

The first route to large pore metal phosphonates†

John A. Groves,^a Stuart R. Miller,^a Stewart J. Warrender,^a Caroline Mellot-Draznieks,^b Philip Lightfoot^a and Paul A. Wright*^a

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The first large pore (free diameter > 7 Å) metal phosphonates have been prepared as divalent metal *N,N'*-piperazinebis(methylenephosphonate)s that possess pores greater than *ca.* 10 Å in free diameter, are stable up to 400 °C and offer a route to chiral adsorbents and catalysts.

Metal phosphonates were among the first microporous organic–inorganic hybrid adsorbents to be investigated. Aluminium methylphosphonates AlMePO- α and - β ,¹ for example, contain channels lined by methyl groups that give them characteristic adsorption properties.² Other microporous phosphonates have subsequently been prepared but, since the discovery of MOF-5,³ many more metal carboxylates with very high adsorption capacities have been discovered, with pore sizes extending into the mesoporous range (>20 Å).^{4,5} Some of these show extraordinary structural flexibility upon adsorption⁶ and exhibit special properties as hosts for gas storage⁷ and the inclusion of metal compounds and clusters.⁸ Microporous metal phosphonates offer an alternative set of chemical and structural possibilities, and the AlMePOs possess greater thermal stability than similar carboxylates.⁹ It has not been possible, however, to prepare crystalline metal phosphonates with pores larger than 6 Å, and typically their uptake of adsorbates has been low,¹⁰ so to be alternative hybrid sorbents, structures with larger pores and adsorption capacities are required.

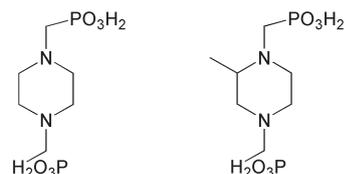
The *N,N'*-piperazinebis(methylenephosphonate) ligand has previously been shown to give small pore metal bis(phosphonate)s of Co(II) and Mn(II)¹¹ and of Al and Ti.¹² Here we report further studies of inorganic–organic hybrids crystallised using *N,N'*-piperazinebis(methylenephosphonic acid) (H₄L), including the first large pore metal phosphonates. This follows up our syntheses of divalent metal piperazinebis(methylenephosphonate)s,¹³ which gave an unidentified phase at higher pH for Co(II) and Mn(II). This phase has now been prepared in pure form for divalent iron, cobalt and nickel. The nickel bis(phosphonate) in particular shows remarkable pore volume and thermal stability, and its discovery opens up important possible applications for this class of material. Furthermore, during exploration of the use of

N,N'-2-methylpiperazinebis(methylenephosphonic acid) (H₄L') another large pore phosphonate has been prepared, with cobalt(II).

Hydrothermal reactions of salts of iron(II), cobalt(II) and nickel(II) with the bis(methylenephosphonic acid)s, H₄L and H₄L' (Scheme 1) were performed using M:H₄L(H₄L'):H₂O ratios of 0.02:0.01:9, and the initial pH was adjusted as required with aqueous potassium hydroxide (ESI†).‡

Reaction of cobalt chloride with H₄L with pH values below 6.5 gives CoLH₂·H₂O.¹¹ Reaction with iron(II) chloride under similar conditions gives the isostructural iron(II) version of this phase, FeLH₂·1.5H₂O, as shown by the single crystal structure, reported here for the first time.^{14,15} In this structure, iron(II) and cobalt(II) exhibit tetrahedral coordination, and chains of tetrahedra are linked by bis(phosphonate) ligands, protonated at the nitrogen, to give a small pore framework, with physically-bound water molecules residing in the channels. Reaction at a similar pH with iron(II) acetate, however, gives a new phase, structure type 1. Reaction of cobalt chloride at higher initial pH, and of nickel chloride and acetate over a range of pH values also gives this structure, which can therefore be prepared for iron, cobalt and nickel, and is favoured by higher pH (for cobalt) and acetate rather than chloride (for iron). The structure of the nickel version of structure type 1 [M₂(H₂O)₂L]·5.4H₂O was determined from laboratory X-ray powder data *via* a combination of direct methods, structure modelling and Rietveld refinement.^{16–19} Comparison of the diffraction patterns indicates iron(II) and cobalt(II) also crystallise with this structure.

The framework is based on inorganic columns of helical chains of edge-sharing NiO₅N octahedra (Fig. 1). Each NiO₅N octahedron consists of nickel coordinated to four oxygen atoms belonging to two phosphonate tetrahedra (on the two shared edges) plus an oxygen atom from a coordinating water molecule and a nitrogen from the piperazine ring of the bis(phosphonic acid). The piperazine ring is on a centre of symmetry. Each chain is linked to three others *via* piperazine groups, so that each bis(phosphonate) ligand coordinates *via* two oxygens and a nitrogen to each of two helical chains of nickel cations, leaving a phosphonate oxygen projecting towards the pore space. This is the



Scheme 1 (Left) *N,N'*-piperazinebis(methylenephosphonic acid) (H₄L) and (right) its racemic 2-methylated derivative (H₄L').

^aSchool of Chemistry, University of St. Andrews, Purdie Building, North Haugh, St. Andrews, Fife, UK KY16 9ST.

E-mail: paw2@st-andrews.ac.uk; Fax: (+44) 1334 463808;

Tel: (+44) 1334 463793

^bDavy-Faraday Laboratories, The Royal Institution of Great Britain, 21 Albemarle Street, London, UK W1X 4BS

† Electronic supplementary information (ESI) available: Powder XRDs of as-prepared and dehydrated samples, TGAs, tabulated experimental conditions, chemical analyses, details of structure solution from powder X-ray data, including Rietveld plot, N₂ adsorption isotherms. See DOI: 10.1039/b605400e

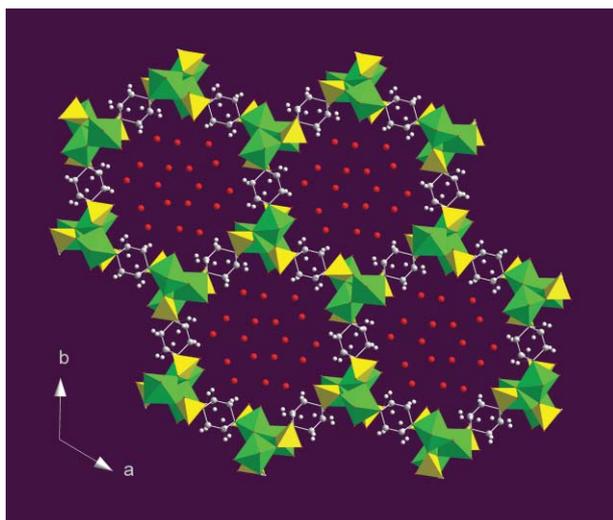


Fig. 1 Structure **1**, $[\text{Ni}_2(\text{H}_2\text{O})_2\text{L}]\cdot 5.4\text{H}_2\text{O}$, viewed down the c axis, including extra-framework water. (Edge-sharing NiO_5N octahedra, green; phosphonate PO_3C tetrahedra, yellow; carbon atoms, grey; nitrogen, blue; oxygen, red; hydrogen, white).

first porous solid in which this ligand coordinates through both oxygen and nitrogen atoms. The arrangement of inorganic chains and organic linkers leaves a structure with a hexagonal array of channels with a free diameter, taking into account van der Waals radii of hydrogen atoms, of *ca.* 10 Å.

In the as-prepared solid, channels are filled with physically adsorbed water molecules. $[\text{Ni}_2(\text{H}_2\text{O})_2\text{L}]\cdot 5.4\text{H}_2\text{O}$ loses water in two steps, attributed to physisorbed and coordinated molecules, at 100 and 200 °C, and ligand decomposition occurs above 400 °C. X-Ray diffraction of samples dehydrated *in vacuo* show that the unit cell is no longer rhombohedral: the X-ray profile can be indexed by a primitive triclinic unit cell with a volume *ca.* one third of the rhombohedral cell, although the slightly broadened reflections do not permit unambiguous assignment. Nitrogen adsorption at 77 K indicates a micropore volume of $0.16 \text{ cm}^3 \text{ g}^{-1}$ (at $p/p_0 = 0.2$). Samples dehydrated at temperatures of up to 400 °C rehydrate reversibly. The cobalt version of the structure shows very similar behaviour but the iron sample collapses upon dehydration. Using the 2-methylpiperazine version of the bis(phosphonic acid) in the syntheses also gives structure type **1** for nickel and cobalt. X-Ray powder diffraction of $\text{Ni}_2\text{L}'$ dehydrated *in vacuo* shows that the symmetry remains rhombohedral. Nitrogen adsorption at 77 K indicates a micropore volume of $0.21 \text{ cm}^3 \text{ g}^{-1}$. This is higher than that of Ni_2L , despite the presence of an additional methyl group in the ligand, because the structure remains rhombohedral upon dehydration.

The chains and pore structure of Ni_2L , $\text{Ni}_2\text{L}'$ and the isostructural iron and cobalt compounds are similar to those observed previously in cobalt and nickel hydroxyterephthalates.²⁰ The phosphonates offer a coordinatively unsaturated metal cation to adsorbates in the same way as these carboxylates but are stable to a higher temperature (by 100 °C).

Using cobalt acetate in reactions with $\text{H}_4\text{L}'$ gives purple crystals of a second novel phase (structure type **2**). Combining crystallography, TGA and chemical analysis gives $[\text{Co}_4\text{L}'_{1.5}(\text{CH}_3\text{CO}_2)_{1.5}(\text{OH},\text{H}_2\text{O})_3]\cdot (\text{NH}_4)_{0.5}(\text{H}_2\text{O})_{5.5}$ as its composition, with only the

framework fully determined by single crystal X-ray diffraction (SCXRD). The structure type has only been observed to form with cobalt(II) and in the presence of acetate. In structure **2**,²¹ the inorganic unit is composed of chains of ‘tetramers’ of octahedral cobalt cations linked by three phosphonate units (Fig. 2). The central cobalt cation is fully coordinated by six phosphonate oxygen atoms to give a CoO_6 octahedron, which shares edges with three CoO_5N octahedra. These outer cobalt ions are each coordinated by three phosphonate oxygens, a nitrogen of the piperazine ring and two remaining oxygens that are in part from acetate groups and in part water molecules or hydroxyl groups. These inorganic columns are linked to three other identical columns by piperazine units in the chair conformation. The disordered methylpiperazine moiety lies about a twofold axis in the crystal. The methyl groups of the piperazine rings project into the channels, and are disordered over the two ring carbon atoms bordering the channel.

Structure **2** loses 15 wt% upon dehydration and remains crystalline, without change in symmetry. Although the crystal structure indicates channels with a free dimension of around 7 Å taking van der Waals radii of H atoms into account, the material does not adsorb nitrogen. This is attributed to the presence of charged species such as ammonium ions in the pores, blocking access to nitrogen molecules.

These phosphonate structures offer considerable scope for future examination as adsorbents, and stimulate further research into microporous phosphonates. In particular, structure type **1** is a promising large pore solid, offering organic and inorganic surface regions, including a metal cation that is able to offer a coordination site to sorbate molecules. Both structures can be prepared with a racemic mixture of *N,N'*-2-methylpiperazinebis(phosphonic acid)s, suggesting that their fully chiral derivatives

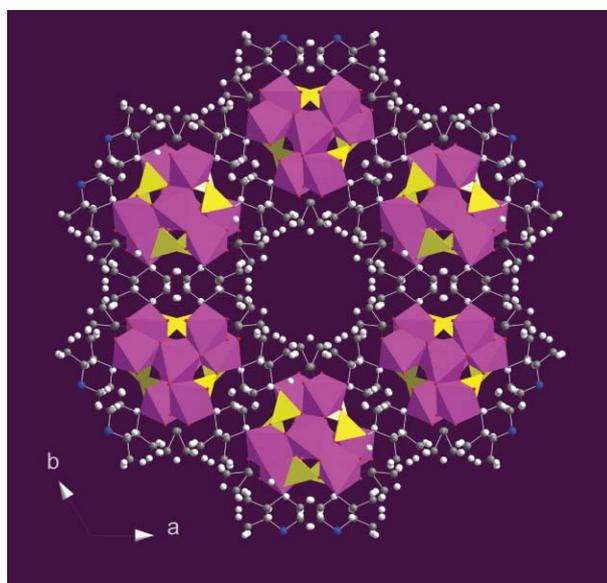


Fig. 2 The $[\text{Co}_4\text{L}'_{1.5}(\text{CH}_3\text{CO}_2)_{1.5}(\text{OH},\text{H}_2\text{O})_3]$ framework of structure **2**. Acetate groups have been shown at full occupancy, although in the measured structure, one-half of these are replaced by water molecules or hydroxyl groups bound to the cobalt cations. (Edge-sharing Co octahedra, purple; phosphonate PO_3C tetrahedra, yellow; carbon atoms, grey; nitrogen, blue; oxygen, red; hydrogen, white).

should be synthetically accessible, and will offer possibilities for chiral separations, particularly structure type 1. The use of the 2-methylpiperazine derivative of the acid has the additional consequence of preventing distortion of structure 1 upon dehydration and increasing rather than decreasing nitrogen adsorption, and suggests a promising approach to the synthesis of large pore solids that we are currently successfully exploring. Accessible metal sites in the frameworks of microporous solids are known to show Lewis acidity, so structure 1 is expected to show catalytic activity. Furthermore, the nature of the inorganic chains in these solids, which possess either columns of edge-sharing octahedra or edge-sharing tetramers of cobalt-centred octahedra, suggests that they will have interesting magnetic properties.^{20a}

Notes and references

‡ Bis(phosphonic acids) were prepared by modifications of reported methods. *N,N'*-Piperazinebis(methylenephosphonic acid) was synthesised using a variation of the modified Mannich reaction of piperazine, using HCl as a catalyst.²² *N,N'*-2-Methylpiperazinebis(methylenephosphonic acid) was prepared from a racemic mixture of 2-*R*- and 2-*S*-methylpiperazine (98% Acros); the solution from the modified Mannich reaction was raised to pH 6 with 2 M NaOH, the volume reduced and the solution cooled to 4 °C. The resulting precipitate was washed with cold water and dried: H₄L'·H₂O: calculated for C₇H₂₀N₂P₂O₆·H₂O, C 27.45%, H 6.60%, N 9.15%; measured, C 27.62%, H 6.63%, N 8.90%. Reaction gels were prepared by mixing the reactants and adjusting the initial pH, by addition of KOH, to values between 5 and 8. The gels were then put into Teflon-lined autoclaves and heated at 140–190 °C. Samples were characterised by powder XRD on a STOE Stad/p diffractometer using Cu K_{α1} X-rays. Chemical analysis of the inorganic component was performed by EDX analysis on a JEOL JSM-5600 SEM with an Oxford INCA Energy 200 analyser and the organic component measured on a Carlo Erba EA 1110 CHNS analyser. TGA was performed under flowing nitrogen at 5 °C min⁻¹, and the structural response to dehydration of the samples followed by XRD of heated samples sealed in 0.7 mm capillaries. N₂ adsorption was performed at 77 K on dehydrated samples on an automated HIDEN gravimetric porosimeter.

In a typical synthesis of structure 1 (Ni₂L·7.4H₂O), 0.002 moles (0.5 g) of Ni(CH₃CO₂)₂·4H₂O and 0.001 moles (0.29 g) of H₄L'·H₂O were dissolved in 0.9 moles water, the pH adjusted to 8 by addition of potassium hydroxide solution and the mixture heated at 160 °C for 120 h. EDX analysis gave Ni/P of 1.0(1): elemental analysis is then consistent with a formula of Ni₂L·7.4H₂O. TGA indicated the structural formula was [Ni₂(H₂O)₂L]·5.4H₂O. Calcd: C, 13.87%; H, 5.16%; N, 5.39%; measured: C, 13.77%; H, 4.87%; N, 5.23%.

Synthesis of structure 2. Typically, 0.001 mole of H₄L'·H₂O (0.31 g) was dissolved in 0.9 mole water with 0.002 moles (0.5 g) of Co(CH₃CO₂)₂·4H₂O (Aldrich, 98%) and heated at 160 °C for 150 h. EDX analysis gave Co/P = 1.3(1). Elemental and crystallographic analysis are in reasonable agreement with the structural formula [Co₄L'_{1.5}(CH₃CO₂)_{1.5}(OH,H₂O)₃](NH₄)_{0.5}(H₂O)_{5.5}. Calcd: C, 17.9%; H, 5.0%; N, 5.5%, measured: C, 17.43%; H, 5.75%; N, 5.72%.

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