JOURNAL OF Materials CHEMISTRY Communication

Synthesis and characterisation of some lamellar indium phosphonates

Julia Morizzi, Malcolm Hobday* and Colin Rix

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

Received 6th January 1999, Accepted 27th January 1999

A new series of layered indium phosphonates, an arsonate and a phosphinate have been prepared in which the phosphonate compounds and the arsonate contain the ligand in both di-anion and mono-anion forms.

Over recent years there has been considerable interest in the synthesis of open-framework metal phosphonates owing to their potential applications in the areas of sorption, ion exchange, catalysis and sensors.[1–5] To date, research in this area has focussed on the synthesis and characterisation of divalent,[6–11] trivalent[8,12,13] and tetravalent metal[14–20] phosphonates of the transition metals. With some exceptions, for example copper[21] and lanthanum,[8,22] the metal ions in these lamellar systems are octahedrally coordinated and the organophosphonate moieties are directed into the interlayer space.

Research into the phosphonates of the p-block Group 13 metals has focussed on aluminium,[23,24,26–29] with some recent interest in gallium.[25] To our knowledge, the present communication reports the first layered indium phosphonate compounds, as well as an indium phosphinate and arsonate. These compounds were synthesised 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. When the indium solution was added to a solution of the appropriate acid, a white precipitate formed immediately. The suspension was then sealed in a Teflon-lined stainless-steel autoclave and heated at 160 °C for 6.5 days. The white solid produced was collected by filtration, washed with milli-Q ultrapure water, dried in air and then dried over phosphorus pentoxide. The resulting compounds were characterised by elemental analysis, FTIR, TG, powder XRD, ^{31}P and ^{13}C MAS NMR.

For the phosphonic and arsonic acid derivatives the elemental analysis is consistent with a 1 : 2 ratio of In to P or As, whereas analysis of the phenylphosphinic acid derivative indicated a 1 : 3 In to P ratio. The elemental analyses for In, P(As), C and H in the phosphonate (arsonate) compounds give very good agreement with the formulation $In(O_3XR)(O_2X(OH)R)\cdot H_2O$ (where R is Ph, or $PhCH_2$ when X is P, R is Ph when X is As), whilst the phosphinate compound analysis is consistent with $In(O_2P(H)Ph)_3$. A typical analysis is that obtained for $In(O_3PPh)(O_2P(OH)Ph)\cdot H_2O$ (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%). These formulations are consistent with the results from FTIR, TG and other characterisation techniques. An unusual result is the combined presence of the phosphonic (or arsonic) acid in both a fully and partially deprotonated form within the same phosphonate (or arsonate) compound. Analogous compounds have previously been obtained involving cerium,[8] lanthanum,[22] uranyl,[30,31] manganese[32] and iron[13] with mono- and di-anionic ligands, and two aluminium phenylphosphonate compounds[29] have been reported. Phenylphosphonates of both aluminium[23,24,29] and gallium[25] have been isolated with some of these compounds[24,29] possessing a 1 : 2 metal to phosphorus ratio. The phenylphosphinic acid can act only as a monoanion and hence the observed difference in the indium to phosphorous ratio for this compound.

Powder XRD results for these indium compounds all display an intense diffraction from the 001 plane, consistent with the proposed lamellar systems.[14,19,23,24] The powder XRD pattern for the phenylphosphonate compound, shown in Fig. 1, exhibited a strong diffraction, d_{001}, with a spacing between layers equal to 15.06 Å, suggesting that the phenyl groups are perpendicular to the indium–oxo layers. The other phosphonate, arsonate, and phosphinate compounds all exhibited similar XRD patterns, with d_{001} spacings of 15.54 Å for the arsonate, 14.81 Å for the benzylphosphonate, and 14.36 Å for the phosphinate. These spacings compare well with those for similar systems.[23,24]

The TG analyses for the phosphonates and arsonate 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 TG of the phenylphosphonate compound 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, at 370–450 and 450–700 °C, are attributed to the decomposition of organics. The phenylphosphinate compound had one major mass loss above 400 °C due to organic decomposition, consistent with lack of water in the proposed formula. The percentage mass loss for the organics in these compounds was less than theoretically expected. This is most likely due to incomplete degradation of the intercalated organic material and is a common observation for this type of intercalated structure.[23] These types of compounds have previously been recognised for their high thermal stability.[23]

FTIR spectra for the compounds all give well resolved peaks, for example a typical spectrum, that for the phenylphosphonate compound, contains one broad band at 3400 cm^{-1} due to the OH stretch, and another band at 1640 cm^{-1} corresponding to the bending vibration for water. The C–H

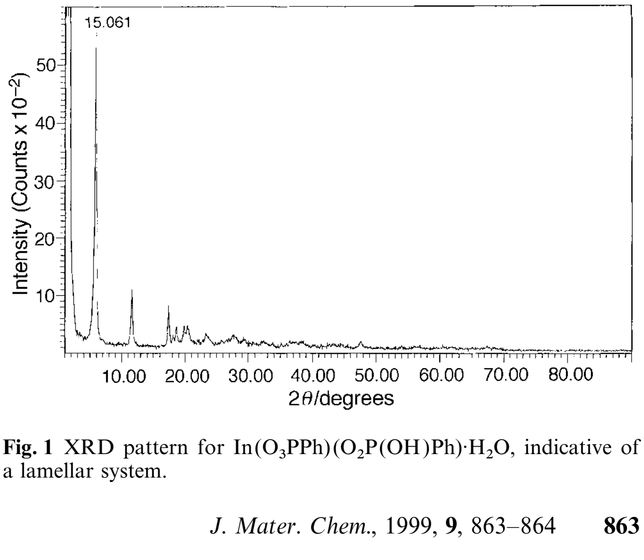

Fig. 1 XRD pattern for $In(O_3PPh)(O_2P(OH)Ph)\cdot H_2O$, indicative of a lamellar system.

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 in the range 1000–1500 cm^{-1} whilst the corresponding AsO_3 peaks in the arsonate compound are observed in the range 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 difference observed between the FTIR spectra for the phosphonates and phosphinate is the presence of a peak of medium intensity in the phosphinate spectrum at 2372 cm^{-1} which is characteristic of a P–H stretching vibration. The benzylphosphonate compound exhibits CH bands located at *ca.* 1400 and 1500 cm^{-1}.

Solid state MAS NMR spectra for all compounds are consistent with the proposed formulations. The ^{31}P MAS NMR spectrum for the phenylphosphonate compound contains only one resonance at 21.9 ppm (relative to potassium dihydrogen orthophosphate as standard), suggesting a single site for phosphorus. This contrasts with the ^{31}P NMR spectrum for the benzylphosphonate compound which clearly has two distinct peaks at 27.6 and 32.4 ppm, indicative of two phosphorus sites in the structure. The phosphinate compound contains one broad ^{31}P peak at 20.7 ppm which could be due to two unresolved peaks. The ^{13}C MAS NMR spectra for these compounds contain aromatic carbon peaks at *ca.* 135 ppm, which is as anticipated, however the peaks are a little asymmetrical, suggesting some site differences for the ring, or that phosphorus couples with the carbon atoms. The benzylphosphonate contains a methylene carbon peak at 43 ppm.

The results described in this communication form part of a more extensive systematic study of layered compounds containing the Group 13 elements Al, Ga and In which will subsequently be fully reported.

Acknowledgements

The authors thank the following people for their assistance: Mr Ian McPhail from RMIT for running XRD on the samples; Dr Craig Morton and Dr Frances Separovic from Melbourne University for recording the MAS NMR spectra, and Dr Caryn Cunningham from Perkin Elmer for obtaining ICP analyses. Julia Morizzi gratefully acknowledges an APA Scholarship. Analyses for In and P were carried out by Perkin Elmer Australia Pty. Ltd., Melbourne, and C, H analyses were carried out by HRL Technology Pty. Ltd., Melbourne.

References

1 J. D. Wang, A. Clearfield and G. Z. Peng, *Mater. Chem. Phys.*, 1993, **35**, 208.

2 B. Z. Wan, R. G. Anthony, G. Z. Peng and A. Clearfield, *J. Catal.*, 1986, **101**, 19.

3 H. Byrd, A. Clearfield, D. M. Poojary, K. P. Reis and M. E. Thompson, *Chem. Mater.*, 1996, **8**, 2239.

4 D. Deniaud, B. Schollorn, D. Mansuy, J. Rouxel, P. Battioni and B. Bujoli, *Chem. Mater.*, 1995, **7**, 995.

5 G. Alberti, M. Casciola and R. Palombari, *Solid State Ionics*, 1993, **61**, 241.

6 G. Cao, H. Lee, V. M. Lynch and T. E. Mallouk, *Inorg. Chem.*, 1998, **27**, 2781.

7 D. Cunningham, P. J. D. Hennelly and T. Deeney, *Inorg. Chim. Acta*, 1979, **37**, 95.

8 G. Cao, V. M. Lynch, J. S. Swinnea and T. E. Mallouk, *Inorg. Chem.*, 1990, **29**, 2112.

9 Y. Zhang and A. Clearfield, *Inorg. Chem.*, 1992, **31**, 2821.

10 K. J. Martin, P. J. Squattrito and A. Clearfield, *Inorg. Chim. Acta*, 1989, **155**, 7.

11 B. Bujoli, O. Pena, P. Palvadeau, J. Lebideau, C. Payen and J. Rouxel, *Chem. Mater.*, 1993, **5**, 583.

12 P. Palvadeu, M. Queignee and J. P. Venien, *Mater. Res. Bull.*, 1988, **23**, 1561.

13 B. Bujoli, P. Palvadeau and J. Rouxel, *Chem. Mater.*, 1990, **2**, 582.

14 A. Clearfield, *Comments Inorg. Chem.*, 1990, **10**, 89.

15 G. Cao, H. Hong and T. E. Mallouk, *Acc. Chem. Res.*, 1992, **25**, 420.

16 M. E. Thompson, *Chem. Mater.*, 1994, **6**, 1168.

17 G. Alberti, U. Constantino, S. Allulli and N. Tomassini, *J. Inorg. Nucl. Chem.*, 1978, **40**, 1113.

18 D. M. Poojary, L. A. Vermeulen, E. Vicenzi, A. Clearfield and M. Thompson, *Chem. Mater.*, 1994, **6**, 1845.

19 G. Huan, A. J. Jacobson, J. W. Johnson and E. W. Corcoran, *Chem. Mater.*, 1990, **2**, 91.

20 J. W. Johnson, J. F. Brody, R. M. Alexander, B. Pilarski and A. R. Katritsky, *Chem. Mater.*, 1990, **2**, 198.

21 Y. P. Zhang, K. J. Scott and A. Clearfield, *Chem. Mater.*, 1993, **5**, 495.

22 R.-C. Wang, Y. Zhang, H. Hu, R. R. Frausto and A. Clearfield, *Chem. Mater.*, 1992, **4**, 864.

23 L. Raki and C. Detellier, *Chem. Commun.*, 1996, 2475.

24 J. E. Haky, J. B. Brady, N. Dando and D. Weaver, *Mater. Res. Bull.*, 1997, **32**, 297.

25 F. Fredoueil, D. Massiot, D. Poojary, M. Bujoli-Doeuff, A. Clearfield and B. Bujoli, *Chem. Commun.*, 1998, 175.

26 L. J. Sawers, V. J. Carter, A. R. Armstrong, P. G. Bruce, P. A. Wright and B. E. Gore, *J. Chem. Soc., Dalton Trans.*, 1996, 3159.

27 K. Maeda, J. Akimoto, Y. Kiyozumi and F. Mizukami, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1199.

28 K. Maeda, J. Akimoto, Y. Kiyozumi and F. Mizukami, *J. Chem. Soc., Chem. Commun.*, 1995, 1033.

29 A. Cabeza, M. A. G. Aranda, S. Bruque, D. M. Poojary, A. Clearfield and J. Sanz, *Inorg. Chem.*, 1998, **37**, 4168.

30 D. M. Poojary, A. Cabeza, M. A. G. Aranda, S. Bruque and A. Clearfield, *Inorg. Chem.*, 1996, **35**, 1468.

31 M. A. G. Aranda, A. Cabeza, S. Bruque, D. M. Poojary and A. Clearfield, *Inorg. Chem.*, 1998, **37**, 1827.

32 A. Cabeza, M. A. G. Aranda, S. Bruque, D. M. Poojary and A. Clearfield, *Mater. Res. Bull.*, 1998, **33**, 1265.

Communication 9/00174C