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Amine-Templated Unidimensional Phosphate−Diphosphates of Gallium and Vanadium, $[NH_3CH_2CH_2NH_3][M(H_2PO_4)(P_2O_7)]$ (M = Ga, V)

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A new one-dimensional gallium phosphate−diphosphate, $[C_2H_{10}N_2][Ga(H_2PO_4)(P_2O_7)]$, has been synthesized under solvothermal conditions at 433 K in the presence of ethylenediamine, and the structure was determined using room-temperature single-crystal X-ray diffraction data ($M_r = 402.76$, monoclinic, space group *Cc*, $a = 8.6139(4)$, $b = 14.929(1)$, and $c = 9.3109(4)$ Å, and $\beta = 106.541(4)°$; $V = 1147.8$ Å^3, $Z = 4$, $R = 4.39\%$, and $R_w = 5.03\%$ for 2049 observed data ($I > 3(\sigma(I))$). The structure consists of anionic chains of formula $[Ga(H_2PO_4)(P_2O_7)]^{2-}$ containing GaO_6 octahedra linked by $PO_2(OH)_2$ and P_2O_7 units, which are charge-balanced by ethylenediamine dications. The chains are held together by a network of hydrogen bonds involving both interchain and chain−diamine interactions. Polycrystalline samples of the isostructural vanadium and mixed vanadium−gallium analogues, $[C_2H_{10}N_2][V(H_2PO_4)(P_2O_7)]$ and $[C_2H_{10}N_2][[V_xGa_{1-x}(H_2PO_4)(P_2O_7)]$ ($x \sim 0.65$), have also been prepared. The former has an effective magnetic moment of 2.70(1) μ_B per vanadium cation consistent with the presence of V^{3+} ions in an octahedral environment.

Introduction

In addition to their use as structure-directing agents in the solvothermal synthesis of three-dimensional zeolite and zeotype frameworks, organic amines have now been employed in the preparation of several low-dimensional metal phosphates. Use of ethylenediamine (T) in particular has led to the formation of both layered and chain materials in which the amine molecules are located in the interlamellar or interchain voids. Examples of two-dimensional metal−phosphate frameworks in which the metal is trivalent include $[TH_2][Al_2(PO_4)_2(OH)_2(H_2O)]$,[1] $[TH_2][(HO(CH_2)_2OH)(HO(CH_2)_2OH_2)][Al_3(PO_4)_4]$,[2] and $[TH_2]_{0.5}[M(PO_4)(OH)]$ (M = Ga,[3] Fe[4]), whereas chains occur in $[TH_2][Al_2(PO_4)(HPO_4)]$,[5] $[TH_2][Ga(PO_4)(HPO_4)]$,[6] and $[TH_2][M(HPO_4)_2(OH)]\cdot H_2O$ (M = V,[7] Fe[8]). These structures are constructed from PO_4 tetrahedra and MO_x ($x = 4$ or 6) polyhedra linked, in the majority of cases, alternately through oxygen atoms. However, in $[TH_2][M(HPO_4)_2(OH)]\cdot H_2O$ (M = V,[7] Fe[8]), the MO_6 octahedra are linked directly through M−O−M bridges. To date, however, there have been no reports of any organically templated materials with continuous structures containing P−O−P linkages. Here, three new chain phosphate−diphosphates, synthesized in the presence of ethylenediamine and containing such structural units, are described: $[TH_2][Ga(H_2PO_4)(P_2O_7)]$ (**I**), $[TH_2][V(H_2PO_4)(P_2O_7)]$ (**II**), and $[TH_2][V_xGa_{1-x}(H_2PO_4)(P_2O_7)]$ ($x \sim 0.65$) (**III**). The materials are unusual in that they contain both PO_4 and P_2O_7 units.

Experimental Section

Single crystals of $[NH_3CH_2CH_2NH_3][V(H_2PO_4)(P_2O_7)]$ **(I)** were prepared under solvothermal conditions (reaction i, Table 1). Ga_2O_3 (0.876 g) was dispersed in ethylene glycol (5.6 cm^3) by stirring followed by addition of ethylenediamine (1.1 cm^3). Aqueous H_3PO_4 (3 cm^3, 85 wt %) was then added with a small amount of the mineralizer $Si(OEt)_4$.[10] The gel was stirred until homogeneous, sealed in a Teflon-lined stainless steel autoclave and heated at 433 K for 7 days. The solid products were collected by filtration, washed copiously with water, and dried in air at 353 K.

$[NH_3CH_2CH_2NH_3][V(H_2PO_4)(P_2O_7)]$ (**II**) and $[NH_3CH_2CH_2NH_3][V_xGa_{1-x}(H_2PO_4)(P_2O_7)]$ ($x \sim 0.65$) (**III**) were synthesized as polycrystalline powders by using the synthetic procedure above and keeping the same amounts of phosphoric acid and organic components as those for reaction i, but by using V_2O_5 (0.728 g) for the vanadium analogue (**II**) (reaction ii), and V_2O_5 (0.364 g) and Ga_2O_3 (0.345 g) for the mixed gallium−vanadium analogue (**III**) (reaction iii).

Powder X-ray diffraction patterns of the bulk products of reactions i−iii were recorded on a Philips PW1710 diffracto-

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Table 1. Summary of Gel Compositions and Reaction Products

reaction	gel composition	products
i	0.283 Ga_2O_3:2.66 H_3PO_4:2.56 H_2O: 1.00 $NH_2(CH_2)_2NH_2$:6.10 $HOCH_2CH_2OH$:0.1 $Si(OEt)_4$	major product: **I** (single crystals, colorless plates) minor product: α-$GaPO_4$ (hexagonal)[9] (single crystals, colorless faceted blocks)
ii	0.243 V_2O_5:2.66 H_3PO_4:2.56 H_2O: 1.00 $NH_2(CH_2)_2NH_2$:6.10 $HOCH_2CH_2OH$:0.1 $Si(OEt)_4$	sole product: **II** (polycrystalline pale-green powder)
iii	0.122 V_2O_5:0.112 Ga_2O_3:2.66 H_3PO_4:2.56 H_2O: 1.00 $NH_2(CH_2)_2NH_2$:6.10 $HOCH_2CH_2OH$:0.1 $Si(OEt)_4$	sole product: **III** (polycrystalline pale-green powder)

Table 2. Powder X-ray Diffraction Data[a] for II in the Range ($0 \le 2\theta \le 40°$)

rel. intensity	$2\theta_{obs}$ (deg)	d_{obs} (Å)	d_{calc} (Å)	h	k	l
100	11.800	7.494	7.478	0	2	0
81	12.235	7.228	7.223	1	1	0
15	13.575	6.517	6.512	1	1	−1
1	15.535	5.777	5.769	0	2	1
7	17.540	5.052	5.056	1	1	1
12	19.575	4.531	4.534	0	0	2
9	20.305	4.370	4.373	1	1	−2
5	20.820	4.263	4.266	1	3	0
23	21.560	4.119	4.124	2	0	0
5	22.950	3.872	3.877	0	2	2
5	23.755	3.743	3.739	0	4	0
23	24.090	3.691	3.693	2	2	−1
26	24.630	3.612	3.611	2	2	0
84	25.745	3.458	3.457	0	4	1
16	26.455	3.366	3.369	1	3	−2
28	27.405	3.252	3.256	2	2	−2
5	28.865	3.096	3.096	2	2	1
11	30.870	2.894	2.897	1	3	2
7	31.930	2.801	2.806	2	4	−1
8	32.395	2.761	2.764	1	5	−1
15	33.440	2.678	2.676	2	2	−3
2	34.495	2.598	2.560	2	4	−2
5	36.100	2.486	2.488	3	3	−1
9	37.435	2.400	2.404	0	6	1
5	39.360	2.287	2.286	2	0	−4

[a] Refined monoclinic lattice parameters at 293 K ($0 \le 2\theta \le 70°$): $a = 8.619(1)$, $b = 14.956(2)$, and $c = 9.476(1)$ Å and $\beta = 106.855(7)°$ (Cu Kα_1 radiation).

meter using graphite-monochromated Cu Kα radiation ($\lambda_1 = 1.5406$ Å, $\lambda_2 = 1.5444$ Å) and the data examined within GSAS.[11] Energy-dispersive X-ray emission analyses were performed using a JEOL 2000FX analytical electron microscope with α-$GaPO_4$[9] and α-$VOPO_4 \cdot 2H_2O$[12] as calibration standards.

The major component of the product of reaction i consisted of colorless rectangular plates of **I** together with some crystals of α-$GaPO_4$ as an impurity phase. Combustion analysis gave the following results: C, 5.70; H, 2.78; N, 6.41%. The C:N ratio is 1, confirming that the ethylenediamine is present intact in the material. The single-crystal study of **I** is described below.

The product of reaction ii consisted of pale-green polycrystalline powder. All peaks in the powder X-ray pattern (Table 2) could be indexed on the basis of the monoclinic cell proposed for **I** with refined lattice parameters: $a = 8.619(1)$, $b = 14.956(2)$, and $c = 9.476(1)$ Å, and $\beta = 106.855(7)°$. Energy-dispersive X-ray and combustion analyses further confirmed that the sample was monophasic. The former technique, performed on a finely ground sample, showed that each of the 20 crystallites examined contained V and P, but no Si, with a P:V ratio of 3.06(7) (the oxygen content cannot be determined from the electron microscopy measurements). Combustion analysis gave the following results: C, 6.37; H, 3.18; N, 7.09%, which compare well with the values calculated from the proposed formula $[NH_3CH_2CH_2NH_3][V(H_2PO_4)(P_2O_7)]$ (**II**): C, 6.26; H, 3.15; N, 7.29%.

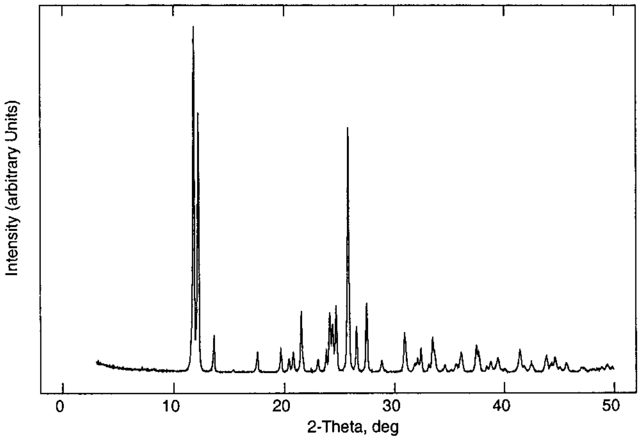

Figure 1. Powder X-ray diffraction pattern of $[NH_3CH_2CH_2NH_3][V(H_2PO_4)(P_2O_7)]$ (**II**) (Cu Kα radiation).

The X-ray pattern of the pale-green product of reaction iii could also be indexed completely on a monoclinic unit cell with the following lattice parameters: $a = 8.603(1)$, $b = 14.932(1)$, and $c = 9.397(1)$ Å, and $\beta = 106.721(2)°$ (Figure 1). Analytical electron microscopy gave a total (V + Ga) content of 1.07(5), a P:(V + Ga) ratio of 2.93(5), and a mean composition of $V_{0.67(4)}Ga_{0.38(6)}P_3O_z$. Combustion analysis gave the following: C, 6.14; H, 3.12; N, 6.79%, which compare well with the values calculated from the approximate proposed formula $[NH_3CH_2CH_2NH_3][V_{0.65}Ga_{0.35}(H_2PO_4)(P_2O_7)]$ (**III**): C, 6.15; H, 3.09; N, 7.17%.

Thermogravimetric analysis, performed on **II** and **III** using a Stanton Redcroft STA 1500 thermal analyzer over the temperature range 293−973K at a heating rate of 10 K min^{-1} under flowing nitrogen, showed smooth weight losses of 17.67 and 17.03%, respectively, over the range 673−823K. (Loss of ethylenediamine from **II** and **III** would correspond to weight losses of 15.65 and 15.39%, respectively). Both of the final products were black and X-ray amorphous.

Magnetic susceptibility measurements were made on a bulk sample of **II** using a Quantum Design MPMS 5 SQUID susceptometer. The sample was loaded into a gelatin capsule at room temperature and data collected over the temperature range $5 \le T \le 300$ K, after cooling the sample in both the zero applied field (zfc) and the 1 kG measuring field (fc). Data were corrected for the diamagnetism of the gelatin capsule and for intrinsic core diamagnetism. The zfc and fc susceptibilities overlie each other at all temperatures and magnetic susceptibility data in the temperature range $15 \le T \le 300$ K can be fitted to a Curie−Weiss law modified by the addition of a temperature-independent paramagnetic component. Derived parameters $\theta = -11.74(7)$ K and $C = 0.914(2)$ cm^3 K mol^{-1} were obtained giving an effective moment of 2.70(1) μ_B per vanadium cation. This compares well with the values of 2.62 and 2.69 μ_B obtained previously for related vanadium (III) phosphates $H_3OVP_2O_7$[13] and $VPO_4 \cdot H_2O$[14] respectively, and is

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Table 3. Crystallographic Data for I

formula	$C_2H_{12}N_2GaP_3O_{11}$
M_r	402.76
crystal size (mm)	0.16 × 0.09 × 0.03
crystal habit	colorless plate
crystal system	monoclinic
space group	*C* c
a (Å)	8.6139(4)
b (Å)	14.929(1)
c (Å)	9.3109(4)
β (°)	106.541(4)
cell volume (Å^3)	1147.8
Z	4
temperature (K)	295
ρ_{calc} (g cm^{-3})	2.331
$\mu_{Cu\ K\alpha}$ (cm^{-1})	79.63
θ_{max}	70
scan type	$\omega - 2\theta$
index ranges	$-10 \leq h \leq 10$ $-1 \leq k \leq 18$ $-11 \leq l \leq 11$
unique data	2116
observed data ($I > 3\sigma(I)$)	2049
R_{merge}	0.0264
weighting scheme	Chebyshev 3 term
res. electron dens. (min, max) (eÅ^{-3})	−2.09, 1.63
no. of parameters refin.	179
R	0.0439
R_w	0.0503

Table 4. Fractional Atomic Coordinates and Isotropic Thermal Parameters (Å^2) for I

atom	x	*y*	*z*	*U*eq[a]
Ga(1)	0.1832(1)	0.49051(4)	0.3041(1)	0.0103
P(1)	0.4448(2)	0.43635(9)	0.6265(2)	0.0107
P(2)	−0.0700(2)	0.53315(9)	−0.0130(2)	0.0126
P(3)	0.0909(2)	0.36694(8)	0.0198(2)	0.0108
O(1)	0.3310(4)	0.4218(2)	0.4733(4)	0.0147
O(2)	0.3754(4)	0.5259(3)	0.2447(4)	0.0148
O(3)	−0.4121(5)	0.5026(3)	0.1198(5)	0.0192
O(4)	0.5173(5)	0.3417(3)	0.6851(5)	0.0223
O(5)	0.0425(5)	0.5570(3)	0.1403(4)	0.0166
O(6)	−0.0009(5)	0.4359(2)	0.3637(4)	0.0138
O(7)	−0.2413(5)	0.5632(3)	−0.0358(4)	0.0190
O(8)	−0.0737(4)	0.4251(3)	−0.0192(5)	0.0183
O(9)	0.1751(4)	0.3780(2)	0.1888(4)	0.0119
O(10)	0.1959(5)	0.5969(2)	0.4285(4)	0.0138
O(11)	0.0362(5)	0.2714(2)	−0.0167(4)	0.0148
N(1)	−0.4793(6)	0.3390(4)	0.2491(6)	0.0232
N(2)	0.1820(7)	0.7474(4)	−0.0547(6)	0.0242
C(1)	−0.4871(8)	0.2974(5)	0.1003(8)	0.0320
C(2)	−0.3173(8)	0.2765(5)	0.1006(7)	0.0330
H(3)	−0.34(1)	0.532(6)	0.07(1)	0.05
H(4)	−0.47(1)	0.703(5)	0.111(8)	0.05

[a] Note that $\boldsymbol{U}_{eq}$ is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

in good agreement with the expected values for V^{3+} ions with a T_{1g} ground term in octahedral coordination.[15] Reduction of V^{5+} to V^{3+} in the presence of an organic amine has been reported previously in the formation of $[NH_3(CH_2)_4NH_3]_2[Ga_{3.6}V_{0.4}(HPO_4)_2(PO_4)_3(OH)_3]\cdot 6H_2O$ from V_2O_5, Ga_2O_3, H_3PO_4, and 1,4 diaminobutane.[16]

Single-Crystal X-ray Diffraction. Room-temperature X-ray diffraction data were collected from a crystal of **I** using an Enraf-Nonius CAD4 diffractometer (graphite-monochromated Cu Kα radiation ($\lambda = 1.5418$ Å)) (Table 3). The unit cell was determined as monoclinic from measurement of 24 well-centered reflections and the cell parameters optimized by least-squares refinement. Intensity data were then measured using the ω-2θ scan technique. Three standard reflections were measured every hour during the data collection, and no significant intensity variations were observed. Data were corrected for absorption using ψ-scans and further corrected for Lorentz and polarization effects within the program *RC93*.[17]

The systematic absences in the reduced data suggested that the space group was either *Cc* (No. 9) or *C*2/*c* (No. 15).[18] Successful solution and refinement of the structure showed that the former space group was correct. The structure was solved using the direct methods program *SIR92*[19] and all non-hydrogen atoms located. All subsequent Fourier calculations and least-squares refinements were carried out using the CRYSTALS suite of programs.[20] The hydrogen atoms of the gallium−phosphate framework hydroxyl groups were then found in difference Fourier maps, and their positions were refined with O−H bond lengths restrained to be 1.00(5) Å and with isothermal parameters fixed at 0.05 Å^2. The hydrogen atoms of the template, which could not be located in the Fourier maps, were placed geometrically. A correction for secondary extinction was applied.[21] In the final cycle, 179 parameters, including anisotropic thermal parameters for all non-hydrogen framework and template atoms, were refined. A three-term Chebyshev polynomial was applied as weighting scheme,[22] and the refinement converged to give $R = 0.0439$ ($R_w = 0.0503$). Atomic coordinates and isotropic thermal parameters are given in Table 4 and selected interatomic distances and bond angles in Table 5.

Powder X-ray diffraction data suitable for Rietveld analysis were collected for **III**. The structural model, refined using GSAS[11] with the metal site having an occupancy fixed at (0.65V + 0.35Ga), showed no significant differences from that obtained from the single-crystal data for **I** (final *R* values: $R_p = 0.0845$, $R_{wp} = 0.1096$).

Discussion

The structure consists of one-dimensional polymeric gallium−phosphate−diphosphate anions of formula $[Ga(H_2PO_4)(P_2O_7)]^{2-}$ running parallel to the *c* axis charge balanced by ethylenediamine dications lying in the interchain spaces.

The one crystallographically distinct gallium atom and three phosphorus atoms are present in octahedral GaO_6 and tetrahedron-based PO_4 and P_2O_7 units (Figure 2). The phosphate group bridges adjacent gallium atoms via O(1) and O(2) (P(1)−O(1), 1.498(4) Å, and P(1)−O(2), 1.504(4) Å). The remaining P(1)−O bonds are substantially longer (P(1)−O(3), 1.549(4) Å, and P(1)−O(4), 1.579(4) Å), suggesting that the oxygen atoms involved are protonated. The location of hydrogen atoms in the difference Fourier maps confirms the assignment of P(1)−OH groups. Diphosphate units with eclipsed conformations also constitute part of the chain; each P atom of the P_2O_7 unit is linked via two oxygen atoms to adjacent Ga atoms (average P(2)−O and P(3)−O bridging lengths are 1.515 and 1.524 Å, respectively) and is also connected to a terminal oxygen atom. The P(2)−

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Table 5. Selected Bond Distances (Å) and Angles (deg) for I

Ga(1)−O(1)	2.003(4)	P(1)−O(1)	1.498(4)
Ga(1)−O(2)	1.961(4)	P(1)−O(2)^a	1.504(4)
Ga(1)−O(5)	1.931(4)	P(1)−O(3)^b	1.549(4)
Ga(1)−O(6)	1.998(4)	P(1)−O(4)	1.579(4)
Ga(1)−O(9)	1.984(4)	P(2)−O(5)	1.522(4)
Ga(1)−O(10)	1.951(4)	P(2)−O(6)^c	1.508(4)
		P(2)−O(7)	1.498(4)
N(1)−C(1)	1.502(8)	P(2)−O(8)	1.615(4)
N(2)−C(2)^d	1.507(9)	P(3)−O(8)	1.613(4)
C(1)−C(2)	1.50(1)	P(3)−O(9)	1.542(4)
		P(3)−O(10)^c	1.506(4)
O(3)−H(3)	1.00(1)†	P(3)−O(11)	1.510(4)
O(4)−H(4)	1.00(1)†		
O(1)−Ga(1)−O(2)	87.8(2)	O(1)−P(1)−O(2)^a	117.5(2)
O(1)−Ga(1)−O(5)	179.4(2)	O(1)−P(1)−O(3)^b	111.1(2)
O(1)−Ga(1)−O(6)	87.1(2)	O(1)−P(1)−O(4)	106.6(2)
O(1)−Ga(1)−O(9)	84.8(1)	O(2)^a−P(1)−O(3)^b	107.2(2)
O(1)−Ga(1)−O(10)	92.0(2)	O(2)^a−P(1)−O(4)	106.4(2)
O(2)−Ga(1)−O(5)	91.7(2)	O(3)^b−P(1)−O(4)	107.5(2)
O(2)−Ga(1)−O(6)	171.5(2)	O(5)−P(2)−O(6)^c	111.0(2)
O(2)−Ga(1)−O(9)	88.7(2)	O(5)−P(2)−O(7)	113.7(2)
O(2)−Ga(1)−O(10)	92.2(2)	O(5)−P(2)−O(8)	105.6(2)
O(5)−Ga(1)−O(6)	93.4(2)	O(6)^c−P(2)−O(7)	112.7(2)
O(5)−Ga(1)−O(9)	95.2(2)	O(6)^c−P(2)−O(8)	106.7(2)
O(5)−Ga(1)−O(10)	88.1(2)	O(7)−P(2)−O(8)	106.6(2)
O(6)−Ga(1)−O(9)	84.0(1)	O(8)−P(3)−O(9)	107.5(2)
O(6)−Ga(1)−O(10)	94.7(2)	O(8)−P(3)−O(10)^c	108.1(2)
O(9)−Ga(1)−O(10)	176.6(2)	O(8)−P(3)−O(11)	105.0(2)
		O(9)−P(3)−O(10)^c	110.7(2)
Ga(1)−O(1)−P(1)	140.5(2)	O(9)−P(3)−O(11)	110.9(2)
Ga(1)−O(2)−P(1)^a	148.3(3)	O(10)^c−P(3)−O(11)	114.2(2)
Ga(1)−O(5)−P(2)	135.2(3)		
Ga(1)−O(6)−P(2)^e	127.0(2)	P(2)−O(8)−P(3)	121.5(2)
Ga(1)−O(9)−P(3)	125.2(2)	P(1)^f−O(3)−H(3)	112.6(56)
Ga(1)−O(10)−P(3)^a	133.3(2)	P(1)−O(4)−H(4)^b	118.6(55)
N(1)−C(1)−C(2)	107.3(5)	N(2)^g−C(2)−C(1)	108.7(6)

$^{a-g}$ Symmetry transformations used to generate equivalent atoms: $^a x, 1 - y, z + {}^1/_2$; $^b x + 1, 1 - y, z + {}^1/_2$; $^c x, 1 - y, z - {}^1/_2$; $^d x + {}^1/_2, y + {}^1/_2, z$; $^e x - {}^1/_2, 1 - y, z + {}^1/_2$; $^f x - 1, 1 - y, z + {}^1/_2$; $^g x - {}^1/_2, y - {}^1/_2, z$. † Chemical restraint applied.

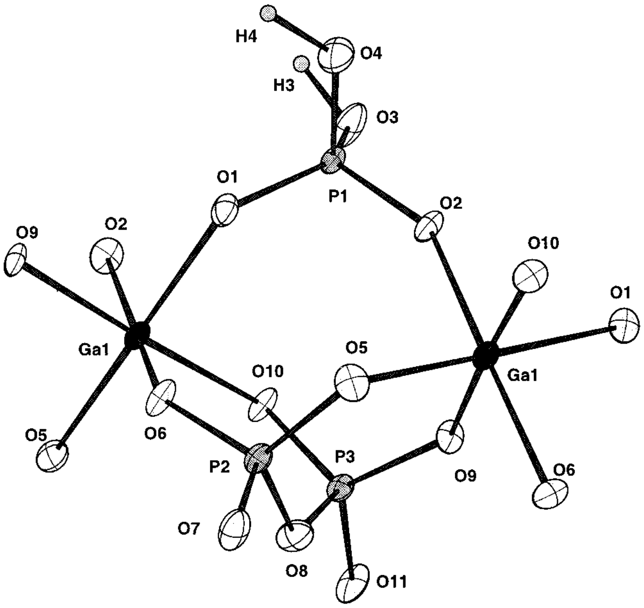

Figure 2. Local coordination of the framework atoms in **I**. Thermal ellipsoids at 50% probability. (Drawing package, CAMERON.[23])

O(7) and P(3)−O(11) bond lengths of 1.498(4) and 1.510(4) Å, respectively, are reasonably short, implying that these bonds have some degree of multiple-bond character. The P−O bonds of the P(2)−O(8)−P(3) bridge are substantially longer (P(2)−O(8), 1.615(4) Å, and P(3)−O(8), 1.613(4) Å), as is generally observed in diphosphate structures,[13,24] and the P−O−P bond angle is 121.5(2)°. The coordination geometry around O(8) is in accordance with the relationship between P−O bridging bond lengths and P−O−P bridging angles in P_2O_7 units observed previously in a number of diphosphate structures: P−O bridging bond lengths in the range 1.63−1.54 Å typically have P−O−P angles in the range 123−180°.[25]

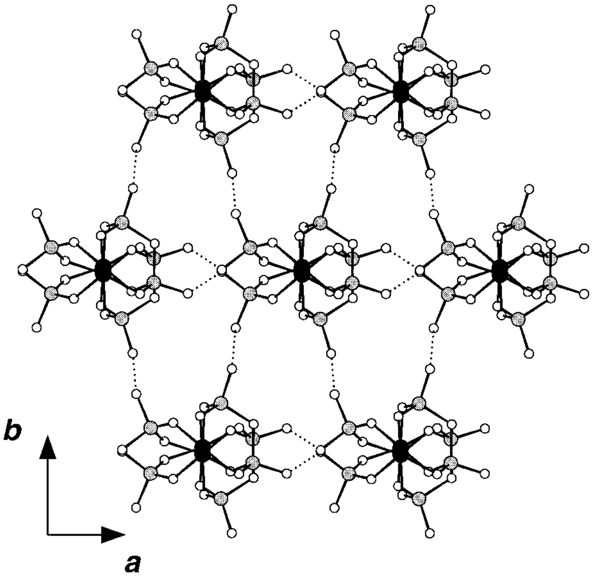

Figure 3. View of **I** along the *c* axis showing the interchain hydrogen bonds as dotted lines. The diamine cations and framework hydrogen atoms have been omitted. Key: large black spheres = Ga, large gray spheres = P, and white spheres = O.

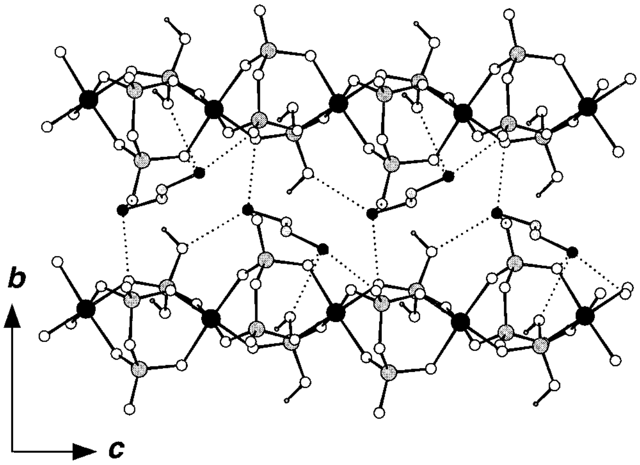

Figure 4. View of **I** along the *a* axis showing two $[Ga(H_2PO_4)(P_2O_7)]^{2-}$ chains with ethylenediamine dications in the interchain space. Framework hydrogen atoms are shown, but those of the diamine have been omitted. Chain−diamine hydrogen bonds are shown as dotted lines. Key: large black spheres = Ga, large gray spheres = P, white spheres = O, small black spheres = N, and small gray spheres = C.

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The structure is held together by both interchain and chain−amine hydrogen bonding. The P−OH groups of the $P(1)O_2(OH)_2$ units are sufficiently close to the terminal P═O units of the diphosphate groups in neighboring chains to suggest the presence of strong interchain interactions. Thus, the chains are linked parallel to both the *a* (O(3)···O(7), 2.509(6) Å) and *b* axes (O(4)···O(11), 2.565(6) Å) to generate a three-dimensional assembly (Figure 3). Each NH_3 group of the diprotonated ethylenediamine forms three hydrogen bonds to framework oxygen atoms (N(1)···O distances in the range 2.831(7)−2.927(6) Å, N(2)...O distances in the range 2.812(7)−2.991(7) Å) (Figure 4).

Conclusion

The three isostructural materials reported here are the first examples of organically templated mixed-anion phosphates in which both PO_4 and P_2O_7 groups coexist as independent units. The synthetic conditions are such that condensation of PO_4^{3-} units from the phosphoric acid generates $P_2O_7^{4-}$ units. The use of pyrophosphoric acid in the synthesis of related iron(III) materials will be reported elsewhere.[26]

Mixed phosphate−diphosphate frameworks with inorganic counterions are themselves reasonably rare.[27] There are no known gallium phases and only three examples of such materials containing vanadium, namely, $Ba_2V_3H(PO_4)_2(P_2O_7)_2$,[28] $KV_4(PO_4)(P_2O_7)(P_4O_{13})$,[29] and $AgV_2(PO_4)(P_2O_7)$,[30] all of which have three-dimensional structures. The chain structure of the present compounds is however related to that of a vanadium (IV) diarsenate, $[NH_3CH_2CH_2NH_3][VO(As_2O_7)(H_2O)]$.[31] In the diarsenate, As_2O_7 units link adjacent octahedrally coordinated vanadium atoms to form chains in a manner similar to the formation of P_2O_7 units in the present structure. The two remaining coordination sites of the vanadium(IV) are occupied by the oxygen atom of a vanadyl group (V═O) and a water molecule rather than bridging PO_4 groups.

In view of the enormous number of organically templated metal−phosphate phases now known, it is likely that numerous other diphosphate and phosphate−diphosphate structures may also exist. These may have chain structures similar to the materials described here, but it is also possible that there may be examples with layered or three-dimensional frameworks. Such materials, as well as the products obtained on removal of the organic templates, have many potential applications, particularly in the area of catalysis where there is currently much interest in related materials such as $(VO)_2P_2O_7$.

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Supporting Information Available: Tables listing coordinates of geometrically placed hydrogen atoms and anisotropic thermal parameters and tables of observed and calculated structure factors for **I**, magnetic measurements for **II**, and GSAS-based refinement parameters including fractional coordinates and observed and calculated diffraction patterns for **III**. This material is available free of charge via the Internet at http://www.pubs.acs.org.

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