ (100) layers between which $[C_9H_{22}N_2]^{2+}$ cations are inserted. A network of hydrogen bonds connects the different components. IR spectra of **I** and **II** show the characteristic bands of amine groups and phosphate anions.*

Keywords Crystal structures; hydrothermal synthesis; infrared spectroscopy; organic phosphates; thermal behavior

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INTRODUCTION

The phosphate chemistry has considerably expanded over the past few years as a reason of their potential applications (ion exchange, surface absorption chemistry, ionic conductivity, gas separation, heterogeneous catalysis, etc.).[1–4] Hybrid metal phosphates generally are prepared by the hydrothermal reaction of a metal salt and phosphoric acid in the presence of an organic amine, which acts as a structure-directing agent.[5] However, Tapp and colleagues.[6] noted that this type of preparation also leads to simple amine phosphates. Our laboratory now is involved in the elaboration of hybrid zinc phosphates in phosphoric acid and fluoride solutions with various amines. 4-amino-2,2,6,6-tetramethylpiperidine was chosen by reason of the presence of one primary function and one strongly hindered secondary function. During this study, one zinc amine phosphate and two amine phosphates were obtained in H_3PO_4-HF-ethanol solutions. Here, we report on the structures of the amine phosphates.

RESULTS AND DISCUSSION

Description of the Structures and Discussion

In **I** and **II**, both primary and secondary amine functions are protonated. Two crystallographically independent organic cations $[C_9H_{22}N_2]^{2+}$ are found in **I** (Table I) while only one is found in **II**. All cations adopt a pseudo mirror symmetry (Figure 1); the C-N_S-C angles, in the range 119.1–119.7°, depart strongly from a tetrahedral angle and lateral C—C_L—C angles lie in the range 112.1–113.4°. All cations are anchored on to the anionic chains through (N—H···O) and (N—H···F) hydrogen bonds.

Structure of $(C_9H_{22}N_2)_2\cdot(H_2PO_4)\cdot(HPO_4)\cdot(F)\cdot H_2O$ (I)

A projection of the structure of **I** onto the (001) plane is given in Figure 2. The $(HPO_4)^{2-}$ and $(H_2PO_4)^-$ units are assembled through hydrogen bonds (O(4)–H···O(5) = 2.79(2) Å and O(7)–H···O(2) = 2.573(2) Å) to form dimers. These dimers, associated with F^- and H_2O by (O–H···O) and (O–H···F) hydrogen bonds, build infinite inorganic $_\infty((H_2PO_4)\cdot(HPO_4)\cdot(F)\cdot H_2O)^{4-}$ chains parallel to the *b* axis (Figure 3). Weak hydrogen bonds [O(w)···O(w) = 3.079(1) Å] link these chains together to form puckered layers lying parallel to the (100) plane (Figure 4). It must be noted that $(HPO_4)^{2-}$ and $(H_2PO_4)^-$ groups are easily identified from P—O distances (d_{P-O} = 1.50–1.53 Å and d_{P-OH} = 1.56–1.60 Å).

TABLE I Selected Interatomic Distances (Å) and Angles (°) in $(C_9H_{22}N_2)_2\cdot(H_2PO_4)\cdot(HPO_4)\cdot(F)\cdot H_2O$ (I)

$(HP(1)O_4)^{2-}$ anion <P(1)-O> = 1.539 (2)				
P(1)	O(1)	O(2)	O(3)	O(4)
O(1)	1.521(2)	2.504(2)	2.512(2)	2.489(2)
O(2)	110.52(9)	1.527(1)	2.534(2)	2.508(2)
O(3)	112.17(9)	113.4(1)	1.506(2)	2.522(2)
O(4)	105.53(9)	106.41(8)	108.3(1)	1.605(2)
$(H_2P(2)O_4)^{-}$ anion <P(2)-O> = 1.535 (2)				
P(2)	O(5)	O(6)	O(7)	O(8)
O(5)	1.515(2)	2.543(2)	2.512(2)	2.522(2)
O(6)	111.4(1)	1.564(2)	2.479(2)	2.444(2)
O(7)	109.27(9)	104.8(1)	1.565(2)	2.529(2)
O(8)	113.7(1)	106.0(1)	111.3(1)	1.497(2)
$[C_9N_2H_{22}]^{2+}$ (A) cation			$[C_9N_2H_{22}]^{2+}$ (B) cation	
N(1)A–C(1A)	1.523(3)		N(1)B–C(1)B	1.524(2)
N(1)A–C(5A)	1.514(2)		N(1)B–C(5)B	1.521(2)
N(2)A–C(3)A	1.489(2)		N(2)B–C(3)B	1.487(3)
C(1)A–C(2A)	1.532(3)		C(1)B–C(2)B	1.527(3)
C(1)A–C(8A)	1.531(3)		C(1)B–C(8)B	1.533(3)
C(1)A–C(9A)	1.528(4)		C(1)B–C(9)B	1.530(4)
C(2)A–C(3A)	1.522(3)		C(2)B–C(3)B	1.520(3)
C(3)A–C(4A)	1.514(3)		C(3)B–C(4)B	1.525(2)
C(4)A–C(5A)	1.521(3)		C(4)B–C(5)B	1.528(3)
C(5)A–C(7A)	1.526(3)		C(5)B–C(6)B	1.525(3)
C(5)A–C(7A)	1.527(4)		C(1)B–C(9)B	1.535(3)

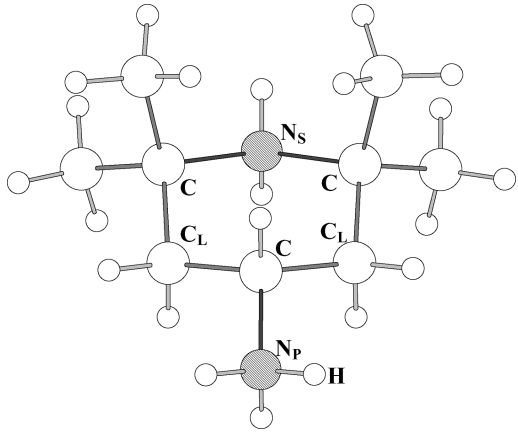

FIGURE 1 View of the organic cation $(C_9H_{22}N_2)^{2+}$ showing the pseudo-mirror symmetry.

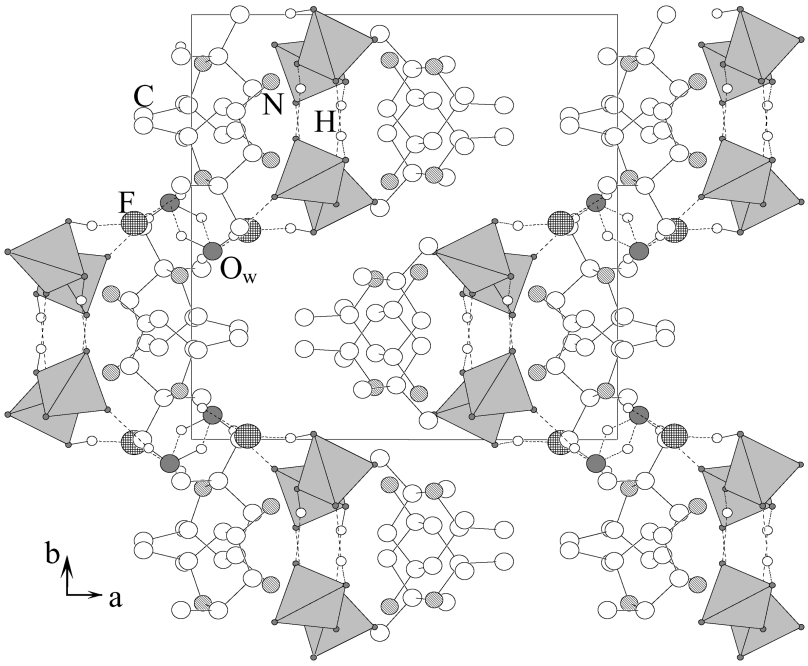

FIGURE 2 Projection of the structure of $(C_9H_{22}N_2)_2{\cdot}(H_2PO_4){\cdot}(HPO_4){\cdot}(F){\cdot}H_2O$ (**I**) along the *c* axis showing the hydrogen bonding interactions between phosphate, fluoride anions, and water molecules. For the clarity of the scheme, the hydrogen atoms of the diprotonated amine molecules have been omitted.

The stability of the structure is ensured in part by hydrogen bonds involving the phosphate units, the water molecules, the fluorine anions, as well as the doubly protonated amine cations. In Table II, the most probable D(donor)-H···A (Acceptor) hydrogen bonds of this compound are listed.

Structure of $(C_9H_{22}N_2)_2{\cdot}(H_2PO_4)_2$(II)

The structure of **II** consists of $_\infty(H_2PO_4)^-$ anionic sheets stacked along the [100] direction. The amine molecules, displayed between the inorganic layers, are stacked in zigzag parallel to the *b*-axis (Figure 5). Within the inorganic layers, phosphate groups, $(H_2P(1)O_4)^-$ and $(H_2P(2)O_4)^-$ (hereafter referred as P_1/P_2) are connected together by strong hydrogen bonds [O(3)···O(3) = 2.57(5) Å; O(3)···O(6) = 2.56(2) Å; O(2)···O(5) = 2.60(1) Å)] (Table III) to form tetramers ($2P_1{+}2P_2$). Every tetramer is connected to 4 neighbors by 4 hydrogen bonds (O(4)···O(7) = 2.58(4) Å), giving rise to an infinite

TABLE II Hydrogen-Bond Scheme in $(C_9H_{22}N_2)_2{\cdot}(H_2PO_4){\cdot}(HPO_4){\cdot}(F){\cdot}H_2O$ (I)

N(O)–H···O	H···O(Å)	N(O)···O (F)	N(O)HO
O(w)–H(wA)···O(w)	2.44(3)	3.079(7)	116(2)
N(1)A–H(1A)···O(8)	1.86	2.747(2)	168.9
N(2)A–H(2A)···O(8)	1.83	2.704(2)	166.6
N(2)A–H(2B)···O(5)	2.2	2.998(2)	148.8
N(2)A–H(2C)···O(1)	1.89	2.697(2)	149.2
N(1)B–H(1D)···F	1.75	2.645(2)	172.8
N(2)B–H(2F)···O(2)	1.89	2.764(2)	166.2
O(4)–H(4)···O(5)	1.99	2.799(2)	166.8
O(7)–H(7)···O(2)	1.77	2.573(2)	166.5
O(w)–H(wA)···O(3)	2.28(3)	2.780(3)	112(2)
O(w)–H(wB)···F	2.5	3.19	119.36
O(6)–H(6)···F	1.70	2.496(2)	163.4
N(1)A–H(1B)···O(1)	1.88	2.740(2)	160.3
N(1)B–H(1C)···O(3)	1.85	2.738(2)	170.8
N(2)B–H(2H)···O(5)	1.96	2.817(2)	160.0
N(2)B–H(2G)···F	1.81	2.658(2)	159.0
N(2)B–H(2F)···O(2)	1.89	2.764(2)	166.2

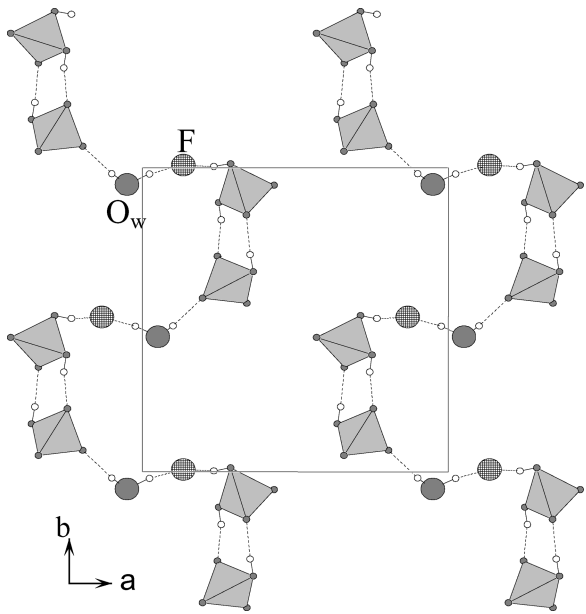

FIGURE 3 $_{\infty}((H_2PO_4){\cdot}(HPO_4){\cdot}(F){\cdot}H_2O)^{4-}$ chains in $(C_9H_{22}N_2)_2{\cdot}(H_2PO_4){\cdot}(HPO_4){\cdot}(F){\cdot}H_2O$ (**I**).

TABLE III Hydrogen-Bond Scheme in $(C_9H_{22}N_2)\cdot(H_2PO_4)_2$(II)

N(O)–H···O	H···O (Å)	N(O)···O	N(O)HO
N(1)–H(1A)···O(1)	1.91	2.765(6)	157.8
O(3)–H(3)···O(3)	1.82	2.579(9)	152.5
O(4)–H(4)···O(7)	1.83	2.596(6)	155.6
N(1)–H(1B)···O(1)	1.92	2.806(6)	168.8
N(2)–H(2A)···O(6)	2.0	2.827(7)	154.8
N(2)–H(2B)···O(7)	2.06	2.876(8)	152.0
N(2)–H(2C)···O(2)	1.87	2.745(6)	165.4

two-dimensional hydrogen-bonded network lying parallel to the (100) plane (Figure 6).

IR Spectroscopy

IR spectra of **I** and **II** are presented in Figure 7. They mainly can be subdivided into three domains: (1) 400–600 cm^{-1}, (2) 900–1200 cm^{-1}, and

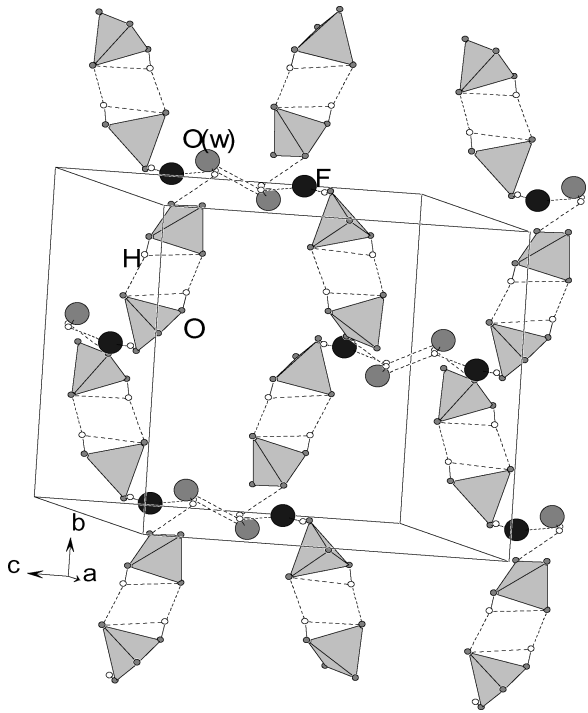

FIGURE 4 View of an inorganic layer in $(C_9H_{22}N_2)_2\cdot(H_2PO_4)\cdot(HPO_4)\cdot(F)\cdot H_2O$ (**I**) showing hydrogen bonding connectivity between chains.

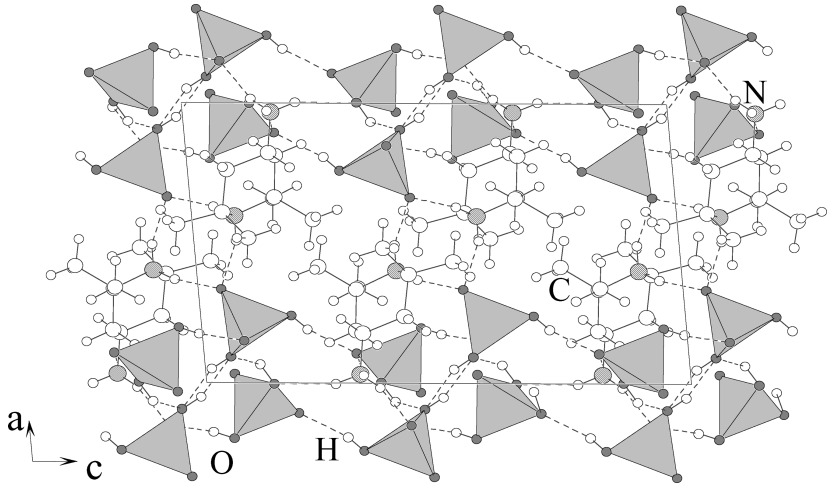

FIGURE 5 Projection of the structure of $[C_9H_{22}N_2]\cdot(H_2PO_4)_2$(**II**) along the *b* axis. The dotted lines represent the hydrogen bond interactions between phosphate tetramers and diprotonated amine molecules.

(3) 1200–3500 cm^{-1}. These ranges correspond, respectively, to bending modes of (PO_4) groups, stretching modes of (PO_4) groups, and a combination of (N(O,C)-H) bending and stretching modes.

Band attribution is carried out by comparison with the spectra of other hydrogen phosphates.[7–11] The proposed vibrational assignments are listed in Table IV.

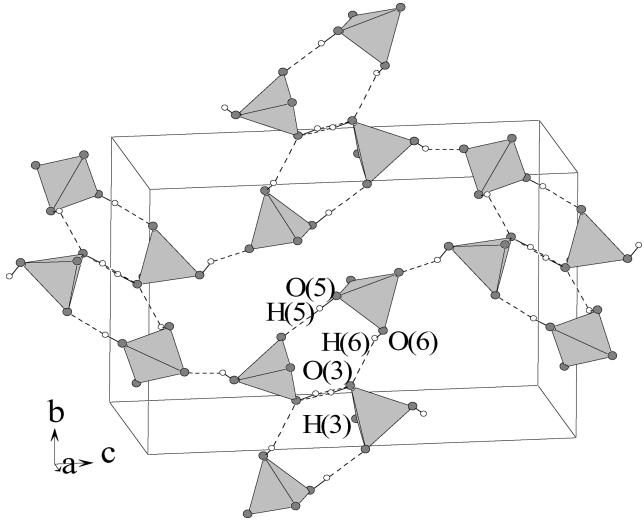

FIGURE 6 View of an organic layer in $(C_9H_{22}N_2)\cdot(H_2PO_4)_2$(II) showing the connectivity between tetramer entities.

TABLE IV Band Attribution of IR Spectra of I and II

I	II	Attribution	I	II	Attribution
417 (m)	417 (m)		1300 (sh)	1345 (w)	
440 (m)	432 (w)	$\nu_2(\delta_{O-P-O})$	1320 (m)	1396 (s)	
478 (m)	442 (w)		1354 (w)		
	472 (m)		1394 (s)	1385 (s)	$\delta_{(P-O-H)(out-of-plane)}$
519 (s)	500 (m)	$\nu_4(\delta_{O-P-O})$	1463 (m)	1466 (m)	δ_{N-H}
534 (s)	535 (m)		1542 (m)	1525 (s)	
558 (w)	546 (sh)		1557 (s)	1578 (s)	
667 (m)		$\rho t(H_2O)$		1617 (m)	
746 (w)	767 (w)	γ_{O-H}	2165 (w)	2342 (w)	$\nu_{(O-H)}$
778 (m)	782 (w)		2344 (w)	2366 (w)	
843 (s)		$\nu_{s(P-O-H)(out-of-plane)}$	2640 (w)	2447 (m)	
875 (w)	870 (sh)			2471 (m)	
892 (w)				2576 (w)	
940 (m)	954 (s)	$\nu_{1(P-O)}$		2630 (w)	
969 (vw)				2763 (w)	
983 (s)	1049 (s)	$\nu_{3(P-O)}$		2807 (w)	
1009 (w)	1081 (vw)		2783 (w)	2836 (m)	$\nu_{as(-CH_2-)}$
1045 (s)	1097 (s)		2851 (w)	2890 (m)	
1081 (s)	1122 (w)		2941 (w)	2937 (m)	
1100 (s)	1182 (m)			2976 (w)	
1144 (m)			3419		$\nu_{(H_2O)}$
1192 (w)			2984 (w)	3141 (w)	$\nu_{(NH_3)}$
1238 (s)	1236 (s)	γ_{CH3}	3020 (w)	3244 (w)	
1252 (s)	1273 (m)	δ_{-CH2-}			
1270 (m)	1321 (m)				

Thermal Analysis

Thermogravimetric analysis of **I** reveals a two-step weight loss at 509 K (38.7%) and 628 K (29%). The first weight loss, occurring between 453 and 557 K, can be attributed to the departure of one organic molecule, one water molecule, one HF molecule, and probably a second water molecule from the dehydration of $(HPO_4)^{2-}$ and $(H_2PO_4)^-$ groups (cal. 39%). Indeed, IR spectrum of **I** heated to 550 K shows a band around 750 cm^{-1} corresponding to the $\nu_{(O-P-O)}$ as well as a large modification of peaks in the range of 900–1200 cm^{-1}, corresponding to $\nu_{(P-O)}$ in independent (PO_4) tetrahedra. The second step, occurring between 557–670 K, corresponds to the departure of the second amine molecule.

For **II**, the TGA curve shows a continuous weight loss of 50% between 493–598 K, corresponding to the progressive degradation of the organic molecule.

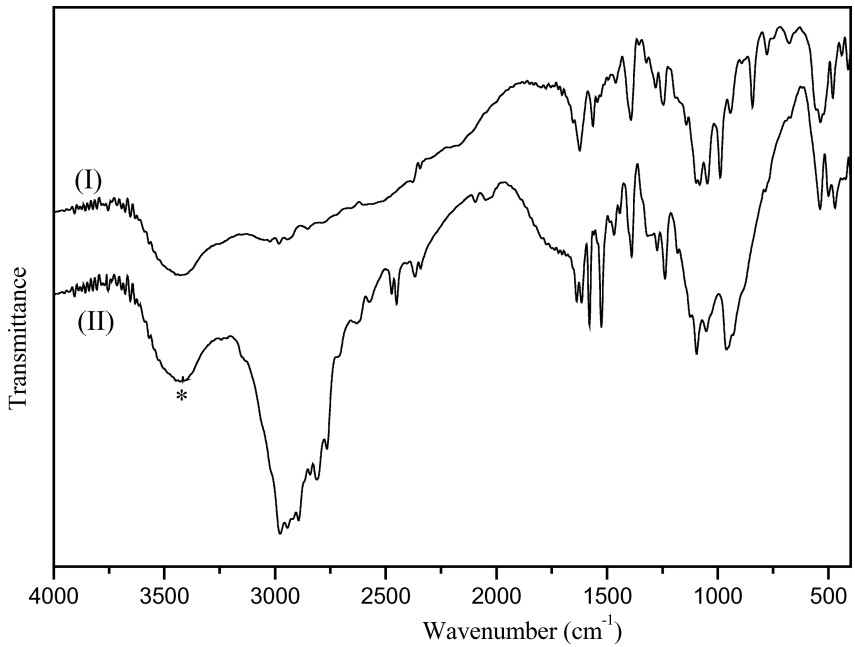

FIGURE 7 Infrared spectra of $(C_9H_{22}N_2)_2{\cdot}(H_2PO_4){\cdot}(HPO_4){\cdot}(F){\cdot}H_2O$ (**I**) and $(C_9H_{22}N_2){\cdot}(H_2PO_4)_2$(**II**) (*peak due to the H_2O (of KBr) modes).

EXPERIMENTAL

Chemical Preparation

Both compounds, $(C_9H_{22}N_2)_2{\cdot}(H_2PO_4){\cdot}(HPO_4){\cdot}(F){\cdot}H_2O$ (**I**) and $(C_9H_{22}N_2){\cdot}(H_2PO_4)_2$(**II**), were synthesized by using mild hydrothermal conditions under autogenous pressure.

I was prepared by dropwise adding 3 mL of ethanol solution of 4-amino-2,2,6,6-tetramethylpiperidine (0.1 M) to 2 mL of an aqueous solution of H_3PO_4 (0.1 M) and HF (0.4 M). The reaction mixture was stirred to homogeneity and placed in a Teflon-lined autoclave (filling factor 55%). After reaction at 393 K over 24 h, transparent crystals of **I** were obtained.

II was prepared from a 1/3/0.5/2/80 mixture of $Zn(OAc)_2.2H_2O$/H_3PO_4/HF/4-amino-2,2,6,6-tetramethylpiperidine/ethanol, heated at 463 K in a Teflon-lined autoclave (filling factor 50%). After reaction during two days, single crystals of **II** appeared together with an unidentified zinc phosphate powder. **II** is obtained whatever the (amine/$Zn(OAc)_2$) ratio between 0.2 and 2.

Investigation Techniques

X-Ray Diffraction

Suitable single-crystals of **I** and **II** were selected under a polarizing microscope and diffraction data were collected at room temperature on a Siemens AED2 four-circle diffractometer using the $\omega/2\theta$ scan technique. A summary of crystal data and details of intensity measurement are presented in Table V.

Intensities were corrected for Lorentz, polarization effects, and absorption. The observed systematic extinctions h0l (l = 2n) and 0k0

TABLE V Crystal Data and Intensity Measurement for $(C_9H_{22}N_2)_2{\cdot}(H_2PO_4){\cdot}(HPO_4){\cdot}(F){\cdot}H_2O$ (I) and $(C_9H_{22}N_2){\cdot}(H_2PO_4)_2$ (II)

	I	II
Formula	$[C_9H_{22}N_2]_2{\cdot}(H_2PO_4){\cdot}(HPO_4){\cdot}(F){\cdot}H_2O$	$[C_9H_{22}N_2]{\cdot}(H_2PO_4)_2$
Molecular weight (g mol^{-1})	546.56	352.26
Space group	$P2_1/c$ (N°14)	
Cell parameters		
a (Å)	14.856 (1)	9.803 (2)
b (Å)	14.092 (2)	0.466 (2)
c (Å)	14.7166 (9)	15.640 (8)
β(°)	118.434 (7)	94.990 (4)
Volume (Å^3); Z	2709.2 (4); 4	1598.68 (7); 4
$\rho_{calc.}$, $\rho_{exp.}$(g cm^{-3})	1.34, 1.296 (3)	1.46, not measured
Diffractometer, T(K)	Siemens AED2, 293 (2)	
Radiation (graphite monochromated)	MoK$_\alpha$ 0.71073 Å	
Scan mode	ω-2θ	
hkl min–max	$0 \le h \le 20$, $-19 \le k \le 0$, $-20 \le l \le 18$	$-10 \le h \le 10$, $0 \le k \le 11$, $0 \le l \le 16$
Absorption correction	Empirical	Empirical
2θ limit	60°	45°
Number of independent reflections	6009	1435
Number of refined parameters	325	144
Final R/R$_w$ indices ($I > 2\sigma(I)$)	0.043/0.149	0.060/0.149
Goodness of fit on F^2	1.129	1.035

($k = 2n$) led to the $P2_1/c$ space group for both compounds. Structures were determined using SHELXS-97[12] and refined using SHELXL-97.[13] For **I** as well as for **II**, P and part of O atoms were first located and then all other non-hydrogen atoms were found by difference Fourier maps analysis. By examining the anisotropic thermal parameters, the site denoted F for **I** (Table VI) was attributed to fluorine rather than to oxygen.

TABLE VI Atomic Coordinates and Equivalent Thermal Parameters in $(C_9H_{22}N_2)_2 \cdot (H_2PO_4) \cdot (HPO_4) \cdot (F) \cdot H_2O$ (I)

Atoms	x	y	Z	$B_{eq.}$(Å^2)
P(1)	0.71855(3)	0.12018(3)	0.27129(3)	1,651(8)
O(1)	0.6590(1)	0.0535(1)	0.3044(1)	2,35(3)
O(2)	0.7542(1)	0.2074(1)	0.3412(1)	2,40(3)
O(3)	0.8038(1)	0.0702(1)	0.2629(1)	2,91(4)
O(4)	0.6374(1)	0.1573(1)	0.1585(1)	3,05(3)
P(2)	0.66923(4)	0.08265(3)	0.68430(4)	1,810(8)
O(5)	0.6599(1)	0.15678(1)	0.6057(1)	2,31(3)
O(6)	0.7122(1)	−0.01308(1)	0.6670(1)	2,99(4)
O(7)	0.7505(1)	0.1161(1)	0.7946(1)	2,96(3)
O(8)	0.5695(1)	0.0587(1)	0.6810(1)	3,02(4)
F	0.1335(1)	0.0079(1)	0.3588(1)	6,99(4)
O(w)	0.0509(3)	0.4433(2)	0.1016(3)	4,05(9)
N(1)A	0.4308(1)	0.3778(1)	0.2407(1)	1,82(3)
N(2)A	0.5346(1)	0.1066(1)	0.3817(1)	2,03(3)
C(1)A	0.3712(1)	0.2927(1)	0.1764(1)	2,11(4)
C(2)A	0.4335(2)	0.2023(1)	0.2232(1)	2,16(4)
C(3)A	0.4731(1)	0.1945(1)	0.33933(1)	1,89(4)
C(4)A	0.5398(2)	0.2798(1)	0.3917(1)	2,24(4)
C(5)A	0.4812(2)	0.3728(1)	0.3575(1)	2,28(4)
C(6)A	0.4021(2)	0.3829(2)	0.3953(2)	3,84(7)
C(7)A	0.5566(2)	0.4555(2)	0.3980(2)	3,65(5)
C(8)A	0.3588(2)	0.3096(2)	0.0682(2)	3,40(5)
C(9)A	0.2653(2)	0.2872(2)	0.1692(2)	3,84(6)
N(1)B	0.0272(1)	0.6145(1)	0.2575(1)	1,78(3)
N(2)B	0.1878(1)	0.842(1)	0.4567(1)	2,12(3)
C(1)B	0.0643(2)	0.5977(1)	0.3722(1)	2,15(4)
C(2)B	0.1448(2)	0.6731(1)	0.4321(1)	2,18(4)
C(3)B	0.1058(1)	0.7729(1)	0.3954(1)	1,84(4)
C(4)B	0.0758(1)	0.7834(1)	0.2814(1)	1,90(4)
C(5)B	−0.0073(1)	0.7132(1)	0.2127(1)	1,79(3)
C(6)B	−0.0159(2)	0.7102(2)	0.1053(2)	2,65(3)
C(7)B	−0.1120(1)	0.7386(2)	0.2031(2)	2,73(5)
C(8)B	0.1147(2)	0.4994(2)	0.3968(2)	3,22(5)
C(9)B	−0.0243(2)	0.5980(2)	0.3976(2)	3,33(6)

*Coordinates of H atoms are determined but not reported in the table.

Qualitative analysis, performed with a Hitachi S2300 scanning electron microscope, confirmed the presence of fluorine in this compound. P and O atoms in compound **II** were refined anisotropically. H atoms, except those of the water molecule in **I**, were geometrically localized. The final refinement factors converged to R = 0.060 (Rw = 0.147) for 6009 reflexions (I $\geq 2\sigma$ (I)) and R = 0.060 (Rw = 0.149) for 1435 reflexions (I $\geq 2\sigma$ (I)) for compound **I** and **II**, respectively. The final atomic coordinates and thermal parameters are deposited at the Cambridge Crystallographic Centre (CCDC 251050 **I**, CCDC 251051 **II**). The atomic coordinates with equivalent isotropic ADPs and the main interatomic distances and angles are reported respectively in Tables VI and I for **I** and Tables VII and VIII for **II**.

Physical Measurements

Thermal analysis. Thermal analyses were carried out between room temperature and 1073 K under argon flow and with a heating rate of 5 K/min for **I** and 10 K/mn for **II** in a multimodule 92 Setaram Analyzer.

TABLE VII Atomic Coordinates and Equivalent Thermal Parameters in $(C_9H_{22}N_2)\cdot(H_2PO_4)_2$(II)

Atoms	x	y	z	B_{eq}(Å^2)
P(1)	0.2073(2)	0.5528(2)	0.0919(1)	2,09(4)
O(1)	0.3350(4)	0.5331(4)	0.0473(3)	2,4(1)
O(2)	0.1507(4)	0.6868(4)	0.0859(3)	2,7(1)
O(3)	0.0939(4)	0.4569(4)	0.0551(3)	3,3(1)
O(4)	0.2413(4)	0.5126(4)	0.1873(3)	3,0(1)
P(2)	0.9316(2)	0.1466(2)	0.1084(1)	2,22(4)
O(5)	0.8026(4)	0.1758(5)	0.0473(3)	3,6(2)
O(6)	0.9979(6)	0.2735(5)	0.1395(3)	4,4(2)
O(7)	0.8937(5)	0.0770(5)	0.1848(3)	4,4(2)
O(8)	1.0318(5)	0.0716(6)	0.0601(3)	5,6(2)
N(1)	0.4026(4)	0.1234(4)	0.4117(3)	1,75(8)
N(2)	0.0323(5)	0.3094(5)	0.3188(3)	2,42(9)
C(1)	0.3351(6)	0.0771(6)	0.3262(4)	2,0(1)
C(2)	0.1875(6)	0.1239(5)	0.3174(4)	2,1(1)
C(3)	0.1776(6)	0.2670(5)	0.3310(4)	1,9(1)
C(4)	0.2384(6)	0.3010(6)	0.4196(4)	2,2(1)
C(5)	0.3887(6)	0.2639(6)	0.4363(4)	2,3(1)
C(6)	0.4818(7)	0.3477(7)	0.3880(4)	3,4(1)
C(7)	0.4344(7)	0.2736(7)	0.5315(4)	3,2(1)
C(8)	0.3398(7)	−0.0680(6)	0.3294(4)	3,0(1)
C(9)	0.4154(6)	0.1220(6)	0.2512(4)	3,0(1)

*Coordinates of H atoms are determined but not reported in the table.

TABLE VIII Selected Interatomic Distances (Å) and Angles (°) in $(C_9H_{22}N_2)\cdot(H_2PO_4)_2$(II)

$(H_2P(1)O_4)^-$anion <P(1)-O> = 1.533(5)				
P(1)	O(1)	O(2)	O(3)	O(4)
O(1)	1.499(4)	2.531(6)	2.507(6)	2.456(6)
O(2)	114.6(3)	1.508(5)	2.507(6)	2.526(6)
O(3)	109.6(3)	109.1(2)	1.569(5)	2.486(6)
O(4)	106.9(2)	110.9(3)	105.3(2)	1.558(5)
$(H_2P(2)O_4)^-$anion <P(2)-O> = 1.517(5)				
P(2)	O(5)	O(6)	O(7)	O(8)
O(5)	1.548(5)	2.512(7)	2.481(6)	2.490(7)
O(6)	109.0(3)	1.538(6)	2.428(7)	2.487(7)
O(7)	110.3(3)	107.5(3)	1.474(5)	2.469(8)
O(8)	109.0(3)	109.4(3)	111.7(3)	1.510(6)
$[C_9N_2H_{22}]^{2+}$cation				
N(1)–C(1)	1.519(8)		C(3)–C(4)	1.503(9)
N(1)–C(5)	1.529(8)		C(4)–C(5)	1.524(8)
N(2)–C(3)	1.488(8)		C(5)–C(7)	1.520(9)
C(1)–C(2)	1.522(8)		C(1)–C(8)	1.520(9)
C(1)–C(9)	1.542(9)		C(5)–C(6)	1.514(9)
C(2)–C(3)	1.517(7)			

Infrared spectroscopy. IR data were collected in the 4000–400 cm^{-1} range with a Perkin-Elmer FT-IR 1000 spectrophotometer using the KBr pellet technique. The resolution was 4 cm^{-1}.

CONCLUSION

The elaboration of two organic hydrogen phosphates, $(C_9H_{22}N_2)_2\cdot(H_2PO_4)\cdot(HPO_4)\cdot(F)\cdot H_2O$ (**I**) and $(C_9H_{22}N_2)\cdot(H_2PO_4)_2$ (**II**), is performed with 4-amino-2,2,6,6-tetramethylpiperidine in solvothermal conditions. Both compounds, obtained in similar amine/H_3PO_4/HF ratios, were investigated by thermal analysis, X-ray diffraction, and vibrational spectroscopy.

A pseudo-mirror symmetry of the organic cations is found in both compounds, which bear no other structural relationship. In **I**, $(HPO_4)^{2-}$ and $(H_2PO_4)^-$ anions are associated as dimers while in **II**, $(H_2PO_4)^-$ groups are arranged in tetramers. Hydrogen bonding ensures the cohesion of the structures. The IR spectra, analyzed by comparison with other hydrogen phosphates, reveal the characteristic bands of phosphate groups, water, and amine cations.

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