

Syntheses, Crystal Structures, and Characterizations of a Series of New Layered Lanthanide Carboxylate-Phosphonates

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Hydrothermal reactions of different lanthanide(III) salts with $(\text{H}_2\text{O}_3\text{PCH}_2)_2\text{NCH}_2\text{COOH}$ (H_5L^1) led to two new layered lanthanide(III) carboxylate-diphosphonates, namely $\text{La}(\text{H}_2\text{L}^1)(\text{H}_2\text{O})_2 \cdot \text{H}_2\text{O}$ (**1**) and $\text{La}(\text{H}_2\text{L}^1)(\text{H}_2\text{O})$ (**2**). The structure of compound **1** features a layered architecture in which the nine-coordinate La^{3+} ions are bridged by phosphonate groups of the ligands. The carboxylate group of the phosphonate ligand remains protonated and is involved in the interlayer hydrogen bonding. Compound **2** features a double layer structure in which the La^{3+} ion is eight-coordinated and the carboxylate group of the ligand is chelated to a La^{3+} ion in a bidentate fashion. Hydrothermal reactions of lanthanide(III) salts with $4\text{-HOOC-C}_6\text{H}_4\text{-CH}_2\text{N}(\text{CH}_2\text{PO}_3\text{H}_2)_2$ (H_5L^2) afforded three new compounds, namely, $\text{La}(\text{H}_4\text{L}^2)(\text{H}_3\text{L}^2)(\text{H}_2\text{O}) \cdot 2\text{H}_2\text{O}$ (**3**), $\text{Er}(\text{H}_3\text{L}^2)(\text{H}_4\text{L}^2)$ (**4**), and $\text{Er}(\text{HL}^3)(\text{H}_2\text{L}^3)(\text{H}_2\text{O})$ (**5**) [$\text{H}_2\text{L}^3 = \text{H}_2\text{O}_3\text{PCH}_2\text{N}(\text{CHO})(\text{CH}_2\text{-C}_6\text{H}_4\text{-COOH})$]. H_5L^2 was formed by the in situ oxidation of one P-C bond of the H_5L^2 ligand. Compound **3** features a (002) lanthanum(III)

phosphonate layer in which the seven-coordinate La^{3+} ions are bridged by diphosphonate moieties of the ligands. The carboxylate group remains protonated and is involved in the interlayer hydrogen bonding. The structure of compound **4** contains a 1D chain along the a axis in which each pair of ErO_6 octahedra is bridged by a pair of phosphonate groups. These 1D chains are further interconnected by hydrogen bonds between noncoordinated phosphonate oxygen atoms into a (002) layer with the phenyl carboxylate groups hanging on the interlayer space. The structure of compound **5** is also layered. The interconnection of Er^{3+} ions by bidentate and tetradentate bridging phosphonate groups resulted in a (002) inorganic layer with the organic groups orientated to the interlayer space. Luminescence properties of compounds **4** and **5** have also been studied.

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Introduction

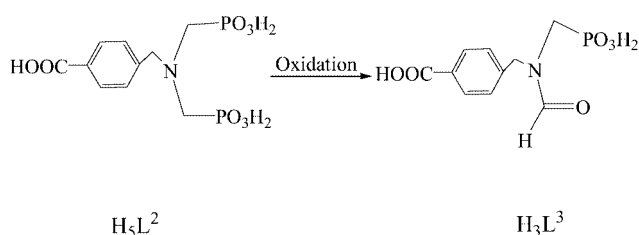
During the past two decades, a lot of research attention has been devoted to the chemistry of metal phosphonates for their potential applications in the areas of catalysis, ion exchange, proton conductivity, intercalation chemistry, photochemistry, and materials chemistry.^[1] Most metal phosphonates exhibit a variety of open framework architectures such as layered and microporous structures. The use of bi-functional or multifunctional anionic units, such as diphosphonates, aminophosphonates, or phosphonocarboxylates, has been found to be an effective method to prepare new materials with microporous or open framework structures.^[2–5] Results from ours and other groups indicate that amino-carboxylic-phosphonic acids are good ligands for building inorganic–organic hybrid open frameworks.^[6] Reports on lanthanide phosphonates are rather limited and a number of them are based on X-ray powder diffraction.^[7–11,13–16] Low solubility and poor crystallinity are two

big obstacles for the structural studies for these lanthanide(III) compounds. The elucidation of the structures of lanthanide phosphonates is very important, as these compounds may exhibit useful luminescent properties in both visible and near IR regions.^[12] A series of lanthanide diphosphonates with a 3D pillared-layer structure were isolated by the Ferey group.^[13] Several lanthanide phosphonates with a crown ether or calixarene moiety have been reported by Clearfield, Bligh, Lukes, and Lin et al.^[8a,14] Their structures normally feature a chelating mononuclear unit or a layer architecture. A series of one-dimensional lanthanide diphosphonates containing a hydroxy group were also reported.^[15] Results from our group indicate that introducing a second ligand such as 5-sulfoisophthalic acid (H_3BTS) or oxalate acid, whose lanthanide compounds have good solubility and very good crystallinity, into the lanthanide–phosphonate system can lead to novel luminescent lanthanide phosphonate hybrids.^[16] Another useful alternative method is the use of a phosphonic acid to which the carboxylate group or amino acid moiety is directly attached. So far, research on this aspect is scarce. Only a few 2D or 3D lanthanide phosphonates with additional carboxylate group or amino acid moiety have been prepared.^[17] We have initiated a research project to systematically study the influence of counteranion, pH value, the ionic size of the lanthanide(III)

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ion and the substituent on the structures, and luminescence properties of lanthanide amino-carboxylate-phosphonates formed. Two carboxylate-phosphonic acids, H_5L^1 [$H_5L^1 = (H_2O_3PCH_2)_2NCH_2COOH$] and H_5L^2 [$H_5L^2 = 4-HOOC-C_6H_4-CH_2N(CH_2PO_3H_2)_2$], in which the carboxylate group is well separated from the diphosphonate moiety were selected. Hydrothermal reactions of the lanthanide(III) salts with the above two phosphonic acids afforded five new compounds, namely, $La(H_2L^1)(H_2O)_2 \cdot H_2O$ (**1**), $La(H_2L^1)(H_2O)$ (**2**), $La(H_4L^2)(H_3L^2)(H_2O) \cdot 2H_2O$ (**3**), $Er(H_3L^2)(H_4L^2)$ (**4**), and $Er(HL^3)(H_2L^3)(H_2O)$ (**5**) [$H_3L^3 = H_2O_3PCH_2N(CHO)(CH_2-C_6H_4-COOH)$]. H_3L^3 resulted from the in situ oxidation of one P–C bond of the H_5L^2 ligand during the reaction (Scheme 1). Herein we report their syntheses, crystal structures, and luminescent properties.



Scheme 1. The formation of H_3L^3 by the in situ oxidation of H_5L^2 .

Results and Discussion

Hydrothermal reactions of different lanthanide(III) salts with $(H_2O_3PCH_2)_2NCH_2COOH$ (H_5L^1) at two different temperatures lead to two new layered lanthanide(III) carboxylate-diphosphonates, namely $La(H_2L^1)(H_2O)_2 \cdot H_2O$ (**1**) and $La(H_2L^1)(H_2O)$ (**2**). The higher temperature used for the synthesis resulted in compound **2** with fewer water molecules. Hydrothermal reactions of lanthanide(III) salts with $4-HOOC-C_6H_4-CH_2N(CH_2PO_3H_2)_2$ (H_5L^2) afforded three new compounds, namely, $La(H_4L^2)(H_3L^2)(H_2O) \cdot 2H_2O$ (**3**), $Er(H_3L^2)(H_4L^2)$ (**4**), and $Er(HL^3)(H_2L^3)(H_2O)$ (**5**) [$H_2L^3 = H_2O_3PCH_2N(CHO)(CH_2-C_6H_4-COOH)$]. The higher number of water molecules present in the lanthanum(III) compound are probably due to the higher coordination number for the La^{3+} ion than that for the Er^{3+} ion. H_2L^3 was formed by the in situ oxidation of one P–C bond of the H_5L^2 ligand by oxidizing nitrate anion. Hence the counteranion, the temperature, and the ionic size of the lanthanide(III) ion have a strong effect on lanthanide phosphonates formed.

Compound **1** features a layered structure. The La^{III} ion is nine-coordinate by seven phosphonate oxygen atoms from five $\{H_2L^1\}^{3-}$ anions and two aqua ligands (Figure 1). The La–O distances are in the range 2.4453(19)–2.888(2) Å, which is comparable to those reported for other La^{III} phosphonates.^[16] The H_2L^1 anion is septadentate; it chelates bidentately with one La^{3+} ion by using a phosphonate group and another La^{III} ion by using two oxygen atoms from two phosphonate groups, and also bridges with three other La^{III}

ions. Two phosphonate oxygen atoms [O(11) and O(12)] are bidentate metal linkers. The carboxylate group of the ligand remains protonated and noncoordinated; so does its amine group. The protonation of the amine group in a phosphonate ligand is well known, as amino-phosphonic acid usually exists as a zwitterion in which a proton of the phosphonate group is transferred to the basic amine group.^[1,5]

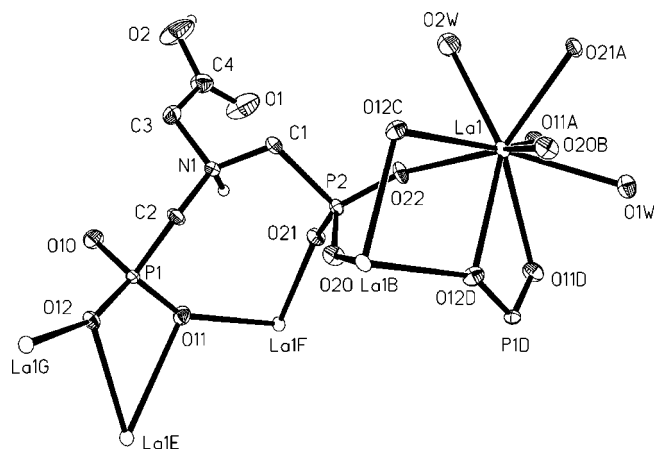


Figure 1. ORTEP representation of the selected unit of compound **1**. The thermal ellipsoids are drawn at 50% probability. The lattice water molecules have been omitted for clarity. Symmetry codes for generated atoms: A) $x, -y + 1/2, -z - 1/2$; B) $-x + 2, -y + 1, -z + 1$; C) $x, -y + 3/2, -z - 1/2$; D) $-x + 2, -y - 1/2, -z + 3/2$; E) $-x + 2, y + 1/2, -z + 3/2$; F) $x, -y + 1/2, z + 1/2$; G) $x, -y + 3/2, z + 1/2$.

The interconnection of the La^{3+} ions by bridging phosphonate ligands resulted in (100) inorganic layers with the carboxylate moieties orientating toward the interlayer space (Figure 2). The interlayer distance is about 12.0 Å. Neighboring layers are held together by hydrogen bonds among carboxylate oxygens, noncoordinated phosphonate oxygen [O(10)], aqua ligand O(2w), and lattice water [O(3w)] (Table 1).

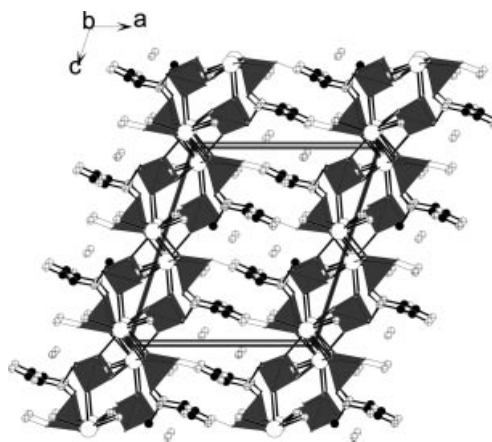


Figure 2. View of the structure of compound **1** down the b axis. The phosphonate tetrahedra are shaded in medium gray. La, C, N, and O atoms are drawn as open, black, octahedron, and crossed circles, respectively.

Compound **2** has a different layered structure. The asymmetric unit of **2** consists of one unique La³⁺ ion, one {H₂L¹}³⁻ anion, and an aqua ligand (Figure 3). The La³⁺ ion is eight-coordinate by five phosphonate oxygen atoms from five phosphonate groups of four {H₂L¹}³⁻ anions, two carboxylate oxygens of another phosphonate ligand, and an aqua ligand. The La–O distances are in the range 2.360(9)–2.728(8) Å, which is comparable to those in compound **1** and other lanthanum(III) phosphonates.^[16] The coordinating mode of the phosphonate anion is different from that

Table 1. Selected bond lengths [Å] for compounds **1–5**.^[a]

Compound 1			
La(1)–O(21)#1	2.445(2)	P(1)–O(12)	1.524(2)
La(1)–O(20)#2	2.485(2)	P(1)–O(10)	1.534(2)
La(1)–O(11)#1	2.509(2)	P(2)–O(22)	1.520(2)
La(1)–O(22)	2.517(2)	P(2)–O(20)	1.523(2)
La(1)–O(1w)	2.564(2)	P(2)–O(21)	1.524(2)
La(1)–O(12)#3	2.587(2)	C(4)–O(1)	1.225(4)
La(1)–O(2w)	2.589(3)	C(4)–O(2)	1.276(4)
La(1)–O(12)#4	2.694(2)	O(2)···O(10)#5	2.478(3)
La(1)–O(11)#4	2.888(2)	O(2)···O(2w)#6	2.835(4)
O(1)···O(2w)#7	2.800(4)	O(10)···O(3w)	2.822(4)
Compound 2			
La(1)–O(11)#1	2.360(9)	La(1)–O(2)	2.728(8)
La(1)–O(22)#2	2.407(9)	P(1)–O(11)	1.499(9)
La(1)–O(21)#3	2.456(8)	P(1)–O(12)	1.504(8)
La(1)–O(12)#3	2.469(9)	P(1)–O(13)	1.562(8)
La(1)–O(23)#4	2.509(9)	P(2)–O(21)	1.489(9)
La(1)–O(1w)	2.630(9)	P(2)–O(22)	1.508(9)
La(1)–O(1)	2.693(8)	P(2)–O(23)	1.515(9)
N(1)···O(13)	3.24(1)	N(1)···O(1w)#5	3.32(1)
Compound 3			
La(1)–O(43)#1	2.409(5)	P(3)–O(32)	1.574(4)
La(1)–O(13)#2	2.430(5)	P(4)–O(43)	1.511(4)
La(1)–O(42)	2.441(5)	P(4)–O(42)	1.515(4)
La(1)–O(33)#1	2.466(5)	P(4)–O(41)	1.520(4)
La(1)–O(22)	2.495(5)	C(10)–O(1)	1.196(8)
La(1)–O(31)#3	2.575(6)	C(10)–O(2)	1.302(8)
La(1)–O(1w)	2.632(7)	O(1)···O(2w)#4	2.732(7)
P(1)–O(13)	1.490(4)	O(2)···O(23)#5	2.700(8)
P(1)–O(11)	1.528(4)	O(4)···O(41)#6	2.505(7)
P(1)–O(12)	1.533(5)	O(11)···O(11)#7	2.474(8)
P(2)–O(22)	1.504(4)	O(12)···O(23)#8	2.493(7)
P(2)–O(23)	1.517(4)	O(21)···O(21)#2	2.606(8)
P(2)–O(21)	1.542(4)	O(32)···O(41)#8	2.539(7)
P(3)–O(33)	1.496(5)	N(2)···O(2w)	2.782(8)
P(3)–O(31)	1.504(4)	N(1)···O(3w)	2.757(8)
Compound 4			
Er(1)–O(12)	2.206(4)	Er(1)–O(23)#1	2.208(4)
Er(1)–O(13)#2	2.230(4)	Er(1)–O(33)#3	2.237(4)
Er(1)–O(42)	2.244(4)	Er(1)–O(43)#1	2.258(4)
P(1)–O(11)	1.512(5)	P(1)–O(13)	1.513(5)
P(1)–O(12)	1.516(5)	P(2)–O(23)	1.495(5)
P(2)–O(22)	1.499(4)	P(2)–O(21)	1.568(4)
P(3)–O(32)	1.494(5)	P(3)–O(33)	1.504(4)
P(3)–O(31)	1.564(5)	P(4)–O(42)	1.501(4)
P(4)–O(43)	1.507(4)	P(4)–O(41)	1.556(5)
C(10)–O(1)	1.192(12)	C(10)–O(2)	1.309(11)
C(20)–O(4)	1.203(11)	C(20)–O(3)	1.323(11)
N(1)···O(32)#1	2.680(7)	N(2)···O(22)#1	2.772(7)
O(3)···O(11)#4	2.624(8)	O(11)···O(41)	2.535(7)
O(21)···O(22)#5	2.558(6)	O(31)···O(32)#6	2.681(6)

Table 1. (continued)

Compound 5			
Er(1)–O(13)#1	2.213(6)	P(2)–O(23)	1.523(6)
Er(1)–O(23)#2	2.239(7)	P(2)–O(21)	1.549(6)
Er(1)–O(12)	2.253(7)	N(1)–C(4)	1.314(13)
Er(1)–O(21)#3	2.290(6)	N(2)–C(21)	1.285(14)
Er(1)–O(1w)	2.356(7)	O(5)–C(4)	1.167(14)
Er(1)–O(21)	2.403(6)	O(6)–C(21)	1.186(14)
Er(1)–O(22)	2.437(6)	C(6)–O(1)	1.266(16)
P(1)–O(12)	1.497(6)	C(6)–O(2)	1.290(14)
P(1)–O(13)	1.502(6)	C(27)–O(4)	1.228(16)
P(1)–O(11)	1.586(8)	C(27)–O(3)	1.270(17)
P(2)–O(22)	1.517(7)	O(1)···O(4)#4	2.614(13)
O(2)···O(3)#4	2.585(13)		

[a] Symmetry transformations used to generate equivalent atoms: For **1**: #1 $x, -y + 1/2, -z + 1/2$; #2 $-x + 2, -y + 1, -z + 1$; #3 $x, -y + 3/2, -z - 1/2$; #4 $-x + 2, y - 1/2, -z + 3/2$; #5 $-x + 1, -y - 1/2, -z + 3/2$; #6 $-x + 1, -y + 1, -z + 1$; #7 $x, 1/2 - y, 1/2 + z$. For **2**: #1 $-x - 1/2, y, z - 1/2$; #2 $x + 1/2, -y, z$; #3 $x + 1, y, z$; #4 $-x - 1/2, y, z + 1/2$; #5 $-1/2 + x, -y, z$. For **3**: #1 $-x + 2, -y + 1, -z + 1$; #2 $-x + 2, -y + 2, -z + 1$; #3 $-x + 1, -y + 1, -z + 1$; #4 $x, y, z + 1$; #5 $-x + 2, -y + 2, -z + 2$; #6 $-x + 2, -y + 1, -z$; #7 $-x + 1, -y + 2, -z + 1$; #8 $x - 1, y, z$. For **4**: #1 $-x + 1, -y + 2, -z + 1$; #2 $-x + 2, -y + 2, -z + 1$; #3 $x + 1, y, z$; #4 $-x + 1, -y + 1, -z$; #5 $-x + 1, -y + 3, -z + 1$; #6 $-x, -y + 1, -z + 1$. For **5**: #1 $-x, -y + 2, -z + 1$; #2 $-x - 1, -y + 1, -z + 1$; #3 $-x, -y + 1, -z + 1$; #4 $x + 1, y + 1, -1 + z$.

in compound **1**. The singly protonated phosphonate group (P1) is bidentate and connects with two La³⁺ ions. The fully deprotonated phosphonate group (P2) is tridentate and is bridged to three La³⁺ ions. Unlike that in compound **1**, the carboxylate group of the phosphonate ligand in compound **2** is deprotonated and forms a four-member chelating ring [La(1)–O(2)–C(4)–O(1)] (Figure 3). The amine group is protonated as in compound **1**.

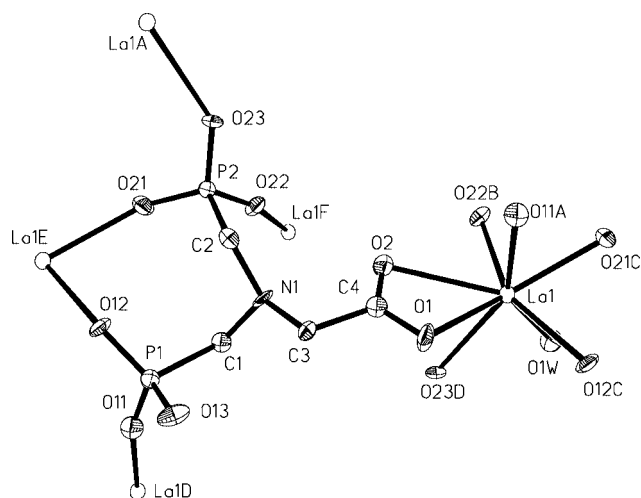


Figure 3. ORTEP representation of the selected unit of compound **2**. The thermal ellipsoids are drawn at 50% probability. Symmetry codes for the generated atoms: A) $-x - 1/2, y, -z - 1/2$; B) $x + 1/2, -y, z$; C) $x + 1, y, z$; D) $-x - 1/2, y, z + 1/2$; E) $x - 1, y, z$; F) $x - 1/2, -y, z$.

The interconnection of La³⁺ ions by phosphonate ligands led to a (010) double layer (Figure 4). The thickness of the double layer is about 9.0 Å. Neighboring 2D layers

are held together by weak hydrogen bonds among the amine group, aqua ligand, and noncoordination phosphonate oxygen, as well as a weak van der Waals force (Table 1, Figure 4).

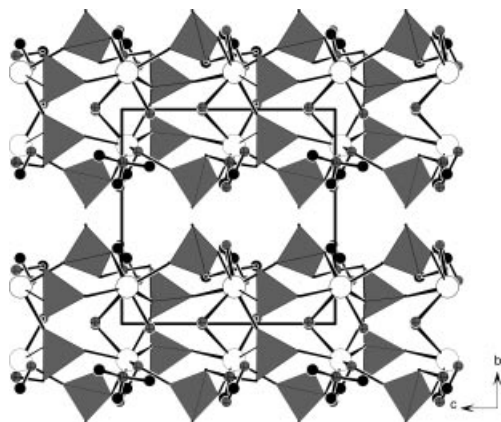


Figure 4. View of the structure of compound **2** down the *a* axis. The phosphonate tetrahedra are shaded in medium gray. La, C, N, and O atoms are drawn as open, black, octand, and crossed circles, respectively.

Compound **3** also features a layered structure. The asymmetric unit of **3** consists of one La^{3+} ion, one $\{\text{H}_4\text{L}^2\}^-$ anion, one $\{\text{H}_3\text{L}^2\}^{2-}$ dianion, an aqua ligand, and two lattice water molecules (Figure 5). The La^{3+} ion is seven-coordinate by six phosphonate oxygen atoms from five phosphonate ligands and an aqua ligand. The La–O distances are in the range 2.409(5)–2.632(7) Å, which is comparable to those in compounds **1** and **2**. The $\{\text{H}_4\text{L}^2\}^-$ anion composed of P(1) and P(2) is bidentate and bridges with two La^{3+} ions; each phosphonate group is singly protonated, as are the amine group and the carboxylate group. The $\{\text{H}_3\text{L}^2\}^{2-}$ anion composed of P(3) and P(4) is tetradentate; it forms an eight-member chelating ring with a La^{3+} ion, and also bridges with two other La^{3+} ions. Only one phosphonate group is singly protonated; the amine group and the carboxylate group are also protonated.

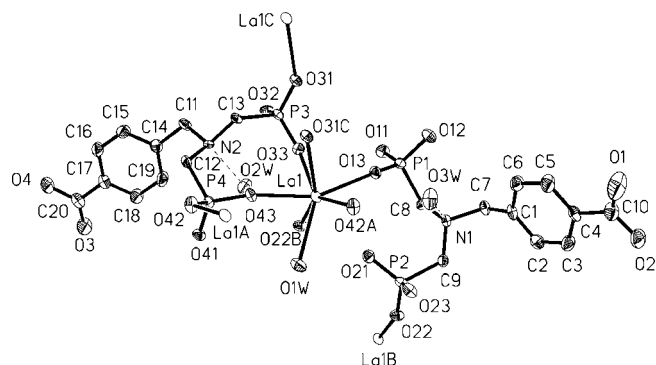


Figure 5. ORTEP representation of the selected unit of compound **3**. The thermal ellipsoids are drawn at 50% probability. Hydrogen bonds are drawn as dashed lines. Symmetry codes for the generated atoms: A: $-x + 2, -y + 1, -z + 1$; B: $-x + 2, -y + 2, -z + 1$; C: $-x + 1, -y + 1, -z + 1$.

Adjacent La^{3+} ions are bridged by the above two types of phosphonate anions into a (002) lanthanide phosphonate

layer with $-\text{C}_6\text{H}_4-\text{COOH}$ moieties hanging on both sides of the layer (Figure 6). Extensive intralayer and interlayer hydrogen bonds further crosslink these layers into a 3D supramolecular network (Figure 6, Table 1). The lattice water molecules are located at the voids of the structure and are involved in hydrogen bonding (Figure 6, Table 1). The interlayer distance of about 16.8 Å is significantly larger than that in compound **1**, which is due to the introduction of the additional phenyl group into the phosphonate ligand.

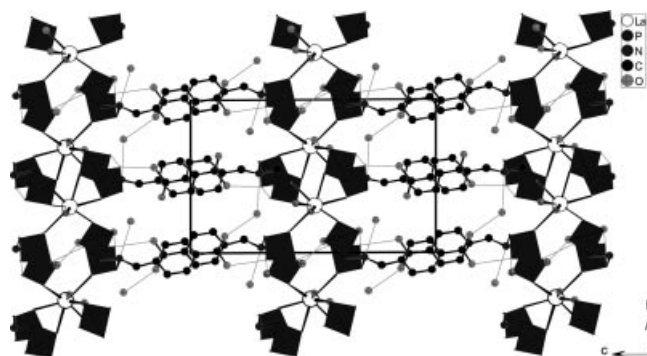


Figure 6. View of the structure of compound **3** down the *a* axis. The phosphonate tetrahedra are shaded in grey. La, N, C, and O atoms are represented by open, dark grey, black, and light grey circles, respectively. Hydrogen bonds are drawn as dashed lines.

The structure of $\text{Er}(\text{H}_3\text{L}^2)(\text{H}_4\text{L}^2)$ (**4**) features a 3D supramolecular network based on 1D erbium(III) phosphonate chains. The asymmetric unit of **4** is composed of one Er^{3+} ion, one $(\text{H}_3\text{L}^2)^{2-}$ dianion, and one $(\text{H}_4\text{L}^2)^-$ anion. The Er^{3+} ion is octahedrally coordinated by six phosphonate oxygens from six different phosphonate ligands (Figure 7). The Er–O distances [2.280(2)–2.331(2) Å] are comparable to those found in the other erbium(III) phosphonate.^[16] The coordination modes for the $(\text{H}_3\text{L}^2)^{2-}$ dianion and $(\text{H}_4\text{L}^2)^-$ anion are similar. One phosphonate group is monodentate whereas the other is bidentate. The amine group and the carboxylate group for both types of anion are singly protonated. The main difference between the two phosphonate anions are that both phosphonate groups are singly protonated for the $(\text{H}_4\text{L}^2)^-$ anion [O(31) and O(41)] whereas only one phosphonate group is singly protonated for the $(\text{H}_3\text{L}^2)^{2-}$ dianion [O(21)].

Each pair of Er^{3+} ions is bridged by a pair of phosphonate groups to form a 1D chain along the *a* axis. Such chains are further interconnected by strong hydrogen bonds between noncoordinated phosphonate oxygens into a (002) layer. These hydrogen bonds are $\text{O}(21)\cdots\text{O}(22)$ 2.558(6) Å (symmetry code: $1 - x, 3 - y, 1 - z$) and $\text{O}(31)\cdots\text{O}(32)$ 2.681(6) Å (symmetry code: $-x, 1 - y, 1 - z$). The $-\text{CH}_2-\text{C}_6\text{H}_4-\text{COOH}$ groups of the phosphonate ligands are hanging on the interlayer space (Figure 8). Intrachain hydrogen bonds are also formed between the amine group and noncoordinated phosphonate oxygens, and between two noncoordinated phosphonate oxygens (Table 1). The interlayer distance is about 14.3 Å, which is shorter than that of compound **3**. These 2D layers are further interlinked by hydro-

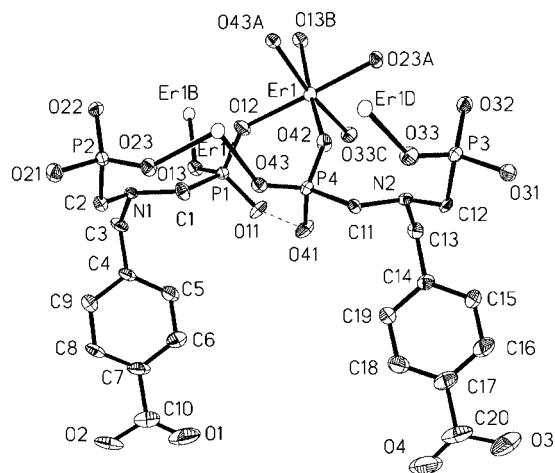


Figure 7. ORTEP representation of the selected unit of compound **4**. The thermal ellipsoids are drawn at 50% probability. Hydrogen bonds are drawn as dashed lines. Symmetry codes for the generated atoms: A) $1 + x, y, z$; B) $2 - x, 1 - y, 1 - z$; C) $2 - x, 2 - y, 1 - z$; D) $-1 + x, y, z$.

gen bonds between carboxylate oxygen and noncoordinated phosphonate oxygen [O(3)⋯O(11) 2.624(8) Å, symmetry code: $1 - x, 1 - y, -z$].

When erbium(III) nitrate was used instead of erbium(III) chloride, compound **5** was isolated. H_5L^2 was also oxidized by the nitrate anion to a new ligand, H_3L^3 (Scheme 1). Such in situ oxidation of the P–C bond has also been observed during the hydrothermal reactions of cobalt(II) nitrate with H_5L .^[2,18] The asymmetric unit of **5** consists of one erbium(III) ion, a $\{H_2L^3\}^-$ anion, a $\{HL^3\}^{2-}$ dianion, and an aqua ligand (Figure 9). The erbium(III) ion is seven-coordinate by six phosphonate oxygens from five phosphonate ligands and an aqua ligand. The Er–O distances range from 2.214(6) to 2.438(6) Å, which is comparable to those in compound **4**. The $\{HL^3\}^{2-}$ dianion is tetradentate; it forms a chelating ring with an erbium(III) ion [Er(1)–O(21)–P(2)–O(22)] and also bridges with two other erbium(III) ions [Er(1b) and Er(1c)]. The phosphonate group is fully deprotonated whereas the amine group remains protonated. The $\{H_2L^3\}^-$ anion is bidentate and bridges with two erbium(III)

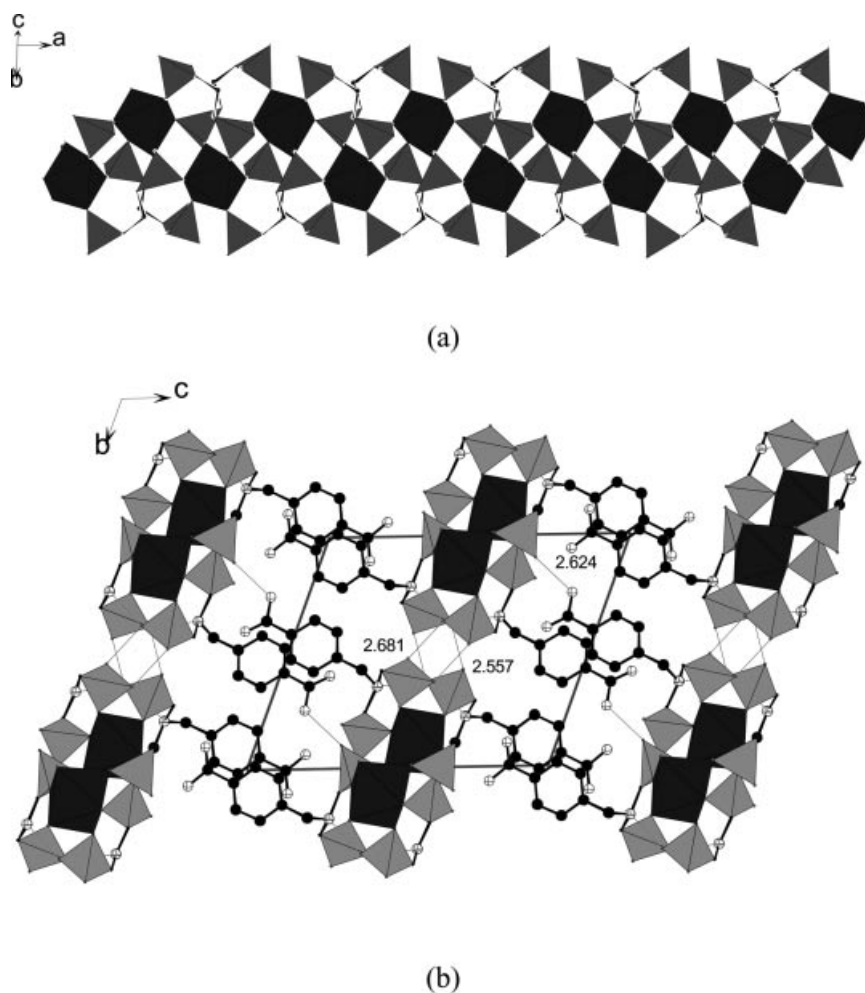


Figure 8. An erbium(III) phosphonate inorganic chain along the a axis (a) and view of the structure of compound **4** down the a axis (b). The ErO_6 octahedra and phosphonate tetrahedra are shaded in dark gray and medium gray, respectively. N, C, and O atoms are represented by octand, black, and crossed circles, respectively.

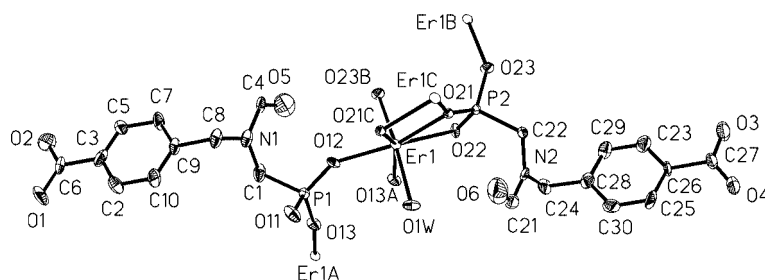


Figure 9. ORTEP representation of the selected unit of compound **5**. The thermal ellipsoids are drawn at 50% probability. Symmetry codes for the generated atoms: A) $-x, -y + 2, -z + 1$; B) $-x - 1, -y + 1, -z + 1$; C) $-x, -y + 1, -z + 1$.

ions using two oxygen atoms [O(12) and O(13)]. The third phosphonate oxygen and the amine group are protonated and noncoordinated. The carboxylate groups in both types of anions are noncoordinated.

The Er^{3+} ions in compound **5** are bridged by phosphonate groups of ligands into a (002) inorganic layer (Figure 10). Within the layer, Er_2O_2 rings and $\text{Er}(\text{O}-\text{P}-\text{O})_2\text{Er}$ rings can be found. Neighboring 2D layers are further interlinked by hydrogen bonds between carboxylate groups. These hydrogen bonds are $\text{O}(1)\cdots\text{O}(4)$ 2.614(13) Å and $\text{O}(2)\cdots\text{O}(3)$ 2.585(13) Å (symmetry codes are the same for both bonds: $1 + x, 1 + y, -1 + z$). The interlayer distance of about 21.6 Å is the largest among five compounds, because the carboxylate groups in other compounds are directly hydrogen bonded to a neighboring inorganic layer, whereas the interlayer hydrogen bonding in compound **5** is between two hanging organic groups (head to head).

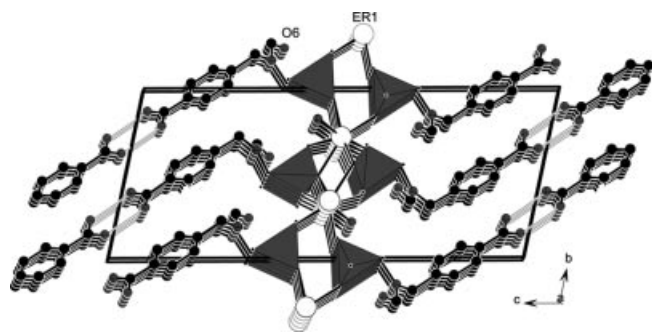


Figure 10. View of the structure of compound **5** down the a axis. The phosphonate tetrahedra are shaded in medium gray. Er, C, N, and O atoms are drawn as open, black, octand, and crossed circles, respectively. Hydrogen bonds are shown as dashed lines.

Based on X-ray powder diffraction studies, compounds **2–5** are prepared as single phases. The measured patterns are in good agreement with those simulated from single-crystal structures (see Supporting Information).

The solid-state luminescent properties of compounds **4** and **5** were investigated at room temperature. The emission spectrum of compound **4** shows three strong near IR emission bands at 1477, 1541, and 1561 nm under 520 nm exci-

tation (Figure 11a), all of which can be attributed to the $^4\text{I}_{13/2} \rightarrow ^4\text{I}_{15/2}$ transition for the Er^{3+} ion.^[16] The splitting of the $^4\text{I}_{13/2} \rightarrow ^4\text{I}_{15/2}$ transition into several sub-bands is due to the low symmetry of the coordination geometry around the Er^{3+} ion (C_1). The luminescence properties of compound **5** are very interesting. Under emission of 330 nm, the excitation spectrum of compound **5** displays one weak

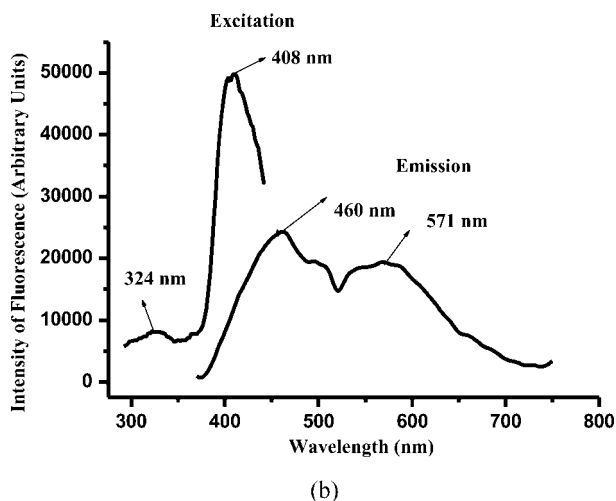
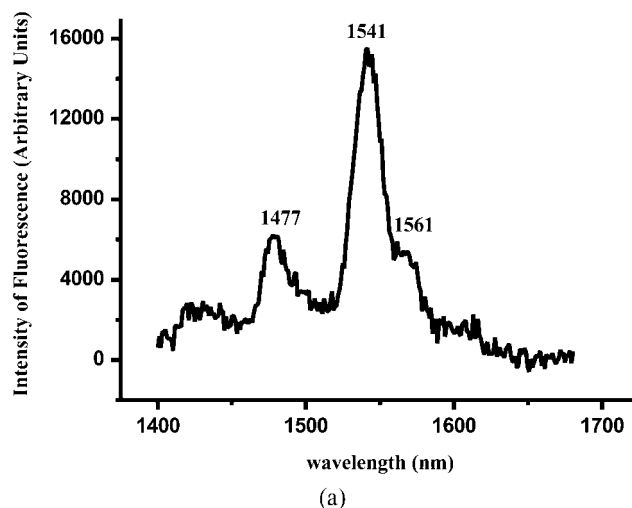


Figure 11. Luminescence spectra for compounds **4** (a) and **5** (b) at room temperature.

absorption peak at 324 nm and a very strong absorption peak at 408 nm. Surprisingly, compound **5** shows no near IR emission band under our experimental conditions. Under excitation of 408 nm, the emission spectrum of compound **5** exhibits a very broad band with two maximum intensity peaks at 460 and 571 nm (Figure 11b), which may be assigned to the intraligand π - π^* fluorescence. The absence of near IR emission is probably due to the quenching effect of the luminescent state by high-frequency vibrating water molecules.^[16a]

TGA curves for compounds **2–5** are shown in Figure 12. TGA curves of compound **2** indicate one main step of weight loss. The weight loss between 260 and 620 °C corresponds to the release of water molecules and the combustion of the phosphonate ligand. The weight loss is about 20.5%. There is small weight loss starting from 800 °C, which can be attributed to the further decomposition of the compound. The total weight loss at 1000 °C is 24.4%. The residue was not characterized. Compound **3** shows no obvious weight loss before 135 °C. The weight loss in the temperature range of 135–270 °C corresponds to the release of two lattice water molecules and an aqua ligand. The observed weight loss of 6.8% is close to the calculated value (6.2%). Then the compound decomposes continuously up to 1000 °C, which corresponds to the combustion of organic groups. The total weight loss at 1000 °C is 48.6% and the residue was not characterized. Compound **4** is stable up to 355 °C. Then it exhibits a sharp weight loss between 355 and 575 °C with a weight loss of 23.8%. The total weight at 1000 °C is 34.3% and the final residue was not characterized. TGA curves for compound **5** display two main steps of weight losses. There is no obvious weight loss before 280 °C. The weight loss in the range of 280–340 °C corresponds to the release of an aqua ligand and the decomposition of the two carboxylate groups of two phosphonate ligands. The observed weight loss of 13.4% is slightly smaller than the calculated one (14.5%). The second weight loss covers a temperature range from 340 to 650 °C, which corresponds to further combustion of the

phosphonate ligands. The total weight loss at 1000 °C is 34.3% and the final residue was not characterized.

Conclusion

In summary, the hydrothermal syntheses, crystal structures, and luminescent properties of five new lanthanide(III) phosphonates with layered structures have been described. Results from this and previous work indicate that we can greatly improve the solubility and crystallinity of lanthanide phosphonates by attaching amino acid moiety to the phosphonic acid or introducing a second ligand such as oxalate or carboxylate-sulfonate. The counteranion used plays an important role. It affects the acidity of the solution and the extent of deprotonation of phosphonate ligands, as well as the coordination mode a phosphonate ligand adopts. Oxidizing anions such as nitrate groups may also trigger the in situ oxidation of P–C bonds. Furthermore, the so-called “lanthanide contraction” is also important. Heavy lanthanide ions usually have smaller coordination numbers than the light ones, which may result in different coordination modes for the phosphonate ligands. However, more systematic studies are still needed to further understand the chemistry of lanthanide phosphonates.

Experimental Section

Materials and Methods: ($\text{H}_2\text{O}_3\text{PCH}_2$)₂NCH₂CO₂H (H_5L^1) and 4-HO₂C–C₆H₄–CH₂N(CH₂PO₃H₂)₂ (H_5L^2) were prepared by a Mannich-type reaction according to the procedures described previously.^[6] All other chemicals were obtained from commercial sources and used without further purification. Elemental analyses were performed on a Vario EL III elemental analyzer. Thermogravimetric analyses were carried out on a NETZSCH STA 449C unit at a heating rate of 15 °C/min under nitrogen. IR spectra were recorded with a Magna 750 FTIR spectrometer photometer as KBr pellets in the range 4000–400 cm^{–1}. Photoluminescence analyses were performed on an Edinburgh FLS920 fluorescence spectrometer. X-ray powder diffraction patterns ($\text{Cu-K}\alpha$) were collected in a sealed glass capillary on a XPERT-MPD θ – 2θ diffractometer.

Preparation of $\text{La}(\text{H}_2\text{L}^1)(\text{H}_2\text{O})_2\cdot\text{H}_2\text{O}$ (1**):** A mixture of $\text{LaCl}_3\cdot 6\text{H}_2\text{O}$ (176.7 mg, 0.5 mmol), H_5L^1 (131.6 mg, 0.5 mmol), and 2-hydroxypyridine (95.1 mg, 1.0 mmol) in 10 mL of distilled water was sealed into an autoclave equipped with a Teflon liner (25 mL) and then heated at 120 °C for 4 days. The initial pH value of the resultant solution was 3.0. Colorless plate-shaped crystals of **1** were collected. Yield: 11.3 mg (5%, based on La). Based on the X-ray powder diffraction study, the majority of impurity was powder of compound **2**. Efforts to prepare a single-phase product of compound **1** were unsuccessful.

Preparation of $\text{La}(\text{H}_2\text{L}^1)(\text{H}_2\text{O})$ (2**):** A mixture of $\text{La}(\text{OH})_3$ (189.9 mg, 1.0 mmol) and H_5L^1 (263.1 mg, 1.0 mmol) in 10 mL of distilled water was sealed into a bomb equipped with a Teflon liner (25 mL) and then heated at 150 °C for 4 days. The initial and final pH values of the resultant solution were 3.5 and 2.5, respectively. Colorless plate-shaped crystals of **2** were collected. Yield: 250 mg (60%, based on La). IR (KBr): $\tilde{\nu}$ = 3359 m, 3139 m, 1607 m, 1448 w, 1407 s, 1371 m, 1305 w, 1214 m, 1164 m, 1083 vs, 1008 m, 974 w, 949 w, 844 w, 768 w, 720 m, 587 w, 496 w, 468 w, 447 w cm^{–1}.

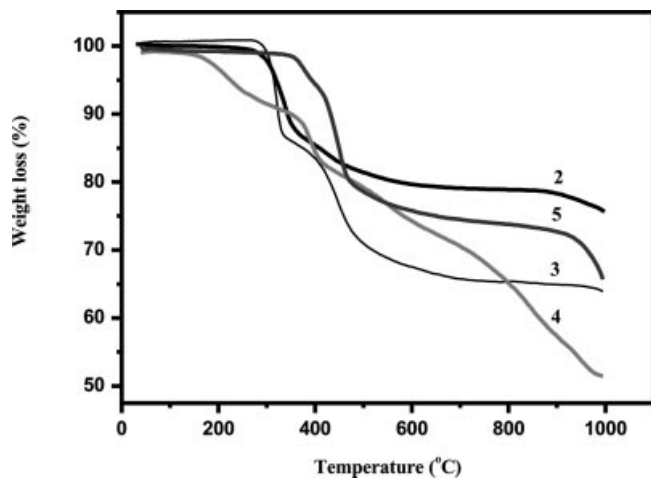


Figure 12. TGA curves for **2** (thick line, black), **3** (thin line, black), **4** (light grey line), and **5** (medium grey line).

$C_4H_{10}LaNO_9P_2$ (416.98): calcd. C 11.52, H 2.42, N 3.36; found C 11.60, H 2.54, N 3.28.

Preparation of $La(H_4L^2)(H_3L^2)(H_2O) \cdot 2H_2O$ (3): A mixture of $La(OH)_3$ (56.98 mg, 0.3 mmol) and H_3L^2 (169.6 mg, 0.5 mmol) in 10 mL of distilled water was sealed into a bomb equipped with a Teflon liner (25 mL) and then heated at 145 °C for 4 days. The initial and final pH values of the resultant solution were 4.5 and 2.5, respectively. Colorless plate-shaped crystals of **3** were collected. Yield: 121.6 mg (56%, based on H_3L^2). IR (KBr): $\tilde{\nu}$ = 3480 m, 3387 m, 3219 m, 3020 w, 3010 w, 2614 w, 1697 s, 1642 m, 1460 w, 1403 m, 1321 w, 1274 w, 1163 m, 1115 vs, 991 m, 931 m, 825 w, 761 m, 644 w, 560 m, 535 m, 484 w, 451 w cm^{-1} . $C_{20}H_{33}LaN_2O_{19}P_4$ (868.27): calcd. C 27.65, H 3.83, N 3.23; found C 27.70, H 3.92, N 3.18.

Preparation of $Er(H_3L^2)(H_4L^2)$ (4): A mixture of $ErCl_3 \cdot 6H_2O$ (95.4 mg, 0.25 mmol) and H_3L^2 (84.8 mg, 0.25 mmol) in 10 mL of distilled water was sealed into an autoclave equipped with a Teflon liner (25 mL) and heated at 145 °C for 5 days. The initial and final pH values of the resultant solution were 3.5 and 2.0, respectively. Pink brick-shaped crystals of **4** were collected. Yield: 147 mg (70%, based on Er). IR (KBr): $\tilde{\nu}$ = 3494 m, 3114 m, 2674 w, 2557 w, 1705 s, 1401 m, 1318 m, 1206 m, 1113 vs, 1020 m, 994 m, 951 m, 908 w, 879 w, 820 w, 808 w, 763 m, 719 m, 681 w, 637 w, 582 m, 515 w, 493 w, 465 w, 413 w cm^{-1} . $C_{20}H_{26}ErN_2O_{16}P_4$ (841.57): calcd. C 28.54, H 3.11, N 3.33; found C 28.50, H 3.17, N 3.39.

Synthesis of $Er(HL^3)(H_2L^3)(H_2O)$ (5): A mixture of $Er(NO_3)_3 \cdot 6H_2O$ (230.70 mg, 0.5 mmol), H_5L^2 (169.6 mg, 0.5 mmol), and 2-hydroxypyridine (95.10 mg, 1.0 mmol) in 10 mL of distilled water was sealed into a bomb equipped with a Teflon liner (25 mL) and then heated at 120 °C for 4 days. The initial and final pH values of the resultant solution were 3.0 and 2.5, respectively. Light yellow brick-shaped crystals of **5** were collected. Yield: 91 mg (25%, based on Er). IR (KBr): $\tilde{\nu}$ = 3494 m, 3116 m, 2674 w, 2557 w, 1686 s, 1611 m, 1579 w, 1511 w, 1453 m, 1430 m, 1324 m, 1296 m, 1239 m, 1175 w, 1104 vs, 1025 m, 994 m, 951 m, 908 w, 879 w, 820 w, 791 w, 763 m, 719 w, 681 w, 641 w, 575 m, 506 w, 493 w, 465 w, 414 w cm^{-1} . $C_{20}H_{23}ErN_2O_{13}P_2$ (728.60): calcd. C 29.59, H 3.18, N 7.51; found C 30.08, H 3.26, N 7.46.

Single-Crystal Structure Determination: Data collections for compounds **1–5** were performed with a Rigaku Mercury CCD diffractometer equipped with graphite-monochromated Mo- K_α radiation (λ = 0.71073 Å). Intensity data were collected by the narrow frame method at 293 K. The data sets were corrected for Lorentz and polarization factors as well as for absorption by the multiscan technique.^[18] All five structures were solved by the direct methods and refined by full-matrix least-squares fitting on F^2 by SHELX-97.^[19] All non-hydrogen atoms were refined with anisotropic thermal parameters, except for C(1), C(4), and O(11) in compound **2**, and C(21) in compound **5**, which were refined isotropically. The lattice water molecule in compound **1** was disordered over two orientations [O(3w) and O(3w')], with an interatomic distance of 0.932 Å. Each orientation was refined with 50% occupancy. Hydrogen atoms attached to carbon atoms, amine groups, and phosphonate groups were located at geometrically calculated positions and refined with isotropic thermal parameters. The protonation for the amine groups as well as phosphonate groups was based on P–O distances and charge balance. Hydrogen atoms for water molecules were not included in refinements.

Crystal Data for 1: $C_4H_{14}LaNO_{11}P_2$ (453.01), monoclinic, space group $P2_1/c$, T = 293(2) K, a = 12.675, b = 7.300, c = 14.212 Å, β = 108.125(2)°, V = 1249.6 Å³, Z = 4, d_{calcd} = 2.408 Mg/m³, $F(000)$ = 880, $\mu(\text{Mo}-K_\alpha)$ = 3.730 mm⁻¹, 9815 reflections collected, 3093

unique (R_{int} = 0.0307). R_1 = 0.0236, wR_2 = 0.0612 [$I > 2\sigma(I)$], R_1 = 0.0263 and wR_2 = 0.0627 (all data) and final Gof = 1.056.

Crystal Data for 2: $C_4H_{10}LaNO_9P_2$ (416.98), orthorhombic, space group $Pca2_1$, T = 293(2) K, a = 9.9649(13), b = 10.5833(15), c = 10.5288(15) Å, V = 1110.4(3) Å³, Z = 4, d_{calcd} = 2.494 Mg/m³, $F(000)$ = 800, $\mu(\text{Mo}-K_\alpha)$ = 4.173 mm⁻¹, 8258 reflections collected, 2418 unique (R_{int} = 0.0891). R_1 = 0.0644, wR_2 = 0.1039 [$I > 2\sigma(I)$], R_1 = 0.0793 and wR_2 = 0.1113 (all data) and final Gof = 1.142.

Crystal Data for 3: $C_{20}H_{33}LaN_2O_{19}P_4$ (868.27), triclinic, space group $P\bar{1}$, T = 293(2) K, a = 8.246(17), b = 10.58(2), c = 16.79(3) Å, α = 90.34(3), β = 90.21(4), γ = 93.52(3)°, V = 1461(5) Å³, Z = 2, d_{calcd} = 1.973 Mg/m³, $F(000)$ = 872, $\mu(\text{Mo}-K_\alpha)$ = 1.772 mm⁻¹, 11453 reflections collected, 6609 unique (R_{int} = 0.0456). R_1 = 0.0542, wR_2 = 0.1036 [$I > 2\sigma(I)$], R_1 = 0.0722 and wR_2 = 0.1143 (all data) and final Gof = 1.088.

Crystal Data for 4: $C_{20}H_{26}ErN_2O_{16}P_4$ (841.57), triclinic, space group $P\bar{1}$, T = 293(2) K, a = 7.9178(7), b = 12.5608(5), c = 15.3008(7) Å, α = 110.453(7), β = 90.296(12), γ = 90.586(13)°, V = 1425.66(15) Å³, Z = 2, d_{calcd} = 1.960 Mg/m³, $F(000)$ = 832, $\mu(\text{Mo}-K_\alpha)$ = 3.247 mm⁻¹, 11127 reflections collected, 6439 unique (R_{int} = 0.0456). R_1 = 0.0528, wR_2 = 0.0984 [$I > 2\sigma(I)$], R_1 = 0.0684 and wR_2 = 0.1072 (all data) and final Gof = 1.107.

Crystal Data for 5: $C_{20}H_{23}ErN_2O_{13}P_2$ (728.60), triclinic, space group $P\bar{1}$, T = 293(2) K, a = 5.752(4), b = 9.382(5), c = 22.050(15) Å, α = 101.507(16), β = 92.62(2), γ = 98.155(19)°, V = 1151.0(12) Å³, Z = 2, d_{calcd} = 1.715 Mg/m³, $F(000)$ = 718, $\mu(\text{Mo}-K_\alpha)$ = 3.839 mm⁻¹, 3176 reflections collected, 2217 unique (R_{int} = 0.0277). R_1 = 0.0440, wR_2 = 0.1207 [$I > 2\sigma(I)$], R_1 = 0.0469 and wR_2 = 0.1239 (all data) and final Gof = 1.033.

CCDC-295013 to -295017 (for **1–5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): X-ray powder diffraction patterns for compounds **2–5**.

Acknowledgments

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