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Synthesis of layered nickel phosphonate materials based on a topotactic approach†

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Layered nickel phosphonate materials $Ni(O_3PR)\cdot H_2O$ [with $R=C_6H_5$, CH_3, $(CH_2)_2CO_2H$, $(CH_2)_2Br$ and $CH_2C_6H_5$] have been prepared by heating nickel(II) hydroxide with a stoichiometric quantity of the relevant phosphonic acid at the melting temperature of the phosphonic acid. Samples of $Ni(O_3PC_6H_5)\cdot H_2O$ and $Ni(O_3PCH_3)\cdot H_2O$ prepared by this method are identical to those prepared previously by other synthetic routes. In addition, the novel materials $Ni[O_3P(CH_2)_2CO_2H]\cdot H_2O$, $Ni[O_3P(CH_2)_2Br]\cdot H_2O$ and $Ni(O_3PCH_2C_6H_5)\cdot H_2O$ have been synthesised by this method. The structural properties of these materials are assessed in detail, and compared with the structural properties of other materials containing the same phosphonates but different divalent metals. The synthetic method reported here appears to be a general approach for preparation of layered metal phosphonates, for cases in which the phosphonic acid undergoes melting rather than decomposition at elevated temperatures.

Introduction

During the past few years, the study of layered metal phosphonate materials has become a well developed field within inorganic solid state chemistry. Early research concentrated on phosphonates of tetravalent metals (particularly Zr and Ti),[1–3] although more recent work has encompassed compounds of divalent and trivalent metals.[4–9] Here, we focus on phosphonates of divalent metals, for which the general formula is $M(O_3PR)\cdot nH_2O$ (in general, $n=1$), with particular interest in the compounds formed between nickel(II) and the following anions: phenylphosphonate [$R=C_6H_5$], methylphosphonate [$R=CH_3$], 2-carboxyethylphosphonate, [$R=(CH_2)_2CO_2H$], 2-bromoethylphosphonate [$R=(CH_2)_2Br$] and benzylphosphonate [$R=CH_2C_6H_5$].

For divalent transition metals, most studies have been carried out on phenylphosphonate and alkylphosphonate materials. There are few reports of phosphonates with other organic functional groups.[6,8] The relative lack of functional variation in the organic group (in contrast, for example, to the functional diversity in studies reported for tetravalent metals) may be due to the fact that the presence of functional groups in the phosphonic acid often induces the formation of specific complexes between the functional group and the metal, rather than layered materials. Another difficulty is the lack of universal synthetic procedures for the formation of isostructural materials containing different metals; thus, the nature of the metal often dictates different preparative conditions, as illustrated by comparisons between iron(II) phenylphosphonate and copper(II) phenylphosphonate.[7]

We now consider relevant structural aspects of layered divalent metal phosphonate materials that have been studied previously. Cunningham and Hennelly[7] reported the synthesis of a series of phenylphosphonates of divalent metals and deduced from electronic spectra that the metals in these materials have octahedral coordination. This interpretation was confirmed subsequently from structural studies.[5,10] Martin *et al.*[5] reported that nickel phenylphosphonate is isostructural with zinc, copper and magnesium phenylphosphonates; the structure is orthorhombic (space group $Pmn2_1$; $a=5.63$ Å, $b=14.34$ Å, $c=8.33$ Å). Cao *et al.*[10] reported similar findings for phenylphosphonates of magnesium, zinc and manganese.

The structures of phosphonates of divalent metals differ markedly from the structures of the extensively studied zirconium phosphonate materials.[11] In zirconium phosphonates, the three oxygens of each phosphonate group are bonded to three different zirconium atoms, and each zirconium atom has octahedral coordination to six oxygens from six different phosphonate groups. It has been shown[5,10] that the structures of divalent metal phosphonates tend to comprise zigzag layers, with the coordination of the metal substantially different from that in zirconium phosphonates. For each phosphonate group (see Fig. 1), two oxygens (described as 'bridging type') form a bridge between a pair of metal atoms, whereas the third oxygen (described as 'terminal type') is coordinated to only one metal atom. Each metal atom (see Fig. 1) is coordinated by six oxygens with approximately octahedral symmetry (we refer to this loosely as 'octahedral coordination'). These six oxygens comprise four of bridging type (from four different phosphonates), one of terminal type (again from a different phosphonate), and one from a water molecule. It has been shown that this water molecule can be removed, allowing the vacant coordination site to be filled by a molecule of ammonia or another small Lewis base.[4]

Zinc 2-carboxyethylphosphonate and copper 2-carboxyethylphosphonate have yet another structure,[9] in which the metal has tetrahedral coordination, with one coordination site around the metal filled by the carbonyl oxygen of the carboxylic acid group rather than a water molecule. Subsequent treatments of these materials were shown to produce the structure described above.

Of the divalent metals, perhaps the least reported in terms of phosphonate chemistry is nickel,[5,7] and in this paper we focus exclusively on a new synthetic approach for the production of nickel phosphonates. We note that a reaction between a $Mg/Al/CO_3$ layered double hydroxide (or its calcined oxide) and molten phenylphosphonic acid has been explored recently[12] as a possible synthetic route to prepare layered phosphonates in a topotactic manner.

In the work reported in the present paper, nickel(II) hydroxide has been shown to undergo solid state reactions with phenylphosphonic acid and methylphosphonic acid to form materials that are identical to the nickel phenylphosphonate and nickel methylphosphonate reported previously. The method has also been applied to synthesise the new materials nickel 2-carboxyethylphosphonate, nickel benzylphosphonate and nickel 2-bromoethylphosphonate.

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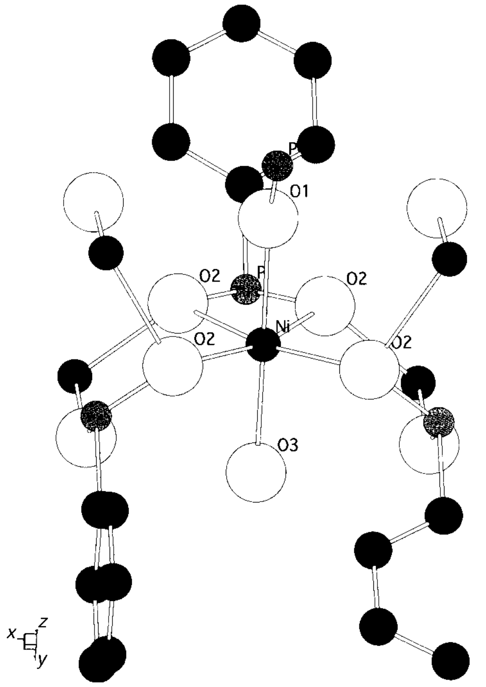

Fig. 1 Specification of the coordination geometry around the metal atoms in a typical layered metal(II) phosphonate material (see text for full discussion). O1 represents oxygens of 'terminal type' in phenylphosphonate anions; O2 represents oxygens of 'bridging type' in phenylphosphonate anions; O3 represents oxygens in water molecules.

Table 1 Melting points (determined in this work) of the phosphonic acids used in the preparation of nickel phosphonates

phosphonic acid	melting point/°C
methylphosphonic acid	104–105
phenylphosphonic acid	166–167
benzylphosphonic acid	164–165
2-carboxyethylphosphonic acid	164–165
2-bromoethylphosphonic acid	85–86
2-aminoethylphosphonic acid	> 300 (decomp.)

Experimental

Starting materials

Nickel(II) hydroxide, phenylphosphonic acid, methylphosphonic acid and 2-carboxyethylphosphonic acid were used as supplied (Aldrich), without further purification.

Benzylphosphonic acid and 2-bromoethylphosphonic acid were prepared by the following method following ref. 9. Diethylbenzylphosphonate or diethyl-2-bromoethylphosphonate (0.02 mol) was refluxed, together with trimethylchlorosilane (0.16 mol) and dry potassium bromide (0.12 mol), in acetonitrile (50 ml) for 2 days. The resultant solution was filtered over Celite to remove the undissolved potassium bromide, and the filtrate was then evaporated and distilled under reduced pressure. Water (10 ml) was added to the resulting liquid and the solution was stirred for 2 h. The aqueous phase was washed with dichloromethane and then evaporated to dryness to leave the acid. Melting points of the benzylphosphonic acid and 2-bromoethylphosphonic acid samples produced by this method were 164–165 °C and 85–87 °C respectively.

Preparation of nickel phosphonate materials

Nickel(II) hydroxide was mixed with a stoichiometric quantity of the relevant phosphonic acid. The mixture was ground thoroughly, and placed in a thick Pyrex tube (capable of withstanding pressures up to 200 psi) which was sealed with a Teflon screw cap. The reaction mixtures were then heated at the melting point of the phosphonic acid (Table 1) for 3 days. All reactions with the phosphonic acids discussed above afforded pale yellow–green materials. The products were suspended in deionised water, recovered by filtration, and then washed thoroughly to remove any unreacted phosphonic acid. The solid products were then dried in air at 60 °C for about 30 min.

The product from an attempted reaction involving 2-aminoethylphosphonic acid was black in colour, indicating that the phosphonic acid had decomposed. Powder X-ray diffraction indicated that this product is amorphous, and no further characterisation of this product was undertaken.

Characterization

Powder X-ray diffraction patterns were recorded using Cu-Kα_1 radiation on a Siemens D5000 diffractometer, operating in transmission mode with a primary beam germanium monochromator. FTIR spectra were recorded as KBr pellets using a Perkin Elmer Paragon 1000 FTIR spectrometer. Room temperature magnetic susceptibility measurements were recorded using a Johnson Matthey magnetic susceptibility balance. Thermogravimetric analyses were carried out using a Stanton Redcroft 870 instrument referenced against recalcined alumina. Samples were heated in air, at 10 °C min^{-1}, to a maximum temperature of 1000 °C. Solid state ^{31}P and ^{13}C MAS NMR spectroscopy was also attempted using a Bruker MSL300 spectrometer, but due to the paramagnetic nature of Ni^{II}, the spectra were too broad to yield any useful information.

Results and Discussion

All materials prepared are pale yellow–green in colour, and are markedly different from the emerald green colour of the nickel(II) hydroxide starting material. There is some variation in the colour of the different samples, with the nickel benzylphosphonate and nickel phenylphosphonate having a more yellow shade than the others.

Results of elemental analyses (carbon and hydrogen percentages) of the materials are given in Table 2, together with values calculated on the assumption that the materials have the stoichiometry $Ni(O_3PR)\cdot H_2O$. The carbon and hydrogen analyses of all five materials are in good agreement with this stoichiometry.

Thermogravimetric curves (Fig. 2) for all materials exhibit stepwise mass losses. The first endothermic mass loss, which is gradual and begins below 100 °C for all materials, may be attributed to loss of water. Clearly this is consistent with the suggestion that all these materials have a removable water molecule in the coordination sphere of the metal, as demonstrated previously for nickel phenylphosphonate.[7] For nickel

Table 2 Elemental analyses (carbon and hydrogen percentages) and total percentage mass losses determined by thermogravimetric analysis for nickel phosphonates (calculated values, as discussed in the text, are in parentheses)

material	% C	% H	% mass loss
$Ni(O_3PCH_3)\cdot H_2O$	7.07 (7.04)	2.85 (2.95)	15.82 (14.67)
$Ni(O_3PC_6H_5)\cdot H_2O$	30.97 (30.95)	2.91 (3.03)	36.19 (36.19)
$Ni[O_3P(CH_2)_2CO_2H]\cdot H_2O$	15.67 (15.75)	3.02 (3.08)	36.76 (36.32)
$Ni(O_3PCH_2C_6H_5)\cdot H_2O$	33.64 (34.07)	3.52 (3.68)	65.95 (66.09)
$Ni[O_3P(CH_2)_2Br]\cdot H_2O$	9.31 (8.75)	2.28 (2.20)	44.98 (44.75)

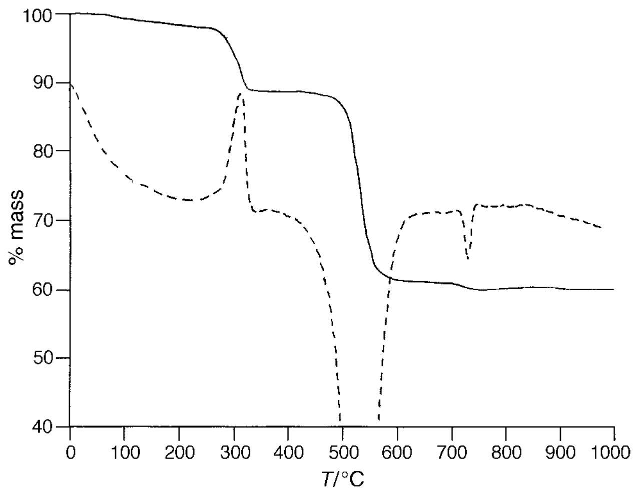

Fig. 2 Thermogravimetric analysis (solid line) and DTA (dotted line) curves for nickel phenylphosphonate

phenylphosphonate, nickel methylphosphonate, nickel benzylphosphonate and nickel 2-bromoethylphosphonate, there is then an exothermic mass loss in the region 520–550 °C, which is attributed to ignition (oxidation) of the organic part of the material. This observation is in good agreement with a previous report[7] of a mass loss at 560 °C for nickel phenylphosphonate, and is consistent with a report[4] that removal of the phenyl ring from zinc and cobalt phenylphosphonates commences above 500 °C. A further exothermic mass loss is observed between 685 °C and 725 °C, as the material is further oxidised. From powder X-ray diffraction, the product of these calcinations is identified as $Ni_2P_2O_7$. The magnitudes of the total mass losses (Table 2) are in good agreement with those calculated on the basis of the formula $Ni(O_3PR)\cdot H_2O$.

The thermogravimetric curve (Fig. 3) for nickel 2-carboxyethylphosphonate is somewhat more complex. The first gradual mass loss begins around 100 °C and is attributed to the loss of a water molecule, as discussed above. Another endothermic mass loss occurs at 460 °C, and is assigned tentatively to condensation of the carboxylic acid groups to form an anhydride. This mass loss overlaps with an exothermic mass loss at 530 °C, as observed for the samples discussed above and ascribed to oxidation of the organic part of the material. A final exothermic oxidative step is observed at 780 °C. The final product is again identified as $Ni_2P_2O_7$ on the basis of powder X-ray diffraction.

Powder X-ray diffraction data (Fig. 4 and Appendix 1), recorded at ambient temperature, show that all materials are highly crystalline and contain no unreacted nickel(II) hydroxide. From these diffractograms, the interlayer spacing (defined as the perpendicular distance between the centres of adjacent layers) is related to the periodic spacing along the *b* axis [determined from the (0*k*0) reflections]. The powder X-ray diffractograms for nickel methylphosphonate and nickel phenylphosphonate are in good agreement with those reported[10] for samples prepared by other synthetic methods, and the interlayer spacings determined for nickel methylphosphonate and nickel phenylphosphonate are 8.70 Å and 14.33 Å respectively. The powder X-ray diffractograms can be indexed on the basis of the orthorhombic unit cells given in Table 3. The interlayer spacings and lattice parameters compare well with those of materials,[10] containing other metals, that are believed to be isostructural (Table 3).

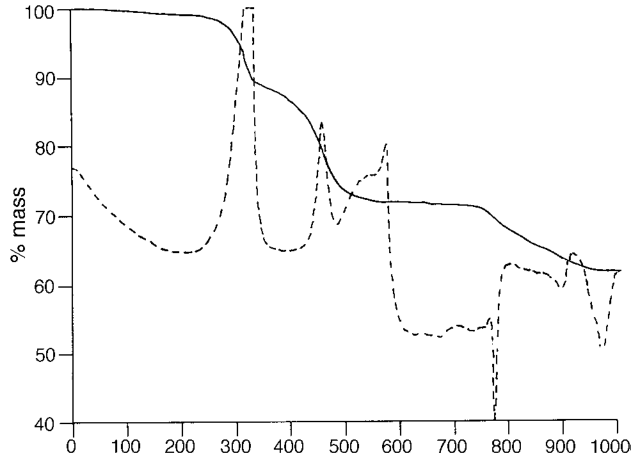

Fig. 3 Thermogravimetric analysis (solid line) and DTA (dotted line) curves for nickel 2-carboxyethylphosphonate

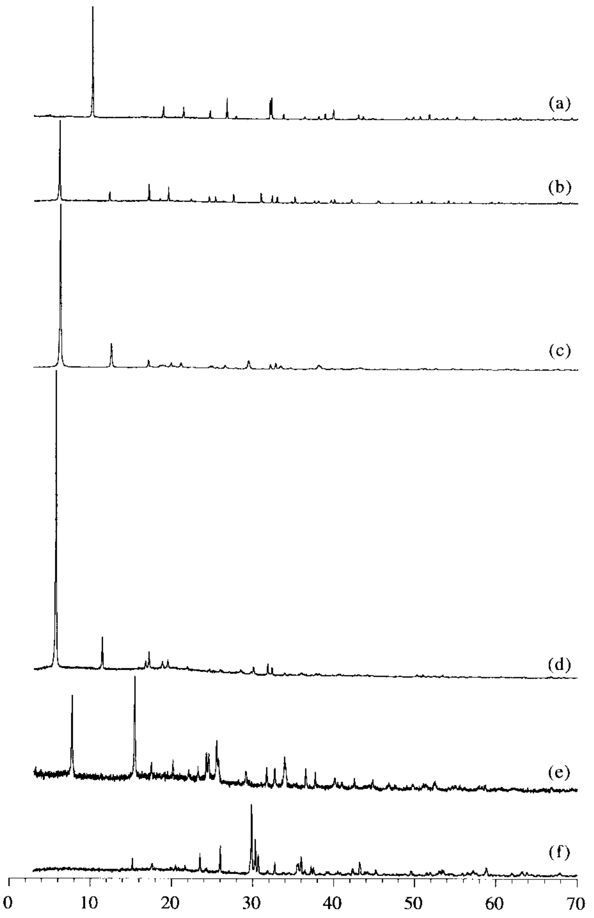

Fig. 4 Powder X-ray diffractograms for: (a) nickel methylphosphonate, (b) nickel phenylphosphonate, (c) nickel 2-carboxyethylphosphonate, (d) nickel benzylphosphonate, (e) nickel 2-bromoethylphosphonate, and (f) the product ($Ni_2P_2O_7$) obtained following thermogravimetric analysis of the nickel phosphonates. The indexing of the powder X-ray diffractograms is specified in the Appendix.

The powder X-ray diffractogram recorded for nickel 2-carboxyethylphosphonate exhibits a strong series of (0*k*0) reflections, as typically observed for layered materials. The interlayer spacing is determined to be 14.13 Å, based on the assumption that the first peak is the (020) reflection. The diffractogram can be indexed on the basis of an orthorhombic unit cell ($a = 5.57$ Å, $b = 28.27$ Å, $c = 4.71$ Å), and initial inspection suggests that the space group is $Pmn2_1$. These results suggest that the material may have essentially the same structure type as nickel phenylphosphonate and nickel methylphosphonate; the metal probably has six-fold coordination with approximately octahedral symmetry (subsequently, this is referred to loosely as 'octahedral coordination'). This differs

Table 3 Lattice parameters for selected layered phosphonate materials of divalent metals

material	reference	a/Å	b/Å	c/Å	β/°
$Ni(O_3PCH_3)\cdot H_2O$	this paper	5.59(1)	8.70(1)	4.73(1)	—
$Mg(O_3PCH_3)\cdot H_2O$	10	5.68	8.72	4.79	—
$Mn(O_3PCH_3)\cdot H_2O$	10	5.82	8.79	4.91	—
$Ni(O_3PC_6H_5)\cdot H_2O$	this paper	5.54(1)	14.33(1)	4.79(1)	—
$Mg(O_3PC_6H_5)\cdot H_2O$	10	5.61	14.28	4.82	—
$Mn(O_3PC_6H_5)\cdot H_2O$	10	5.73	14.33	4.95	—
$Ni[O_3P(CH_2)_2CO_2H]\cdot H_2O$	this paper	5.57(1)	28.27(1)	4.71(1)	—
$Ni(O_3PCH_2C_6H_5)\cdot H_2O$	this paper	5.62(1)	30.86(2)	4.76(1)	—
$Ni[O_3P(CH_2)_2Br]\cdot H_2O$	this paper	5.64(1)	11.46(1)	4.77(1)	90.6(8)

from the structures[9] of zinc 2-carboxyethylphosphonate and copper 2-carboxyethylphosphonate, both of which have tetrahedral coordination of the metal, as discussed in the Introduction. Furthermore, the interlayer spacings are considerably smaller for copper 2-carboxyethylphosphonate (7.55 Å) and zinc 2-carboxyethylphosphonate (9.43 Å) than for nickel 2-carboxyethylphosphonate (14.13 Å). On the basis of the above comparisons, we propose that in nickel 2-carboxyethylphosphonate, the nickel is not coordinated by oxygens from the carboxylic acid group. The fact that the periodicity of the structure along the b axis is double the interlayer spacing ($b \approx 2 \times 14.13$ Å) is probably due to a slight distortion in the structure induced by hydrogen bonding between the carboxylic acid groups, as also observed in zirconium 2-carboxyethylphosphonate.[13]

The powder X-ray diffraction pattern for nickel benzylphosphonate is again indexed on the basis of an orthorhombic unit cell (Table 3), with space group $Pmn2_1$. Unlike nickel phenylphosphonate, the b axis is doubled, probably due to distortions in the structure relating to the orientations of the phenyl rings.

The powder X-ray diffraction pattern for nickel 2-bromoethylphosphonate is indexed by a monoclinic unit cell ($a = 5.64$ Å, $b = 11.46$ Å, $c = 4.77$ Å, $\beta = 90.6°$). Although there is a reduction in symmetry in comparison with the materials discussed above, the distortion of the lattice from orthorhombic metric symmetry is not large (the angle β is close to 90°), and on the basis of magnetic susceptibility measurements (see below) the metal is thought to have essentially the same octahedral environment as that in the other materials studied. On this basis, the structure of nickel 2-bromoethylphosphonate probably does not differ substantially from the structures of the other materials reported here.

The IR spectra (Fig. 5) of nickel methylphosphonate and nickel phenylphosphonate are relatively straightforward to assign. Bands at around 3450 and 3420 cm^{-1} are attributed to stretching vibrations of coordinated water molecules; the strong sharp nature of these bands indicates that the water is coordinated to the metal, rather than located in the interlayer region (which would lead to broadening of the band due to the formation of hydrogen bonds between water molecules). Bands in the 1150–980 cm^{-1} region for both materials are associated with P—O vibrations. For nickel phenylphosphonate, aromatic C—H stretching bands are at 3080 and 3030 cm^{-1} and there is a strong deformation band at 1436 cm^{-1}. For nickel methylphosphonate, aliphatic C—H stretching bands are at 2994 and 2925 cm^{-1}.

The IR spectrum of nickel 2-carboxyethylphosphonate provides good insight into the coordination around the metal. Sharp bands at 3455 and 3417 cm^{-1} are attributed to water molecules coordinated to the metal. These bands are superimposed on a broad band, centred around 3400 cm^{-1}, which is due to the hydroxyl groups of the carboxylic acid and broadened as a result of hydrogen bonding between groups at the interface between adjacent layers. A strong band at 1698 cm^{-1} is due to the C=O group of the carboxylic acid. For zinc 2-carboxyethylphosphonate and copper 2-carboxyethylphosphonate,[9] this band is at about 1583 cm^{-1}, with the lower frequency due to coordination of the C=O group to the metal in these materials; an attempt to intercalate a base into these materials was reported to lead to disruption of this coordination, with the C=O stretching band moving to 1703 cm^{-1}. The clear conclusion is that the C=O group in nickel 2-carboxyethylphosphonate is not bound to the metal, and instead participates in the hydrogen bonding between carboxylic acid groups at the interface between adjacent layers. Finally, bands in the region 3120–2930 cm^{-1} are assigned as C–H stretching modes of the methylene groups, and bands in the region 1150–980 cm^{-1} are associated with P—O vibrations.

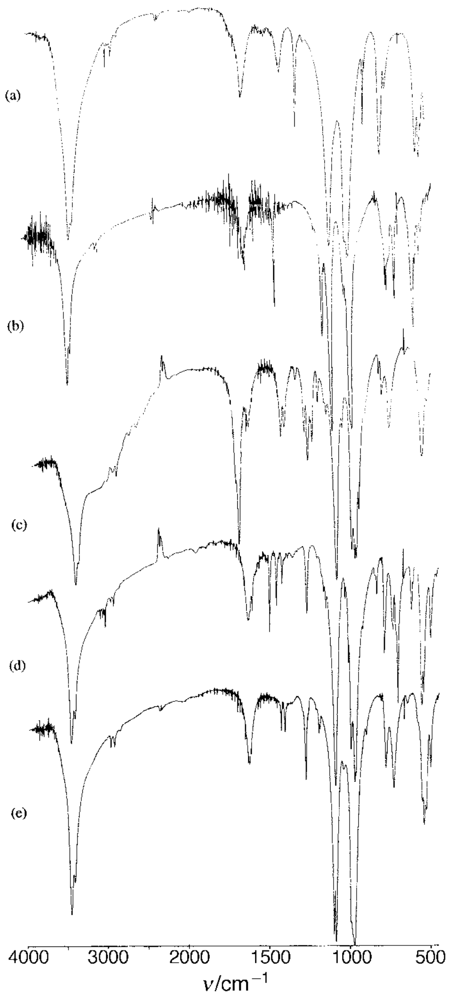

Fig. 5 FTIR spectra for: (a) nickel methylphosphonate, (b) nickel phenylphosphonate, (c) nickel 2-carboxyethylphosphonate, (d) nickel benzylphosphonate, and (e) nickel 2-bromoethylphosphonate

IR spectra of the products retrieved from the thermogravimetric analyses for all materials confirm that the calcination product is $Ni_2P_2O_7$[ν(P—O—P) 980 cm^{-1}] in each case.

Table 4 Magnetic moments calculated from room temperature magnetic susceptibility data

	μ/μ_B
hydrated materials	
$Ni(O_3PCH_3)\cdot H_2O$	3.54
$Ni(O_3PC_6H_5)\cdot H_2O$	3.16
$Ni[O_3P(CH_2)_2CO_2H]\cdot H_2O$	3.14
$Ni(O_3PCH_2C_6H_5)\cdot H_2O$	3.11
$Ni[O_3P(CH_2)_2Br]\cdot H_2O$	3.31
dehydrated materials	
$Ni(O_3PCH_3)$	3.23
$Ni(O_3PC_6H_5)$	2.88
$Ni[O_3P(CH_2)_2CO_2H]$	2.98
$Ni(O_3PCH_2C_6H_5)$	2.90
$Ni[O_3P(CH_2)_2Br]$	2.95

The magnetic moments, calculated from the room temperature magnetic susceptibilities, are in the range 3.1–3.6 μ_B for all materials (Table 4. These values are typical of compounds in which Ni^{2+} has an octahedral environment.[14] For nickel 2-bromoethylphosphonate, this provides some evidence that the environment around the metal is still close to octahedral, despite the suggestion that the crystal symmetry is different from that in the other materials. All observed values are in excess of the spin only magnetic moment for Ni^{2+} ($\mu_S = 2.83\ \mu_B$), but less than the value expected if orbital angular momentum is accounted for ($\mu_{S+L} = 4.47\ \mu_B$), due to partial quenching.

On heating above 100 °C, all materials lose the water molecule coordinated to the metal, resulting in a decrease in the magnetic moment. This has also been observed for cobalt phenylphosphonate,[4] and is consistent with a decrease in the coordination number of the metal. IR spectra also confirm the removal of the water molecule coordinated to the metal, from the loss of the sharp bands around 3455 cm^{-1} and 3417 cm^{-1}.

Conclusions

The method reported here for synthesis of layered metal phosphonates is straightforward and appears to be a general approach for phosphonic acids that undergo melting rather than decomposition at elevated temperatures. Considering the general equation for the synthesis:

$$Ni(OH)_2 + H_2O_3PR \rightarrow Ni(O_3PR)\cdot H_2O + H_2O$$

the reaction might be considered as a mild, hydrothermal synthesis. There are, however, two major differences between this method and conventional hydrothermal experiments. First, the pressure in the experiments reported here is *ca.* 10–12 atm (estimated on the basis of the quantities of materials and the reaction vessels used), which is lower than typical pressures (50–100 atm) for high pressure syntheses. Second, a layered host matrix that is insoluble in water is used, and the lack of excess water means that the phosphonic acid is not dissolved; mobility of the constituent ions within the molten phase and within the growing product solid phase is clearly implicated.

Syntheses of nickel phenylphosphonate and nickel methylphosphonate result in materials with physical characteristics that are in good agreement with those reported previously. The novel functionalised materials nickel 2-carboxyethylphosphonate, nickel benzylphosphonate and nickel 2-bromoethylphosphonate have been synthesised by our method. The layers within these materials comprise nickel in octahedral coordination, with a removable water molecule included in the coordination sphere around the nickel.

Further preliminary investigations have shown that the preparative method reported here is successful for synthesis of phenylphosphonates of other divalent metals such as copper, cobalt, zinc, manganese and magnesium, the hydroxides of which all have the brucite (magnesium hydroxide) structure. Interestingly, layered hydroxides with other structures (such as aluminium, calcium and barium hydroxides) also yield layered phosphonates by this method. Further work on syntheses involving other metals, and more complex phosphonic acids, is currently in progress.

We are grateful to the Nuffield Foundation and EPSRC for financial support. We wish to thank Dr Colin Greaves for access to thermogravimetric analysis equipment, and Dr Abil Aliev (University of London Intercollegiate Research Services) for solid state NMR experiments on the materials reported here.

Appendix

Indexing of the powder X-ray diffractograms (see Fig. 4) for the materials discussed in the text.

(a) Nickel methylphosphonate $Ni(O_3PCH_3)\cdot H_2O$:

2θ/degrees	d/Å	h k l
10.15	8.707	0 1 0
18.86	4.700	1 1 0
21.39	4.151	0 1 1
24.65	3.608	1 0 1
26.73	3.332	1 1 1
27.86	3.200	0 2 1
32.04	2.791	2 0 0
32.23	2.775	1 2 1
33.68	2.659	2 1 0
36.32	2.472	0 3 1
38.05	2.363	0 0 2
38.83	2.317	2 1 1
39.48	2.280	0 1 2
39.86	2.260	1 3 1

(*b*) Nickel phenylphosphonate $Ni(O_3PC_6H_5)\cdot H_2O$:

2θ/degrees	d/Å	h k l
6.13	14.409	0 1 0
12.31	7.184	0 2 0
17.13	5.171	1 1 0
18.51	4.790	0 3 0
19.51	4.545	0 1 1
22.28	3.987	0 2 1
24.55	3.623	1 3 0
25.31	3.516	1 1 1
26.28	3.388	0 3 1
27.55	3.235	1 2 1
30.91	2.890	1 3 1
32.28	2.771	2 0 0
32.88	2.721	2 1 0
34.66	2.586	2 2 0
35.14	2.551	1 5 0
36.39	2.467	0 5 1
37.51	2.395	2 0 1
38.02	2.365	2 1 1
39.57	2.275	2 2 1
39.99	2.253	1 5 1

(*c*) Nickel 2-carboxyethylphosphonate
$Ni[O_3P(CH_2)_2CO_2H]\cdot H_2O$:

2θ/degrees	d/Å	h k l
6.23	14.165	0 2 0
12.51	7.068	0 4 0
17.08	5.187	1 2 0

18.54	4.781	1 3 0
18.82	4.710	0 0 1
19.07	4.650	0 1 1
19.85	4.468	0 2 1
20.26	4.379	1 4 0
21.08	4.212	0 3 1
22.67	3.919	0 4 1
24.70	3.601	1 0 1
24.91	3.571	1 1 1
25.52	3.487	1 2 1
26.50	3.360	1 3 1
27.80	3.207	1 4 1
29.41	3.034	1 5 1
31.22	2.863	1 6 1
32.09	2.786	2 0 0
32.73	2.734	1 9 0
33.34	2.685	1 7 1

(*d*) Nickel benzylphosphonate $Ni(O_3PCH_2C_6H_5)\cdot H_2O$

2θ/degrees	d/Å	$h\ k\ l$
5.72	15.431	0 2 0
11.45	7.724	0 4 0
16.79	5.276	1 2 0
17.21	5.149	0 6 0
18.85	4.704	0 1 1
19.52	4.543	0 2 1
21.91	4.053	0 4 1
24.65	3.609	1 1 1
25.14	3.539	1 2 1
25.99	3.425	0 9 0
27.07	3.291	1 4 1
28.47	3.132	1 5 1
29.78	2.998	0 8 1
30.09	2.968	1 6 1
31.84	2.808	2 0 0
32.35	2.765	2 2 0
33.90	2.642	1 8 1
34.57	2.592	0 10 1
36.00	2.493	1 9 1
37.24	2.413	2 1 1

(*e*) Nickel 2-bromoethylphosphonate $Ni[O_3P(CH_2)_2Br]\cdot H_2O$

2θ/degrees	d/Å	$h\ k\ l$
7.71	11.459	0 1 0
15.45	5.730	0 2 0
17.51	5.059	1 1 0
20.17	4.398	0 1 1
22.09	4.020	1 2 0
23.27	3.819	0 3 0
24.29	3.661	0 2 1
24.58	3.619	1 0 1
25.54	3.485	1 1 −1
25.76	3.455	1 1 1
28.20	3.162	1 3 0
29.17	3.059	1 2 1
31.74	2.817	2 0 0
32.71	2.735	2 1 0
33.90	2.642	1 3 −1
35.41	2.532	2 2 0
36.56	2.455	0 4 1
37.73	2.382	2 1 −1
40.12	2.246	1 4 1
40.99	2.200	1 0 −2

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