



$\text{Ln}_2(\text{O}_2\text{CCH}_2\text{PO}_3)_2(\text{H}_2\text{O})_3 \cdot \text{H}_2\text{O}$ (Ln = La, Pr, Nd, Sm): Layered lanthanide phosphonoacetates containing two-dimensional $-\text{Ln}-\text{O}-$ linkages

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ABSTRACT

Four novel isostructural lanthanide phosphonate compounds with formula $\text{Ln}_2(\text{O}_2\text{CCH}_2\text{PO}_3)_2(\text{H}_2\text{O})_3 \cdot \text{H}_2\text{O}$ [Ln = La (**1**), Pr (**2**), Nd (**3**), Sm (**4**)] have been prepared through hydrothermal reactions of phosphonoacetate acid and lanthanide nitrates. All show layered structures made up of $\{\text{LnO}_9\}$ polyhedra and $\{\text{CPO}_3\}$ tetrahedra with the lattice water molecules locating between the layers. Within the layer, chains of edge-sharing $\{\text{LnO}_9\}$ polyhedra are connected via corner-sharing by phosphonate oxygens forming a two-dimensional $-\text{Ln}-\text{O}-$ linkage. Thermal analyses and XRD measurements reveal that the framework structures can be maintained up to 400 °C.

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1. Introduction

The introduction of lanthanide centers into the inorganic–organic hybrid solids has been of great interest because it may create unusual architectures, and give unique properties due to their f–f electronic transitions [1,2]. A number of lanthanide phosphonates have been reported so far, most of which contain functional groups in the phosphonate ligands in order to improve the solubility and hence the crystallization of the products [3]. However, despite impressive progress in this field, one challenge that remains is the control of the dimensionality of the $\text{Ln}-\text{O}$ linkages. Most of the lanthanide phosphonates discovered up to now are polymers in which the metallic moieties are either single polyhedra or isolated small clusters, which could reduce their performance and/or their thermal stability for application purpose. Only in a few cases, the rare-earth polyhedra are linked by edge-sharing to form chains which are further connected by phosphonate groups into a two- or three-dimensional network. These examples include $\text{La}(\text{O}_3\text{PCH}_2\text{C}_6\text{H}_5)(\text{HO}_3\text{PCH}_2\text{C}_6\text{H}_5)(\text{H}_2\text{O})_2$, $\text{La}(\text{O}_3\text{PC}_6\text{H}_5)(\text{HO}_3\text{PC}_6\text{H}_5)$ [4], $\text{LnH}[\text{O}_3\text{P}(\text{CH}_2)_n\text{PO}_3]$ ($n = 1-3$; Ln = Pr, Nd, Eu, Gd) [5], $\text{Pr}[\text{O}_3\text{P}(\text{CH}_2)_2\text{CO}_2]$ [6], $\text{Gd}[(\text{O}_3\text{PCH}_2)(\text{HO}_3\text{PCH}_2)\text{N}(\text{H})(\text{CH}_2)_4\text{N}(\text{H})(\text{CH}_2\text{PO}_3\text{H}_2)] \cdot 2\text{H}_2\text{O}$ [7], and $\text{Sm}[(\text{O}_3\text{PCH}_2)_2\text{NHCH}_2\text{C}_6\text{H}_4\text{COOH}] \cdot \text{H}_2\text{O}$ [8]. As far as we are aware, lanthanide phosphonates containing two- or three-dimensional $-\text{Ln}-\text{O}-\text{Ln}-\text{O}-$ linkages have never been reported.

In this paper, we employ a hydrothermal synthetic route by using phosphonoacetate and the lanthanide nitrates as the starting materials. Four new compounds are crystallized with formula

$\text{Ln}_2(\text{O}_2\text{CCH}_2\text{PO}_3)_2(\text{H}_2\text{O})_3 \cdot \text{H}_2\text{O}$ [Ln = La (**1**), Pr (**2**), Nd (**3**), Sm (**4**)]. All contain edge-sharing $\{\text{LnO}_9\}$ polyhedra chains linked via corner-sharing into a layer. Hence, compounds **1–4** provide first examples of lanthanide phosphonates that contain two-dimensional $-\text{Ln}-\text{O}-\text{Ln}-\text{O}-$ linkages.

2. Experimental

2.1. Materials and instruments

All starting materials were of reagent quality and were obtained from commercial sources without further purification. Elemental analyses were performed on a Perkin Elmer 240 C elemental analyzer. The IR spectra were obtained as KBr disks on a VECTOR 22 spectrometer. Thermal analyses were performed in nitrogen with a heating rate of 10 °C/min on a TGA V5.1A Dupont 2100 instrument. XRD were performed on an XRD-6000 X-ray diffractometer.

2.2. Preparations

A mixture of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (0.2 mmol, 0.0866 g) and phosphonoacetate acid (0.2 mmol, 0.0280 g) in 8 mL H_2O , stirred for 10 min at room temperature, was transferred to a Teflon-lined autoclave and heated at 160 °C for 2 days. After slowly cooled to room temperature, flake crystals of **1** were obtained as a monophasic product, judged by the XRD measurements. Compounds **2–4** were synthesized following the same procedure as compound **1** except different lanthanide nitrates. Yield: 0.0450 g (72% based on La) for **1**, 0.0530 g (85% based on Pr) for **2**, 0.0520 g (82% based on Nd) for **3**, 0.0430 g (68% based on Sm) for **4**, respectively. Anal. Calc.

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Table 1
Crystallographic data for compounds **1–4**

Compound	1	2	3	4
Formula	C ₄ H ₁₂ La ₂ O ₁₄ P ₂	C ₄ H ₁₂ Pr ₂ O ₁₄ P ₂	C ₄ H ₁₂ Nd ₂ O ₁₄ P ₂	C ₄ H ₁₂ Sm ₂ O ₁₄ P ₂
<i>M</i>	623.9	627.90	634.56	646.78
Crystal system	triclinic	triclinic	triclinic	triclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> (Å)	9.0299(12)	8.9447(13)	8.924(2)	8.9090(12)
<i>b</i> (Å)	9.0376(12)	8.9579(12)	8.934(3)	8.9207(12)
<i>c</i> (Å)	9.8256(13)	9.7446(14)	9.727(3)	9.7032(13)
α (°)	110.241(2)	110.089(2)	109.960(4)	109.949(2)
β (°)	108.157(2)	107.864(2)	107.774(4)	107.763(2)
γ (°)	91.563(2)	91.653(3)	91.804(4)	91.762(2)
<i>V</i> (Å ³)	706.62(16)	690.02(17)	686.1(3)	682.45(16)
<i>Z</i>	2	2	2	2
<i>D</i> _{calc} (g cm ⁻³)	2.932	3.022	3.072	3.148
μ (Mo K α) (mm ⁻¹)	6.263	7.283	7.791	8.829
<i>F</i> (000)	584	592	596	604
Total	2811, 2372,	2900, 2455,	3516, 2985,	2824, 2441,
Unique	0.0300	0.0489	0.0882	0.0324
Data, <i>R</i> _{int}				
Observed data	2078	2213	2842	2204
[<i>I</i> > 2.0 σ (<i>I</i>)]				
<i>R</i> ₁ , <i>wR</i> ₂ , ^a	0.0300,	0.0314,	0.0639,	0.0263, 0.0684,
GOF	0.0696, 1.001	0.0816, 1.014	0.1792, 1.059	1.031
($\Delta\rho$) _{max} , ($\Delta\rho$) _{min} (e Å ⁻³)	1.173, -0.894	1.692, -1.194	4.827, -3.358	1.054, -0.849

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|; wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}.$$

for **1**: C, 7.70; H, 1.94. Found: C, 7.67; H, 1.81%. *Anal. Calc.* for **2**: C, 7.65; H, 1.93. Found: C, 7.42; H, 1.71%. *Anal. Calc.* for **3**: C, 7.57; H, 1.91. Found: C, 7.38; H, 1.83%. *Anal. Calc.* for **4**: C, 7.43; H, 1.87. Found: H, 7.36; H, 1.78%. IR (KBr, cm⁻¹) for **1**: 3374 (s), 1572 (s), 1416 (vs), 1232 (w), 1172 (m), 1109 (vs), 1019 (vs), 992 (s), 981 (s), 945 (m), 808 (w), 755 (w), 730 (w), 606 (m), 563 (m), 527 (m), 481 (m), 421 (w).

2.3. Crystallographic studies

Single crystals of dimensions 0.12 × 0.10 × 0.04 mm³ for **1**, 0.11 × 0.10 × 0.04 mm³ for **2** and 0.11 × 0.08 × 0.03 mm³ for **3**, 0.10 × 0.08 × 0.03 mm³ for **4** were used for structural determinations on a Bruker SMART APEX CCD diffractometer using graphite-monochromatized Mo K α radiation ($\lambda = 0.71073$ Å) at room temperature. A hemisphere of data was collected using a narrow-frame method with scan widths of 0.30° in ω and an exposure time of 5 s/frame. The data were integrated using the Siemens SAINT program [9] with the intensities corrected for Lorentz factor, polarization, air absorption, and absorption due to variation in the path length through the detector faceplate. Empirical absorption corrections were applied. The structures were solved by direct methods and were refined on *F*² by full matrix least squares using SHELXTL [10]. All the non-hydrogen atoms were located from the Fourier maps, and were refined anisotropically. All H atoms were refined isotropically, with the isotropic vibration parameters related to the non-H atom to which they are bonded. Crystallographic data for compounds **1–4** are listed in Table 1. Selected bond lengths and angles are given in Table 2.

3. Results and discussion

3.1. Description of the structures

Compounds **1–4** are isostructural, confirmed by both the XRD measurements (Fig. 1) and single crystal structural analyses. Take

Table 2
Selected bond lengths (Å) and angles (°) for compounds **1–4**^a

	1 (La)	2 (Pr)	3 (Nd)	4 (Sm)
Ln(1)–O(10)	2.444(4)	2.408(4)	2.394(5)	2.398(4)
Ln(1)–O(5A)	2.463(4)	2.411(4)	2.398(5)	2.390(4)
Ln(1)–O(10B)	2.523(4)	2.494(4)	2.481(5)	2.480(4)
Ln(1)–O(3)	2.537(5)	2.496(4)	2.479(5)	2.478(4)
Ln(1)–O(1W)	2.569(4)	2.526(4)	2.514(5)	2.500(4)
Ln(1)–O(2W)	2.579(5)	2.536(4)	2.518(6)	2.523(4)
Ln(1)–O(7)	2.606(5)	2.581(4)	2.574(6)	2.573(4)
Ln(1)–O(4)	2.630(4)	2.582(4)	2.576(5)	2.568(4)
Ln(1)–O(9B)	2.820(4)	2.826(4)	2.832(5)	2.832(4)
Ln(2)–O(8C)	2.440(4)	2.399(4)	2.393(5)	2.376(4)
Ln(2)–O(4)	2.467(4)	2.419(4)	2.403(5)	2.403(4)
Ln(2)–O(9D)	2.512(4)	2.466(4)	2.456(5)	2.445(4)
Ln(2)–O(1)	2.519(4)	2.494(4)	2.478(5)	2.482(4)
Ln(2)–O(3W)	2.575(4)	2.520(5)	2.500(6)	2.489(4)
Ln(2)–O(1E)	2.595(4)	2.555(4)	2.538(5)	2.534(4)
Ln(2)–O(7)	2.598(4)	2.562(4)	2.552(6)	2.544(4)
Ln(2)–O(2E)	2.648(4)	2.607(4)	2.607(6)	2.596(4)
Ln(2)–O(6)	2.752(5)	2.744(5)	2.738(6)	2.738(5)
P(1)–O(3)	1.519(4)	1.520(4)	1.524(5)	1.520(4)
P(1)–O(4)	1.528(5)	1.534(4)	1.528(6)	1.524(4)
P(1)–O(5)	1.509(5)	1.512(4)	1.512(5)	1.510(4)
P(2)–O(8)	1.515(4)	1.522(4)	1.518(5)	1.526(4)
P(2)–O(9)	1.519(4)	1.519(4)	1.516(5)	1.519(4)
P(2)–O(10)	1.541(5)	1.536(4)	1.541(5)	1.530(4)
O(1)–C(1)	1.267(7)	1.261(7)	1.260(8)	1.256(7)
O(2)–C(1)	1.240(7)	1.238(7)	1.254(9)	1.238(7)
O(6)–C(3)	1.244(7)	1.239(7)	1.256(9)	1.242(7)
O(7)–C(3)	1.266(8)	1.262(7)	1.250(10)	1.257(7)
Ln(2)–O(1)–Ln(2E)	114.4(2)	114.3(2)	114.7(2)	114.5(2)
Ln(2)–O(4)–Ln(1)	118.9(2)	120.3(2)	120.6(2)	120.4(2)
Ln(2)–O(7)–Ln(1)	115.1(2)	115.0(2)	115.1(2)	115.0(2)
Ln(2F)–O(9)–Ln(1B)	120.9(2)	122.9(2)	123.5(2)	123.5(1)
Ln(1)–O(10)–Ln(1B)	115.9(2)	115.3(2)	115.3(2)	114.9(2)

^a Symmetry codes: (A) $-x + 1, -y, -z + 2$; (B) $-x, -y, -z + 2$; (C) $-x, -y, -z + 1$; (D) $x + 1, y, z$; (E) $-x + 1, -y, -z + 1$; (F) $x - 1, y, z$.

1 as an example. Compound **1** crystallizes in the triclinic space group *P* $\bar{1}$. The asymmetric unit consists of two La atoms, two 4-pa³⁻, and four water molecules (Fig. 2). There are two crystallographically distinguished La atoms, both locating in general positions. The La(1) atom is nine-coordinated, six sites are occupied by phosphonate oxygen atoms [O(3), O(4), O(5A), O(9B), O(10), O(10B)] from four 4-pa³⁻ ligands. The other three sites are filled with the carboxylate oxygen atom [O(7)] and two water molecules [O(1W), O(2W)]. The La(2) atom is also nine-coordinated. Five coordination positions are provided by carboxylate oxygen atoms [O(1), O(1E), O(2E), O(6), O(7)] from three 4-pa³⁻ ligands and three by phosphonate oxygen atoms [O(4), O(8C), O(9D)] from three 4-pa³⁻ ligands. The water oxygen atom [O(3W)] fills in the remaining site. The La–O bond lengths are in the range of 2.440(5)–2.820(5) Å.

Two 4-pa³⁻ ligands are crystallographically distinguished, each serves as a multi-dentate ligand by using its three phosphonate and two carboxylate oxygens (Scheme 1). The 4-pa³⁻(P1) ligand chelates to the La(1) atom through phosphonate oxygens O(3) and O(4), while to the La(2) atom through carboxylate oxygens O(1) and O(2) forming four-membered rings. It also chelates to the equivalent La(2) atom through both phosphonate [O(4)] and carboxylate [O(1)] oxygen atoms, forming a six-membered ring. The phosphonate oxygen O(4) and the carboxylate oxygen O(1) act as μ_3 -O bridges and connect the La atoms (Scheme 1a). The coordination mode of the 4-pa³⁻(P2) ligand (Scheme 1b) may be compared with that of the 4-pa³⁻(P1) ligand. In this case, however, there are two phosphonate oxygen [O(9), O(10)] and one carboxylate oxygen [O(7)] atoms that behave as μ_3 -O bridges, and the same ligand is coordinated to five La atoms including two La(1) and three La(2) atoms (Scheme 1b). Consequently, the {La(1)O₉} and {La(2)O₉} polyhedra are edge-shared through O(4) and O(7) atoms.

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