$[Ga_4(C_{10}H_9N_2)_2(PO_4)(H_{0.5}PO_4)_2(HPO_4)_2(H_2PO_4)_2(H_2O)_2] \cdot H_2O$: a novel one-dimensional chain structure containing four different types of monophosphate

Ching-Yeh Chen,[a] Fang-Rey Lo,[a] Hsien-Ming Kao[a] and Kwang-Hwa Lii*[ab]

[a] Department of Chemistry, National Central University, Chungli, Taiwan 320. E-mail: liikh@cc.ncu.edu.tw
[b] Institute of Chemistry, Academia Sinica, Nankang, Taipei, Taiwan 115

The title compound is unique in such a way that among the vast number of synthetic phosphates and naturally occurring phosphate minerals it is the first example in which four different types of monophosphate, PO_4, $H_{0.5}PO_4$, HPO_4 and H_2PO_4, are present in the same structure.

Metal phosphates have been the subject of intense research owing to their rich structural chemistry and potential applications as ion exchangers, ionic conductors, catalysts and nonlinear optical materials.[1–6] In addition to the metal phosphates prepared in laboratories, phosphate minerals are also found in natural rocks; one example is the well known naturally occurring iron phosphate, cacoxenite, with a remarkable open-framework structure.[7] Some of the synthesized aluminophosphates or derived materials adopt structures that are similar to the naturally occurring aluminosilicates.[8] Anhydrous phosphates such as $LiTi_2P_3O_{12}$ and $LiZr_2P_3O_{12}$ have been prepared using high-temperature solid-state reactions. Many other metal phosphates containing PO_4, HPO_4, H_2PO_4 or combinations of the three have also been synthesized by hydrothermal methods. Hydrogen bonds are often formed in these crystalline hydrogen phosphates and unsymmetrical O–H⋯O bonds are usually observed. Symmetrical hydrogen bonds, which occur in many dicarboxylates with O⋯O distances of < 2.5 Å, are rarely found in phosphates. Here, we present the synthesis and characterization of a novel gallophosphate $[Ga_4(C_{10}H_9N_2)_2(PO_4)\-(H_{0.5}PO_4)_2(HPO_4)_2(H_2PO_4)_2(H_2O)_2] \cdot H_2O$ **1**. Among the vast numbers of metal phosphates that have been synthesized, none has the unique composition of **1** which contains four different types of monophosphates, *viz.* PO_4, $H_{0.5}PO_4$, HPO_4 and H_2PO_4, in the same structure. For $H_{0.5}PO_4$ there is an inversion center at the center of the short, symmetrical O–H–O bonds. We have prepared the monophasic phase and single-crystal X-ray diffraction and ^{31}P magic angle spinning (MAS) NMR have been applied to study the four different coordination environments for phosphorus.

Solvothermal reaction of $Ga(NO_3)_3 \cdot 4H_2O$, 4,4′-bipyridine, H_3PO_4, H_2O and butan-1-ol in the molar ratio of 1:3:8:55.5:76.5 in a Teflon-lined acid digestion bomb at 165 °C for 3 d produced compound **1** in 66% yield based on Ga. A suitable colorless crystal was selected for structure determination by single-crystal X-ray diffraction.† The bulk product is monophasic as judged by powder X-ray diffraction (Anal. Calc.: C, 18.25; H, 2.27; N, 4.01. Found: C, 18.21; H, 2.37; N, 4.25%). ^{31}P MAS NMR spectra were acquired at a ^{31}P frequency of 161.73 MHz on a Bruker DSX-400 spectrometer under conditions of high-power proton decoupling. A pulse length of 4 μs (π/4) and a repetition time of 30 s were used. The ^{31}P chemical shifts were reported relative to 85% H_3PO_4 as external reference. The Hartmann–Hahn condition for ^1H to ^{31}P CP experiments was determined using $(NH_4)_2HPO_4$. The $^1H \rightarrow$ ^{31}P CP spectra were recorded using a single-contact pulse sequence with reversal of spin temperature in the rotating frame and with proton decoupling during the ^{31}P signal acquisition. This pulse sequence was used for ordinary CP experiments as well as for $T_{1\rho}^H$ and $T_{1\rho}^P$ relaxation measurements.

Compound **1** has a one-dimensional chain structure. The fundamental building unit consists of two $Ga(1)O_5N$ octahedra, two monoprotonated 4,4′-bipyridine molecules which coordinate to $Ga(1)$, two $Ga(2)O_4$ tetrahedra and seven phosphates of four different types. The connectivity between units is made by $P(1)O_4$ groups that join the GaO_5N and GaO_4 polyhedra to those in the neighboring units and thus form infinite chains parallel to the [001] direction (Fig. 1). $H_{0.5}P(4)O_4$ coordinates to one GaO_4 tetrahedron and two GaO_5N octahedra. The hydrogen atom in $H_{0.5}PO_4$ lies on an inversion center and is shared by two $H_{0.5}P(4)O_4$ groups on the adjacent chains. The O–H bond length in the symmetrical O–H–O bonds is 1.231 Å.[9] $HP(3)O_4$ has one oxygen bridging to GaO_4 and extends away from the chain as a pendant group, which accounts for the relatively larger thermal parameters of the atoms in the group. Of the three remaining $P(3)–O$ bonds, the longest one constitutes the P–OH group, while the other two receive hydrogen bonds from adjacent chains. $H_2P(2)O_4$ is connected to GaO_5N and GaO_4 with the two hydroxo groups being H-bonded to two adjacent chains. All H atoms except those for O_w were found in difference Fourier maps and refined isotropically. The infinite chains are held in position by a network of hydrogen bonds, generating tunnels parallel to [001], within which the monoprotonated 4,4′-bipyridine and lattice water molecules reside (Fig. 2). The lattice water molecule has a site occupancy of 0.5 and is held in the crystal lattice by hydrogen bonds.

Fig. 3 shows the room temperature ^{31}P MAS NMR spectrum of **1**. Four resonances at −0.4, −9.2, −11.3 and −17.9 ppm with relative intensities very close to 1:1:1:0.5 respectively are observed. These signals correspond to the four distinct crystallographic phosphorus sites. In studies of a series of layered Ti, Zr and Al phosphates by MAS NMR spectroscopy, Nakayama *et al.* reported that the isotropic ^{31}P chemical shifts of H_2PO_4, HPO_4 and PO_4 groups appear around −10, −20 and −30 ppm, respectively.[10] Turner *et al.* noted that with increasing radius of the metal ion within one group of elements, the ^{31}P signal shifts downfield (*e.g.* BPO_4: −29.5 ppm, $AlPO_4$:
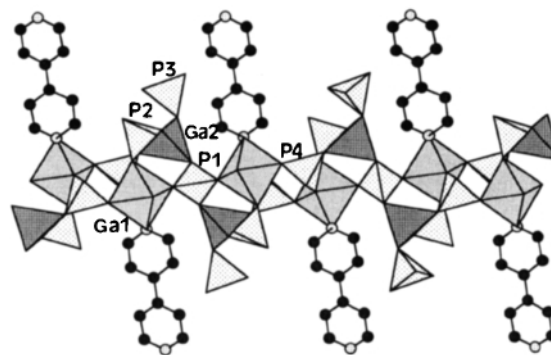

Fig. 1 Section of an infinite chain in **1** viewed along the [010] direction. GaO_5N octahedra are medium gray, GaO_4 tetrahedra are dark gray and PO_4 tetrahedra are light gray. Solid circles and stippled circles are the C and N atoms of 4,4′-bipyridine ligand, respectively.
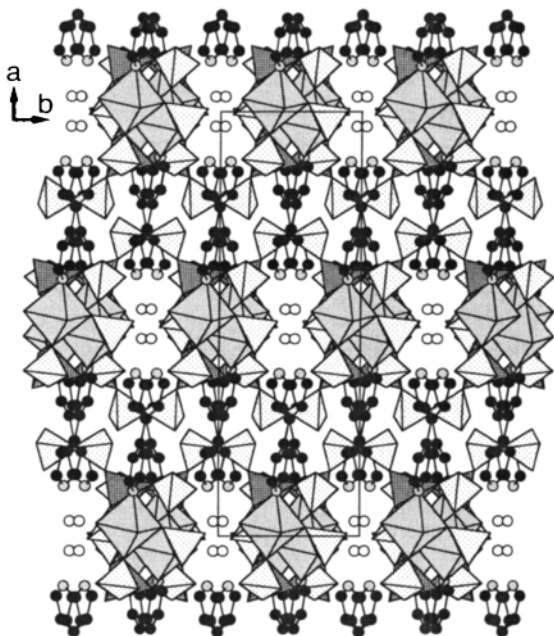
Fig. 2 Structure of **1** viewed along the [001] direction. Open circles are water oxygen atoms.
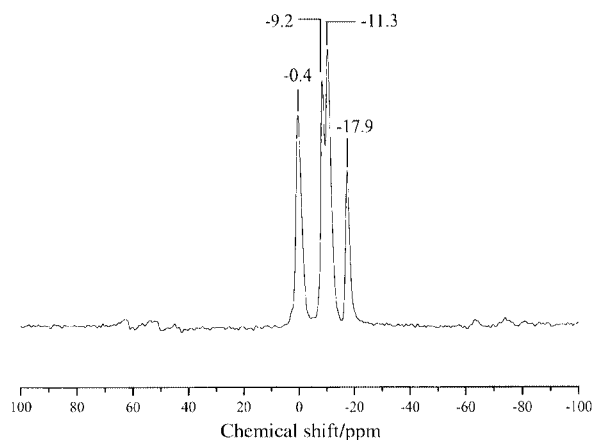

Fig. 3 Proton-decoupled ^{31}P MAS NMR spectrum of **1** acquired at a spinning frequency of 10 kHz. The isotropic chemical shifts are labeled; all other peaks in this spectrum are spinning sidebands. The peaks from left to right are assigned to H_2PO_4, HPO_4, $H_{0.5}PO_4$ and PO_4 groups, respectively.

−24.5 ppm, $GaPO_4$: −9.8 ppm).[11] Wessels *et al.* indicated that for microporous gallophosphates chemical shifts in the range from −10 to −20 ppm generally correspond to Q^4 groups, whereas values close to −5 ppm correspond to Q^3 groups.[12] Based on the above results we conclude that for gallophosphates the isotropic ^{31}P chemical shifts move to high-field values with decreasing protonation and the signals of Q^4 groups shift upfield relative to Q^3 groups. Consequently, the component at −17.9 ppm is assigned to P(1) (PO_4 group), which is also in agreement with the peak intensity. The other three peaks at −0.4, −9.2 and −11.3 ppm can be assigned to the three distinct P sites P(2) (H_2PO_4 group), P(3) (HPO_4 group) and P(4) ($H_{0.5}PO_4$ group), respectively. The HPO_4 peak is located at nearly equal distance from the H_2PO_4 and PO_4 peaks.

^{1}H → ^{31}P CP experiments at various contact times have been performed to estimate the proximity of the protons and the phosphorus atoms. In theory, the growth of the ^{31}P CP intensity depends on the contact time, the rate constant of magnetization transfer (T_{cp}), the ^{31}P/^{1}H population ratios (ε) and the $T_{1\rho}$ values for both nuclei. The poor CP efficiency for the resonance at −17.9 ppm indicates that the phosphorus atom is not in close proximity to the protons, consistent with the assignment of this resonance to the PO_4 group. On the other hand, the enhance-

ment of signal intensities for the resonances at −0.4, −9.2 and −11.3 ppm at short-contact times is observed. $T_{1\rho}$ values measured for the ^{1}H spins (*ca.* 22 ms) are much shorter than those of the ^{31}P spins in the different phosphate groups (320–580 ms). Fits to these CP intensity data with the measured $T_{1\rho}$ values, using modified versions of the expressions by Mehring[13] and Walter *et al.*[14] and ignoring the contributions from distant water and bipyridyl molecules, demonstrate that the ^{31}P/^{1}H population ratios involved in the CP transfer for the resonances at −0.4, −9.2 and −11.3 ppm are close to 0.5, 1.1 and 2.1, respectively. In addition, T_{cp} values, which are related to the dipolar coupling between ^{1}H and ^{31}P nuclei, are 0.6, 0.85 and 2.15 for the resonances at −0.4, −9.2 and −11.3 ppm, respectively. Both ^{31}P/^{1}H population ratios and T_{cp} values are reasonably in agreement with the above assignment.

In summary, this work illustrates that a novel 1-D gallium phosphate with an unique composition is synthesized under solvothermal conditions and structurally characterized by single-crystal X-ray diffraction and ^{31}P MAS NMR spectroscopy. The compound is unique in that, among the vast number of synthetic phosphates and naturally occurring phosphate minerals it is the first example in which four different types of phosphate, PO_4, $H_{0.5}PO_4$, HPO_4 and H_2PO_4 are present.

Notes and references

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