

www.elsevier.com/locate/ica Inorganica Chimica Acta 320 (2001) 67-74 Inorganica Chimica Acta

# Gallium(III) organophosphonate adducts with the bidentate amines 2,2'-bipyridyl and 1,10-phenanthroline

Julia Morizzi, Malcolm Hobday\*, Colin Rix

Department of Applied Chemistry, RMIT University, 124 La Trobe St., Melbourne, Victoria 3000, Australia

Received 27 December 2000; accepted 17 April 2001

### Abstract

A number of gallium(III) organophosphonates form adducts with the bidentate amines 2,2'-bipyridyl and 1,10-phenanthroline. These adducts contain a 1:2:1 molar ratio of metal/phosphorus/amine and have the proposed formulations  $Ga(O_3PR)(O_2P(OH)R)(C_{10}H_8N_2)$ ·H<sub>2</sub>O and  $Ga(O_3PR)(O_2P(OH)R)(C_{12}H_8N_2)$ ·H<sub>2</sub>O (where  $R = CH_3$ ,  $C_6H_5$  and  $CH_2C_6H_5$ ;  $C_{10}H_8N_2$  is 2,2'-bipyridyl and  $C_{12}H_8N_2$  is 1,10-phenanthroline). Unlike the parent gallium(III) organophosphonates, which conform to the general formula  $Ga(OH)(O_3PR)$ ·xH<sub>2</sub>O (x = 0 or 1), the amine adducts lack the hydroxo group, but contain the organophosphonate ligand in the partially as well as fully deprotonated forms. All compounds were isolated from aqueous solutions as monohydrates, with the exception of the bipyridyl adduct of gallium(III) phenylphosphonate, which is anhydrous. TGA measurements suggest that for the hydrates, the water molecule is not coordinated to the metal. The bipyridyl adducts of gallium(III) phenylphosphonate and gallium(III) methylphosphonate, like the parent gallium(III) organophosphonates, are very likely layered, as indicated by the powder XRD patterns. In contrast, the corresponding phenanthroline adducts are non-layered, and both the bipyridyl and phenanthroline adducts of gallium(III) benzylphosphonate are amorphous solids. FTIR, powder XRD, TGA, XPS, solid state <sup>31</sup>P/<sup>13</sup>C MAS-NMR and BET surface area data are presented and discussed. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Gallium complexes; Organophosphonate complexes; Layered complexes

#### 1. Introduction

Lamellar metal organophosphonates are found to have well-defined void spaces and coordination sites which usually allow access of intercalating agents into the internal surface of the layered structure [1]. Intercalation of alcohols [2–7] and amines [1,8–18] into metal organophosphonates has received considerable attention. For example, vanadium(IV) organophosphonates have been studied in terms of mono- and di-alcohol intercalation, where the interlayer spacing is found to increase according to the size of the alcohol chain [7]. Amine intercalation of vanadium(IV) organophosphonates has also been studied [15], with these types of intercalates reported for a number of other metal phosphonate systems [1,8-14,16-18]. Similar work has been conducted with mono- and bidentate compounds [19-26], for instance, 2,2'-bipyridyl and 1,10-phenanthroline have been intercalated into layered titanium [24] and zirconium [20,21,25,26] phosphate structures, resulting in an increased interlayer spacing.

A series of lamellar gallium(III) organophosphonates [27–29] have previously been prepared. In this study, the potentially bidentate ligands 2,2'-bipyridyl and 1,10-phenanthroline were combined with certain gallium(III) organophosphonates to determine if the lamellar structure was retained on adduct formation, and if so, what effect amine coordination would have on the interlayer spacing. The corresponding organophosphonates of indium(III) have also been investigated [29,30] and analogous amine indium(III) organophosphonates prepared [31].

<sup>\*</sup> Corresponding author. Tel.: + 61-39-925-2117; fax: + 61-39-639-1321.

E-mail address: malcolm.hobday@rmit.edu.au (M. Hobday).

#### 2. Experimental

The gallium(III) compounds 1-6 were synthesised from solutions of gallium(III) chloride, the organophosphonic acid and the amine ligand in a 1:2:2 or 1:3:2 molar ratio for the aromatic and alkylphosphonic acids, respectively. The same products were obtained in both water/ethanol (70% ethanol) and aqueous solvent systems (water/ethanol was used initially for the reactions of 2.2'-bipyridyl due to limited water solubility). All chemicals were obtained from Aldrich Chemical Co. or BDH Laboratory Supplies and were AR grade. The metal ion solution was added with stirring to the combined ligands in solution and the mixture sealed in a Teflon-lined stainless-steel autoclave and heated at 160 °C for 2 days. A white solid was produced for the methyl- and phenylphosphonate gallium(III) adducts for both bipyridyl and phenanthroline. For the corresponding benzylphosphonate compounds, the reaction solutions were evaporated to half the volume before a precipitate formed. The solids were washed with ultrapure water, then air-dried and stored over phosphorus pentoxide prior to characterisation. (Note that the reaction solutions were clear and colourless prior to autoclave treatment, but were transparent red and peach, for the bipyridyl and phenanthroline derivatives, respectively, following the autoclave treatment, presumably due to the presence of gallium bipyridyl and phenanthroline complexes.) The resulting compounds were characterised by elemental analysis, FTIR, TGA, powder XRD, XPS, <sup>31</sup>P/<sup>13</sup>C MAS-NMR and BET surface area measurements. Analyses for Ga and P were carried out at Perkin-Elmer Australia Ptv. Ltd.; analyses for C, H and N were carried out by HRL Technology Pty. Ltd., Melbourne, Australia. Thermogravimetric analyses (TGA) were performed under flowing nitrogen gas 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 XRD patterns were acquired on a Philips automated diffractometer using monochromatised Cu Ka radiation. A VG Scientific Scanning Auger Nanoprobe was used to obtain X-ray photoelectron spectra using a nonmonochromatised magnesium filament (Mg K $\alpha$ ) as the radiation source. Cross-polarisation solid state MAS-NMR for <sup>13</sup>C and <sup>31</sup>P were acquired using a Varian 300 NMR spectrometer at 75.45 MHz for <sup>13</sup>C and 121.46 MHz for <sup>31</sup>P, with the <sup>13</sup>C chemical shifts referenced to TMS and the <sup>31</sup>P chemical shifts referenced to potassium dihydrogen orthophosphate. BET surface areas were measured using a Micromeritics ASAP 2000 surface area analyser with nitrogen as the absorbate gas.

The elemental analyses for Ga, P, C, H and N in the bipyridyl and phenanthroline derivatives of gallium(III) organophosphonates gave good agreement with the proposed formulations  $(C_{10}H_8N_2 = 2,2'$ -bipyridyl,  $C_{12}H_8N_2 = 1,10$ -phenanthroline).

Anal. Found: Ga, 13.3; P, 11.7; C, 48.9; H, 3.1; N, 5.0. Calc. for  $Ga(O_3PC_6H_5)(O_2P(OH)C_6H_5)(C_{10}H_8N_2)$ (1): Ga, 13.0; P, 11.5; C, 49.2; H, 3.2; N, 5.2% (% yield = 58).

Anal. Found: Ga, 12.3; P, 11.0; C, 50.1; H, 4.1; N, 5.0. Calc. for  $Ga(O_3PCH_2C_6H_5)(O_2P(OH)CH_2C_6H_5)-(C_{10}H_8N_2)\cdot H_2O$  (2): Ga, 12.3; P, 11.0; C, 51.0; H, 4.1; N, 5.0% (% yield = 71).

*Anal.* Found: Ga, 16.0; P, 14.4; C, 33.4; H, 3.5; N, 6.2. Calc. for  $Ga(O_3PCH_3)(O_2P(OH)CH_3)(C_{10}H_8N_2)$ ·  $H_2O$  (3): Ga, 16.2; P, 14.4; C, 33.4; H, 3.5; N, 6.5% (% yield = 33).

*Anal.* Found: Ga, 11.9; P, 10.6; C, 49.3; H, 3.7; N, 4.9. Calc. for  $Ga(O_3PC_6H_5)(O_2P(OH)C_6H_5)(C_{12}H_8N_2)$ ·  $H_2O$  (4): Ga, 12.0; P, 10.7; C, 49.6; H, 3.6; N, 4.8% (% yield = 54%).

Anal. Found: Ga, 11.5; P, 10.4; C, 50.1; H, 4.0; N, 4.9. Calc. for  $Ga(O_3PCH_2C_6H_5)(O_2P(OH)CH_2C_6H_5)-(C_{12}H_8N_2)\cdot H_2O$  (5): Ga, 11.7; P, 10.4; C, 50.4; H, 3.9%; N, 4.7% (% yield = 73%).

*Anal.* Found: Ga, 15.2; P, 13.5; C, 36.7; H, 3.8; N, 6.1. Calc. for  $Ga(O_3PCH_3)(O_2P(OH)CH_3)(C_{12}H_8N_2)$ ·  $H_2O$  (6): Ga, 15.3; P, 13.6; C, 36.8; H, 3.8; N, 6.1% (% yield = 32%).

#### 3. Results and discussion

#### 3.1. Elemental analysis

For the bipyridyl and phenanthroline adducts of gallium(III) methyl- (3, 6), phenyl- (1, 4) and benzylphosphonate (2, 5), the elemental analyses indicate a 1:2:1 molar ratio of Ga/P/amine, consistent with the organophosphonate being present in both the fully and partially deprotonated forms. Analogous organophosphonate compounds with mono- and di-anionic organophosphonate groups have previously been obtained for indium [29,30], as well as cerium [32], lanthanum [33], uranyl [34], manganese [35], iron [36] and aluminium [37,38]. The bipyridyl and phenanthroline amine adducts of indium(III) organophosphonates have been shown to possess the same In/P/amine composition of 1:2:1 [31]. Compounds 2, 3, 4, 5, and 6 are monohydrates, whereas 1 is anhydrous. These formulations are consistent with the results from FTIR, TGA and other characterisation techniques. It is interesting to note that the parent gallium organophosphonates have the general form  $Ga(OH)(O_3PR) \cdot xH_2O$  (where R is an organic group, x = 0 or 1), whereas the bidentate amine adducts are generally Ga(O<sub>3</sub>PR)(O<sub>2</sub>P- $(OH)R)(amine) \cdot xH_2O$ . The presence of the hydroxo group in the parent gallium(III) organophosphonates

was attributed [29] to the polarisation of coordinated water by the metal, leading to hydroxo formation by the loss of protons. Presumably for compounds 1-6, where there are no hydroxo groups, the coordination of the amine reduces the polarising ability of the metal ion, preventing hydroxo group formation.

#### 3.2. Fourier transform infrared spectroscopy (FTIR)

The FTIR spectra of 1-6 are typical of this class of compounds, with peaks that are well resolved. For the bipyridyl adducts, the spectrum of the gallium phenylphosphonate derivative (1) is representative (see Fig. 1) and is discussed here in detail. This spectrum contains a broad band due to an OH stretch vibration at 3434 cm<sup>-1</sup> attributed to the undissociated phosphonic acid group. A relatively weak peak observed at 3056  $cm^{-1}$  is due to the CH stretching mode for the phenyl ring, with a very sharp and intense peak located at 1437  $cm^{-1}$  also due to the aromatic CH. The vibrations associated with the PO<sub>3</sub> moiety are observed between 1000 and 1200 cm<sup>-1</sup>. The peaks characteristic of the out-of-plane CH vibrations in C<sub>6</sub>H<sub>5</sub> are located at 734, 718 and 697 cm<sup>-1</sup>. These peaks are characteristic of phenylphosphonate systems and very similar absorptions are found in the parent gallium(III) phenylphosphonate [29]. Other peaks observed in this region are associated with the bipyridyl ligand, as are the peaks at 1601, 1578, 1475, and 1445 cm<sup>-1</sup>. Corresponding peaks are observed at slightly lower frequencies in the uncomplexed 2,2'-bipyridyl [39] ligand. The increase in bipyridyl absorption frequencies is consistent with the coordination of the amine ligand to the metal, rather than the amine non-covalently lodged between the layers of the lamellar parent gallium(III) phenylphosphonate. The FTIR spectrum of the benzylphosphonate (2) differs from that of 1 only marginally, exhibiting a very sharp peak around 1420  $\text{cm}^{-1}$  due to the additional  $CH_2$  group. The methylphosphonate (3) derivative has



Fig. 1. FTIR spectrum for  $Ga(O_3PC_6H_5)(O_2P(OH)C_6H_5)(C_{10}H_8N_2)$  (1).

a similar spectrum to those of 1 and 2, with the phenyl group absorptions absent and a slight shift in peak frequencies. The only major difference is an absorption due to the CH<sub>2</sub> bending vibration around 1300 cm<sup>-1</sup> arising from the methyl group. As observed for 1, both the benzyl(2) and methylphosphonate (3) derivatives contain a broad peak around 3400 cm<sup>-1</sup> due to an OH stretch associated with both water and the undissociated phosphonic acid group, but unlike 1 a weak absorption is observed in 2 and 3 around 1630 cm<sup>-1</sup> due to the OH bending vibration of water.

The FTIR spectra for the phenanthroline analogues are very similar to the corresponding bipyridyl derivatives, for example the phenylphosphonate(4) derivative exhibits a broad peak at 3424 cm<sup>-1</sup> due to the OH stretch, and a weak peak at 1627 cm<sup>-1</sup> due to the OH bending vibration of water. A relatively weak band due to the CH stretching mode for the phenyl ring is observed at 3047 cm<sup>-1</sup>, with a very sharp and intense peak located at 1428 cm<sup>-1</sup> also due to the aromatic CH bend. The vibrations associated with the PO<sub>3</sub> moiety are observed between 1000 and 1200 cm<sup>-1</sup>. The peaks characteristic of the out-of-plane CH vibrations are located at 753, 717 and 698 cm<sup>-1</sup>. Other peaks observed in this region, and those at 1587, 1520, and 1491 cm<sup>-1</sup> are associated with the phenanthroline ligand and are consistent with coordination of the amine to the metal [39]. The phenanthroline derivative of gallium(III) benzylphosphonate (5) displays similar absorptions to (4), with the only major difference due to the  $CH_2$  group absorbing at 1428 cm<sup>-1</sup>. The methylphosphonate derivative (6) contains the methyl CH band at 1314 cm<sup>-1</sup>.

## 3.3. Thermogravimetric analyses (TGA)

The TGA of 1 shows two major thermal decompositions, the first mass loss occurring between 300 and 400 °C and the second between 540 and 670 °C. These mass losses are attributable to the loss of the amine ligand and the organic group of the organophosphonate, respectively (see Fig. 2). The TGA of the parent gallium(III) phenylphosphonate showed a mass loss at above 500 °C due to the phenyl group decomposition [28]. This suggests that the second mass loss in 1 arises from the loss of the organic phenyl group, and consequently the first mass loss can be attributed to the bipyridyl ligand (observed mass loss 29.2%, expected 28.9%). In metal organophosphonates, decomposition of the organophosphonate group is usually incomplete [40]. These TGA assignments are supported by the observation that 2,2'-bipyridyl incorporated into a zirconium phosphate system decomposed between 330-400 °C [21]. The TGA for the benzylphosphonate (2) showed thermal decompositions due to loss of water (30-100 °C), loss of bipyridyl (270-400 °C) and loss



Fig. 2. TGA for (a)  $Ga(O_3PC_6H_5)(O_2P(OH)C_6H_5)(C_{10}H_8N_2)$  (1) and (b)  $Ga(O_3PC_6H_5)(O_2P(OH)C_6H_5)(C_{12}H_8N_2)\cdot H_2O$  (4).

of the benzyl group (510-600 °C). The methylphosphonate derivative (**3**) showed corresponding mass losses between 33 and 130 °C due to loss of water, and between 217–412 °C and 454–611 °C, for the amine and organophosphonate, respectively.

The TGA results for the phenanthroline adducts are similar to those of the bipyridyl analogues. Compounds 4, 5 and 6 exhibit three major mass losses consistent with the loss of water, loss of amine ligand and decomposition of the organophosphonate. The thermal decompositions for the phenylphosphonate (4) are observed between 20-120 °C (water), 210-400 °C (phenanthroline; observed 29.5%, expected 31.0%) and 420-610 °C (see Fig. 2). The thermal decompositions in the benzylphosphonate (5) system are found over the temperature ranges 20-100 °C (water), 200-380 °C (phenanthroline; observed 30.0%, expected 29.6%) and 400-600 °C. Similarly, for the methylphosphonate (6), the three mass losses occur at 66-222 °C, 225-343 °C and 347-697 °C. In all cases, the thermal decomposition of the organic group of the organophosphonate is incomplete [40]. The relatively low temperature range corresponding to the loss of water for compounds 2-6indicates that the water is not coordinated to the metal. This is in contrast to coordinated or interlamellar water loss in the gallium(III) benzylphosphonate, Ga(OH)- $(O_3PCH_2C_6H_5)$ ·H<sub>2</sub>O, which occurred over the temperature range 100-150 °C [29].

## 3.4. Powder X-ray diffraction (XRD)

The powder XRD pattern for the previously reported gallium(III) phenylphosphonate [29] compound dis-

played strong 001 diffractions, consistent with the proposed lamellar structure. One reason for synthesising the bidentate amine adducts 1-6 in this study, was to investigate the influence of the coordinated ligands on layering and interlayer spacing, relative to the parent gallium(III) organophosphonates. The powder XRD pattern of the bipyridyl derivative of gallium(III) phenyphosphonate (1) contains a strong 001 diffraction, suggesting a lamellar structure with an interlayer spacing of 14.08 Å, which is slightly less than that observed in the parent gallium(III) phenylphosphonate (14.52 Å) [29]. In contrast, the XRD pattern for the corresponding phenanthroline derivative (4) does not contain a strong 001 diffraction, suggesting a non-lamellar structure (see Fig. 3).

Gallium(III) benzylphosphonate has a smaller interlayer spacing (13.04 Å) than the corresponding gallium(III) phenylphosphonate [29]. The reduced spacing for the gallium(III) benzylphosphonate relative to the phenyl analogue is indicative of the greater flexibility, and hence reduced steric demands, of the benzyl group containing the methylene (CH<sub>2</sub>) link. The addition of the bipyridyl and phenanthroline ligands to form the compounds 2 and 5, respectively, produces compounds with amorphous solid state structures, as indicated by powder XRD patterns. The compounds 2 and 5 did not precipitate from the reaction mixture, as observed for other compounds in the series, but were precipitated by slow evaporation from a gel-like solution. These solubility properties are consistent with a non-polymerised solid state structure. Presumably, bidentate amine coordination with the gallium(III) benzylphosphonate produces coordinately saturated gallium(III) without the involvement of polymerisation. The bipyridyl (3) derivative of gallium(III) methylphosphonate exhibited an XRD pattern indicative of a lamellar system with a  $d_{001}$  spacing of 8.98 Å, a reduced interlayer spacing compared with that in the parent gallium(III) methylphosphonate (9.76 Å) [29]. The XRD pattern for the phenanthroline adduct (6) indicated a non-lamellar structure.

## 3.5. Solid state MAS-NMR

The <sup>31</sup>P MAS-NMR spectrum of 1, the bipyridyl derivative of gallium(III) phenylphosphonate, contained two phosphorus resonances (7 and -5 ppm), consistent with the presence of di- and mono-anion forms of the phosphonate ligand. The <sup>13</sup>C MAS-NMR for the original phenylphosphonate compound contained one peak at 135 ppm due to the aromatic phenyl carbons [29]. The <sup>13</sup>C MAS-NMR spectrum for 1 contained a broad peak centred at 134 ppm (phenyl group), with two smaller peaks at 147 and 153 ppm attributable to the aromatic carbons associated with the heterocyclic groups in the bipyridyl ligand (see Fig. 4a). The <sup>31</sup>P MAS-NMR spectrum of the corresponding phenanthroline derivative (4) contained a broad <sup>31</sup>P signal due to two unresolved peaks centred at -1.4 ppm (shoulder at 4 ppm). The <sup>13</sup>C MAS-NMR spectrum contained one broad <sup>13</sup>C peak at 126 ppm attributed to the aromatic carbons in the phenyl and phenanthroline groups, together with a smaller peak at 138 ppm, attributed to the aromatic carbons in the heterocyclic portions of the phenanthroline ligand (see Fig. 4b). In the same way, <sup>31</sup>P and <sup>13</sup>C MAS-NMR spectra for 2, 3, 5 and 6 are consistent with at least two <sup>31</sup>P sites, and with the presence of the organic group and amine ligand, respectively. The <sup>31</sup>P MAS-NMR spectra for 2 and 5 contain a broad peak at about 10 ppm with a shoulder at about 8 ppm. For **3** and **6**, a very broad  ${}^{31}P$ peak is observed (peak width at half height is 6 ppm), indicative of at least two sites, as suggested by others [23]. The <sup>13</sup>C MAS-NMR spectra for2 and 5 display signals due to the aromatic phenyl ring and amine group centred at 134 ppm, with another peak at 153 ppm for 2, and two small shoulders at 144 and 154 ppm for 5 due to the aromatic carbons in the bipyridyl and phenanthroline groups, respectively. The <sup>13</sup>C MAS-NMR spectra for both 2 and 5 contain peaks at ap-

proximately 43 ppm due to the  $CH_2$  of the benzyl group, whereas the <sup>13</sup>C spectra of **3** and **6** contain peaks at approximately 23 ppm due to the methyl group. The <sup>13</sup>C MAS-NMR signal due to the aromatic carbons in the amine ligands, the only aromatic group present in the methylphosphonate systems **3** and **6**, is present at around 134 ppm, with a small shoulder at 154 ppm.

## 3.6. BET surface areas

The lamellar nature of metal organophosphonates suggests that these compounds may have accessible surface areas that are larger than corresponding nonlamellar systems. Others [41] have found that for bis(methylphosphonato)zirconium(IV), surface area is influenced by particle size, with surface areas increasing as particle size is decreased. A direct correlation was also found between molecular volume and interlayer spacing for a series of isostructural lamellar metal(IV) phosphates and phosphonates [42]. The BET surface areas for compounds 1-6, the parent gallium(III) organophosphonates and related indium(III) compounds, are summarised in Table 1, where data is either from this study, or from Morizzi et al. [29,31]. The



Fig. 3. Powder XRD patterns for (a)  $Ga(O_3PC_6H_5)(O_2P(OH)C_6H_5)(C_{10}H_8N_2)$  (1) and (b)  $Ga(O_3PC_6H_5)(O_2P(OH)C_6H_5)(C_{12}H_8N_2) \cdot H_2O$  (4).

Fig. 4. Solid state  ${}^{13}C$  MAS-NMR spectra for (a)  $Ga(O_3PC_6H_5)-(O_2P(OH)C_6H_5)(C_{10}H_8N_2)$  (1) and (b)  $Ga(O_3PC_6H_5)(O_2-P(OH)C_6H_5)(C_{12}H_8N_2)\cdot H_2O$  (4).

parent gallium(III) and indium(III) organophosphonate compounds are found to have surface areas in the ranges  $17-52 \text{ m}^2 \text{g}^{-1}$  and  $14-46 \text{ m}^2 \text{g}^{-1}$ , respectively. In all cases, adduct formation with bipyridyl or phenanthroline produces a decrease in BET surface area that is often substantial. The one exception occurs for gallium(III) benzylphosphonate (surface area 25 m<sup>2</sup> g<sup>-1</sup>) where conversion to the phenanthroline adduct produces a relatively minor decrease (to  $20 \text{ m}^2 \text{ g}^{-1}$ ). From these observations, however, there appears to be no simple correlation between interlayer spacing and BET surface area.

## 3.7. X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) is a useful tool for the analysis of surface composition, surface atom oxidation states and the estimation of core-electron binding energies. XPS involves X-ray stimulation of electron emission from the valence and inner shells of the surface atoms [43]. In the present study, the area of particular interest was the binding energies associated with the C- and N-bonds of the heterocyclic amine ligands incorporated into the organophosphonate systems.

As shown earlier, comparison of the FTIR spectra for the free molecules, 2,2'-bipyridyl and 1,10-phenanthroline, and the same molecules held in the metal(III) organophosphonate systems, demonstrated slight increases in peak frequencies associated with the amine ligand in the metal complexes. The increase in these absorption frequencies is consistent with coordination of the amine ligand to the metal, rather than a simple mixture, or the amine groups non-covalently lodged between the layers of the lamellar parent metal(III) organophosphonate. To verify these observations in the FTIR spectra, XPS studies were conducted on the bipyridyl(1) and phenanthroline(4) adducts of gallium(III) phenylphosphonate. In addition to the samples analysed by XPS, the free ligand 1,10-phenanthroline was also analysed and used as a reference. It should be

Table 1

BET surface areas and interlayer spacing for gallium(III) and indium(III) organophosphonates and their 2,2'-bipyridyl and 1,10-phenanthroline adducts

Compound (bipy = $2,2'$ -bipyridyl) (phen = $1,10$ -phenanthroline)	BET surface area $(m^2 g^{-1})$	Interlayer spacing (Å)
$Ga(OH)(O_3PC_6H_5)$ (parent)	52	14.52
$Ga(O_3PC_6H_5)(O_2P(OH)C_6H_5)$ bipy (1)	4	14.10
$Ga(O_3PC_6H_5)(O_2P(OH)C_6H_5)$ phen·H <sub>2</sub> O (4)	6	NL <sup>a</sup>
$Ga(OH)(O_3PCH_2C_6H_5) \cdot H_2O$ (parent)	25	13.04
$Ga(O_3PCH_2C_6H_5)(O_2P(OH)CH_2C_6H_5)bipy \cdot H_2O$ (2)	10	NL <sup>a</sup>
$Ga(O_3PCH_2C_6H_5)(O_2P(OH)CH_2C_6H_5)$ phen·H <sub>2</sub> O(5)	20	NL <sup>a</sup>
$Ga(OH)(O_3PCH_3)$ (parent)	17	9.76
$Ga(O_3PCH_3)(O_2P(OH)CH_3)bipy \cdot H_2O(3)$	5	8.90
$Ga(O_3PCH_3)(O_2P(OH)CH_3)$ phen·H <sub>2</sub> O(6)	6	NL <sup>a</sup>
$In(O_3PC_6H_5)(O_2P(OH)C_6H_5) \cdot H_2O$ (parent)	30	15.06
$In(O_3PC_6H_5)(O_2P(OH)C_6H_5)bipy \cdot H_2O$	18	11.34
$In(O_3PC_6H_5)(O_2P(OH)C_6H_5)phen \cdot H_2O$	13	NL <sup>a</sup>
$In(O_3PCH_2C_6H_5)(O_2P(OH)CH_2C_6H_5) \cdot H_2O$ (parent)	14	14.81
$In(O_3PCH_2C_6H_5)(O_2P(OH)CH_2C_6H_5)bipy \cdot H_2O$	4	NL <sup>a</sup>
$In(O_3PCH_2C_6H_5)(O_2P(OH)CH_2C_6H_5)phen \cdot H_2O$	7	NL <sup>a</sup>
$In_2(O_3PCH_3)_3 \cdot 2H_2O$ (parent)	46	7.58
In(OH)(O <sub>3</sub> PCH <sub>3</sub> )bipy	9	8.83
In(OH)(O <sub>3</sub> PCH <sub>3</sub> )phen·2H <sub>2</sub> O	7	NL <sup>a</sup>

<sup>a</sup> NL = non-layered.



noted that 2,2'-bipyridyl completely sublimed under the sample analysis conditions, and hence could not be analysed by XPS, however, similar results would be anticipated for both compounds.

The binding energy data associated with carbon (1s) in the phenanthroline ligand indicated only one type of carbon with a peak maximum at 284.40 eV, whilst 1 and 4 were found to have two carbon sites, associated with the presence of heterocyclic amine carbons of phenanthroline or bipyridyl ( $\sim 284$  eV) and the aromatic carbons of the phenyl group ( $\sim 286$  eV). The change in the binding energies of carbon ( $\Delta C$ ) associated with the phenanthroline group vary by 0.1-0.15 eV, from the free ligand to the metal complexes. The binding energies of carbon associated with phenanthroline are not expected to change significantly from the free ligand to the metal complexes because on complexation of the heterocyclic amine to the organophosphonate system, the carbon atoms do not form any new bonds. The small variations in the binding energy of the free ligand and metal complexes are indicative of this.

The binding energies associated with nitrogen (1s) in the free phenanthroline molecule indicated only one type of nitrogen with a peak maximum of 398.39 eV, and similarly, 1 and 4 were also found to have one nitrogen site as expected, due to the presence of either the phenanthroline or bipyridyl ligand. The change in the binding energies of nitrogen ( $\Delta N$ ) from the free ligand to the metal complex is in the range 0.98-1.15 eV. This increase in the binding energy associated with nitrogen when the heterocyclic amine becomes incorporated into the organophosphonate system suggested that the nitrogen atoms are indeed involved in different types of bonds in comparison to the free ligand. For example, the binding energies of BN and NH<sub>3</sub> were found to be 398.1 and 398.8 eV [44], respectively, which illustrates that the binding energies of an element, such as nitrogen, varies marginally when bonded to a different species. The variation in binding energies of nitrogen from the free ligand to the metal complexes strongly suggests that nitrogen binds to the metal on addition to the organophosphonate system.

## 4. Conclusions

The gallium(III) organophosphonates (1-6) contain the organophosphonate in both the dianionic and partially deprotonated monoanionic forms, and with the amine coordinated to the metal, as suggested by XPS data. All compounds except 1 were isolated as monohydrates, however, the water appears to be in lattice sites and not directly coordinated to the metal. Powder XRD patterns suggest that 1 and 3 are layered in the solid state, with the interlayer spacings slightly decreased relative to those in the parent gallium(III) organophosphonates. Compounds 4 and 6 were found to be non-lamellar in the solid state, whereas 2 and 5 were amorphous solids. There appears to be no correlation between BET surface area and the layering of these compounds in the solid state, however, BET surface areas of the gallium(III) organophosphonates and their indium analogues are substantially decreased by amine coordination.

## Acknowledgements

The authors thank the following people for their assistance: Ian McPhail from RMIT for XRD measurements; Matthew Glenn from RMIT for XPS measurements; Tracy Lam and Dr Frances Separovic from Melbourne University for assisting with MAS-NMR spectra; and Vesna Dolic from Perkin–Elmer, Australia, for assisting in ICP analyses. The authors thank Bayswater Dental Pty.Ltd. for a donation of gallium metal. Julia Morizzi gratefully acknowledges an APA Scholarship.

#### References

- [1] G. Cao, T. Mallouk, Inorg. Chem. 30 (1991) 1434.
- [2] F. Abbona, R. Boistelle, R. Haser, Acta Crystallogr., Sect. B 35 (1979) 2514.
- [3] J.W. Johnson, A.J. Jacobson, J.F. Brody, J.T. Lewandowski, Inorg. Chem. 23 (1984) 3842.
- [4] J.W. Johnson, A.J. Jacobson, W.M. Butler, S.E. Rosenthal, J.F. Brody, J.T. Lewandowski, J. Am. Chem. Soc. 111 (1989) 381.
- [5] P. Gendraud, M.E. de Roy, J.P. Besse, J. Solid State Chem. 106 (1993) 517.
- [6] P. Gendraud, L. Bigey, C. Gueho, M.E. de Roy, J.P. Besse, Chem. Mater. 9 (1997) 539.
- [7] E.M. Sabbar, M.E. de Roy, J.P. Besse, Mater. Res. Bull. 34 (1999) 1023.
- [8] K.J. Frink, R. Wang, J.L. Colon, A. Clearfield, Inorg. Chem. 30 (1991) 1438.
- [9] Y. Zhang, A. Clearfield, Inorg. Chem. 31 (1992) 2821.
- [10] Y. Zhang, K.J. Scott, A. Clearfield, Chem. Mater. 5 (1993) 495.
- [11] G. Cao, V.M. Lynch, L.N. Yacullo, Chem. Mater. 5 (1993) 1000.
- [12] S. Drumel, P. Janvier, P. Barboux, M. Bujoli-Doeuff, B. Bujoli, Inorg. Chem. 34 (1995) 148.
- [13] D.M. Poojary, A. Clearfield, J. Am. Chem. Soc. 117 (1995) 11278.
- [14] S. Drumel, P. Janiver, M. Bujoli-Doeuff, B. Bujoli, J. Mater. Chem. 6 (1996) 1843.
- [15] P. Gendraud, M.E. de Roy, J.P. Besse, Inorg. Chem. 35 (1996) 6108.
- [16] E. Jaimez, A. Bortun, G.B. Hix, J.R. Garcia, J. Rodriguez, R.C.T. Slade, J. Chem. Soc., Dalton Trans. (1996) 2285.
- [17] F. Fredueil, D. Massiot, P. Janiver, F. Gingl, M. Bujoli-Doeuff, M. Evain, A. Clearfield, B. Bujoli, Inorg. Chem. 38 (1999) 1831.
- [18] P. Gerbier, C. Guerin, B. Henner, J.R. Unal, J. Mater. Chem. 9 (1999) 2559.
- [19] C. Ferragina, M.A. Massucci, A. La Ginestra, P. Patrono, A.A.G. Tomlinson, J. Chem. Soc., Chem. Commun. (1984) 1204.

- [20] C. Ferragina, A. La Ginestra, M.A. Massucci, P. Patrono, A.A.G. Tomlinson, J. Phys. Chem. 89 (1985) 4762.
- [21] C. Ferragina, M.A. Massucci, P. Patrono, A. La Ginestra, A.A.G. Tomlinson, J. Chem. Soc., Dalton Trans. (1986) 265.
- [22] J.L. Colon, C.Y. Yang, A. Clearfield, C.R. Martin, J. Phys. Chem. 92 (1988) 5777.
- [23] J.L. Colon, C.Y. Yang, A. Clearfield, C.R. Martin, J. Phys. Chem. 94 (1990) 874.
- [24] C. Ferragina, M.A. Massucci, A.A.G. Tomlinson, J. Mater. Chem. 6 (1996) 645.
- [25] C. Ferragina, P. Cafarelli, A. De Stefanis, G. Mattei, Mater. Res. Bull. 34 (1999) 1039.
- [26] S.K. Shakshooki, H.B. El Hanash, R.M. El-Mehdawi, M.A. El-Mellah, E.A. Arafa, A.M. Bejey, J. Radioanal. Nucl. Chem. 240 (1999) 433.
- [27] F. Fredoueil, D. Massiot, P. Janvier, F. Gingl, M. Bujoli-Doeuff, M. Evain, A. Clearfield, B. Bujoli, Inorg. Chem. 38 (1999) 1831.
- [28] M. Bujoli-Doeuff, M. Evain, F. Fayon, B. Alonso, D. Massiot, B. Bujoli, Eur. J. Inorg. Chem. 12 (2000) 2497.
- [29] J. Morizzi, M. Hobday, C. Rix, J. Mater. Chem. 10 (2000) 1693.
- [30] J. Morizzi, M. Hobday, C. Rix, J. Mater. Chem. 9 (1999) 863.
- [31] J. Morizzi, M. Hobday, C. Rix, J. Mater. Chem. 11 (2001) 794.

- [32] G. Cao, V.M. Lynch, J.S. Swinnea, T.E. Mallouk, Inorg. Chem. 29 (1990) 2112.
- [33] R-C Wang, Y. Zhang, H. Hu, R.R. Frausto, A. Clearfield, Chem. Mater. 4 (1992) 864.
- [34] D.M. Poojary, A. Cabeza, M.A.G. Aranda, S. Bruque, A. Clearfield, Inorg. Chem. 35 (1996) 1468.
- [35] A. Cabeza, M.A.G. Aranda, S. Bruque, D.M. Poojary, A. Clearfield, Mater. Res. Bull. 33 (1998) 1265.
- [36] B. Bujoli, P. Palvadeau, J. Rouxel, Chem. Mater. 2 (1990) 582.
- [37] A. Cabeza, M.A.G. Aranda, S. Bruque, D.M. Poojary, A. Clearfield, J. Sanz, Inorg. Chem. 37 (1998) 4168.
- [38] G.B. Hix, V.J. Carter, D.S. Wragg, R.E. Morris, P.A Wright, J. Mater. Chem. 9 (1999) 179.
- [39] Mudasir, N. Yoshioka, H. Inoue, Transition Met. Chem. 24 (1999) 210.
- [40] L. Raki, C. Detellier, J. Chem. Soc., Chem. Commun. 21 (1996) 2475.
- [41] M.B. Dines, P.C. Griffith, J. Phys. Chem. 86 (1982) 571.
- [42] M.B. Dines, P.M. Digiacomo, Inorg. Chem. 20 (1981) 92.
- [43] W.L. Jolly, Modern Inorganic Chemistry, McGraw-Hill, New York, 1985.
- [44] D. Briggs, M.P. Seah, Practical Surface Analysis-Auger and X-ray Photoelectron Spectroscopy, Wiley, London, 1985.