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Synthesis and characterisation of a series of lamellar gallium and indium phosphonates and related compounds†

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A series of new layered gallium(III) and indium(III) phosphonates, phenylarsonates and phenylphosphinates have been prepared and characterised. The methylphosphonate, phenylphosphonate and phenylarsonate derivatives of gallium(III) possess a metal to ligand ratio of 1 : 1 and properties consistent with the formulation $Ga(OH)(O_3XR)$ (where X = P or As for $R = C_6H_5$, and where X = P for $R = CH_3$), whereas the benzylphosphonate derivative forms the monohydrate $Ga(OH)(O_3XCH_2C_6H_5)\cdot H_2O$. The corresponding phosphinate derivative of gallium(III) has a metal to ligand ratio of 1 : 2 with the formulation $Ga(OH)(O_2P(H)C_6H_5)_2$. The gallium compounds all contain a hydroxo group bonded to the metal, unlike the corresponding indium(III) compounds. The phenylphosphonate and phenylarsonate derivatives of indium(III) have a 1 : 2 metal to ligand ratio and formula $In(O_3XR)(O_2X(OH)R)\cdot H_2O$ (where $R = C_6H_5$ or $CH_2C_6H_5$ when X = P and $R = C_6H_5$ when X = As), where the ligand is present as both a mono- and di-anion. The methylphosphonate of indium(III) has the unexpected formulation $In_2(O_3PCH_3)_3\cdot 2H_2O$ whereas the indium(III) phenylphosphinate compound is $In(O_2P(H)C_6H_5)_3$. These compounds were characterized by elemental analysis, thermal gravimetry, X-ray powder diffraction (XRD) and solid state $^{31}P/^{13}C$ MAS NMR spectroscopy. Powder XRD measurements indicate these compounds contain layered solid state structures.

Due to their potential applications in areas such as sorption, ion exchange, catalysis and as sensors,[1–5] there has been an interest in open-framework metal phosphonate compounds since the early seventies. The synthesis and characterization of divalent,[6–14] trivalent[8,15–16] and tetravalent metal[17–23] phosphonates has focussed mainly on the transition metals. In the solid state these compounds are mostly lamellar systems containing octahedrally coordinated metal cations with the organophosphonate moieties directed into the interlayer space. There are exceptions to the octahedral arrangement about the metal ion, for example copper[24] and lanthanum[8,25] where the coordination is tetrahedral, and uranyl[26] where the coordination is a distorted pentagonal bipyramidal geometry. The actual structure of these materials is highly dependent on, for example, the metal used, the organic groups and the extent to which they protrude into the interlayer region, and synthesis conditions such as pH and temperature.

Investigations into phosphonates of the p-block Group III metals have focussed on aluminium,[27–35] in particular the methyl and phenyl derivatives, with some recent interest in gallium[36–41] and indium.[39,41–42] The methylphosphonate of aluminium has a layered solid state structure with different polymorphic forms.[29–31,33,35] Depending on conditions of synthesis, the aluminium phosphonates have Al : P ratios of 2 : 3, 1 : 1 and 1 : 2. Recently reported gallium phosphonates, with Ga : P ratios of 1 : 1 and 3 : 2, have been characterised using ^{71}Ga and ^{31}P solid state NMR.[36] In the present study, we report on the synthesis and structural features of a series of gallium(III) and indium(III) phenylphosphonates, phenylphosphinates and phenylarsonates. Some of the results of this study have been reported previously in a communication.[42]

Experimental

The gallium(III) compounds were prepared from aqueous solutions of gallium(III) chloride and the corresponding phosphonic or arsonic acid using a 1 : 2 molar ratio of metal to ligand.

The indium compounds were synthesized from aqueous solutions of indium(III) chloride tetrahydrate and the corresponding phosphorus- or arsenic-containing acid using a 1 : 3 molar ratio of metal to ligand. All chemicals were obtained from Aldrich Chemical Co. and were of AR grade. For the aryl derivatives when the metal ion solution was added to a solution of the acid, a white precipitate formed immediately. The suspension was sealed in a Teflon-lined stainless-steel autoclave and heated at 160 °C for 6.5 days. For the alkyl derivatives no precipitate formed on the addition of the metal ion solution to the acid solution. The pH of the solution was adjusted from 1 to 4 by addition of 1 M NaOH solution, and then placed in a Teflon lined stainless steel autoclave. The autoclave was placed in an oven and heated at 190 °C for 3 days. The white solid produced was collected by filtration, washed with ultrapure water, air dried and then dried over phosphorus pentoxide. The resulting compounds were characterised by elemental analysis, FTIR, TGA, powder XRD, ^{31}P and ^{13}C MAS NMR. Analyses for Ga, In, P and As were carried out by Perkin-Elmer Australia Pty. Ltd., analyses for C and H were carried out by HRL Technology Pty. Ltd., Melbourne, Australia.

$Ga(OH)(O_3XC_6H_5)$ (where X = P or As), $Ga(OH)(O_3PCH_3)$, $Ga(OH)(O_3PCH_2C_6H_5)\cdot H_2O$ and $Ga(OH)(O_2P(H)C_6H_5)_2$

The elemental analyses for Ga, P(As), C and H in the phosphonate(arsonate) compounds gave good agreement with the proposed formulations:

$Ga(OH)(O_3PC_6H_5)$ (1). Found Ga, 29.3%; P, 13.1%; C, 29.9%; H, 2.5%, calc. Ga, 28.7%; P, 12.8%; C, 29.7%; H, 2.5%.

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†Electronic supplementary information (ESI) available: XRD powder patterns of (a) $Ga(OH)(O_3PC_6H_5)$ **1** and (b) $Ga(OH)(O_3PCH_3)$ **3**. See http://www.rsc.org/suppdata/jm/b0/b000011f/

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$Ga(OH)(O_3AsC_6H_5)$ (2). Found Ga, 24.0%; As, 24.6%; C, 24.8%; H, 2.1%, calc. Ga, 24.2%; As, 26.0%; C, 25.0%; H, 2.5%.

$Ga(OH)(O_3PCH_3)$ (3). Found Ga, 38.8%; P, 14.8%; C, 6.7%; H, 2.8%, calc. Ga, 38.4%; P, 16.6%; C, 6.7%; H, 2.2%.

$Ga(OH)(O_3PCH_2C_6H_5)\cdot H_2O$ (4). Found Ga, 25.3%; P, 11.6%; C, 30.0%; H, 3.6%, calc. Ga, 25.4%; P, 11.3%; C, 30.6%; H, 3.7%.

$Ga(OH)(O_2P(H)C_6H_5)_2$ (5). Found Ga, 19.6%; P, 17.8%; C, 39.8%; H, 3.5%, calc. Ga, 18.9%; P, 16.8%; C, 39.1%; H, 3.6%.

$In(O_3XR)(O_2X(OH)R)\cdot H_2O$ (where $R = C_6H_5$ or $CH_2C_6H_5$ when $X = P$, $R = C_6H_5$ when $X = As$), $In_2(O_3PCH_3)_3$ and $In(O_2P(H)C_6H_5)_3\cdot 2H_2O$

The elemental analyses for these compounds are as follows:

$In(O_3PC_6H_5)(O_2P(OH)C_6H_5)\cdot H_2O$ (6). Found In, 25.3%; P, 14.4%; C, 32.5%; H, 3.0%, calc. In, 25.7%; P, 13.9%; C, 32.3%; H, 2.9%.

$In(O_3PCH_2C_6H_5)(O_2P(OH)CH_2C_6H_5)\cdot H_2O$ (7). Found In, 25.8%; P, 13.4%; C, 34.4%; H, 3.7%, calc. In, 24.2%; P, 13.1%; C, 35.5%; H, 3.6%.

$In(O_3AsC_6H_5)(O_2As(OH)C_6H_5)\cdot H_2O$ (8). Found In, 20.9%; P, 29.0%; C, 27.8%; H, 2.5%, calc. In, 21.5%; P, 28.1%; C, 27.0%; H, 2.5%.

$In_2(O_3PCH_3)_3$ (9). Found In, 40.4%; P, 16.8%; C, 6.5%; H, 2.2%, calc. In, 41.9%; P, 16.9%; C, 6.6%; H, 2.3%.

$In(O_2P(H)C_6H_5)_3$ (10). Found In, 21.7%; P, 17.2%; C, 39.0%; H, 3.4%, calc. In, 21.3%; P, 17.3%; C, 40.2%; H, 3.4%.

Thermogravimetric analyses (TGA) were performed under flowing air in a Perkin-Elmer TGA 7/DX thermogravimetric analyser. Infrared spectra were obtained on a Perkin-Elmer 2000 Fourier Transform Infrared Spectrometer using KBr discs. Powder X-ray diffraction patterns were acquired on a Philips automated diffractometer using monochromatized Cu-Kα radiation. Cross polarization solid state magic angle spinning NMR for ^{13}C and ^{31}P were acquired using a Varian 300 NMR spectrometer at 75.45 MHz for ^{13}C and 121.46 MHz for ^{31}P, with ^{13}C chemical shifts referenced to TMS and ^{31}P referenced to potassium dihydrogen orthophosphate.

Results and discussion

Elemental analysis

For the phenylphosphonic, phenylarsonic, methylphosphonic and benzylphosphonic acid derivatives of gallium(III), compounds **1**, **2**, **3** and **4** respectively, the elemental analyses are consistent with a 1 : 1 ratio of Ga to P or As, with **4** isolated as the monohydrate. All of the gallium compounds contained a hydroxo group, unlike the analogous indium compounds. The presence of the OH group does not appear to be directly related to the pH of the reaction solution, since both gallium and indium solutions were adjusted to the same pH before reaction. Since an excess of ligand was present in the reaction mixture (a metal to ligand ratio of 1 : 2 was used), a deficiency in the amount of ligand does not explain the presence of the hydroxo group. Presumably this difference is due to the higher charge density of the gallium(III) ion causing polarisation of the O–H bond of coordinated water, with subsequent deprotonation to form hydroxo groups. The corresponding effect is not observed for the indium(III) compounds due to the larger size and lower charge density of indium(III) compared to gallium(III). (This deprotonation effect is illustrated in, for example, the acidic properties of the aquated cations $[M(H_2O)_6]^{3+}$, where $pK_a = 2.6$ for M = Ga and $pK_a = 3.7$ for M = In.) The presence of the hydroxo groups in these compounds is unusual but not unknown. Recently reported gallium phosphonates,[36–38,40] as well as an aluminium phosphonate[35] and a copper phosphonate,[43] also contain hydroxo groups.

The phosphinic acid derivative of gallium(III) (**5**) has a 1 : 2 Ga to P ratio, typical for this type of system[43] where the ligand acts as a mono-anion. This compound can be difficult to isolate, since reaction conditions that avoid the oxidation of phenylphosphinic acid to phenylphosphonic acid are required. If oxidation occurs the corresponding phenylphosphonate is formed, as indicated from the FTIR spectrum of the product, and in particular the loss of the characteristic phosphinate P–H absorption peak between 2300–2400 cm^{-1}.

For the phenylphosphonic (**6**), benzylphosphonic (**7**) and phenylarsonic (**8**) acid derivatives of indium(III), elemental analyses are consistent with a 1 : 2 ratio of In to P or As, whereas analysis of the methylphosphonate (**9**) gives a 2 : 3 ratio and the phenylphosphinic (**10**) acid derivative a 1 : 3 In to P ratio. The formulations based on these ratios are consistent with the results from FTIR, TGA and other characterization techniques.

An unusual result is the combined presence of the aromatic phosphonic and arsonic acids in both fully and partially deprotonated forms within the same compound. Analogous compounds with mono- and di-anion phosphonate ligands have previously been obtained involving cerium,[8] lanthanum,[25] uranyl,[45,46] manganese,[47] iron,[16] and aluminium.[31] Recently, both aluminium[27,28,32] and gallium[36] phosphonates have been isolated, and three of these compounds[28,32] possess a 1 : 2 metal to phosphorus ratio.

Powder X-ray diffraction (XRD)

Powder XRD results for the indium and gallium compounds all display an intense diffraction from the 001 plane, consistent with the proposed lamellar structures as observed in other related systems.[17,22,27,28] The powder XRD pattern for **1** exhibited a strong diffraction with an inter-layer spacing (d_{001}) equal to 14.52 Å, a value similar to that observed in other layered phosphonates[17,22,27,28] and consistent with the phenyl groups protruding into the inter-layer space between the gallium oxo layers. The compounds **4** (benzylphosphonate) and **5** (phenylphosphinate) exhibited similar XRD patterns, with inter-layer spacings of 13.04 and 14.32 Å, respectively. These spacings also compare well with those for similar systems.[27,28] The phenylarsonate derivative **2** displayed a d_{001} spacing of 14.82 Å. Isomorphous phenylarsonate compounds of magnesium, manganese, cobalt, nickel, copper, zinc and cadmium have been reported.[7] The methylphosphonate (**3**) exhibited an XRD pattern with a d_{001} spacing of 9.76 Å, which is expected for lamellar phosphonate systems containing small alkyl groups.

The indium(III) compounds exhibit powder XRD diffraction patterns similar to those observed for the corresponding gallium compounds. The methyl (**9**), phenyl (**6**) and benzylphosphonate (**7**) compounds exhibited XRD patterns with d_{001} spacings of 7.58, 15.06 and 14.81 Å respectively. The spacing for the arsonate (**8**) was 15.54 Å and the phosphinate (**10**) derivative 14.36 Å. These d_{001} spacings agree well with values from similar systems in the literature[17,22,27,28] and are consistent with a lamellar solid state structure where the organic moieties are positioned between the indium–oxo layers.

Thermal gravimetric analysis (TGA)

For the gallium compounds the TGA measurements for **1**, **2**, **3** and **5** all contained two major mass losses indicative of the loss of the hydroxo group (between 300 and 400 °C) and the loss of organics (above 400 °C). The TGA for the benzylphosphonate (**4**) derivative differs in that it contains three major mass losses. These are associated with the loss of coordinated or interlamellar water (100–150 °C), loss of the hydroxo group (250–300 °C) and loss of organics (above 450 °C). These observed mass losses are consistent with those observed for the thermal decomposition of analogous compounds.[12–14,46] Previously, arsonates[7] were found to be less thermally stable than phosphonates, but this is not the situation for gallium, where the phenylarsonate (**2**) decomposes at a similar temperature to the corresponding phosphonate (**1**). Fig. 1 compares the TGA of gallium and indium phenylphosphonates (**1** and **6**) with gallium phenylarsonate (**2**). The percentage mass loss for the organics in these compounds was less than theoretically expected. This is most likely due to incomplete combustion of the intercalated organic material and is common for this type of compound.[27] These compounds have also been previously recognized for their high thermal stability.[27]

The TGAs for the phosphonates and arsonate of indium, compounds **6–10**, all contain a mass decrease in the 200–300 °C region consistent with the loss of interlamellar or coordinated water, plus a large mass decrease above 400 °C due to breakdown of the organic groups. As an example, the TGA of the phenylphosphonate compound [shown in Fig. 1(b)] exhibited three mass losses. The first mass loss over the range 200–300 °C corresponds to the loss of water (observed 4.08%, expected 4.04%). The second and third mass losses, 370–450 and 450–700 °C, are attributed to the decomposition of the organic component of the ligand. The phenylphosphinate **10** had one major mass loss above 400 °C due to organic decomposition, consistent with lack of water in the proposed formula.

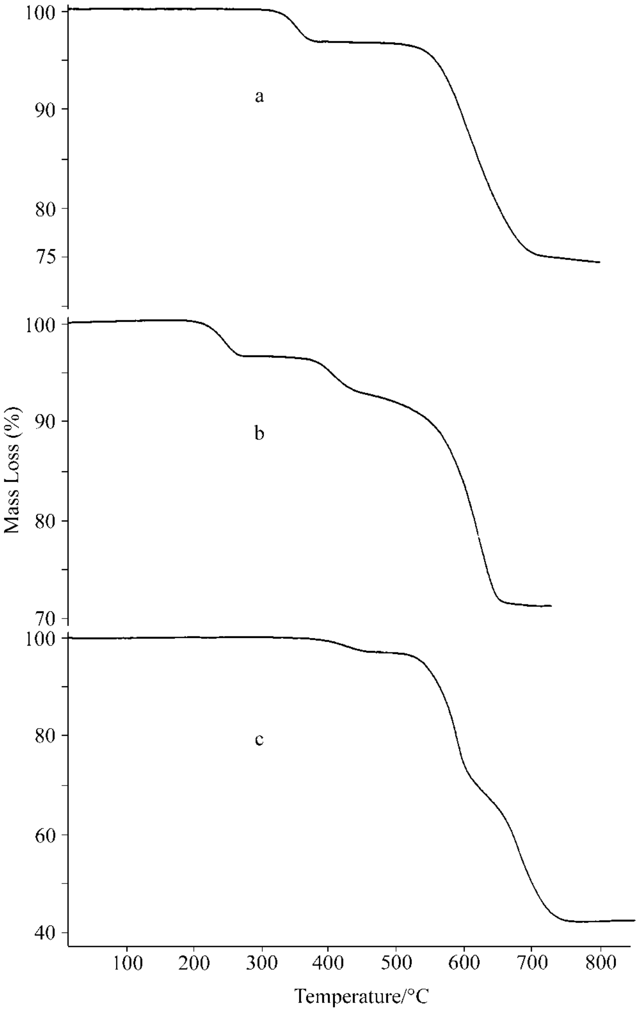

Fig. 1 TG curves for (a) $Ga(OH)(O_3PC_6H_5)$ (**1**), (b) $In(O_3PC_6H_5)(O_2P(OH)C_6H_5)\cdot H_2O$ (**6**) and (c) $Ga(OH)(O_3AsC_6H_5)$ (**2**).

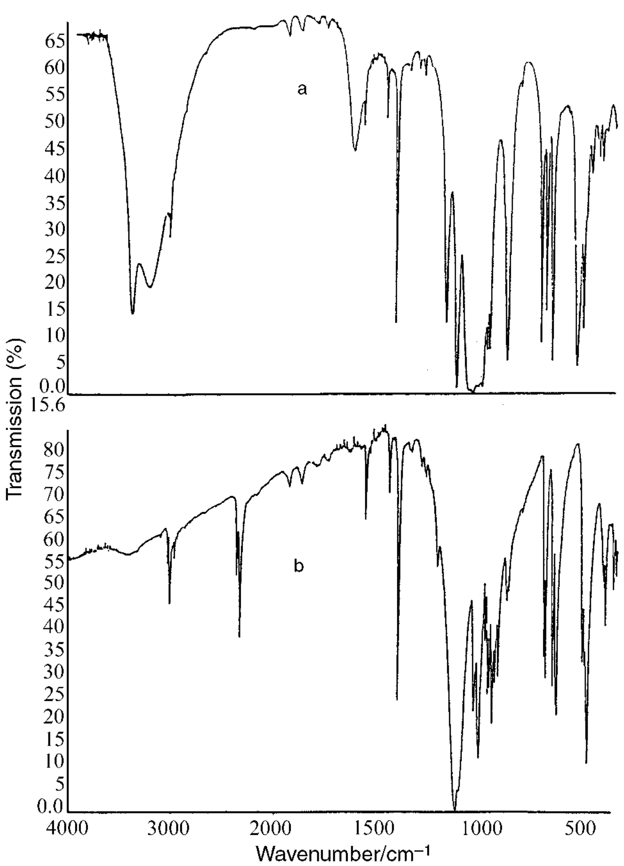

Fig. 2 IR spectra for (a) $In(O_3PC_6H_5)(O_2P(OH)C_6H_5)\cdot H_2O$ (**6**) and (b) $In(O_2P(H)C_6H_5)_3$ (**10**) showing the presence of the P–H absorption at 2372 cm^{-1}.

Fourier transform infrared spectroscopy

FTIR spectra for the indium (see Fig. 2 for examples) and gallium compounds all give well-resolved peaks. For **1** there is a sharp peak at 3530 cm^{-1} due to the OH group. The C–H stretching mode for the phenyl ring is relatively weak and is observed at 3055 cm^{-1}, with a very sharp and intense peak located at 1438 cm^{-1} also due to the aromatic ring. Three absorptions in the 700–800 cm^{-1} region are diagnostic for C_6H_5. The vibrations associated with the PO_3 moiety are observed between 1000–1200 cm^{-1}. The FTIR spectra for **2** (arsonate) and **5** (phosphinate) are similar to that of **1** (phosphonate). However there are two notable differences, the presence of the P–H band in the phosphinate spectrum at 2402 cm^{-1} and the lower frequency of the AsO_3 bands in the arsonate spectrum relative to the absorptions of PO_3, as expected from the difference in the masses of the heteroatoms. The FTIR spectrum of **4** (benzylphosphonate) differs from that of **1** (phenylphosphonate) only marginally, containing one broad band at 3510 cm^{-1} due to the OH stretch, and another broad band at 1640 cm^{-1} corresponding to the bending vibration for water. The benzylphosphonate (**4**) exhibits C–H bands located around 1413 cm^{-1}. The methyl derivative also contains C–H bands around 1300 cm^{-1}, but obviously lacks the C–H aromatic absorptions.

The FTIR spectra for the indium(III) compounds are very similar to those of the corresponding gallium compounds, but there appears to be a general slight shift to lower frequencies. This shift is expected and is attributed to the mass increase in going from gallium to indium. The spectrum for **6** [phenylphosphonate, Fig. 2(a)], contains two broad bands at 3400 and 3246 cm^{-1} due to the OH stretch of coordinated water and the free OH group on the phenylphosphonate monoanion ligand, with another absorption at 1640 cm^{-1} corresponding to the bending vibration for water. The C–H stretching mode for the phenyl ring is relatively weak and is observed at 3057 cm^{-1}, with a very sharp and intense peak located at 1437 cm^{-1} also due to the aromatic ring. The vibrations associated with the PO_3 moiety are observed between 1000–1200 cm^{-1}, whilst corresponding AsO_3 peaks in the arsonate compound are observed between 800–900 cm^{-1}. Peaks characteristic of the out-of-plane C–H vibrations are located at 746, 722, 692 and 576 cm^{-1}. The main differences observed between the FTIR spectra for the phosphonates and **10** [phosphinate, Fig. 2(b)] is the presence of a medium intensity peak at 2372 cm^{-1} in the phosphinate spectrum, characteristic of a P–H stretching vibration. The benzylphosphonate (**7**) exhibits C–H bands around 1400 cm^{-1}, whilst the methyl compound (**9**) exhibits C–H bands around 1300 cm^{-1}.

Solid state NMR

Solid state MAS-NMR spectra for all compounds are consistent with the proposed formulations. The ^{31}P MAS-NMR spectra for the gallium(III) compounds **1**, **3**, **4**, and **5** all contain one resonance at 17.3, 17.4, 16.3, and 17.4 ppm respectively, suggesting a single site for phosphorus in these compounds. The ^{13}C NMR spectra for these compounds contain aromatic carbon peaks at approximately 135 ppm, which is as anticipated. The benzylphosphonate (**4**) contains a methylene carbon peak at 42 ppm. Like those for the phosphonates, the phosphinate (**5**) and arsonate (**2**) spectra only contain aromatic carbon peaks at 135 ppm, whereas the methylphosphonate (**3**) derivative contains a methyl carbon peak at 24 ppm.

The phosphorus NMR spectra for the indium compounds are a little different to those of the corresponding gallium compounds as a result of their different formulations. The ^{31}P MAS-NMR spectrum for **6** (phenylphosphonate) contains one resonance at 21.9 ppm (relative to potassium dihydrogen orthophosphate as standard), suggesting a single site for phosphorus. This is in contrast to the ^{31}P spectrum for **7** (benzylphosphonate) which clearly has two distinct peaks at 27.6 and 32.4 ppm, indicative of two phosphorus sites in the solid state structure. The two sites correspond to phosphorus being present in the monoanion and dianion forms. Similarly **9** (methyl) also contains two ^{31}P peaks at 24.4 and 26.5 ppm. The phosphinate compound **10** contains one broad ^{31}P peak at 20.7 ppm which could be due to two unresolved peaks. The ^{13}C NMR spectra for the phosphorus containing compounds exhibit aromatic carbon peaks at approximately 135 ppm. These peaks are a little asymmetrical, suggesting some site differences for the ring, or possibly phosphorus coupling with the carbons, although such couplings are usually small (10–20 Hz) and would not normally be observed in solid state NMR spectra where linewidths are of the order of 100 Hz. This spectral pattern is also observed in **7** (arsonate), where there is normally no arsenic coupling observed. Along with the aromatic carbons, the benzylphosphonate (**7**) contains a methylene carbon peak at 43 ppm, and the methylphosphonate (**9**) derivative a methyl carbon peak at 24 ppm.

Conclusion

Gallium(III) and indium(III) form a range of phosphonates and related compounds with stoichiometries that provide metal to phosphorus (arsenic) ratios of 1 : 1, 1 : 2, 1 : 3, and 2 : 3. The phosphonic and arsonic acids are fully deprotonated when reacting with gallium(III), forming hydroxophosphonates or hydroxoarsonates. The corresponding indium(III) compounds do not involve hydroxide, but contain the phosphonic or arsonic acid as both the fully deprotonated dianion and the partially deprotonated monoanion. These compounds have similar characteristics and are typical of this class of compound. The data obtained from powder XRD measurements strongly suggest the compounds exist as lamellar structures in the solid state. Interlayer spacings vary from approximately 14 Å for gallium(III) and indium(III) compounds with aromatic organic groups, to much less than this for compounds with a corresponding methyl group. FTIR and solid state MAS-NMR spectra are consistent with the formulations proposed for these compounds.

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