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Polymorphism in nickel phosphonates: synthesis of layered and microporous $Ni(O_3PCH_2C(O)NH_2)\cdot H_2O$

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Two new polymorphic nickel phosphonates have been prepared by a reaction between nickel acetate and diethyl cyanomethylphosphonate. The acidity of the nickel solution affects the hydrolysis of the phosphonate to produce the phosphonic acid *in situ*.

Examples of nickel phosphonates, $Ni(O_3PR)\cdot H_2O$, reported in the literature to date are all layered materials.[1,2] Whilst no single crystal data has been reported, almost all of these materials have been shown by powder XRD data to be isostructural with layered Co or Mn phosphonates containing the same organic functional group; indexing yields a = 5.57–5.64 Å, c = 4.71–4.79 Å with b varying with the size of the organic functional group, R. On this basis, we expect the nickel atoms to always have a slightly distorted octahedral coordination environment, composed of five oxygen atoms from phosphonate $-PO_3$ groups and one from a water molecule. The organic functional group is pendant between nickel phosphate layers.[1,2]

The use of bi- and trifunctional phosphonic acids in the synthesis of metal phosphonates can result in the formation of porous materials.[3–6] The metal atoms in these structures are coordinated by the oxygen atoms of the $-PO_3$ group and a donor atom (usually oxygen or nitrogen) of the group at the other end of an alkyl chain. In some cases this coordination is truly bidentate,[3,5] with both ends of the phosphonate anion bonding to the same metal atom, but more usually two different metal atoms are linked in this manner. In the latter case the phosphonate has been referred to as 'double coordinating'.[4,6]

In a recent article the synthesis and crystal structure of $Zn(O_3PCH_2C(O)NH_2)\cdot H_2O$ was reported.[6] The procedure used for synthesising this material used the diethyl phosphonate ester, $(EtO)_2P(O)CH_2CN$, which was hydrolysed *in situ* using the acidity of the zinc solution to yield the acid which subsequently combined with the Zn ions. However, under the conditions of the experiment, the nitrile group was partially hydrolysed resulting in the formation of an amide group. Subsequently, an attempt was made to synthesise a Ni derivative; the results of this attempt are described herein.

The title compound was hydrothermally synthesised by placing a mixture of a solution of 0.92 g nickel acetate tetrahydrate in 10 ml distilled water and 0.656 g (3.7 mmol) diethyl cyanomethylphosphonate in a Teflon-lined stainless steel autoclave of 23 ml volume and heating at 433 K for 48 h. The green $Ni(O_3PCH_2C(O)NH_2)\cdot H_2O$ product was recovered by filtration, washed with distilled water and dried in air at room temperature prior to subsequent investigations. Inspection under a microscope revealed the presence of a few small (0.20 × 0.04 × 0.04 mm) needle shaped crystals amongst the polycrystalline bulk. Single crystal X-ray diffraction data were collected at low temperature (150 K) using a Bruker AXS SMART CCD area-detector diffractometer on the high flux single crystal diffraction station 9.8 at CCLRC Daresbury Laboratory Synchrotron Radiation Source, Cheshire, UK.[7,8]

The single crystal structure determination† showed the crystals to be microporous with two perpendicular channel systems. We believe this to be the first example of a porous nickel phosphonate.

The asymmetric unit contains only one Ni atom, which is tetrahedrally coordinated by 3 oxygen atoms and 1 nitrogen atom. A bond valence calculation[9] yields a value of 1.93 implying a good coordination sphere about the Ni ion. The three oxygens occupying coordination sites are supplied by three different phosphonate groups, in such a way as to form chains parallel to the c-axis. The three oxygens of the phosphonate group are all bonded to Ni atoms, such that each is directly connected to only one nickel atom; this is referred to as (111) connectivity.[10] The amide nitrogen from the phosphonate part of a neighbouring chain occupies the remaining coordination position. This results in cross-linked chains that give rise to the formation of two orthogonal channel systems; one parallel to the c-axis (Fig. 1) and one parallel to the a-axis (Fig. 2). The channels that run in the [001] direction have an elongated shape (Fig. 1), and dimensions of *ca.* 13.5 Å × 3.9 Å (H–H distance is 2.9 Å). The other channel system running in the [100] direction is roughly triangular in shape, with one 'corner' occupied by carbonyl oxygen of the amide groups. This restricts the size of the channel to *ca.* 3.5 Å. Water molecules are situated at the intersections of the two channel systems. The C═O bond length of 1.247 Å is slightly longer than that expected for a carbonyl bond (1.16–1.21 Å). The protons on the amide group ($-NH_2$) were not located in the structural analysis.

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† Crystal data for $Ni(O_3PCH_2C(O)NH_2\cdot H_2O$: M_w = 213.76, orthorhombic, a = 9.5378(10), b = 12.5720(14), c = 5.1830(6) Å, U = 621.49(12) Å^3, T = 150 K, space group $Pna2_1$ (No. 33), D_{calc} = 2.285 g cm^{-3}, Z = 4, λ = 0.687 70 Å, μ(Mo–K) = 3.340 mm^{-1}, 4162 reflections measured, 1682 reflections unique, 1543 reflections observed (R_{int} = 0.0614) which were used in all calculations. The final $wR(F_{all\ data}^2)$ was 0.1341 and $R(F_{all\ data})$ was 0.0541. The crystal structure was solved using direct methods and refined by full matrix least-squares on F^2. Corrections were made for synchrotron beam intensity decay as part of the standard inter-frame scaling procedure. CCDC reference numbers [CCDC NUMBER(S)]. See http://www.rsc.org/suppdata/nj/b4/b411740a/ for crystallographic data in .cif or other electronic format.

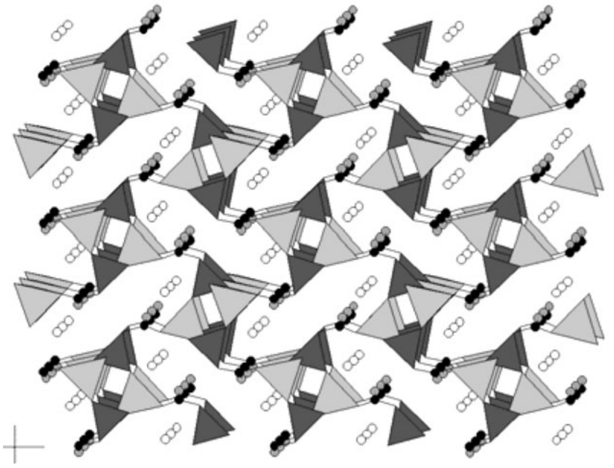

Fig. 1 A view of the channel system in the [001] direction. The CPO_3 and NiO_3N tetrahedra are shown as dark grey and light grey tetrahedra, respectively. Carbon atoms are shown as black circles, nitrogen atoms as grey circles and oxygen atoms as open circles. Hydrogen atoms have been omitted for clarity.

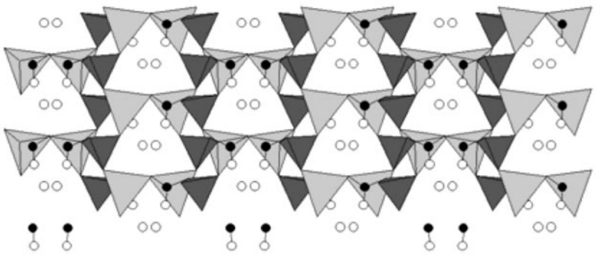

Fig. 2 A view of the channel system along the *a* axis. The CPO_3 and NiO_3N tetrahedra are shown as dark grey and light grey tetrahedra respectively. Carbon atoms are shown as black circles, nitrogen atoms as grey circles and oxygen atoms as open circles. Hydrogen atoms have been omitted for clarity.

The CHN and EDX analyses are consistent with the stoichiometry obtained from the single crystal analysis, $Ni(O_3PCH_2C(O)NH_2)\cdot H_2O$. In order to verify that the bulk polycrystalline powder has the same structure as the single crystal chosen for analysis, powder diffraction data were recorded.‡ However, the powder XRD profile (Fig. 3) of the polycrystalline material, differs from that simulated from the single crystal structure. This clearly shows that the product is a two phase mixture with the polycrystalline bulk of the sample having the same chemical composition as the single crystals *i.e.* two polymorphs. Since the single crystal component of the two phase mixture is so small, the subsequent analysis of the reaction products can be assumed to describe the polycrystalline material, with the microporous component having no appreciable effect upon the experimental observations made.

The powder XRD pattern of the bulk phase resembles those observed for layered nickel phosphonates,[2] although it has not been possible to index the pattern with a high degree of certainty. The major peak at the beginning of the pattern indicates a possible interlayer distance of 8.5 Å: a value that agrees with the potential unit cells that were obtained in indexing, but that is inconsistent with other layered phosphonates that have interlayer organic groups of a similar size, *e.g.* $Zr(O_3PCH_2CO_2H)_2$, in which one observes an interlayer distance of 11.1 Å.[11] If the material is layered, then the small apparent interlayer distance may be explained by considering the arrangement of the pendant organic groups. If the alkyl amide groups are fully interdigitated, it is possible that either the oxygen or the nitrogen of the amide group is co-ordinated to a Ni atom in the next layer. Interdigitation of this type was observed by Stock *et al.*[12] in $Mn_3(O_3PCH_2CH_2CO_2)_2$, where the carboxylate group co-ordinates Mn atoms in adjacent layers *via* the $-PO_3$ and the carboxylate groups. On the basis of the IR data obtained for the carbonyl group (*vide infra*), co-ordination of Ni by the oxygen atom can be discounted, whilst the broad peak around 3200 cm^{-1} could indicate co-ordination by the amine group. Co-ordination of metal atoms by both ends of the amidophosphonate in this manner would serve to reduce the interlayer distance from the expected value to the observed value of approximately 8.5 Å.

The IR spectrum of $Ni(O_3PCH_2C(O)NH_2)\cdot H_2O$ contains peaks assigned as C–H(str) at 3027, 2929 and 2800 cm^{-1}, P–C(str) at 1436 cm^{-1} and P–O(str) as a series of sharp bands in the region 1150–950 cm^{-1}. There is no evidence in the spectrum of a peak at 2256 cm^{-1}, which is observed in the spectrum of diethyl cyanomethylphosphonate and arises from the $-C\equiv N$ stretching mode. The C=O stretching frequency seen at 1743 cm^{-1} is similar to that expected for an amide; the effective lowering of the frequency that has been previously observed in the IR spectra of $Zn(O_3P(CH_2)_2CO_2H)\cdot 1.5H_2O$ [5] and $Al(O_3PCH_2CO_2)\cdot 3H_2O$,[13] arising from the coordination of the carbonyl group to a metal atom in a neighbouring phosphonate chain, is not observed. This indicates that carbonyl oxygen is not coordinated to the nickel atoms in opposite layers.

Thermogravimmetry yields an overall mass loss of 30.97%, which is consistent with the value of 31.85% calculated on the basis of stoichiometry. These figures correspond to the formation of nickel pyrophosphate, $Ni_2P_2O_7$, upon the removal of the water and organic parts of the phosphonate from within the material. The product recovered after calcination at 1000 °C has the characteristic yellow colour of $Ni_2P_2O_7$ and the identity of this product was confirmed by powder XRD.

The synthesis of metal phosphonates directly from the relevant dialkylphosphonate has previously been shown to be a productive adaptation of the traditional hydrothermal methods employed in the synthesis of a porous zinc phosphonate. As demonstrated in the synthesis of $Zn(O_3PCH_2OH)$,[6] the metal salt solution is sufficiently acidic to carry out the hydrolysis of the phosphonate to produce the phosphonic acid *in situ*, without having to introduce additional mineral acids.

The benefits of this method are that the synthesis of phosphonate esters is often far simpler that the corresponding phosphonic acid since the latter can be difficult to purify.

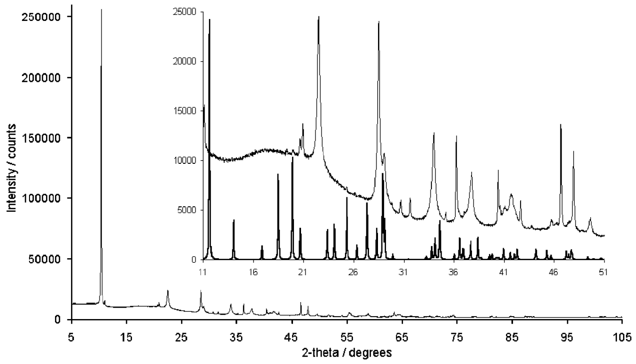

Fig. 3 Powder X-ray diffraction profile for layered $Ni(O_3PCH_2C(O)NH_2.H_2O$. Inset shows comparison of experimental data (top) with simulated profile for microporous $Ni(O_3PCH_2C(O)NH_2\cdot H_2O$ (bottom).

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‡ Powder XRD data collection: The sample was ground and placed between two pieces of transparent tape. The powder diffraction data ($4 \leq 2\theta \leq 105°$ in 0.019° steps over 15 h) were collected in transmission mode on a Bruker-AXS D5000 using Ge monochromated $CuK\alpha_1$ radiation and a linear PSD covering 8° in 2θ. A second data set was collected at 150 K, and although this generated only poor quality data, the powder pattern matches that collected at room temperature.

A possible source of impurity and a step in the overall synthetic procedure have been removed.

The porous $Ni(O_3PCH_2C(O)NH_2)\cdot H_2O$ phase synthesised demonstrates that Ni can adopt tetrahedral coordination in the formation of porous phosphonate materials, opening up the possibility of some interesting magnetic or catalytic applications in these materials.

It has already been noted that functionalised phosphonic acids can act as efficient building blocks for the synthesis of open framework three-dimensional materials.[4,6,14] The material reported here reiterates this point, and demonstrates that the synthetic method employed in the synthesis is applicable not only to the synthesis of porous zinc phosphonates, but can also be used to produce porous materials containing different metals and phosphonate groups.

Perhaps the most important discovery in this work is that polymorphs of TM phosphonates can be formed, although we have been unable to elucidate the structure of one of the materials. It is likely that there are other systems in which polymorphism might be observed, and we would suggest that it is prudent to continue with the investigation of a particular system even if a structure has been elucidated. In light of this work, we have revisited a number of systems and have found other instances of polymorphism arising from subtle changes in the experimental procedure. The results of these studies will be published elsewhere.

In summary, the synthesis of phosphonate materials directly from the dialkylphosphonates simplifies the synthetic procedure. We have demonstrated that the use of this method in conjunction with phosphonates that are bifunctional, can yield porous materials. Work is currently in progress to develop the synthesis to make $Ni(O_3PCH_2C(O)NH_2)\cdot H_2O$ as a single phase product.

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