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Preparation and Structural Characterization of Two Metallophosphate Frameworks Clathrating Diprotonated Ethylenediamine: $AlPO_4$-12(en) and $GaPO_4$-12(en)

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Two isostructural framework structures of empirical formula $M_3(PO_4)_3\cdot H_2O\cdot en$, with M = Al, Ga and en = ethylenediamine, have been synthesized as single crystals and characterized by X-ray crystallography. Both compounds crystallize in space group $P2_1/c$, $Z = 4$, with $a = 14.542$ (2) Å, $b = 9.430$ (2) Å, $c = 9.630$ (2) Å, $\beta = 98.21$ (1)° and $a = 14.656$ (2) Å, $b = 9.625$ (1) Å, $c = 9.672$ (1) Å, $\beta = 97.90$ (1)°, for $AlPO_4$-12 and $GaPO_4$-12, respectively. The structure type is characterized by the intergrowth of *sheets*, containing alternating corner-linked AlO_4 (or GaO_4) and PO_4 tetrahedra, with *slabs* containing tetramers composed of Al- (or Ga-) centered trigonal bipyramids cross-linked by PO_4 tetrahedra. These building units, infinite in (100), alternate along the *a* axis and sandwich molecules of diprotonated ethylenediamine between them. Hydrogen atoms are located only on the diprotonated en molecule, $C_2N_2H_{10}^{2+}$. All oxygen atoms, save one, are linked to at least two (or, in the case of O10 in the tetramer, three) metal atoms. The exception is O1, bonded to P3 in the sheet. The P3–O1 bond is directed toward the en molecule in the cavity between the sheet and the slab and is considerably shorter than other P–O bonds (1.502 (3) Å for $GaPO_4$-12) due to its direct bonding to only P3. Strong hydrogen bonds bind the en molecule to the framework via interactions such as the following: N1–H1···O1, H1···O1, 1.78 (1) Å; N1–H2··O7, H2··O7, 1.83 (1) Å.

Introduction

New families of aluminophosphate ($AlPO_4$-*n*)[1-8] and gallophosphate ($GaPO_4$-*n*)[9,10] structures with open frameworks contain members that are related to the microporous aluminosilicate molecular sieves[11] (zeolites) as well as unique structural types. These compounds are designated MPO_4-*n*, where M = Al, Ga and *n* denotes the framework type. Although the composition need not be MPO_4, the designation is maintained in order to be consistent with the patent literature.[1,2] The phases are characterized by metal to phosphorus ratios close to 1.0 and are typically synthesized by heating a gel of appropriate composition at between 150 and 250 °C.[1] An amine, believed to behave as a structure-directing or "templating" agent, organizing the metallophosphate framework about it in accord with its shape, size, and hydrogen-bonding requirements,[2,4,8] is added to the gel prior to hydrothermal treatment. Structurally, the families are divided into three groups,[8] on the basis of the types of metal-centered polyhedra in the framework: those frameworks consisting only of alternating corner-linked tetrahedra, those dense phases containing only octahedra and tetrahedra, and finally those frameworks composed of some combination of 4-, 5-, and 6-coordinated aluminum (or gallium) polyhedra and PO_4 tetrahedra. This last class has been described structurally in terms of intergrowths of elements of structure from the first and second classes.[4,5,8] A brief description of one member of this group ($AlPO_4$-12) has been given.[4] This report is concerned with the structure of this compound and its gallium analogue. Particularly, synthesis of high-quality single crystals of $GaPO_4$-12 has permitted a more positive definition of the hydrogenous species entrapped by the metallophosphate framework.

Experimental Section

All preparations were carried in a slightly modified manner[8,10] compared to that described in the patent literature.[1] The procedures described here were used because of their convenience and tendency to result in large single crystals of the required phase. They are not necessarily the optimal ones for other purposes, such as the production of single phase, gel-free products.

The alumina source (CATAPAL, a pseudobohemite phase with reported composition $Al_2O_3\cdot{}^3/_2H_2O$), was kindly provided by CONOCO Chemicals Corp. Ethylenediamine (en) and phosphoric acid were purchased from Koch-Light and Ajax Corp., respectively. All Chemicals were used as received. Hydrothermal syntheses were carried out in Pyrex glass capsules sealed under vacuum ($<10^{-5}$ torr) and placed in stainless steel bombs fitted with Teflon seals. Reaction products were identified by noting their crystal morphology under the optical microscope and from a comparison of Guinier X-ray powder photographs with published data.[1] The inhomogeneity of the samples produced (see below) precluded analysis of the amount of template taken up in a particular phase. This has been inferred from the structural analysis.

Preparation of $AlPO_4$-12(en). This compound was obtained by combining the reactants to give a 1:1:1:40 Al_2O_3:P_2O_5:en:H_2O gel composition. A typical synthesis run combined 8.0 g of 85% H_3PO_4, 20.8 g of water, and 4.8 % of CATAPAL, to give a thick, lumpy gel into which 1.0 g of en was folded. This gel was then sealed into a glass capsule and heated at 200 °C for 21 h in a box furnace. The technique resulted in the formation of clear crystals of four phases with distinct crystal morphologies:[8] $AlPO_4$-12 (thin plates), $AlPO_4$-21 (blades), $AlPO_4$-EN3 (tablets), and $AlPO_4$-EN4 (needles). A series of experiments, with varying digestion times at 200 °C, indicated the following crystallization sequence: EN4 followed by 12 and 21 with EN3 the last phase to form.

Preparation of $GaPO_4$-12(en). A source of gallium was prepared by dissolving 1.9 g of gallium metal in 35.0 mL of warm HNO_3. This was then filtered and ammonia solution added dropwise until the pH of the filtrate was 10.5. The resultant gel was filtered and washed with warm water. After drying at 90 °C overnight, this product was fired in air over a Bunsen burner to produce a white powder, which gave an essentially featureless X-ray powder diffraction pattern. Chemical analysis indicated a composition of $Ga_2O_3\cdot{}^1/_2H_2O$. A 1.0-g sample of this material was stirred into a solution of 1.0 g of 85% H_3PO_4 and 2.6 g of water. To this slurry was added 0.14 g of en. The thickened product was placed in a capsule and heated at 200 °C for 63 h. Clear crystals of a phase, designated $GaPO_4$-12, having a X-ray powder pattern and crystal morphology similar to those of $AlPO_4$-12, was predominent in the product. The only other crystalline phase detected was one with needle-shaped crystals and a unique X-ray powder diagram.[9]

X-ray Crystallography. Atomic positional parameters parameters for the non-hydrogen atoms in the $AlPO_4$-12(en) framework[4] were used as

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Table I. Crystallographic Data for $AlPO_4$-12(en) and $GaPO_4$-12(en)

	$AlPO_4$-12(en)	$GaPO_4$-12(en)
formula	$Al_3(PO_4)_3 \cdot H_2O \cdot C_2N_2H_8$	$Ga_3(PO_4)_3 \cdot H_2O \cdot C_2N_2H_8$
formula weight	444.0	572.2
space group	$P2_1/c$	
a, Å	14.542 (2)	14.656 (2)
b, Å	9.430 (2)	9.625 (1)
c, Å	9.630 (2)	9.672 (1)
β, deg	98.21 (1)	97.90 (1)
V, Å^3	1307.0	1351.5
D_{calcd}, g/cm^3	2.26	2.81
cryst shape; size, mm	(100) plate; 0.11 × 0.08 × 0.02	(100) plate; 0.16 × 0.16 × 0.03
μ(Mo Kα), cm^{-1}; absorption	6.0; 0.95 < abs < 0.99	62.8; 0.67 < abs < 0.91
diffractometer	Picker-FACSI	
radiation (graphite monochromator)	Mo Kα (λ = 0.7107 Å)	
range of hkl	$\pm h,k,l$	$-h,k,\pm l$
no. and 2θ of refs for cell	12, 35.4–44.0°	12, 34.6–42.6°
temp, °C	22	
scan method, speed, background	θ–2θ, 2°/min, fixed 20 s	
data colln range	$3° \leq 2\theta \leq 55°$	
no. of measd intensities	3604	3763
no. of unique intensities (I>0)	2657	3295
no. of intensities used (N_o)	2132 [$I > \sigma(I)$]	3295
no. of parameters refined (N_p)	227	227
R(INT) from combin equivalent	0.05	0.02
R, R_w, s[a]	0.074, 0.075, 0.96	0.030, 0.033, 1.02
scattering factors	neutral[12]	
(shift/esd)$_{max}$, final cycle	+0.01	−0.02
range in final ΔF map, e/Å^3	−0.82, +0.86	−0.67, +0.56
computer programs	TOMPA, SHELX-76,[13] ORTEP[14]	

[a] $R = \Sigma[|F_o| - |F_c|]/\Sigma|F_o|$, $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w = 1/[\sigma(F_o^2) + xF_o^2]$, x = 0.001 for $GaPO_4$-12 and 0.002 for $AlPO_4$-12; $s = [\Sigma w(F_o - F_c)^2/(N_o - N_p)]^{1/2}$.

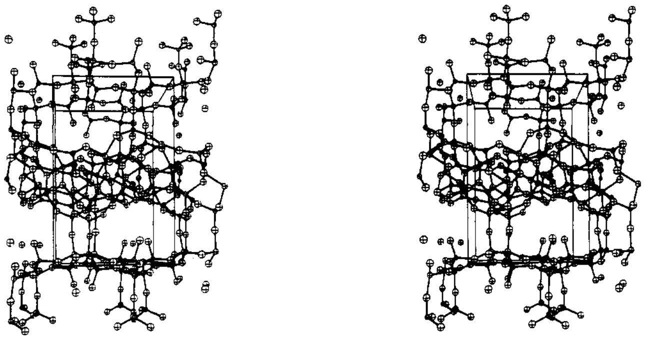

Figure 1. Stereoscopic ORTEP drawing of the structure of $GaPO_4$-12 and $AlPO_4$-12. The a axis is approximately vertical, while c is across the page. The infinite sheet and slab [in (100)] are close to each other at x = 0 and $^1/_2$, respectively. The ethylenediamine molecule, which resides in the pores between the sheet and the slab (see Figure 2), has been omitted for clarity. All atoms have arbitrary radii.

a starting point for the refinement of the structure of $GaPO_4$-12(en). The hydrogen atoms were located by a difference Fourier synthesis. They were then used in the refinement of the total structure of $AlPO_4$-12(en). Following the assignment of anisotropic thermal parameters, to all non-hydrogen atoms, both structures were refined to convergence. The relevent data pertaining to the data collection and structure refinement are summarized in Table I. Lorentz, polarization, and absorption corrections were applied.

Results and Discussion

The framework topologies for both $AlPO_4$-12 and $GaPO_4$-12 are essentially identical. As for the other structures belonging to this class,[8] it is best visualized by dividing it into two distinct structural units.[4,5] The decription given here will concentrate on $GaPO_4$-12; of course it applies equally well (except in the case of the geometry of Al-centered polyhedra) to $AlPO_4$-12. Atomic parameters and selected interatomic distances for the two phases are given in Table II–V. A stereoscopic drawing (Figure 1) of the structure and an ORTEP drawing of the environment around the en molecule (Figure 2) are provided for their interpretation.

Framework Topology and Geometry. The structure consists of the infinite *sheets* and *slabs* (in (100) at x = 0 and x = $^1/_2$, respectively) shown alternating along the a axial direction in Figure 1.

Table II. Atomic Positional[a] (×10^4) and Thermal (×10^3) Parameters for $AlPO_4$-12

atom	x	y	z	U or U(eq),[b,c] Å^2
Al1	3936 (1)	1562 (2)	2499 (2)	7
Al2	618 (1)	1747 (2)	4222 (2)	7
Al3	4214 (1)	−785 (2)	5039 (2)	6
P1	2813 (1)	1587 (1)	4932 (1)	6
P2	5670 (1)	3427 (1)	2914 (1)	7
P3	−275 (1)	3699 (1)	1940 (1)	9
O1	−1227 (3)	3247 (5)	2184 (5)	18
O2	4625 (3)	3170 (4)	2634 (5)	11
O3	5888 (3)	4930 (4)	3483 (4)	13
O4	478 (3)	3231 (5)	3165 (5)	13
O5	6791 (3)	−150 (4)	4499 (5)	12
O6	6102 (3)	3192 (4)	1551 (4)	9
O7	6147 (3)	2367 (4)	3986 (4)	8
O8	1771 (3)	1571 (5)	5002 (5)	13
O9	3264 (3)	2192 (4)	796 (4)	9
O10	4636 (3)	741 (4)	4047 (4)	7
O11	2931 (3)	1763 (5)	3385 (4)	12
O12	−54 (3)	1969 (5)	5560 (5)	17
O13	187 (3)	4682 (5)	8191 (5)	18
N1	−1967 (4)	3083 (6)	4694 (7)	20
N2	−3282 (4)	4732 (6)	6360 (6)	17
C1	−2249 (5)	4808 (8)	6559 (8)	20
C2	−1837 (5)	4564 (8)	5229 (8)	19
H1	−1737 (47)	2948 (81)	3763 (37)	44 (9)
H2	−2654 (12)	2884 (82)	4529 (75)	44 (9)
H3	−1684 (46)	2314 (61)	5347 (62)	44 (9)
H4	−3504 (53)	3720 (29)	6243 (76)	44 (9)
H5	−3580 (49)	5257 (67)	5497 (45)	44 (9)
H6	−3566 (52)	5151 (66)	7164 (51)	44 (9)
H7	−2041 (5)	5846 (8)	6959 (8)	44 (9)
H8	−1979 (5)	4012 (8)	7315 (8)	44 (9)
H9	−1102 (5)	4787 (8)	5434 (8)	44 (9)
H10	−2166 (5)	5279 (8)	4433 (8)	44 (9)

[a] H7–H10 refined on a riding model with respect to atoms C1 and C2. [b] Thermal parameters of H atoms tied to a common value during refinement. [c] $U(eq) = {}^1/_3(U_{11} + U_{22} + U_{33})$; anisotropic thermal parameters have been deposited as supplementary material.

Table III. Atomic Positional[a] (×10^4) and Thermal (×10^3) Parameters for $GaPO_4$-12

atom	x	y	z	U or U(eq),[b,c] Å^2
Ga1	3930 (1)	1630 (1)	2498 (1)	6
Ga2	614 (1)	1656 (1)	4178 (1)	9
Ga3	4196 (1)	−832 (1)	4970 (1)	6
P1	2788 (1)	1489 (1)	4948 (1)	7
P2	5675 (1)	3529 (1)	3040 (1)	7
P3	−259 (1)	3638 (1)	1945 (1)	10
O1	−1182 (2)	3163 (3)	2270 (3)	23
O2	4636 (2)	3282 (2)	2716 (3)	12
O3	5865 (2)	5019 (3)	3584 (3)	11
O4	541 (2)	3170 (3)	3044 (3)	16
O5	6826 (2)	−86 (2)	4471 (3)	11
O6	6144 (2)	3236 (2)	1739 (3)	12
O7	6140 (1)	2550 (2)	4161 (3)	10
O8	1758 (2)	1476 (3)	5122 (3)	14
O9	3260 (2)	2299 (2)	764 (3)	12
O10	4640 (2)	776 (2)	4053 (3)	9
O11	2869 (2)	1664 (3)	3382 (3)	11
O12	−129 (2)	1962 (4)	5507 (3)	24
O13	149 (2)	4775 (3)	8093 (4)	28
N1	−1958 (2)	3138 (4)	4730 (4)	19
N2	−3276 (2)	4699 (4)	6401 (4)	18
C1	−2241 (3)	4838 (5)	6571 (5)	22
C2	−1853 (3)	4597 (5)	5242 (5)	22
H1	−1663 (29)	3037 (54)	3863 (29)	39 (5)
H2	−2618 (11)	2870 (53)	4495 (49)	39 (5)
H3	−1668 (28)	2476 (45)	5451 (40)	39 (5)
H4	−3486 (34)	5040 (45)	7275 (28)	39 (5)
H5	−3506 (35)	3725 (20)	6275 (48)	39 (5)
H6	−3597 (32)	5224 (43)	5591 (32)	39 (5)
H7	−1944 (3)	4089 (5)	7335 (5)	39 (5)
H8	−2057 (3)	5874 (5)	6938 (5)	39 (5)
H9	−1128 (3)	4848 (5)	5413 (5)	39 (5)
H10	−2202 (3)	5275 (5)	4451 (5)	39 (5)

[a] H7–H10 refined on a riding model with respect to atoms C1 and C2. [b] Thermal parameters of H atoms tied to a common value during refinement. [c] $U(\mathrm{eq}) = {}^1/_3(U_{11} + U_{22} + U_{33})$; anisotropic thermal parameters have been deposited as supplementary material.

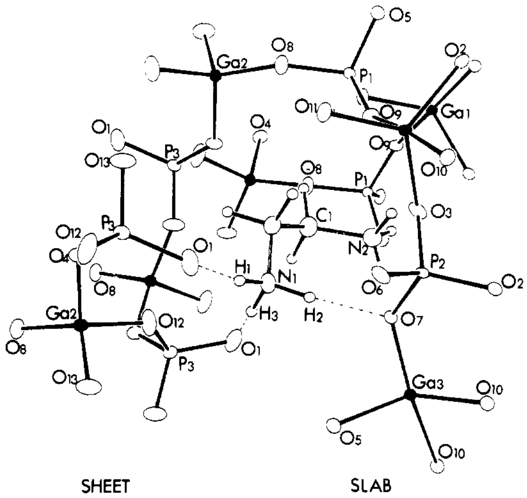

Figure 2. ORTEP drawing of the environment around ethylenediamine in $GaPO_4$-12(en). Atoms are represented by ellipsoids of thermal vibrations at the 50% probability level. Solid ellipsoids represent Ga and the atom numbers are as per Tables II–V.

Table IV. Selected Interatomic Distances (Å) and Angles (deg) for $AlPO_4$-12[a]

O3–Al1	1.844 (5)	O10–Al3	1.775 (5)
O11–Al1	1.804 (5)	O6–Al3	1.813 (5)
O10–Al1	1.850 (5)	O5–Al3	1.817 (5)
O9–Al1	1.881 (5)	O7–Al3	1.877 (5)
O2–Al1	1.812 (5)	O10*–Al3	1.879 (5)
O3–Al1–O11	120.7 (2)	O10–Al3–O6	122.6 (2)
O3–Al1–O10	88.0 (2)	O10–Al3–O5	127.0 (2)
O3–Al1–O9	84.7 (2)	O10–Al3–O7	94.7 (2)
O3–Al1–O2	128.4 (2)	O10–Al3–O10*	83.2 (2)
O11–Al1–O2	110.8 (2)	O6–Al3–O5	110.5 (2)
O11–Al1–O9	91.4 (2)	O6–Al3–O7	86.8 (2)
O11–Al1–O10	93.0 (2)	O6–Al3–O10*	92.3 (2)
O10–Al1–O2	93.3 (2)	O5–Al3–O7	88.3 (2)
O10–Al1–O9	172.7 (2)	O5–Al3–O10*	94.9 (2)
O9–Al1–O2	90.6 (2)	O7–Al3–O10*	176.7 (2)
O13–Al2	1.738 (5)	O5–P1	1.542 (5)
O12–Al2	1.739 (5)	O9–P1	1.514 (5)
O4–Al2	1.725 (5)	O8–P1	1.527 (5)
O8–Al2	1.744 (5)	O11–P1	1.533 (5)
O13–Al2–O12	108.8 (3)	O5–P1–O9	111.2 (3)
O13–Al2–O4	106.8 (3)	O5–P1–O8	107.3 (3)
O13–Al2–O8	114.8 (3)	O5–P1–O11	110.7 (3)
O12–Al2–O4	107.9 (3)	O9–P1–O8	109.8 (3)
O12–Al2–O8	107.5 (3)	O9–P1–O11	110.6 (3)
O8–Al2–O4	110.9 (3)	O8–P1–O11	107.1 (3)
O7–P2	1.530 (5)	O1–P3	1.499 (5)
O6–P2	1.550 (5)	O13–P3	1.539 (5)
O2–P2	1.524 (5)	O12–P3	1.546 (5)
O3–P2	1.536 (5)	O4–P3	1.555 (5)
O7–P2–O2	111.1 (3)	O1–P3–O13	112.6 (3)
O7–P2–O3	108.1 (3)	O1–P3–O12	109.2 (3)
O7–P2–O6	106.1 (3)	O1–P3–O4	111.6 (3)
O6–P2–O2	110.0 (3)	O13–P3–O12	107.7 (3)
O6–P2–O3	110.3 (3)	O13–P3–O4	106.6 (3)
O3–P2–O2	111.1 (3)	O12–P3–O4	109.0 (3)
O1–N1	2.786 (8)		
O7–N1	2.811 (7)	O3–N2	2.865 (7)
O1†–N1	2.783 (8)		

[a] O10* is related to O10 by the operation ($1 - x, -y, 1 - z$). O1† is related to O1 by the operation ($x, {}^1/_2 - y, {}^1/_2 + z$).

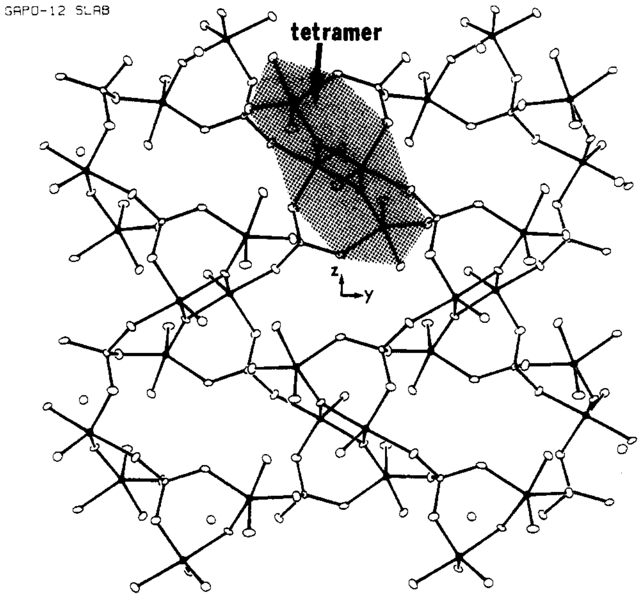

Figure 3. ORTEP drawing of the Ga-centered trigonal-bipyramidal tetramers, found in the slab at $x = {}^1/_2$ (see text and Figure 1), showing how these are cross-linked by PO_4 tetrahedra. Solid ellipsoids represent Ga in $GaPO_4$-12 (or Al in the case of $AlPO_4$-12). The center of the diagram is at (${}^1/_2$, 0, 0).

The slab, with composition $[Ga_2P_2O_9]^{2-}$, consists of tetramers of 5-coordinated gallium cross-linked via PO_4 tetrahedra (Figure 3). The tetramers are formed by two edge-sharing trigonal bipyramids (Ga3). This edge is then corner-linked, at atom O10, to two additional bipyramids (Ga1). Unlike the case of the five-coordinate polyhedra found in framework type 21 of this series,[5,8,10] deviations from the ideal trigonal-bipyramidal configuration are small. This deviation is no greater than 6° on average[15] from the ideal angles expected for this geometry (3 × 120°, 1 × 180°, 6 × 90°). This deviation is about 11° in the case of $AlPO_4$-21.[5,10] There is a tendency toward elongation of the

Table V. Selected Interatomic Distances (Å) and Angles (deg) for GaPO$_4$-12[a]

O2–Ga1	1.894 (3)	O10*–Ga3	1.940 (3)
O9–Ga1	1.935 (3)	O5–Ga3	1.883 (3)
O10–Ga1	1.895 (3)	O7–Ga3	1.949 (3)
O3–Ga1	1.918 (3)	O10–Ga3	1.833 (3)
O11–Ga1	1.875 (3)	O6–Ga3	1.887 (3)
O11–Ga1–O2	114.2 (1)	O10–Ga3–O5	124.0 (1)
O11–Ga1–O9	92.0 (1)	O10–Ga3–O6	125.6 (1)
O11–Ga1–O10	92.7 (1)	O10–Ga3–O10*	82.3 (1)
O11–Ga1–O3	117.7 (1)	O10–Ga3–O7	94.4 (1)
O10–Ga1–O2	92.5 (1)	O5–Ga3–O6	110.4 (1)
O10–Ga1–O9	172.2 (1)	O5–Ga3–O10*	95.0 (1)
O10–Ga1–O3	88.4 (1)	O5–Ga3–O7	90.9 (1)
O9–Ga1–O3	83.9 (1)	O6–Ga3–O10*	92.5 (1)
O9–Ga1–O2	91.2 (1)	O6–Ga3–O7	85.5 (1)
O2–Ga1–O3	128.1 (1)	O10*–Ga3–O7	174.1 (1)
O8–P1	1.542 (3)	O4–Ga2	1.816 (3)
O11–P1	1.544 (3)	O8–Ga2	1.803 (3)
O5–P1	1.539 (3)	O13–Ga2	1.809 (3)
O9–P1	1.519 (3)	O12–Ga2	1.821 (3)
O9–P1–O9	111.4 (2)	O12–Ga2–O4	107.7 (2)
O9–P1–O8	109.4 (2)	O12–Ga2–O8	105.3 (2)
O9–P1–O11	109.6 (2)	O12–Ga2–O13	108.7 (2)
O5–P1–O8	105.6 (1)	O8–Ga2–O4	110.8 (1)
O5–P1–O11	112.3 (2)	O8–Ga2–O13	118.0 (1)
O8–P1–O11	108.3 (2)	O13–Ga2–O4	106.0 (1)
O2–P2	1.530 (3)	O1–P3	1.502 (3)
O3–P2	1.539 (3)	O4–P3	1.540 (3)
O6–P2	1.542 (3)	O13–P3	1.535 (3)
O7–P2	1.524 (3)	O12–P3	1.542 (3)
O7–P2–O2	112.7 (2)	O1–P3–O13	113.9 (2)
O7–P2–O3	106.9 (2)	O1–P3–O4	112.9 (2)
O7–P2–O6	105.1 (2)	O1–P3–O12	107.5 (2)
O6–P2–O2	110.3 (2)	O13–P3–O4	103.6 (2)
O6–P2–O3	111.7 (2)	O13–P3–O12	109.1 (2)
O3–P2–O2	110.0 (2)	O4–P3–O12	109.6 (2)
O1–N1	2.775 (1)		
O7–N1	2.822 (1)	O3–N2	2.856 (1)
O1†–N1	2.852 (1)		

[a] O10* is related to O10 by the operation $(1 - x, -y, 1 - z)$. O1† is related to O1 by the operation $(x, {}^1/_2 - y, {}^1/_2 + z)$

apial bonds in these polyhedra with Ga3–O7 (1.949 Å) and Ga3–O10* (1.940 Å) longer than the average value for this polyhedron (1.90 (5) Å; see ref 15 for an explanation of the esd's given for these averages). These figures are 1.877, 1.879, and 1.83 (3) Å, respectively, for AlPO$_4$-12. Similar tetramers occur in AlPO$_4$-15,[3,16] where they are made up of Al-centered octahedra, and in a new gallium phosphate framework,[9] where they consist of both octahedra and trigonal bipyramids. One difference is the absence of hydrogen attached to these units in the case of framework type 12. The pivotal oxygen atom (O10) is connected to three metal atoms and hydrogen in types 15 and 14, whereas the framework is hydrogen free in type 12. These tetramers are cross-linked by PO$_4$ tetrahedra to form the slab with distorted eight-membered-ring openings (Figure 3).

The sheet, with composition [GaPO$_4$], consists exclusively of metal-centered tetrahedra, which are corner-linked to form four-membered and elliptical eight-membered-rings. Gallium (Ga2) and phosphorus (P3) are in perfect alternation around the net formed (Figure 4). With the exception of the P3-centered polyhedron, all tetrahedra are close to ideal with the following average values and deviations:[15] Ga2–O = 1.812 (8) Å, P1–O = 1.536 (11) Å, and P2–O = 1.534 (8) Å for GaPO$_4$-12, and Al2–O = 1.737 (8) Å, P1–O = 1.529 (8) Å, and P2–O = 1.535 (11) Å for AlPO$_4$-12. In both structures P3–O1 is considerably shorter than these values (1.502 and 1.499 Å for GaPO$_4$-12 and AlPO$_4$-12, respectively). The atom O1 is bonded directly only to P3.

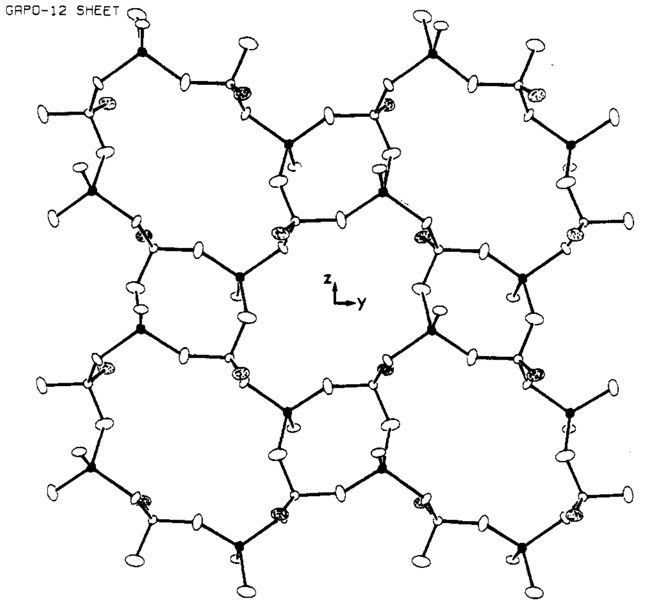

Figure 4. ORTEP drawing of the sheet (at $x = 0$ in Figure 1). Hatched ellipsoids represent Ga in GaPO$_4$-12 (or Al in AlPO$_4$-12). Stippled ellipsoids are the O1 oxygen atoms attached only to P3 and hydrogen bonded to ethylenediamine (see text). The center of the diagram is at (0, 0, 0).

The sheet and slab are joined via Ga(sheet)–O–P(slab) connections (Figure 2). There are no P–O–P connections within the structure nor are there any Ga–O–Ga linkages outside the slab (Figures 1 and 2). Building the framework from these units leaves distorted eight-membered-ring openings in the *a* and *c* axial directions. Molecules of ethylenediamine reside in the pores formed the slab and the sheet.

Position and Hydrogen Bonding of Ethylenediamine. The en molecule is incorporated into the structure as a doubly charged $N_2C_2H_{10}^{2+}$ species. Protonation of the templating amine might be expected since the pH during synthesis varies from about 2 at the beginning to 6 when reaction is halted. Protonated isopropylamine has been reported in the structure of other compounds related to framework type 12.[7,9,10]

Figure 2 shows the disposition of en with respect to the framework. One C–N bond is directed toward the distorted eight-membered ring in the slab while the other is involved in hydrogen bonding to O1. The N1–C2–C1–N2 torsion angles are −66.9 (5) and −56 (2)° for GaPO$_4$-12 and AlPO$_4$-12, respectively. On purely electrostatic grounds a torsion angle close to 180° would be expected for the diprotonated species. The observed value, close to 60°, is usually associated with the conformation stabilized by intramolecular hydrogen bonding[17] in the gas-phase calculations. The rigidity of the molecule and its gauche conformation are due to the hydrogen bonds between it and oxygen in the framework. The strongest of these have the following parameters (Å, deg). For GaPO$_4$-12: N1–H1···O1, 1.78 (1), 170 (5); N1–H2···O7, 1.83 (1), 172 (5); N1–H3···O1, 1.81 (2), 157 (5). For AlPO$_4$-12: 1.81 (2), 163 (7); 1.81 (2), 171 (6); 1.88 (2), 148 (6). The first and second figure in each group are the H···O distance and N–H···O angle, respectively. Hydrogen atoms attached to N2 are involved in weaker bonds with O5 and O7. Complete details of the hydrogen bond geometry have been deposited as supplementary material. Selected interatomic distances between the amine and the metallophosphate frameworks are given in Tables IV and V.

General Remarks and Conclusions. Framework type 12 can be constructed from either aluminophosphate or gallophosphate

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[15] Deviations from ideal geometries are calculated as $[\sum_n(\alpha_i - \alpha_o)^2/(n - 1)]^{1/2}$, where α_i and α_o are the ideal and observed angles, respectively, and n is the number of unique angles in the polyhedron. A similar formulation also applies to the calculation of the esd for average interatomic distance in the polyhedron. In this case the "ideal" is replaced by the mean value.

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compositions by using ethylenediamine, added to the synthesis gel, as a template. The structure is constructed from two distinct elements of structure. These are sheets containing alternating tetrahedra joined to produce four-membered and elliptical eight-membered rings and slabs composed of trigonal-bipyramidal tetramers cross-linked by PO_4 tetrahedra. These units, infinite in (100), alternate along *a*. By way of comparison, frameworks 21 and EN3[8] are composed of corrugated sheets containing 5-coordinated aluminum between which run chains (crankshafts in the case of type 21; zigzag for type EN3) of alternating AlO_4 and PO_4 tetrahedra.[5,8] This class of open frameworks contains elements of structures containing only alternating tetrahedra (analogous to the zeolites) and those dense phases containing no 4-coordinate aluminum (or gallium) such as $AlPO_4$-15.[3,16] One feature not shared with the class by type 12 is a protonated framework. All protons reside on the amine with the framework carrying two negative charges, leading to the formula $[(MPO_4)(M_2P_2O_9^{2-})(N_2C_2H_{10}^{2+})]$. The dehydration of the framework, to produce a four-connected all-tetrahedral net, is not likely. Such a dehydration does occur for type 21 to produce type 25, a molecular sieve with eight-membered-ring apertures.

The only significant differences between $AlPO_4$-12 and $GaPO_4$-12 concern the geometry of the Ga- and Al-centered polyhedra.

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Registry No. $AlPO_4$-12(en), 98218-54-3; $GaPO_4$-12(en), 98218-56-5; Al_2O_3, 1344-28-1; Ga_2O_3, 12024-21-4; H_3PO_4, 7664-38-2; en, 107-15-3.

Supplementary Material Available: Tables of anisotropic thermal parameters, details of hydrogen bonds, and structure factors (26 pages). Ordering information is given on any current masthead page.

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Synthesis, Stability, and Fluxional Behavior of Binuclear Mixed-Hydride–Tetrahydroborate Complexes of Hafnium(IV): X-ray Crystal Structure of $[[(Me_2PCH_2SiMe_2)_2N]Hf(BH_4)_2](\mu\text{-}H)_3[Hf(BH_4)[N(SiMe_2CH_2PMe_2)_2]]$

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Addition of PMe_3 to the mononuclear tris(tetrahydroborate) complex of hafnium $Hf(BH_4)_3[N(SiMe_2CH_2PMe_2)_2]$ (**4**) results in the formation of the binuclear mixed-hydride–tetrahydroborate derivative $[Hf[N(SiMe_2CH_2PMe_2)_2]]_2(\mu\text{-}H)_3(BH_4)_3$ (**6**). The X-ray data for **6** are as follows: triclinic, space group $P\bar{1}$; $a = 13.333$ (3), $b = 18.722$ (3), and $c = 9.690$ (3) Å; $\alpha = 94.02$ (2), $\beta = 107.04$ (2), and $\gamma = 109.14$ (2)°; $V = 2147$ Å^3; $Z = 2$; $R = 0.042$ and $R_w = 0.057$ for 7675 reflections with $I \geq 3\sigma(I)$ from 9827 unique reflections using 328 variables; $\mu(\text{Mo K}\alpha) = 50.6$ cm^{-1}. The solid-state structure shows three bridging hydrides between the two hafnium centers and three different BH_4^- ligands: one bound in a tridentate fashion to one hafnium and the remaining two BH_4^- units bound to the other hafnium in a bidentate mode and a distorted monodentate mode of attachment. To explain the simple ^1H and $^{31}P\{^1H\}$ NMR spectra, it is proposed that an intramolecular BH_4^- migration from one hafnium to the other occurs in the fast-exchange limit. Addition of excess NMe_3 to **4** or **6** results in further BH_3 cleavage to generate the binuclear tetrahydride $[Hf[N(SiMe_2CH_2PMe_2)_2]]_2(\mu\text{-}H)_4(BH_4)_2$ (**7**). The solution spectroscopic data are consistent with fast rotation of the ends of the dimer on the NMR time scale; an activation barrier of 13.4 kcal mol^{-1} was calculated for this rotational process. On the basis of product analysis and deuterium-labeling studies, a mechanism for the formation of these binuclear mixed-hydride–tetrahydroborate complexes is proposed that involves fragmentation of the unstable binuclear intermediate $[Hf[N(SiMe_2CH_2PMe_2)_2]]_2(\mu\text{-}H)_2(BH_4)_4$ followed by recombination; simple BH_3 cleavage is not involved.

Transition-metal complexes containing metal–hydride bonds are implicated in many stoichiometric and catalytic organic transformations.[2] For this reason, the synthesis, structural characterization, and chemical behavior of new metal–hydride complexes continues to be an endeavor of numerous research groups.[3]

It is now well established that hydride complexes of the group 4 transition metals, specifically zirconium and hafnium, offer reactivity patterns that are more comparable to boron or aluminum hydrides than to some of the "later"-transition-metal–hydride complexes.[4,5] However, the vast majority of the known group 4 metal hydrides contain cyclopentadienyl or substituted-cyclopentadienyl groups as ancillary ligands (e.g. $[(\eta^5\text{-}C_5H_5)_2Zr(H)Cl]_x$,[6] $[(\eta^5\text{-}C_5H_4Me)_2ZrH_2]_2$,[7] and $(\eta^5\text{-}C_5Me_5)_2ZrH_2$[8]). If the reactivity of a given transition-metal complex can be fine tuned to some extent by modifying these ancillary ligands, then donor types other than cyclopentadienyl must be investigated to expand the potentially rich chemistry of this particular group.

We have recently[9,10] devised a strategy whereby *soft* donors, such as phosphines, can form stable adducts with the *hard* metal centers, Zr(IV) and Hf(IV). The apparent mismatching[11] of *hard–soft* pairs is overcome by incorporating the *soft* donors into a chelating array (as in **1**) that also contains a *hard* donor such as an amide ligand, $^-NR_2$ (R = alkyl or silyl); since amides of Zr(IV) and Hf(IV) are known[12] to be stable, the tendency for

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