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Synthesis, crystal structures, and luminescent properties of two types of lanthanide phosphonates

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ABSTRACT

Hydrothermal reactions of different lanthanide(III) salts with an amino-diphosphonate ligand ($H_4L = C_6H_5CH_2N(CH_2PO_3H_2)_2$) led to two series of lanthanide phosphonates, namely, $Ln(H_2L)(H_3L)$ (Ln = La, **1**; Pr, **2**; Nd, **3**; Sm, **4**; Eu, **5**; Gd, **6**; Tb, **7**). Compounds **1–5** feature a one-dimensional (1D) chain structure in which dimers of two edge-sharing LnO_8 polyhedra are interconnected by bridging phosphonate groups, such 1D arrays are further interlinked via strong hydrogen bonds between non-coordinated phosphonate oxygen atoms into a two-dimensional (2D) layer with the phenyl groups of the ligands orientated toward the interlayer space. Compounds **6** and **7** also show a different 1D array in which the LnO_6 octahedra are bridged by phosphonate groups via corner-sharing, such chains are also further interlinked by hydrogen bonds into a 2D supramolecular layer. Compounds **5** and **7** emit red and green light with a lifetime of 2.1 and 3.7 ms, respectively.

1. Introduction

Chemistry of metal phosphonates is expanding rapidly in recent years due to these compounds' versatile architectures and topologies as well as their potential applications in catalysis, ion exchange, magnetism, and materials chemistry [1–5]. The strategy of modification of the phosphonic acid with various functional groups such as crown ether, amine, hydroxyl, or/and carboxylate groups has been proven to be an extremely effective route for the construction of metal phosphonates with open framework structures [6–15]. So far, a variety of intriguing networks have been well documented in several reviews [4,16]. Lanthanide phosphonates are important since they can exhibit intense luminescence that has found applications in fluorescent probes and electroluminescent devices [17–20]. However, lanthanide phosphonates are still relatively unexplored, due to their low solubility in water and other organic solvents as well as their poor crystallinity; hence, it is still a difficult task to obtain single crystals suitable for X-ray structural analysis. Results from our previous studies indicate that phosphonic acid, in conjunction with a suitable ancillary ligand such as 5-sulfoisophthalic acid (H_3BTS) or oxalate, is an effective route for the preparation of crystalline lanthanide phosphonates [21–23]. Another useful alternative method is the use of the phosphonic acid attached with functional groups with additional coordination atoms such as the carboxylate acid or amino acid [24–27]. As an extension of our previous work, in this work we used an amino-diphosphonate ligand, *N*-benzyliminobis(methylenephosphonic acid), $C_6H_5CH_2N(CH_2PO_3H_2)_2$ (H_4L), whose transition metal complexes have been reported to exhibit two-dimensional (2D) layers or one-dimensional (1D) arrays [28–31]. We hope to get better understandings of the effects of different metal cations on the final structures and the photoluminescence properties. Our research efforts afforded two series of lanthanide phosphonates, namely, $Ln(H_2L)(H_3L)$ (Ln = La, **1**; Pr, **2**; Nd, **3**; Sm, **4**; Eu, **5**) and $Ln(H_2L)(H_3L)$ (Ln = Gd, **6**; Tb, **7**). Both types of compounds feature 2D supramolecular networks based on 1D arrays interconnected via hydrogen bonds.

2. Experimental section

2.1. Materials and methods

$LnCl_3 \cdot nH_2O$ (Ln = La, Pr, Nd, Sm, Eu, Gd, Tb) were prepared by dissolving lanthanide oxide in hydrochloric acid, and then the mixture was heated at ~100 °C in the air until a lot of powder appeared. $C_6H_5CH_2N(CH_2PO_3H_2)_2$ (H_4L) were prepared by a Mannich-type reaction according to procedures described previously [32–34]. All other chemicals were obtained from commercial sources and used without further purification. Elemental analyses (C, H, and N) were carried out on a Vario EL III elemental analyser. IR spectra were recorded on a Magna 750 FT-IR

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spectrophotometer using KBr pellets in the range 4000–400 cm^{-1}. Thermal gravimetric analyses (TGA) analysis was performed on a NETZSCH STA 449C unit under oxygen flow at a heating rate of 10 °C min^{-1}. Photoluminescence analyses were performed on a Perkin-Elemer LS55 fluorescence spectrometer. XRD powder patterns (Cu$K\alpha$) were collected on an XPERT-MPD 2θ diffractometer.

2.2. Syntheses of Ln(H_2L)(H_3L) (Ln = La, 1*; Pr,* 2*; Nd,* 3*; Sm,* 4*; Eu,* 5*)*

A mixture of $LnCl_3 \cdot nH_2O$ (0.25 mmol), H_4L (0.295 g, 1 mmol) in 10 mL of distilled water was sealed in an autoclave equipped with a Teflon liner (23 mL) and its pH value is ~1. Then the solution was heated at 165 °C for 5 days. Crystals of **1** (colourless), **2** (green), **3** (purple), **4** (colourless), and **5** (yellow) were collected in ca. yields of 78%, 81%, 82%, 73%, and 75% (based on lanthanide), respectively. The measured XRD patterns are comparable with the simulated ones (see Supporting Information). Anal. Calcd. for $C_{18}H_{27}N_2O_{12}P_4La$: C, 29.77; H, 3.75; N, 3.86%. Found: C, 29.49; H, 3.98; N, 3.68%. IR data (KBr, cm^{-1}): 3005 (m), 2944 (m), 2815 (m), 2746 (m), 2601 (m), 1458 (m), 1249 (s), 1170 (s), 1118 (s), 920 (m), 852 (w), 811 (w), 738 (m), 588 (m), 565 (w), 531 (m). Anal. Calcd. for $C_{18}H_{27}N_2O_{12}P_4Pr$: C, 29.69; H, 3.74; N, 3.85%. Found: C, 29.48; H, 3.96; N, 3.61%. IR data (KBr, cm^{-1}): 3007 (m), 2945 (m), 2813 (m), 2745 (m), 2565 (m), 1458 (m), 1249 (s), 1171 (s), 1134 (s), 920 (m), 740 (m), 589 (w), 567 (w), 531 (m). Anal. Calcd. $C_{18}H_{27}N_2O_{12}P_4Nd$: C, 29.55; H, 3.72; N, 3.83%. Found: C, 29.32; H, 3.89; N, 3.63%. IR data (KBr, cm^{-1}): 3007 (m), 2944 (m), 2814 (m), 2745 (m), 2595 (m), 1458 (m), 1248 (s), 1171 (s), 1134 (s), 920 (m), 895 (m), 739 (m), 589 (w), 569 (w), 530 (m). Anal. Calcd. for $C_{18}H_{27}N_2O_{12}P_4Sm$: C, 29.31; H, 3.69; N, 3.80%. Found: C, 29.02; H, 3.91; N, 3.65%. IR data (KBr, cm^{-1}): 3008 (m), 2956 (m), 2813 (m), 2746 (m), 2546 (m), 1459 (m), 1249 (s), 1173 (s), 1133 (s), 920 (m), 740 (m), 590 (w), 568 (w), 530 (m). Anal. Calcd. for $C_{18}H_{27}N_2O_{12}P_4Eu$: C, 29.24; H, 3.68; N, 3.79%. Found: H, 3.95; C, 28.06; N, 3.57%. IR data (KBr, cm^{-1}): 3007 (m), 2946 (m), 2814 (m), 2746 (m), 2545 (m), 1458 (m), 1248 (s), 1172 (s), 1134 (s), 920 (m), 739 (m), 589 (w), 569 (w), 530 (m).

2.3. Syntheses of Ln(H_2L)(H_3L) (Ln = Gd, 6*; Tb,* 7*)*

A mixture of $LnCl_3 \cdot 6H_2O$ (0.25 mmol), H_4L (0.295 g, 1 mmol) in distilled water (10 mL) was sealed in an autoclave equipped with a Teflon liner (23 mL) and its pH value is ~1. Then the solution was heated at 165 °C for 5 days. Needle-like crystals of **6** (colourless) and **7** (colourless) were collected in ca. 64% and 82% yield (based on lanthanide), respectively. The measured XRD powder patterns are comparable with the simulated ones (see Supporting Information). Anal. Calcd. for $C_{13}H_{27}N_2O_{12}P_4Gd$: C, 29.04; H, 3.66; N, 3.76%. Found: C, 28.78; H, 3.82; N, 3.57%. IR data (KBr, cm^{-1}): 3007 (m), 2945 (m), 2850 (m), 2745 (m), 2545 (m), 1458 (m), 1247 (s), 1172 (s), 1133 (s), 920 (m), 739 (m), 589 (w), 568 (w), 529 (m). Anal. Calcd. for $C_{13}H_{27}N_2O_{12}P_4Tb$: C, 28.97; H, 3.65; N, 3.75%. Found: C, 28.65; H, 3.78; N, 3.56%. IR data (KBr, cm^{-1}): 3007 (m), 2966 (m), 2756 (m), 2722 (m), 1430 (m), 1246 (s), 1164 (s), 1099 (s), 912 (m), 739 (m), 591 (m), 565 (m), 535 (m).

2.4. Single-crystal structure determination

Based on the measured XRD powder patterns, compounds **1–5** are isostructural, so are compounds **6** and **7** (see Supporting Information). Therefore, only compounds **4** and **7** were subject to single-crystal structural analyses. Date collections for compounds **4** and **7** were performed on a Siemens Smart CCD diffractometer equipped with graphite-monochromated Mo$K\alpha$ radiation ($\lambda = 0.71073$ Å). Intensity data were collected by the narrow frame method at 293 K and corrected for Lorentz and polarization effects as well as for absorption by the SADABS programme [35,36]. Both structures were solved by direct methods and refined by full-matrix least-squares cycles in SHELX-97 [37]. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms attached to the C and N atoms were located at geometrically calculated positions and refined with isotropic thermal parameters. Crystallographic data and structural refinement parameters for compounds **4** and **7** are summarized in Table 1. Important bond distances are listed in Table 2.

CCDC-684385 (**4**) and CCDC-684386 (**7**) contain the supplementary crystallographic materials for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

3. Results and discussion

The isolations of compounds **1–7** rely on the hydrothermal techniques. Results indicate that the reaction conditions play an important role in the formation of the title compounds. Pure phases were obtained at the L/Ln ratio of 4:1, low pH values of the reaction mixture favour the protonation of some phosphonate groups and facilitate the formation of low-dimensional coordination polymers. When the L/Ln ratio is less than 1:1 at the same conditions, we could not obtain the single crystals but only unknown precipitates.

3.1. Structure description for Ln(H_2L)(H_3L) (Ln = La, 1*; Pr,* 2*; Nd,* 3*; Sm,* 4*; Eu,* 5*)*

Compounds **1–5** are isostructural, hence the structure of compound **4** was described representatively. The asymmetric unit of **4** consists of a Sm(III) ion, a $\{H_2L\}^{2-}$ and a $\{H_3L\}^{-}$ anion (Fig. 1). The Sm(III) center is eight-coordinated by three oxygen atoms from three $\{H_3L\}^{-}$ anions and five oxygen atoms from three $\{H_2L\}^{2-}$ anions. The Sm–O distances are in the range of 2.345(5)–2.725(6) Å. The two phosphonate ligands adopt two different types of coordination modes (Scheme 1). The $\{H_3L\}^{-}$ anion acts as a tridentate ligand, one phosphonate group is monodnetate whereas the other one is bidentate bridging (Scheme 1a), both phosphonate groups are singly protonated (O7, O11) based on P–O distances (Table 2), so is the amine group.

Table 1
Crystal data and structure refinements for **4** and **7**

Compound	**4**	**7**
Formula	$C_{18}H_{27}N_2O_{12}P_4Sm$	$C_{18}H_{27}N_2O_{12}P_4Tb$
fw	737.65	746.22
Crystal system	Triclinic	Orthorhombic
Space group	$P{-}1$	$P2_12_12_1$
a (Å)	8.056(3)	7.994(2)
b (Å)	12.755(5)	25.351(7)
c (Å)	13.498(7)	25.589(8)
α (deg)	115.395(9)	90
β (deg)	92.49(2)	90
γ (deg)	93.030(2)	90
V ($Å^3$)	1247.8(9)	5186(3)
Z	2	8
D_c ($g\,cm^{-3}$)	1.963	1.911
μ (mm^{-1})	2.676	3.038
R_1, wR_2 [$I > 2\sigma(I)$]	$R1 = 0.0545$, w$R2 = 0.1441$	$R1 = 0.0587$, w$R2 = 0.1133$
R_1, wR_2 (all data)	$R1 = 0.0576$, w$R2 = 0.1460$	$R1 = 0.0780$, w$R2 = 0.1267$
GOF^c	1.087	1.093

$R_1 = \Sigma \| F_0| - |F_c \| / \Sigma |F_0|$, $wR_2 = \Sigma[w(F_0^2 - F_c^2)^2] / \Sigma[w(F_0^2)^2]^{1/2}$.