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Some bidentate amine adducts of indium(III) organophosphonates

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A series of indium(III) organophosphonates with coordinated 2,2′-bipyridyl and 1,10-phenanthroline ligands have been prepared and characterised. The bipyridyl and phenanthroline derivatives of indium(III) phenyl- and benzyl-phosphonates have a 1 : 2 : 1 molar ratio of metal : phosphorus : amine ligand, with proposed formulations $In(O_3PR)(O_2P(OH)R)(C_{10}H_8N_2)\cdot H_2O$ and $In(O_3PR)(O_2P(OH)R)(C_{12}H_8N_2)\cdot H_2O$ respectively (where $R = C_6H_5$ and $CH_2C_6H_5$). Like the parent compounds, these adducts contain the organophosphonate ligand in both fully and partially deprotonated forms. In contrast, the bipyridyl and phenanthroline indium(III) methylphosphonates contain a 1 : 1 : 1 molar ratio of indium : phosphorus : amine, with proposed formulations $In(OH)(O_3PCH_3)(C_{10}H_8N_2)$ and $In(OH)(O_3PCH_3)(C_{12}H_8N_2)\cdot 2H_2O$ respectively. Powder XRD measurements indicate that the bipyridyl phenylphosphonate and methylphosphonate compounds are layered, with interlayer spacing for the former (11.34 Å) reduced, and for the latter slightly increased (8.83 Å), relative to the parent indium(III) phenylphosphonate and methylphosphonate, respectively. The corresponding phenanthroline adducts of indium(III) phenylphosphonate and methylphosphonate do not possess layered structures. Both the bipyridyl and phenanthroline indium(III) benzylphosphonates are amorphous solids. FTIR, powder XRD, TGA and solid state $^{31}P/^{13}C$ MAS NMR data are presented.

Introduction

The recent rapid growth in knowledge of metal organophosphonate chemistry derives from an interest in the structural chemistry of these compounds and their potential applications as hosts in intercalation reactions, ion exchangers, proton conductors, sorbents, catalysts and sensors.[1–5] The structure of metal organophosphonates is dependent on a number of factors, including the metal cation, the organic group attached to the phosphonate anion, and synthetic conditions such as temperature, pressure and reaction solution pH. Generally, these compounds possess layered solid state structures, where the octahedrally coordinated metal cation is within the layer and the organic moiety directed into the interlamellar space. The synthesis and characterisation of tetravalent[6–9] metal phosphonates has received most attention, but divalent[10–13] and trivalent[10,14–19] metal phosphonates have also been extensively investigated. Recent work on phosphonates of the p-block group-III metals has predominately focussed on aluminium,[15–19] in particular the methyl and phenyl derivatives, with some recent interest in gallium[20–25] and indium.[24–26]

Layered phosphonates are found to have structurally and chemically well-defined internal spaces and coordination sites,[27] providing relatively easy access to intercalating reagents. Intercalation of alcohols into layered phosphonates has been investigated for a number of systems. Vanadyl organophosphonates[28] intercalate monoalcohols and dialcohols by coordination of the alcohol to vanadium in the phosphonate layer. These intercalated systems exhibit an increase in the interlayer spacing consistent with the length of the alcohol molecule. More recently, intercalation of aliphatic amines into vanadium phosphonate[29] also increased the interlayer spacing, but by an interlamellar packing process. These types of amine intercalates have been prepared for a number of different metal phosphonate systems[11,27,30,31] involving monodentate and bidentate amines. For example, pyridine has been intercalated into a layered titanate[32] structure, resulting in increased interlayer spacing, and similarly 2,2′-bipyridyl and 1,10-phenanthroline have been intercalated into a titanium phosphate[33] and zirconium phosphate[34–39] (where pre-swelling is required).

In the present study, the potentially bidentate ligands 2,2′-bipyridyl and 1,10-phenanthroline were reacted with the metal ion and phosphonic acid to produce a mixed phosphonate/amine ligand system. The objectives were to extend the knowledge of the chemistry of layered phosphonates of the p-block group-III[25,26] metals, to introduce ligands into the system that are potentially capable of increasing the interlayer spacing, and to gain a better understanding of coordinated/intercalated phosphonates.

Experimental

The indium(III) compounds **1**–**6** were synthesised from solutions of indium(III) chloride tetrahydrate, organophosphonic acid and the amine ligand in a 1 : 3 : 2 molar ratio, for both the aromatic and alkylphosphonic acids. Both a water–ethanol (70% ethanol) and aqueous solvent system produced the same results. (Water–ethanol was used initially for reactions of 2,2′-bipyridyl due to limited water solubility.) All chemicals were obtained from Aldrich Chemical Co. or BDH Chemical Supplies and were AR grade. The metal solution was added to the combined ligand solutions with stirring. The solution was then sealed in a Teflon-lined stainless steel autoclave and heated at 160 °C for 2 days. A white solid was produced for the indium(III) methyl- and phenyl-phosphonates, for both the bipyridyl and phenanthroline derivatives. For the benzylphosphonate compounds, the reaction solutions were evaporated to half volume before a precipitate formed. The solids were washed with ultrapure water, air-dried, then dried 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 traces of indium bipyridyl and phenanthroline complexes.) The resulting compounds were characterised by

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elemental analysis, FTIR, TGA, powder XRD, ^{31}P and ^{13}C MAS NMR, and BET surface areas. Analyses for In and P were carried out by Perkin-Elmer Australia Pty. Ltd. Analyses for C, H and N were carried out by HRL Technology Pty. Ltd., Melbourne, Australia.

Thermogravimetric analyses (TGA) were performed under nitrogen 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 monochromatized CuKα radiation. Cross polarization solid state MAS NMR spectra 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. BET surface areas were measured using a Micromeritics ASAP 2000 Surface Area Analyser with nitrogen as the adsorbate gas.

The elemental analyses for In, P, C, H and N in the bipyridyl and phenanthroline derivatives of indium(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):

$In(O_3PC_6H_5)(O_2P(OH)C_6H_5)(C_{10}H_8N_2){\cdot}H_2O$ (**1**): Found: In, 19.0; P, 10.5; C, 44.4; H, 3.1; N, 4.6; Calc.: In, 19.1; P, 10.3; C, 44.0; H, 3.2; N, 4.7%. $In(O_3PCH_2C_6H_5)(O_2P(OH)CH_2C_6H_5)(C_{10}H_8N_2){\cdot}H_2O$ (**2**): Found: In, 18.8; P, 10.5; C, 45.2; H, 4.0; N, 4.2; Calc.: In, 18.2; P, 9.8; C, 45.7; H, 3.7; N, 4.4%. $In(OH)(O_3PCH_3)(C_{10}H_8N_2)$ (**3**): Found: In, 31.1; P, 8.5; C, 35.9; H, 2.7; N, 7.5; Calc.: In, 30.2; P, 8.2; C, 34.8; H, 2.7; N, 7.4%. $In(O_3PC_6H_5)(O_2P(OH)C_6H_5)(C_{12}H_8N_2){\cdot}H_2O$ (**4**): Found: In, 18.7; P, 9.8; C, 46.7; H, 3.2; N, 4.2; Calc.: In, 18.3; P, 9.9; C, 46.0; H, 3.4; N, 4.5%. $In(O_3PCH_2C_6H_5)(O_2P(OH)CH_2C_6H_5)(C_{12}H_8N_2){\cdot}H_2O$ (**5**): Found: In, 17.5; P, 9.8; C, 47.2; H, 4.2; N, 4.3; Calc.: In, 17.6; P, 9.5; C, 47.8; H, 3.8; N, 4.3%. $In(OH)(O_3PCH_3)(C_{12}H_8N_2){\cdot}2H_2O$ (**6**): Found: In, 25.5; P, 7.3; C, 35.0; H, 3.8; N, 6.2; Calc.: In, 26.0; P, 7.0; C, 35.3; H, 3.7; N, 6.3%

Results and discussion

Elemental analysis

For the bipyridyl **1** and phenanthroline **4** indium(III) phenylphosphonates and corresponding bipyridyl **2** and phenanthroline **5** indium(III) benzylphosphonates, the elemental analyses indicate a 1 : 2 : 1 molar ratio of In : P : amine, consistent with the phosphonate being present in both the fully and partially deprotonated forms. Analogous compounds with mono- and di-anionic phosphonate groups have previously been obtained for indium,[25,26] as well as for cerium,[10] lanthanum,[40] uranyl,[41] manganese,[42] iron,[14] and aluminium.[16] The compounds **1**, **2**, **4** and **5** are monohydrates. In contrast, the bipyridyl **3** and phenanthroline **6** methylphosphonates possess a 1 : 1 : 1 molar ratio of In : P : amine and involve dianionic phosphonate groups, with a hydroxy group providing charge balance. Methylphosphonatobipyridylindium(III) **3** is anhydrous, whereas the phenanthroline analogue **6** is a dihydrate. These formulations are consistent with the results from FTIR, TGA and other characterisation techniques.

Fourier transform infrared spectroscopy (FTIR)

The FTIR spectra for the indium(III) compounds all display well resolved peaks. The spectrum for phenylphosphonatobipyridylindium(III) **1** contains a weak broad peak due to OH stretching at 3435 cm^{-1}, with a corresponding weak water OH bending absorption at 1636 cm^{-1}. A relatively weak peak at 3055 cm^{-1} is due to the CH stretching mode of the phenyl ring, with a very sharp and intense peak located at 1443 cm^{-1} also due to aromatic CH. Very similar absorptions are found in phenylphosphonatoindium(III),[25,26] as seen from Fig. 1, which compares the FTIR spectra of **1** and the parent compound, $In(O_3PC_6H_5)(O_2P(OH)C_6H_5){\cdot}H_2O$. Absorptions in **1** due to the PO_3 moiety are observed in the region between 1000 and 1200 cm^{-1}. Three absorptions in **1** due to out-of-plane CH vibrations of C_6H_5, are located at 733, 717 and 697 cm^{-1}, and are characteristic of phenylphosphonates in general. Other absorptions in the same region are associated with the bipyridyl ligand, as are the peaks observed at 1601, 1597, 1577 and 1476 cm^{-1}. Corresponding peaks are observed at slightly lower frequencies in uncomplexed 2,2′-bipyridyl.[43] The increase in bipyridyl absorption frequencies is consistent with coordination of the amine ligand, rather than intercalation of the amine between the layers of the parent lamellar indium phosphonate. The FTIR spectrum of **2** differs from that of **1** only marginally. The benzylphosphonate exhibits a very sharp peak at around 1400 cm^{-1} due to the additional CH_2 group. The methylphosphonate **3** derivative has a spectrum similar to those for the phenyl **1** and benzylphosphonates **2**, with the phenyl group absorption absent and a slight shift in peak frequencies. The only major difference is the presence of methyl CH bands at 1322 cm^{-1}. The phenyl- **1**, benzyl- **2** and methyl-phosphonate **3** derivatives all contain a broad peak around 3400 cm^{-1} due either to the OH stretch in water and the partially deprotonated phosphonate anion, or for **3** the hydroxy group. For **1** and **2** a weak absorption is observed around 1630 cm^{-1} due to the OH bending vibration of water.

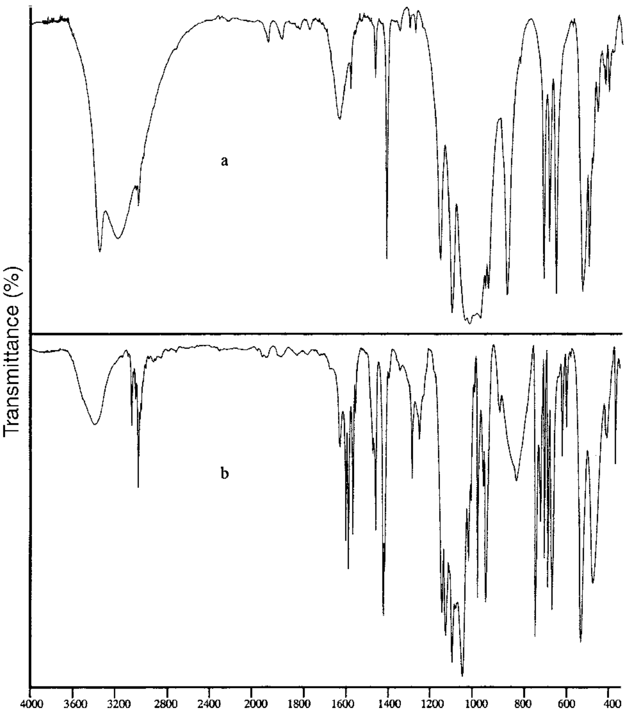

Fig. 1 IR spectra for (a) $In(O_3PC_6H_5)(O_2(OH)PC_6H_5){\cdot}H_2O$ and (b) $In(O_3PC_6H_5)(O_2P(OH)C_6H_5)(C_{10}H_8N_2){\cdot}H_2O$ **1**.

The FTIR spectra for the phenanthroline analogues are very similar; for example, phenylphosphonatophenanthrolineindium(III) **4** exhibits broad peaks at 3568 and 3508 cm^{-1} due to the OH stretch, with a small weak peak at 1615 cm^{-1} due to the OH bending vibration of water. The higher frequency of the OH stretch suggests that the water is non-coordinated. A relatively weak band due to the CH stretching mode of the phenyl ring is present at 3056 cm^{-1}, with a very sharp and intense peak 1433 cm^{-1} due to the aromatic CH bend. The vibrations associated with the PO_3 moiety are observed between 1000 and 1200 cm^{-1}. The peaks characteristic of the out-of-plane CH vibrations are located at 734, 722 and 695 cm^{-1}. Peaks appearing due to the phenanthroline ligand are observed at 1601, 1586, 1525 and 1497 cm^{-1}, consistent with the coordination of the amine to the metal.[43] The phenanthroline derivative of indium(III) benzylphosphonate **5** displays similar absorptions, with the only major difference being the presence of a CH vibration due to the CH_2 group in the benzylphosphonate appearing at 1431 cm^{-1}. The methylphosphonate **6** derivative contains the methyl CH absorption at 1322 cm^{-1}.

Thermal gravimetric analyses (TGA)

The TGA of **1** indicates a small mass loss below 150 °C due to water (observed 3.0%, expected 3.0%). Two major thermal decompositions observed between 390 and 490 °C (observed 25.0%, calculated 25.2%) and between 495 and 700 °C (observed 20.2%, calculated 25.2%) are attributed to the loss of organic groups. The TGA of the indium(III) phenylphosphonate contained a mass loss above 500 °C[25,26] due to phenyl group decomposition. This suggests that the second mass loss in **1** is attributable to the bipyridyl ligand and the third mass loss to the organic phenyl group attached to the phosphonate, as suggested by the observed percentage decomposition figures. Decomposition of the organophosphonate group is often incomplete,[19] as observed in this case. The bidentate 2,2′-bipyridyl ligand incorporated into a zirconium phosphate system was found to decompose between 330 and 400 °C,[36] consistent with these assignments. The TGA for the benzylphosphonate **2** contained four mass losses, the two observed between 50 and 145 °C and betweem 200 and 250 °C being attributable to the combined loss of water (observed 2.7%, expected 2.9%). This observation suggests two types of water are present, probably lattice/intercalated and coordinated water.[36] Observed mass losses occurring between 245 and 390 °C and between 415 and 615 °C are due to decomposition of the bipyridyl and benzyl groups respectively. The methylphosphonate **3** displays three major thermal decompositions, observed at 330–400, 400–500 and 500–650 °C. The first two mass losses almost appear as one, but are thought to be due to decomposition of the OH group in **3** (observed 4.4%, calculated 4.5%) and the amine ligand (observed 42.6%, calculated 40.6%). The third mass loss is due to decomposition of the methyl group (observed 4.0%, calculated 4.0%). The TGA for **1** and the parent organophosphonatoindium(III) are shown in Fig. 2.

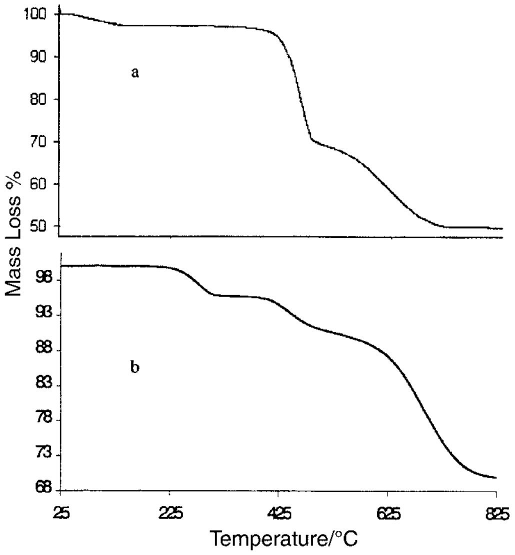

Fig. 2 TGA for (a) $In(O_3PC_6H_5)(O_2P(OH)C_6H_5)(C_{10}H_8N_2)\cdot H_2O$ **1** and (b) $In(O_3PC_6H_5)(O_2(OH)PC_6H_5)\cdot H_2O$.

The TGAs for the phenanthroline derivatives are similar to those of their bipyridyl analogues. Compounds **4** and **5** both exhibit three major mass losses. Consistent with previous suggestions, these are attributed to loss of water, loss of amine ligand and decomposition of the organophosphonate. The thermal decompositions for the phenylphosphonate **4** are observed in the ranges 50–114, 320–400, and 415–590 °C, and those for the benzylphosphonate **5** over 20–110, 270–400 and 450–610 °C. The methylphosphonate **6** displays two major thermal decompositions, observed at 20–110 °C and 420–500 °C, with a minor mass loss at 320–380 °C. The major mass losses are attributed to the loss of water and combined loss of organic material, with the small thermal decomposition between 320 and 380 °C possibly due to the loss of the hydroxy group. The relatively low temperatures for water removal in compounds **4**, **5** and **6** suggest that the water is not directly bonded to the metal [for comparison, the parent compound of **4**, $In(O_3PC_6H_5)(O_2P(OH)C_6H_5)\cdot H_2O$, loses water in the 200–300 °C range[25,26]]. Comparison of the TGA results of the mixed phosphonate/amine ligand systems with those of the corresponding parent indium(III) phosphonates[25,26] indicates a reduced thermal stability for the former. The percentage mass loss of the organics in these compounds was less than theoretically expected due to incomplete combustion of the organic constituents.[19]

Powder X-ray diffraction (XRD)

The powder XRD patterns for previously reported[25,26] indium(III) organophosphonates displayed strong 001 diffractions, consistent with a lamellar solid state structure. One of the reasons for producing the bidentate amine adducts **1** to **6** was to investigate the influence of the coordinated ligands on layering and the inter-layer spacings [relative to the parent indium(III) organophosphonates]. The bipyridyl derivative of indium(III) phenylphosphonate **1** displayed a strong 001 diffraction, consistent with a lamellar solid state structure. However, the d_{001} spacing of 11.34 Å for **1** is significantly less than the d-spacing of the parent indium(III) phenylphosphonate (15.06 Å).[24,25] The inter-layer spacing in metal organophosphonates is governed to some extent by the size of the organic group on the phosphorus, but may also be influenced by the angle of the organic group relative to the metal–oxo plane. The reduced d_{001} spacing for **1** may be explained if bipyridyl coordination reduces the angle of the organophosphonate group relative to the indium–oxo layer. In contrast, the XRD pattern for the phenanthroline derivative **4** does not contain a strong 001 diffraction and is indicative of a non-lamellar structure. Refer to Fig. 3 for powder XRD patterns of **1**, **4** and the parent indium(III) phenylphosphonate.

Indium(III) benzylphosphonate is a lamellar system with a d_{001} spacing of 14.81 Å,[25,26] less than the spacing in the corresponding indium(III) phenylphosphonate (15.06 Å). The reduced spacing for the larger benzyl derivative relative to the phenyl analogue is no doubt indicative of the greater flexibility, and hence reduced steric demands, of the benzyl group containing the methylene (CH_2) link. Addition of the bipyridyl ligand to form **2** and phenanthroline to form **5** in both cases produces compounds with amorphous solid state structures, as indicated by powder XRD patterns. These compounds did not precipitate from the reaction mixture, as observed for the other compounds in this series, but were precipitated by slow evaporation from a gel-like solution. These solubility properties are consistent with a non-polymeric solid state structure. Presumably, bidentate amine coordination with indium(III) benzylphosphonate produces coordinately saturated indium(III) without the involvement of polymerisation. The bipyridyl **3** derivative of indium(III) methylphosphonate exhibited an XRD pattern indicative of a lamellar system, with a d_{001} spacing of 8.83 Å, an increased inter-layer spacing

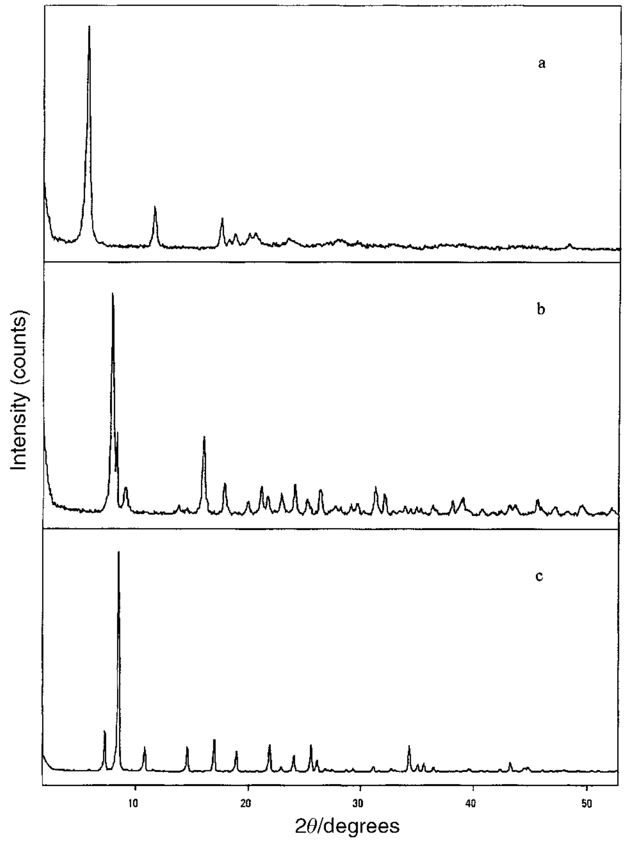

Fig. 3 Powder XRD patterns for (a) $In(O_3PC_6H_5)(O_2(OH)PC_6H_5)\cdot H_2O$, (b) $In(O_3PC_6H_5)(O_2P(OH)C_6H_5)(C_{10}H_8N_2)\cdot H_2O$ **1** and (c) $In(O_3PC_6H_5)(O_2P(OH)C_6H_5)(C_{12}H_8N_2)\cdot H_2O$ **4**.

compared with that in the parent indium(III) methylphosphonate (7.58 Å).[24,25] The XRD pattern for the phenanthroline adduct **6** indicated a non-lamellar structure.

In the phenyphosphonate **1** and methylphosphonate **3** bipyridyl adducts, the changes in the inter-layer spacings are consistent with coordination of the amine to the metal, rather than the alternative of intercalation between layers. If intercalation had occurred, a substantial increase in d_{001} is anticipated. For example, Ferragina *et al.*[36–39] found that intercalation of bipyridyl into lamellar zirconium phosphate increased the interlayer spacing from 6.30 Å in the original zirconium phosphate (α-$Zr(HPO_4)_2\cdot H_2O$) to 10.90 Å, with a corresponding inter-layer spacing of 13.58 Å[36] in the phenanthroline intercalate. The above results also indicate that coordination of bipyridyl in indium(III) phosphonate systems in some cases retains the lamellar structure, unlike phenanthroline coordination.

Solid state NMR

The ^{31}P NMR spectrum for the bipyridyl derivative of indium(III) phenylphosphonate **1** contained one broad phosphorus resonance at δ 2.5, and the ^{13}C NMR spectrum one broad peak (δ 126) and two smaller shoulders (at δ 145 and 139). The NMR spectrum of the phenanthroline derivative **4** contained two ^{31}P peaks (δ 1.7 and −6.7) and one broad ^{13}C peak at δ 123, with a small shoulder at approximately δ 140. The single broad peak for **1** and the two resonances for **4** suggest at least two phosphorus sites, presumably due to the presence of the monoanionic and dianionic forms of phenylphosphonate. This has been observed for similar compounds.[16] The ^{13}C NMR for the parent phenylphosphonate compound contained one peak at δ 136 due to aromatic phenyl carbon peaks,[25,26] with some asymmetry suggesting site differences for the ring, and/or possibly phosphorus coupling with the carbons. These types of 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. The aromatic carbon peaks associated with the bidentate amine ligands also appear in this region, hence giving rise to quite broad peaks with some fine structure in the ^{13}C spectra for both **1** and **4**. The ^{31}P and ^{13}C NMR spectra for **1** are shown in Fig. 4.

The ^{31}P NMR for the bipyridyl **2** and phenanthroline **5** derivatives of indium(III) benzylphosphonate both contained one very broad peak at δ 22.5. Since peaks in the ^{31}P NMR spectra indicative of a single phosphorus site are usually very narrow, the broadness of the peaks observed for **2** and **5** suggest at least two phosphorus sites, corresponding to the monoanionic and dianionic forms of the phosphonate anion. The ^{13}C NMR spectra for these compounds both contain a very broad peak at δ 134, with shoulders around δ 150 due to aromatic group carbons. An additional peak around δ 43 is due to the benzyl CH_2 group.

The ^{31}P NMR spectrum for the bipyridyl indium(III) methylphosphonate **3** contains one phosphorus peak at δ 20, which is a little broad, possibly indicative of unresolved peaks, but only one chemical site is anticipated based on the proposed formulation. The phenanthroline derivative **6** on the other hand contains two peaks at δ 18.5 and 21, clearly indicative of two phosphorus sites that are not represented in the proposed chemical formulation, although two peaks may arise from isomerism about the metal centre induced by the asymmetry of the ligand bonding. The ^{13}C NMR spectra for **3** and **6** contain the methyl group signal appearing as a small peak around δ 24, as expected for methylphosphonates. A peak due to aromatic carbons in the amine ligands, the only aromatic groups present in the methylphosphonate systems, is present around δ 134, with a small shoulder at δ 154.

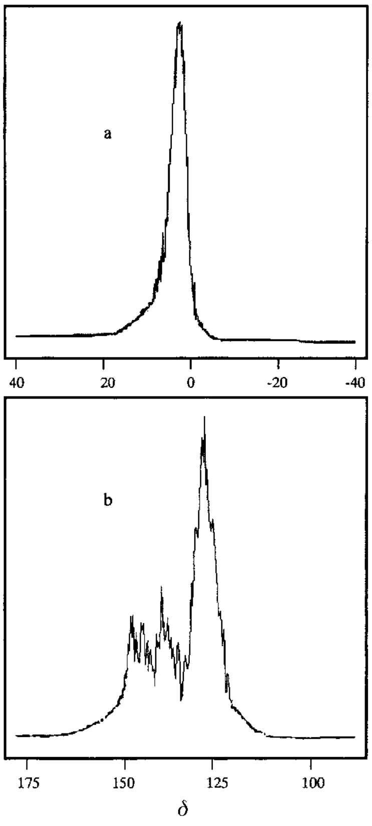

Fig. 4 (a) Solid state ^{31}P NMR of $In(O_3PC_6H_5)(O_2P(OH)C_6H_5)(C_{10}H_8N_2)\cdot H_2O$ **1** and (b) solid state ^{13}C NMR for $In(O_3PC_6H_5)(O_2P(OH)C_6H_5)(C_{10}H_8N_2)\cdot H_2O$ **1**.

Conclusion

Indium(III) phosphonates prepared in the presence of bidentate amine ligands 2,2′-bipyridyl and 1,10-phenanthroline result in mixed phosphonate/amine systems **1** to **6**, where the amine is coordinated to the metal. For compounds **1**, **2**, **4** and **5**, the bidentate amine derivatives of the phenyl- and benzylphosphonates contain the phosphonate in both the dianionic and partially deprotonated monoanionic forms. For the methylphosphonates **3** and **6** the phosphonate is present in the dianionic form only. The FTIR and MAS-NMR spectra of these compounds were consistent with these formulations. All compounds except **3** were found to be hydrated systems, with both coordinated and non-coordinated water in **1** and **2**, and non-coordinated water in **4**, **5** and **6**. Powder XRD measurements suggest that **1** and **3** are layered in the solid state, with inter-layer spacings decreased and increased respectively relative to the parent indium(III) organophosphonates. For both of these layered compounds, coordination of the bidentate amine removes some of the interconnectivity of the bonding. The question then arises as to how layering is achieved. In most binary metal organophosphonates, connectivity is achieved through octahedral coordination around the metal cation. This normally involves five oxygen atoms from phosphonate groups and a single oxygen from a water molecule or hydroxo group. In the ternary compounds **1** and **3**, which do not have water directly bonded to the indium cation, the replacement of two oxygens by bipyridyl would still retain sufficient connectivity through phosphonate oxygens to maintain a lamellar system. Coordination of the bipyridyl amine leads to a decreased inter-layer spacing for the phenylphosphonate **1**, but a slightly increased inter-layer dimension for the methylphosphonate **3**. These observations reflect the different abilities of the organophosphonate ligands in the indium(III) coordination sphere to accommodate the steric demands of the bipyridyl ligand. Observed FTIR and solid state MAS-NMR spectra are consistent with the formulations proposed for these compounds.

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