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Two Closely Related Lanthanum Phosphonate Frameworks Formed by Anion-Directed Linking of Inorganic Chains

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Two novel three-dimensional lanthanum coordination polymers have been prepared with the phosphonic acid $H_2O_3PCH_2N(C_2H_4)_2NCH_2PO_3H_2$ (**L**H_4). La_2(**L**H_2)$_2$(**L**H_4)Cl_2 (**I**) and La_2(**L**H_2)$_2$(**L**H_3)Cl (**II**) arise from similar hydrothermal reactions but differing sources of La. A one-dimensional "lanthanum-phosphate" chain, comprising corner-linked LaO_7 and PO_3C polyhedra, forms the basis for the two different structures. The two structures differ in the mode of connectivity of the inorganic chains via the phosphonate groups. Both materials include extraframework chloride ions, the different amounts of which apparently direct the polytypic structures. In **II**, the chloride ions are incorporated in a noncentrosymmetric manner leading to a polar framework topology.

1. Introduction

The intense current interest in hybrid organic–inorganic materials is driven by the potential they possess as functional solids. Microporous metal carboxylate[1–3] and metal phosphonate[4–6] frameworks show unique properties of adsorption, ion exchange, and proton conductivity. Phosphonate groups are promising chemical building blocks for such structures, because of the thermally and chemically stable M–O–P bonds that they make with a range of metals. The synthetic chemistry of phosphonic acids is also well developed, so that many organic functional groups can be readily incorporated into the phosphonic acids. One particularly promising research direction is in the synthesis of diphosphonates of metals such as aluminum,[7] group 4 metals (titanium and zirconium),[8] transition metals,[9] and rare earth metals.[10] Most of these possess a common structural motif of inorganic layers pillared by the phosphonate moieties, which can lead to interlayer porosity and reversible adsorption behavior.[11]

Many of the crystallographic studies of such pillared structures have centered on methylene, ethylene, and propylene diphosphonates, but more complex phosphonic acids have also been used successfully, including the dimethylenephosphonic acid derivative of piperazine ($H_2O_3PCH_2N(C_2H_4)_2NCH_2PO_3H_2$). This has been found to yield porous metal organic frameworks with vanadium,[12] cadmium,[13] cobalt, and manganese.[14] This readily prepared diphosphonic acid is attractive because it possesses tertiary amine groups, the protonation/deprotonation behavior of which might be inherited by any product metal phosphonates. As part of a program of investigating metal diphosphonates, we have prepared lanthanum diphosphonates by hydrothermal synthesis with this acid. Lanthanides are known to form organodiphosphonate[6] and phosphonate carboxylate frameworks,[10] some of which display reversible adsorption and, with the appropriate lanthanide, luminescence. Our aim was the synthesis of metal diphosphonate frameworks with additional functionality.

2. Experimental Section

2.1. Synthesis. Piperazine (99%), phosphorous acid (98%), formaldehyde (37%), and hydrochloric acid (18%) were obtained from Fisher Scientific and used as received. *N,N′*-Piperazine (bis

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methylene phosphonic acid) was synthesized using a modified Mannich reaction:[15] piperazine (0.1 mol) was mixed with phosphorous acid (0.2 mol), and 50 mL of HCl solution was mixed with 50 mL of water. Formaldehyde (0.4 mol) was added dropwise over 1 h, and the mixture was then refluxed at 120 °C. After 4 h, a white solid had precipitated, which was filtered, washed, and dried. Analysis was based on one HCl associated with the product: C 23.27%, H 5.51%, N 8.84% (calcd. for $C_6H_{17}N_2P_2O_6Cl_1$: C 23.20%, H 5.52%, N 9.02%). Overall yield 68%. Next, 0.0015 mol of this product was added to 0.002 mol of $LaCl_3 \cdot 7H_2O$ (Aldrich, 99.9%) in 25 mL of water and stirred for 1 h at 80 °C, before being added to an autoclave and heated at 170 °C for 240 h. The initial pH of the reaction mixture was 6. The white crystalline residue was filtered, washed, and dried. The predominant phase present consisted of needlelike crystals, one of which was selected for single-crystal X-ray analysis (**I**). The bulk material was separated by sonication in a water bath, from which a pure bulk crystalline phase, representative of the single-crystal analysis, was isolated. This was confirmed by powder X-ray diffraction (Supporting Information) and analysis: C 18.09%, H 3.88%, N 7.05% (calcd. for $C_9H_{22}ClLaN_3P_3O_9$: C 18.52%, H 3.80%, N 7.20%). Thermogravimetric analysis (in air) of the pure material revealed a sharp weight loss of 19% centered around 370 °C, followed by a more gradual weight loss up to 600 °C; the total weight loss of 28% agrees well with that calculated for loss of all of the organic moiety (29.5%); the product of this heat treatment was amorphous to X-ray powder diffraction.

Several further reactions were carried out to isolate a pure as-made sample of **I**. An analogous reaction using 0.0015 mol of ligand and 0.002 mol of La_2O_3 (i.e., twice the La:P molar ratio) again produced **I** as the predominant phase. The initial pH of the reaction mixture was again 6. However, platelike crystals of **II** were isolated in trace amounts. Although this phase could not be isolated in bulk quantities from several different variants of this reaction (e.g., by reaction of 0.0015 mol of ligand and 0.001 mol of La_2O_3 under identical conditions), crystals of **II** could be isolated from two independent reactions. We note that the chloride present in the products of these La_2O_3-based reactions arises from the preparation of the original phosphonic acid as the mono-hydrochloride.

2.2. Crystallography. Single-crystal X-ray diffraction studies were carried out on Bruker SMART (for **I**) or Rigaku Mercury CCD diffractometers (compound **II**) with graphite monochromated Mo Kα radiation. Intensity data were collected using 0.3° steps to give at least a full hemisphere of coverage. All data sets were corrected for absorption via multiscan methods. Data analyses used the SHELXS and SHELXL packages. Relatively poor crystal quality and significant pseudo-symmetry precluded a fully anisotropic refinement for **II**. Details of the crystal structure determinations are given in Table 1, and selected bond lengths are in Table 2. Powder X-ray diffraction data were collected on a Stoe STADI/P transmission diffractometer using Cu $K_{\alpha 1}$ radiation.

Table 1. Crystallographic Data for **I** and **II**

	I	II
formula	$C_9H_{22}Cl LaN_3O_9P_3$	$C_9H_{21.5}Cl_{0.5}La N_3O_9P_3$
crystal system	monoclinic	monoclinic
space group	$P2_1/c$	Cc
a (Å)	6.1071(6)	6.039(1)
b (Å)	21.710(2)	26.524(5)
c (Å)	13.732(1)	23.431(5)
β (deg)	102.521(2)	93.71(3)
V (Å^3)	1777.3(3)	3745(1)
Z	4	8
ρ (g cm^{-3})	2.18	2.00
crystal morphology	needle	plate
data collection temperature	295 K	93 K
total/unique reflections	10 645/3259	13 823/5185
ind. reflections ($I > 2\sigma(I)$)	2588	4779
parameters	237	215
final R1, wR2	0.079, 0.126	0.082, 0.211
Flack parameter		0.23(4)

Table 2. Selected Bond Lengths (Å) for **I** and **II**

I	
La1 O4	2.429(7)
La1 O6	2.434(8)
La1 O1	2.461(8)
La1 O2	2.492(8)
La1 O5	2.511(7)
La1 O3	2.572(8)
La1 O7	2.576(8)
P1 O1	1.504(8)
P1 O2	1.515(8)
P1 O3	1.545(8)
P1 C1	1.829(11)
P2 O6	1.499(9)
P2 O5	1.509(8)
P2 O4	1.513(8)
P2 C6	1.831(12)
P3 O9	1.488(8)
P3 O7	1.501(8)
P3 O8	1.589(8)
P3 C7	1.825(11)

II			
La1 O14	2.42(2)	La2 O10	2.41(2)
La1 O4	2.43(2)	La2 O15	2.43(1)
La1 O9	2.46(1)	La2 O11	2.44(2)
La1 O18	2.48(2)	La2 O1	2.50(1)
La1 O12	2.51(1)	La2 O8	2.50(2)
La1 O6	2.52(2)	La2 O5	2.51(1)
La1 O13	2.57(1)	La2 O7	2.54(2)
P1 O1	1.48(1)	P2 O5	1.53(2)
P1 O2	1.51(2)	P2 O6	1.56(2)
P1 O3	1.58(2)	P2 O4	1.58(2)
P1 C1	1.83(2)	P2 C6	1.86(2)
P3 O9	1.49(2)	P4 O12	1.49(2)
P3 O8	1.51(2)	P4 O11	1.51(2)
P3 O7	1.53(2)	P4 O10	1.55(2)
P3 C11	1.82(2)	P4 C16	1.86(2)
P5 O13	1.53(1)	P6 O18	1.47(2)
P5 O14	1.56(2)	P6 O17	1.47(2)
P5 O15	1.57(2)	P6 O16	1.51(2)
P5 C17	1.79(2)	P6 C18	1.90(3)

3. Results and Discussion

The two compounds have marked similarities in both composition and crystal structure. Both materials adopt three-dimensional framework structures with topologically the same connectivity around the "inorganic" (i.e., lanthanum-phosphate) part of the structure. Compositionally, **II** has a 50% lower chloride content than **I**, and it is tempting to suggest that this may be a cause of the differing framework topologies. A key structural element in each phase is a continuous chain of lanthanum centers, linked via bridging phosphonate groups to other chains, extending in the *a*-direction (Figure 1). The differences between the two structures arise in the way these "lanthanum phosphate" chains are connected. In **I**, there is one crystallographically unique La and three P atoms. Two of these phosphonate groups bridge three adjacent La sites within the same chain; the third acts as a monodentate ligand only, giving 7-fold

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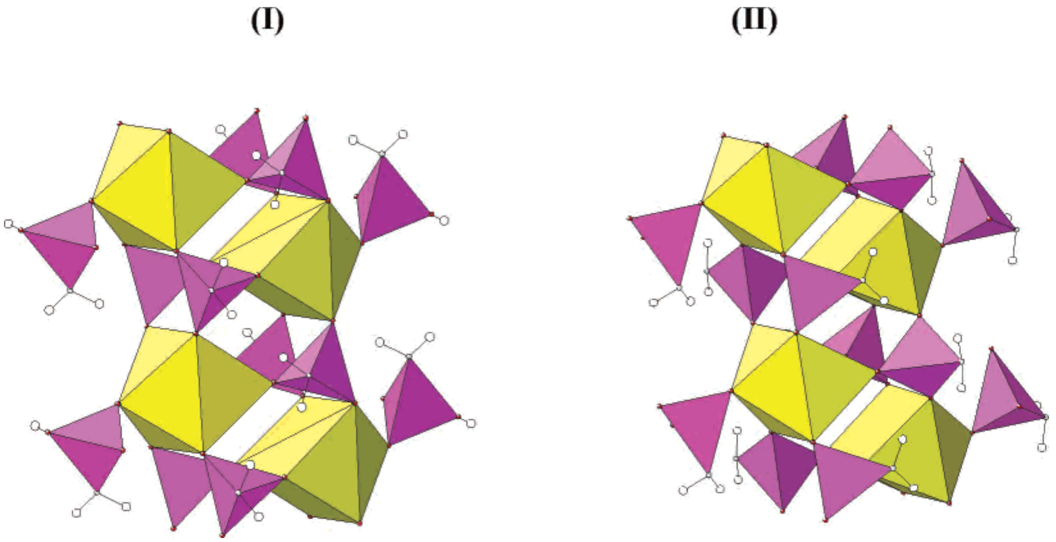

Figure 1. Polyhedral view of the “lanthanum phosphate” chain viewed approximately down the *b*-axis; La−O polyhedra in yellow, P−O tetrahedra in purple.

coordination around the La center. Charge balance requirements result in one of the two “dangling” P−O bonds of this group being protonated, together with protonation of all of the amine N atoms. Phase **I** may thus be formulated as $La_2(O_3PCH_2NH(C_2H_4)_2NHCH_2PO_3)_2(HO_3PCH_2NH(C_2H_4)_2NHCH_2PO_3H)Cl_2$.

The location of the P−O−H moiety can be clearly seen from both the lengthening of the P(3)−O(8) bond and the proximity of the Cl^- anion (3.06 Å), which acts as a H-bond acceptor. In addition, the H position could be located from difference Fourier maps.

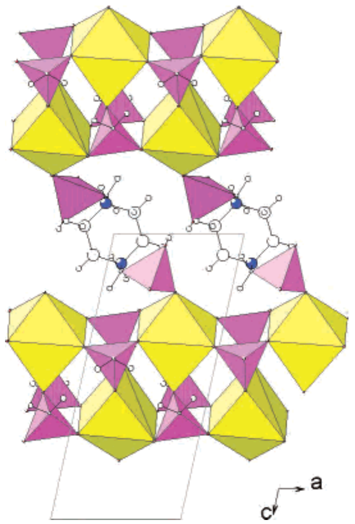

Figure 2. Linkage of adjacent inorganic chains via phosphonate groups in **I**. Note that each chain links to six adjacent chains via a single bridge per repeat unit.

In **II**, the symmetry is lowered such that there are now two inequivalent La and six inequivalent P atoms. The space group is confirmed as *Cc*. A search for centrosymmetric (*C*2/*c*) symmetry using PLATON[16] showed no evidence for the higher symmetry, which would require a considerable disorder around the phosphonate groups. The local structural coordination around the La−O−P chain is compared to that of **I** in Figure 1. It can be seen that, although the presence of four triply bridging phosphate groups and two monodentate groups corresponds to that in (**I**), there are significant differences in the distortion and rotation of the LaO_7 and PO_3C polyhedra relative to each other between the two structures. This arises because the nature of the connectivity between adjacent La−O−P chains differs between the two, giving rise to substantially different overall framework architectures. In **I**, each La center bridges via six **L** groups to six adjacent La chains (Figures 2 and 4). In **II**, on the other hand, each La center bridges to only four adjacent chains, with four of the six **L** groups forming two “double” bridges (Figures 3 and 5). In both cases, the connectivity results in channels along the *a*-axis in which the Cl^- ions reside (Figures 4 and 5). It can be seen that the connectivity in **II** results in a significantly lower framework density (Table 1), and a much more “open” channel system. Due to the lower Cl^- content in **II** versus **I**, only one of the P−O groups needs to be protonated, assuming that all of the tertiary amine groups are protonated. Although the location of this proton could not be determined crystallographically, its position on O(3) can clearly be inferred due to the short, H-bonded contact to the Cl^- anion (O(3)−Cl = 3.06 Å). Compound **II** may therefore be formulated as $La_2(O_3PCH_2NH(C_2H_4)_2NHCH_2PO_3)_2(O_3PCH_2NH(C_2H_4)_2NHCH_2PO_3H)Cl$. A particularly interesting feature of **II** is the noncentric occupancy of the channels by Cl^-. The local environment around a single *a*-axis channel is shown in Figure 6. A pseudo-2-fold axis runs through the center of the channel along the *b*-axis. Refinements were carried out involving occupancy at both the Cl(1) and the Cl(2) positions. These refined to 95(2)/5(2) %, respectively, confirming a genuine “polar” ordering of the Cl^- anions within the channels. The final refinement kept these values fixed at 100/0%. This unusual Cl^- ordering can be seen to cooperate with ordering of the piperazine groups such that favorable H-bonding can occur via both N(5)−H---Cl(1) and O(3)−H---Cl(1). Simultaneous H-bonding to the Cl(2) site cannot occur without partial occupancy

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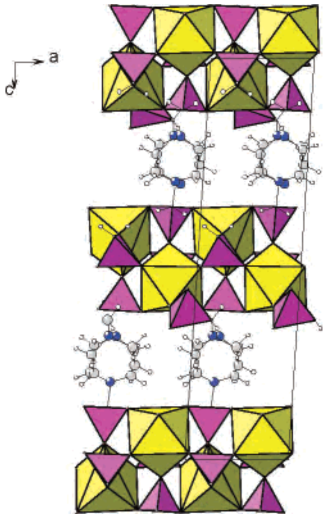

Figure 3. Linkage of adjacent inorganic chains via phosphonate groups in **II**. Note that each chain links to only four adjacent chains: two of these linkages consist of a "double" bridge per repeat unit.

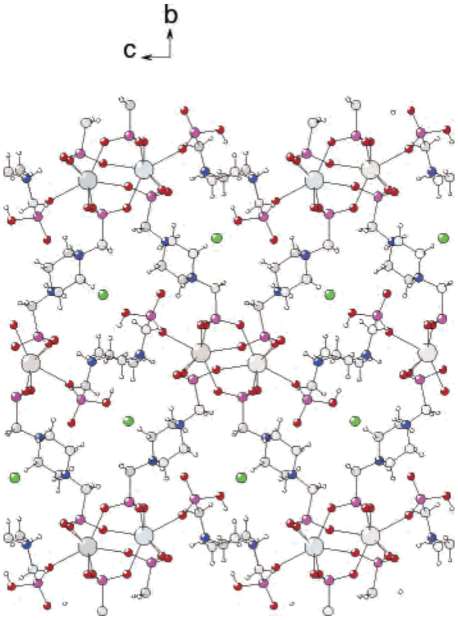

Figure 4. Framework structure of **I** viewed down the *a*-axis; La, C, gray; P, purple; O, red; N, blue; Cl, green.

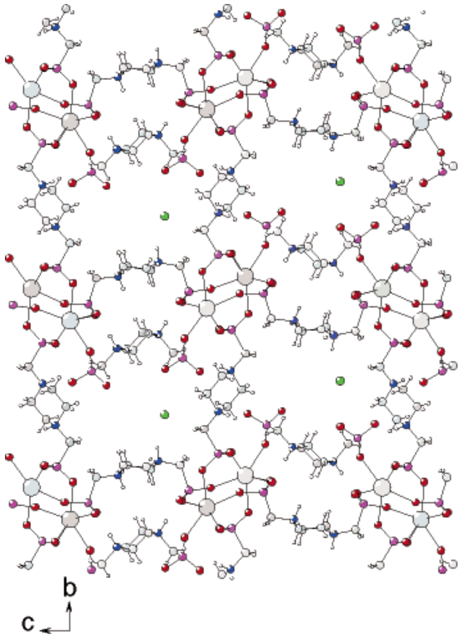

Figure 5. Framework structure of **II** viewed down the *a*-axis.

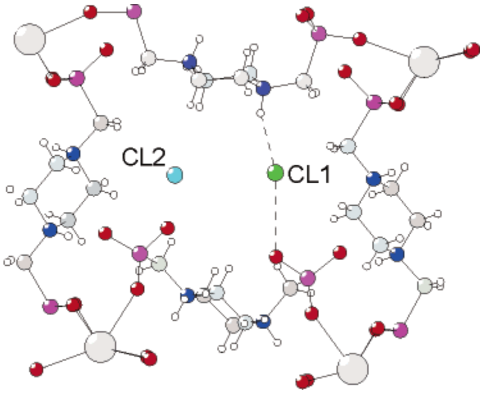

Figure 6. Expanded view of Cl^- anion location in **II**. Note that the Cl(1) site is fully occupied and the Cl(2) site is vacant, leading to the imposition of polarity on the framework itself. H-bonds are shown as dotted lines.

of the two Cl sites and disorder of the piperazine groups, which can be seen not to occur, from the refinements. This is an unusual phenomenon, the reasons for which are not yet clear, although we have seen a similar "polar templating" effect by F^- in the zeolite ITQ-4.[17]

4. Conclusion

Two novel lanthanum phosphonate framework materials have been prepared and structurally characterized. Subtle differences in reaction conditions lead to subtle differences in product composition but marked differences in overall structural architecture of the resultant phases. Topologically similar inorganic "lanthanum phosphate" chains are linked in two quite different ways by the organic ligands, the nature of which appears to depend on both the amount of and the supramolecular coordination preferences of the guest Cl^- ions. Further studies are merited to explore whether this type of guest ordering, and the cooperative imposition of framework polarity, can be controlled and used in the design of novel optical materials.

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Supporting Information Available: X-ray powder diffraction patterns for $La_2(\mathbf{L}H_2)_2(\mathbf{L}H_4)Cl_2$ (compound **I**). Top: Observed pattern. Bottom: Simulated pattern based on the single-crystal structure. Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org. CCDC contains the supplementary crystallographic data for this paper. These data can be obtained online free of charge (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax, (+44) 1223-336-033; e-mail, deposit@ccdc.cam.ac.uk).

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