

Chiral Crown Ether Pillared Lamellar Lanthanide Phosphonates

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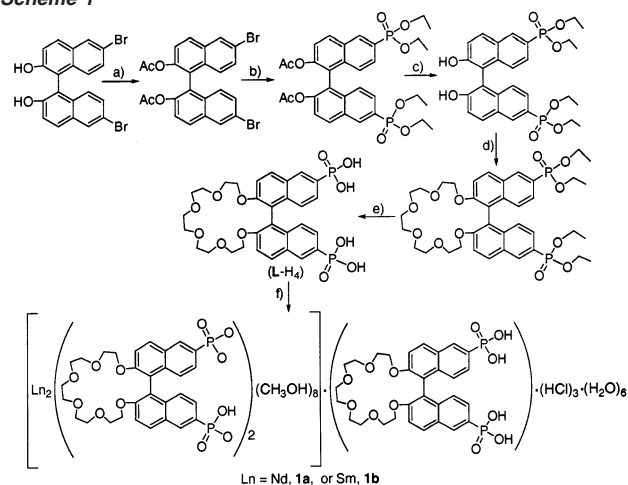
The design and synthesis of functional solids based on metal-organic coordination networks have undergone revolutionary growth over the past decade, driven by the prospect of incorporating and fine-tuning desired properties via judicious choices of metal connecting points and bridging ligands.¹ The synthesis of porous solids based on metal-organic frameworks has been a particularly fertile research area.² In contrast, despite their potential utility in heterogeneous asymmetric catalysis and chiral separations, there have been few reports on crystalline chiral porous solids based on metal-organic coordination networks.³ We have recently explored the design and synthesis of robust, single-crystalline, chiral porous solids based on metal bisphosphonates for potential applications in enantioselective processes.^{3a,b} Herein we wish to report the first homochiral porous lamellar lanthanide bisphosphonates that are pillared with chiral crown ethers.

Macrocyclic ligands such as crown ethers have been a subject of intense studies for several decades owing to their superior selectivity in complexation with metal ions and organic cations.⁴ Immobilization of crown ethers on polymeric and oxide supports presents an attractive approach toward hybrid materials that are exploitable for a wide range of applications such as industrial separations, ion transportations, isotope extractions, and catalysis.⁵ Of particular interest to us is silica gel dispersed chiral crown ether, 2,2'-pentaethylene glycol-3,3'-diphenyl-1,1'-binaphthalene, which has proven extremely powerful for analytical chiral separations of α -amino acids.⁶ Moreover, recent results have indicated that macrocyclic ligands can be incorporated into layered frameworks of zirconium phosphonates as well as network structures of other metal phosphonates.⁷ We thus envision that metal phosphonates containing pendant chiral crown ethers can be designed using a new rigid bisphosphonic acid ligand, 2,2'-pentaethylene glycol-1,1'-binaphthyl-6,6'-bis(phosphonic acid), **L-H**₄, was synthesized in five steps starting from known 6,6'-dibromo-2,2'-dihydroxy-1,1'-binaphthalene in 40.7% overall yield (Scheme 1). The key steps involve Pd-catalyzed phosphonation reaction of 6,6'-dibromo-2,2'-diacetyl-1,1'-binaphthalene to give 2,2'-diacetyl-1,1'-binaphthyl-6,6'-bis-(diethylphosphonate) and cyclization reaction of 2,2'-dihydroxy-1,1'-binaphthyl-6,6'-bis(diethylphosphonate) with pentaethylene glycol ditosylate to afford 2,2'-pentaethylene glycol-1,1'-binaphthyl-6,6'-bis(diethylphosphonate). All of the intermediates and **L-H**₄ were characterized by ¹H, ¹³C{¹H}, and ³¹P{¹H} NMR spectroscopies.

Enantiopure atropisomeric 2,2'-pentaethylene glycol-1,1'-binaphthyl-6,6'-bis(phosphonic acid), **L-H**₄, was synthesized in five steps starting from known 6,6'-dibromo-2,2'-dihydroxy-1,1'-binaphthalene in 40.7% overall yield (Scheme 1). The key steps involve Pd-catalyzed phosphonation reaction of 6,6'-dibromo-2,2'-diacetyl-1,1'-binaphthalene to give 2,2'-diacetyl-1,1'-binaphthyl-6,6'-bis-(diethylphosphonate) and cyclization reaction of 2,2'-dihydroxy-1,1'-binaphthyl-6,6'-bis(diethylphosphonate) with pentaethylene glycol ditosylate to afford 2,2'-pentaethylene glycol-1,1'-binaphthyl-6,6'-bis(diethylphosphonate). All of the intermediates and **L-H**₄ were characterized by ¹H, ¹³C{¹H}, and ³¹P{¹H} NMR spectroscopies.

Single crystals of homochiral lanthanide bisphosphonates with the general formula of [Ln₂(**L-H**)₂(MeOH)₈](**L-H**)₄·(HCl)₃·(H₂O)₆

Scheme 1^a



^a Reagents and conditions: (a) Ac₂O, Py, CH₂Cl₂, 99%; (b) diethyl phosphite, Pd(PPh₃)₄, 95%; (c) K₂CO₃, 95%; (d) pentaethylene glycol ditosylate, NaH, 47%; (e) Me₃SiBr in CH₂Cl₂, then MeOH, 99%; (f) Ln(NO₃)₃, H₂O, MeOH, HCl, 59% for both **1a** and **1b**.

(Ln = Nd, **1a** and Sm, **1b**) were synthesized in good yields by slow evaporation of an acidic mixture of Ln(NO₃)₃ and **L-H**₄ in methanol at room temperature (Scheme 1). The IR spectra of **1a** and **1b** display strong P–O stretches at 950–1150 cm⁻¹ and intense and broad O–H stretching vibrations at ~3350 cm⁻¹. Thermogravimetric analyses show that **1a** and **1b** lose three hydrogen chloride and six water molecules per formula unit by 100 °C. Formulations of **1a** and **1b** have been supported by microanalysis results.⁹

A single-crystal X-ray diffraction study of (*R*)-**1a** reveals a 2-D lamellar structure consisting of eight-coordinate Nd centers and monoprotonated **L-H** bridging groups. **1a** crystallizes in the chiral space group C₂.¹⁰ The asymmetric unit of **1a** contains two Nd centers lying on crystallographic two-fold axes, one **L-H** bridging ligand, four coordinated methanol molecules, one-half of a non-coordinating **L-H**₄ ligand, one and a half hydrogen chloride, and three water molecules. Both Nd centers adopt a square anti-prismatic geometry by coordinating to four methanol molecules and four phosphonate oxygen atoms of four different **L-H** ligands (Figure 1a). The dihedral angle between the naphthyl rings in coordinating **L-H** ligand is 107.56°, while the dihedral angle between the naphthyl rings in free **L-H**₄ ligand is 103.37°. Both phosphonate groups of the **L-H** ligand adopt a κ₂,μ₂ binding mode and link adjacent Nd centers to form doubly bridged 1-D lanthanide phosphonate chains along the *b* axis. The binaphthyl backbones of the **L-H** ligands link adjacent 1-D lanthanide phosphonate chains to form a 2-D coordination network lying in the *ab* plane (Figure 1b). This lamellar structure is entirely different from that of another family of lanthanide phosphonates reported recently.^{3a}

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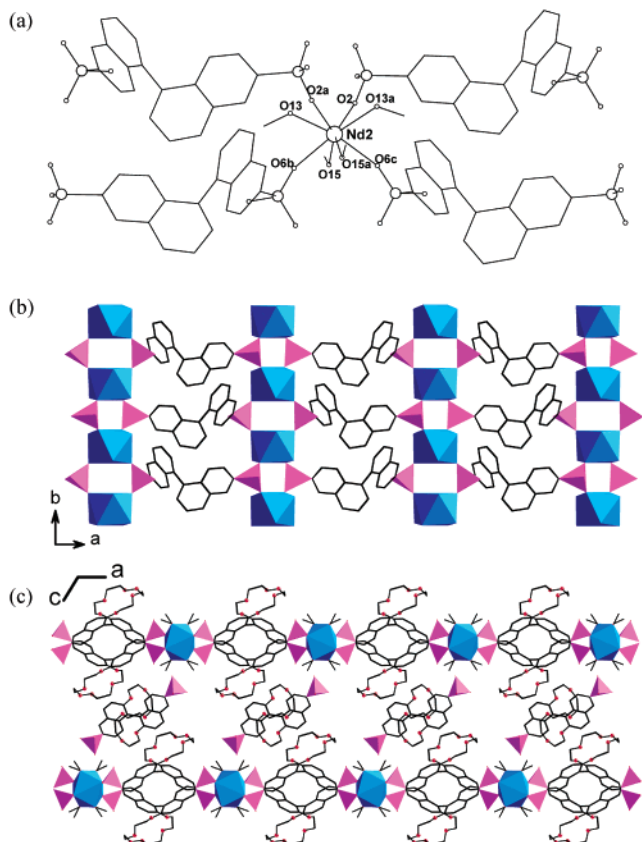


Figure 1. (a) Coordination environment of **1a**. For clarity, the crown ether groups of **L-H** ligands have been omitted. The circles with decreasing sizes represent Nd, P, O, and C atoms, respectively. (b) A view of the lamellar structure of **1a** down the *c* axis. For clarity, the crown ether groups of **L-H** ligands and the carbon atoms of coordinated methanol molecules have been omitted. (c) A view showing chiral crown ether pillared lanthanide phosphonate lamellae as well as the intercalation of free **L-H₄** molecules.

The most striking feature of **1a** is the placement of chiral crown ether groups between the lanthanide phosphonate layers (Figure 1c). Such chiral crown ether pillars have the potential to enantioselectively interact with organic cations such as protonated amino acids and thereby provide a novel material for bulk chiral separations. Interestingly, however, the lamellae of **1a** are intercalated with free **L-H₄** molecules, and, as a result, there is only enough void space in **1a** to accommodate three hydrogen chloride and six water molecules per formula unit.¹¹ The limited porosity of **1a** has thus precluded its application in bulk chiral separations.

Powder X-ray diffraction (PXRD) studies indicated that compound **1b** is isostructural to **1a**. We have also prepared **1a** and **1b** using (*S*)-**L-H₄**. CD spectra of both **1a** and **1b** made from *R*- and *S*-**L-H₄** are mirror images of each other, indicating their supramolecular enantiomeric nature. The framework stability of **1a** and **1b** was studied using PXRD. Upon evacuation at room temperature, **1a** and **1b** experienced weight losses consistent with the removal of three hydrogen chloride and six water molecules per formula unit. Powder patterns of the evacuated solids are essentially the same as those of pristine solids (Figure 2). These results unambiguously demonstrated the retention of framework structures of **1a** and **1b** after the removal of guest molecules.

In summary, we have synthesized and characterized the first porous lamellar lanthanide bisphosphonates that are pillared with chiral crown ethers. Current efforts are centered on increasing the porosity of these materials via modifications of the bridging bisphosphonic acids and exploring their applications in enantioselective processes.

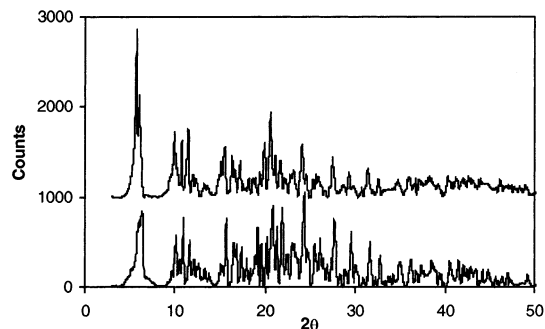


Figure 2. XRPD of **1a** before (top) and after (bottom) the removal of three hydrogen chloride and six water molecules.

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Supporting Information Available: Experimental procedures and four figures (PDF). A crystallographic data file in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (9) Anal. Calcd (found) for C₉₈H₁₄₃Cl₃Nd₂O₅₀P₆, **1a**: C, 43.6(41.7); H, 5.33(4.65); N, 0(0.22); Cl, 3.94(3.69%). Anal. Calcd (found) for C₉₈H₁₄₃Cl₃-Sm₂O₅₀P₆, **1b**: C, 43.4(41.0); H, 5.31(4.16); N, 0(0.27); Cl, 3.92(3.77%). The samples are consistently low in C and H content.
- (10) X-ray data for **1a** were collected on a Bruker SMART CCD diffractometer equipped with Mo K α radiation. Crystal data for **1a**: monoclinic, space group C2, with *a* = 32.758(3), *b* = 10.733(1), *c* = 20.008(2) Å, β = 121.888(1)°, *V* = 5972.7(8) Å³, *Z* = 2, *D*_{calc} = 1.50 g/cm³. Least-squares refinement based on 6024 reflections with *I* > 2 σ (*I*) and 531 parameters led to convergence, with a final value of R1 = 0.084 and wR2 = 0.208. Flack parameter = 0.06(4).
- (11) Microanalysis results indicated the absence of Cl in the evacuated solids of **1a** and **1b** and thus unambiguously demonstrated the presence of HCl as the guest molecules.

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