Hydrothermal synthesis and structural characterization of ammonium ion-templated lanthanide(III) carboxylate-phosphonates

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INTRODUCTION

The complexing ability of phosphonic acids have been extensively exploited in the design and synthesis of metal-organophosphonate-type metal organic frameworks (MOFs) with the formation of new and interesting compounds (Clearfield, 1988; Gagnon et al., 2012). The great interest in metal phosphonates is not only for their many unusual structural features, but also for their potential applications in different fields including adsorption, separation, gas storage, catalysis, photoluminescence, and drug delivery (Zhang and Clearfield, 2012). The use of highly flexible and/or aromatic-based organic linkers has been the focus of many research groups (Galdecka et al., 2000; Paz et al., 2005; Ananias et al., 2006; Soares-Santos et al., 2006; Bao et al., 2007; Cunha-Silva et al., 2007; Girginova et al., 2007; Paz and Klinowski, 2007, 2008; Tang et al., 2007; Chelebaeva et al., 2008; Ferreira et al., 2008; Rodrigues et al., 2008; Shi et al., 2008). The use of highly flexible and/or aromatic-based organic moieties in conjunction with two or more chelating phosphonate groups has enabled the isolation of a number of structures in recent times (Serpaggi and Ferey, 1998; Evans et al., 2001; Groves et al., 2005, 2006; Ying and Mao, 2006). In the last two decades, we and others have investigated the use of a versatile chelating organic ligand: N-(phosphonomethyl) iminodiacetic acid (H₄PMIDA), as a complexing agent, two new complexes, (NH₄)La(PMIDA)(H₂O)●H₂O, 1 and (NH₄)Yb(PMIDA), 2 have been synthesized hydrothermally. In both compounds, the metal ions are trapped by a three five-membered chelate rings by the chelating PMIDA anions giving a tricapped trigonal prismatic LaO₈N and monocapped trigonal prismatic YbO₆N geometries for 1 and 2, respectively. The structure of 1 consists of La(PMIDA)(H₂O) chelating units, linked together by the phosphonate oxygen atoms O1 and O3 to form a chain along the c-axis. The chains are then connected together by the bridging phosphonate oxygen O2 to form a 2D layered structure with alternating 4- and 8-membered apertures. The structure of 2 consists Yb(PMIDA) chelating units, which are connected by alternating bridging carboxylate and phosphonate groups along the [010] direction forming chains with a corrugated pattern. The third phosphonate oxygen bridges the chains together along the [001] direction to build the two-dimensional layer with 4- and 6-membered apertures in the bc-plane. Under excitation of 330 nm, compound 2 shows a broad emission band at λₘₐₓ = 460 nm. This emission is essentially in the blue luminescent region, which corresponds to ligand centered fluorescence.

Keywords: hydrothermal synthesis, carboxylate-phosphonate hybrid material, metal organophosphonate frameworks, aminopolyacid ligand, flexible coordination
agent in the presence of phosphoric acid, a mixed phosphate phosphonate layered zirconium compound was obtained by our group (Zhang et al., 1996). A linear chain compound was isolated when the reaction was carried out in the absence of phosphoric acid (Zhang et al., 1998). In both cases, the iminodiacetic moieties are only involved in hydrogen bonding, and are available for further metal complexing. An antiferromagnet K$_2$Co(PMIDA)$_2$·xH$_2$O, whose crystal structure features a hexameric ring in the chair conformation was isolated by Wood and co-workers through the interaction of the salt of cobalt with H$_2$PMIDA as ligand (Gutschke et al., 1999). Also with H$_4$PMIDA ligand, we reported two divalent metal carboxylate-phosphonate hybrid compounds of composition [Co$_2$(PMIDA)($\text{H}_2$O)$_2$·H$_2$O and [Zn$_2$(PMIDA)(CH$_3$CO$_2$H)]·2H$_2$O. The structure of cobalt compound contains double layers of Co(II)carboxylate interconnected by layers of Co(II)phosphonate, while the crystal structure of zinc compound features a zinc carboxylate-phosphonate hybrid layer along the [202] plane (Mao and Clearfield, 2002). Mao and co-workers isolated isostructural lanthanide carboxyphosphonates Ln(HPMIDA)·3H$_2$O (Ln = Gd, Tb, Dy, Er, Yb, Lu), based on H$_2$PMIDA anion, which exhibit a three-dimensional (3D) open-framework structures with helical tunnels (Tang et al., 2006a). Several research groups have constructed multi-dimensional frameworks by using [V$_2$O$_2$(PMIDA)$_2$]$_{\infty}$ anionic unit, as well as a one-dimensional coordination polymer containing H$_2$PMIDA residues and Fe$_2$O$_3$ centers (Almeida Paz et al., 2004; Shi et al., 2005, 2006). In a typical syntheses of 1, LaCl$_3$·7H$_2$O (0.557 g, 1.5 mmol) was dispersed in 2 ml of water followed by the addition of 0.26 ml HCl and 0.84 ml 1,4-dioxane. To this mixture was added H$_2$PMIDA (0.34g, 1.5 mmol), urea (0.20 g, 3.3 mmol) and potassium acetate (0.10 g, 1.0 mmol). The resulting suspension with a pH of 1 was sealed in a Teflon-lined steel autoclave and heated at 160°C for 6 days. The product, a crop of colorless plate-like crystals was filtered and washed with distilled water and dried at ambient temperature. Compound 2 was obtained similarly from the composition Yb$_2$O$_3$(0.28 g, 1.5 mmol); 0.26 ml HCl; 2 ml H$_2$O; 0.84 ml Dioxiane; H$_2$PMIDA(0.34 g, 1.5 mmol); and Urea (0.20 g, 3.3 mmol). The final pH was 3.5 and 2 for compounds 1 and 2, respectively. Initial characterization was carried out by powder X-ray diffraction (PXRD), inductively coupled plasma-atomic emission spectrometry (ICP-AES), and elemental analysis (CHN). Inorganic materials with multifunctions (Song and Mao, 2005; Ying and Mao, 2006; Liu et al., 2007; Mao, 2007). The successful synthesis of the first open-framework lanthanide carboxyphosphonate Pr$_4$(H$_2$O)$_2$[(O$_3$PCH$_2$NC$_5$H$_4$COO)$_4$(H$_2$O), opened the way for a number of other lanthanide hybrid solids to be isolated (Massiot et al., 1997; Legendziewicz et al., 1998; Serre et al., 2004; Bauer et al., 2006; Tang et al., 2006a,b; Huang et al., 2007; Zhou et al., 2010). For example, using lanthanide chlorides and N-((carboxymethyl)iminodiacetylphosphonic acid)(H$_5$cmp) a series of layered [Ln(H$_2$cmp)(H$_2$O)]$_{\infty}$ materials [where Ln$^{3+}$ = Y$^{3+}$, La$^{3+}$, Pr$^{3+}$, Nd$^{3+}$, Sm$^{3+}$, Eu$^{3+}$, Gd$^{3+}$, Tb$^{3+}$, Dy$^{3+}$, Ho$^{3+}$, and Er$^{3+}$], and the mixed-lanthanide [(Gd$_{0.95}$Eu$_{0.05}$)(H$_5$cmp)(H$_2$O)]$_{\infty}$ material, have been successfully isolated from hydrothermal synthesis as phase-pure micro-crystalline compounds, (Cunha-Silva et al., 2009) and found to be supramolecular polymorphs of the compound that was reported by Mao and co-workers (Massiot et al., 1997; Bauer et al., 2006; Tang et al., 2006b; Zhou et al., 2010). Using phosphonoacetic acid as a complexing agent, a linear chain aluminum(III)carboxyphosphonate with ammonium ion as counter cation has been reported (Ayi et al., 2011). The ammonium cations were generated in-situ from the partial decomposition of urea. By employing a similar technique with the rare earth elements, we have been able to isolate two new materials (NH$_4$)[La(PMIDA)(H$_2$O)]·H$_2$O, 1, and (NH$_4$)[Yb(PMIDA)], 2, exhibiting 2D structures.

This paper reports the synthesis and characterization of these two lanthanide(III)carboxyphosphonates.

### EXPERIMENTAL

#### SYNTHESES AND CHEMICAL ANALYSIS

The two compounds (NH$_4$La(PMIDA)(H$_2$O))·H$_2$O, 1 and (NH$_4$)Yb(PMIDA), 2 were hydrothermally synthesized (autogenous pressure for 6 days) at 160°C from a mixture of lanthanum chloride heptahydrate LaCl$_3$·7H$_2$O (Aldrich, 98%) for 1, ytterbium oxide Yb$_2$O$_3$ for 2, HCl ( Fisher Scientific), N-(phosphonomethyl)iminodiacid acid, H$_2$PMIDA (Aldrich, 95%), potassium acetate ( Fisher Scientific), urea (EM Science), and H$_2$O/dioxane in the molar ratio 1:2:1; 2:2.2:80/10. In a typical synthesis of 1, LaCl$_3$·7H$_2$O (0.557 g, 1.5 mmol) was dispersed in 2 ml of water followed by the addition of 0.26 ml HCl and 0.84 ml 1,4-dioxane. To this mixture was added H$_2$PMIDA (0.34 g, 1.5 mmol), urea (0.20 g, 3.3 mmol) and potassium acetate (0.10 g, 1.0 mmol). The resulting suspension with a pH of 1 was sealed in a Teflon-lined steel autoclave and heated at 160°C for 6 days. The product, a crop of colorless plate-like crystals was filtered and washed with distilled water and dried at ambient temperature. Compound 2 was obtained similarly from the composition Yb$_2$O$_3$(0.28 g, 1.5 mmol); 0.26 ml HCl; 2 ml H$_2$O; 0.84 ml Dioxiane; H$_2$PMIDA(0.34 g, 1.5 mmol); and Urea (0.20 g, 3.3 mmol). The final pH was 3.5 and 2 for compounds 1 and 2, respectively. Initial characterization was carried out by powder X-ray diffraction (PXRD), inductively coupled plasma-atomic emission spectrometry (ICP-AES), and elemental analysis (CHN).

#### Table 1 | Crystal data and structure refinement for 1 and 2.

| 1       | 2       |
|---------|---------|
| Formula | CaH$_{14}$N$_2$O$_3$P La                | CsH$_{10}$N$_2$O$_7$P Yb               |
| Formula mass | 416.06          | 414.16             |
| Crystal system | Monoclinic          | Monoclinic             |
| Space group | P 2/c               | P 2/c               |
| a (Å) | 7059(4)               | 9.1813(3)          |
| b (Å) | 23.577(12)            | 8.8993(3)          |
| c (Å) | 6.8713(3)              | 12.827(4)          |
| β (°) | 94.3296(10)            | 101.4114(3)       |
| V (Å$^3$) | 1140.4(10)             | 1026.0(5)          |
| Z | 4                      | 4                   |
| $\rho_c$ (Mg m$^{-3}$) | 2.423               | 2.681               |
| $\mu$(Mo-K$\alpha$)(mm$^{-1}$) | 3.931               | 9.294               |
| F(000) | 808                   | 780                 |
| Reflections collected | 7029               | 8719              |
| Independent reflections | 2460 | [R(int) = 0.1268]  | 2454 [R(int) = 0.0718] |
| GOF on F$^2$ | 1.015              | 1.028              |
| Final R indices [I > 2σ(I)] | $R_I = 0.0688$, $wR_I = 0.1361$ | $R_I = 0.0321$, $wR_I = 0.0880$ |
| Final R indices (All data) | $R_F = 0.1483$, $wR_F = 0.1680$ | $R_F = 0.0363$, $wR_F = 0.0928$ |

$a$ Final R indices [I > 2σ(I)] = $\Sigma||F_O|-|F_C||/\Sigma|F_O|$, $wR_F = (\Sigma w(F_O^2 - F_C^2)^2/\Sigma w(F_O^2))^0.5$. 

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emission spectroscopy (ICP-AES), thermogravimetric analysis (TGA), elemental CHN analysis, and IR spectroscopy. The PXRD patterns of 1 and 2 compared with their simulated patterns from single crystal analyses are presented in Figure S1. ICP-AES gave a Ln: P ratio of 1:1 in agreement with the formula. C₆H₁₄N₂O₅Pla (416.06) 1, (based on single-crystal data): calcd. La 33.55, P 7.48, C 14.43, H 3.39, N 6.73; found La 34.54, P 7.32, C 14.21, H 3.35, N 6.49; C₆H₁₀N₂O₅PYb (414.16) 2, (based on single-crystal data): calcd. Yb 41.77, P 7.48, C 14.51, H 2.43, N 6.76. found Yb 40.80, P 7.18, C 14.52, H 2.37, N 6.63. TGA data (mass losses), I: 43–197°C 4.72% (DTG peak at 62°C); 231–393°C 6.89% (DTG peaks at 267, 294, and 326°C); 436–893°C 41.2% (DTG peaks at 638, 755, 794, and 845°C). 2: 260–460°C 28.82% (DTG peak at 362°C); 860–958°C 35.9% (DTG peak at 958°C); Selected ATR-FTIR data (cm⁻¹): 1: υ(O-H and N-H involved in hydrogen bonding interactions) = 3440–3000 s⁻¹ (very broad), υ(C-H in –CH₂-) = 2981 w, υ asym(CO) = 1558 vs. υ sym(CO) = 1399 s, δ(O-H...O) = 1338 m, υ(C=O) = 1247 m, υ(C-N) 1117, υ asym(P-O) = 1018 s, υ sym(P-O) = 981 s, υ(P-C) = 787 m. 2: υ(C-H in –CH₂-) = 2948 w, υ asym(CO) = 1593 vs. υ sym(CO) = 1405 s, 1384 s, δ(-CH₂-) = 1448 m, υ(C=O) = 1341 m, 1333 sh, 1257 w, 1232 m, δ(C=C-N, amines) = 1154 m, υ(C=N) = 1122 w, υ sym(P-O) = 1084 vs. υ asym(P-O) = 1020 s, 1006 m, 974 w, υ(P-C) = 786 w, 713 s.

INSTRUMENTATION

A PXRD pattern was recorded at ambient temperature on a Bruker D8 Advance diffractometer (CuKα radiation λ = 1.54056 Å) fitted with Lynx EYE detector. Data were collected using a flat plate sample holder. Intensity data were collected by the continuous counting method (step 0.03° and time 3 s) in the range 5–50° 20. Excel and Origin 7 were used to analyse the data. Elemental analysis (C, H, and N) was performed by Atlantic Microlab, Inc. For La/P and Yb/P ratios, samples were digested in conc HNO₃ and Anderson Analytical determined the relative amounts by ICP-AES. Thermal analysis was carried out with a Rigaku Thermoflex 8110 unit at a heating rate of 5°C/min to 1100°C. The data were reduced using SAINTPLUS, (Bruker, 2005) and an empirical absorption correction was applied using the SADABS program (Sheldrick, 2008b). The structures were solved by direct methods and refined by the full-matrix least-squares technique against F² with the anisotropic displacement parameters for all non-hydrogen atoms using SHELXL-2008 (Sheldrick, 2008a). All hydrogen atoms except those for the water molecules and ammonium, were added in idealized positions and refined using a riding model with Uiso = nUeq for carbon atoms connected to the relevant H-atom where n = 1.5 for methyl and n = 1.2 for other H-atoms. The hydrogen atoms for the water molecules and ammonium ions in both compounds were located from difference Fourier maps and were refined using a riding mode. Anisotropic displacement parameters were established for all non-hydrogen atoms. Selected data collection and refinement parameters are summarized in Table 1. More details on crystallographic studies as well as atom displacement parameters are given in the Supporting Information (CCDC 847459) and (CCDC 847460) for compounds 1 and 2, respectively.

RESULTS AND DISCUSSION

The hydrothermal treatment of H₄PMIDA with the lanthanides (Ln = La, 1; Yb, 2) in the presence of HCl-urea afforded two new lanthanide(III)carboxylate-phosphonates, namely (NH₄)[La(PMIDA)(H₂O)]•H₂O, 1, and (NH₄)[Yb(PMIDA)], 2 incorporating ammonium ions to balance the anionic framework [Ln(PMIDA)]⁻ charge of -1. The ammonium cations are generated in-situ from the partial decomposition of urea and are crucial in the reaction as structure directors. The pH of the reaction mixtures significantly influences the formation of the product. The initial pH for both compounds was 1.0. Whereas a final pH in the range of 3.5–4.0 favors the formation of compound 1, a pH of 2.0 was found to favor compound 2. The addition of urea and potassium acetate in the reaction vessel were needed to control the pH of the reaction media and to yield crystalline samples as direct addition of ammonia solution to the synthetic mixture could not lead to the formation of the products. The two compounds exhibit two-dimensional layered structures with distinct features.

The asymmetric unit of 1 consists of one crystallographically independent Lanthanum(III) ion, a PMIDA⁴⁻ anion, and two new lanthanide(III)carboxylate-phosphonates, namely (NH₄)[La(PMIDA)(H₂O)]•H₂O, 1, and (NH₄)[Yb(PMIDA)], 2 incorporating ammonium ions to balance the anionic framework [Ln(PMIDA)]⁻ charge of -1. The ammonium cations are generated in-situ from the partial decomposition of urea and are crucial in the reaction as structure directors. The pH of the reaction mixtures significantly influences the formation of the product. The initial pH for both compounds was 1.0. Whereas a final pH in the range of 3.5–4.0 favors the formation of compound 1, a pH of 2.0 was found to favor compound 2. The addition of urea and potassium acetate in the reaction vessel were needed to control the pH of the reaction media and to yield crystalline samples as direct addition of ammonia solution to the synthetic mixture could not lead to the formation of the products. The two compounds exhibit two-dimensional layered structures with distinct features.

The asymmetric unit of 1 consists of one crystallographically independent Lanthanum(III) ion, a PMIDA⁴⁻ anion,
aqua ligand, a lattice water and an ammonium ion for charge balancing. The PMIDA$^{4-}$ anion coordinates to the central La ion in a tetradeurate fashion via one oxygen atom from each of the carboxylates (O4 and O6), one oxygen atom from the phosphonate (O1), and a nitrogen atom from the amino group (N1). This forms three five-membered chelation rings. The one independent La(III) ion is nine-coordinate and to fulfill the coordination, three other PMIDA anions coordinates to the metal center through the phosphonate oxygen atoms (O3A, O2B, O3C, and O2C) as shown in Figure 1. The geometry about the central atom is trigonal prismatic tricapped by N(1) and O(8). The interatomic distances are well defined. La-O distances are within the 2.458(9)–2.732(9) Å range [La-Oav = 2.568 Å] and La-N distance is 2.821(12) Å, while the C-O and P-O distances are within the 1.248(16)–1.271(16), and 1.508(9)–1.543(10) Å ranges, respectively and are indicative of complete deprotonation of both the carboxylate and phosphonate groups. The longest P-O distance belongs to the $\mu_2$-bridging oxygen atoms. The P-C distance is 1.791(14) Å. These distances are in good agreement with similar compounds in the literature (Legendziewicz et al., 1998; Serre et al., 2004; Song and Mao, 2005; Tang et al., 2006a; Ying and Mao, 2006; Huang et al., 2007; Liu et al., 2007; Mao, 2007).

The PMIDA$^{4-}$ anion is a polydentate ligand, which chelates with a lanthanum(III) ion in a tetradeurate fashion and bridges three other lanthanum ions using the phosphonate oxygen atoms. The phosphorus atom P(1) on the tetradeurate ligand coordinating to La(1) via O1, forms multiple bonds to three equivalent lanthanum atoms [La(1A), La(1B), and La(1C)] through the remaining two oxygen atoms O2 and O3 giving rise to a [122] connectivity mode (Massiot et al., 1997; Bauer et al., 2006; Tang et al., 2006a,b; Zhou et al., 2010). While the phosphonate oxygen O2 and O3 both chelate with the La(1A) center, O3 also bridges with La(1B) to form a chain propagating along the [001] direction as shown in Figure 2. Within the chain, the La...La distances over $\mu_3$-O3 and O1–P1–O3 bridges are 4.227(2) and 6.871(3) Å, respectively. The chains are then connected together by the
bridging phosphonate oxygen O2 to form a 2D layered structure with alternating 4- and 8-membered rings as shown in Figure 3. Each of the two carboxylate oxygen coordinates to the La(III) center in a monodentate fashion. The two non-coordinating carboxylate oxygen atoms [O5, O7] point into the interlamellar space and interact with the lattice water and ammonium ions in the interlayers via hydrogen bonds (Figure 2, Table 2). The adjacent layers separated by 12.467(6) Å, are connected together via these multiple hydrogen bonds.

The asymmetric unit of 2 consists of one crystallographically independent ytterbium(III) ion, a PMIDA$^{4-}$ anion, and an ammonium ion for charge balance (Figure 4). The Yb(III) ion is coordinated by a polydentate PMIDA anion in a tetradeinate fashion via one oxygen atom from each of the carboxylates (O5 and O6), one oxygen atom from the phosphonate (O1), and a nitrogen atom from the amino group (N1). This forms three five-membered chelation rings similar to the lanthanum compound, 1. Three other PMIDA anions coordinating through two phosphonate oxygen atoms [O2A and O3A] and one carboxylate oxygen atom (O4B) completes the coordination number of seven around the central Yb(III) ion. Interestingly, the two carboxylate groups in PMIDA$^{4-}$ adopt different coordination modes. One carboxylate group is only coordinated to Yb atom by O6 in a monodentate fashion, while the other is bidentate bridging through O4 and O5. The geometry about the central metal ion is a capped trigonal prism YbO$_6$N. The Yb-O distances are in the range

Table 2 | Hydrogen bonds for compounds 1 and 2.

| D-H...A | (D-H-A)/° | d(D...A)/Å | Symmetry operation |
|---------|-----------|------------|--------------------|
| COMPOUND 1 | | | |
| N2-H2-O7 | 152.54 | 2.820(16) | 1 + x, y, z |
| N2-H3-O5 | 163.65 | 2.825(15) | x, y, z |
| N2-H4-O10 | 168.50 | 2.962(14) | x, y, z |
| O10-H10A-O4 | 114.58 | 2.919(16) | x, y, 1 + z |
| O8-H8A-O6 | 122.54 | 2.656(14) | 1 – x, 2 – y, 2 – z |
| COMPOUND 2 | | | |
| N2-H2C-O7 | 167.14 | 2.794(5) | –1 + x, y, z |
| N2-H2D-O6 | 150.82 | 3.032(4) | 1 – x, ½ + y, ½ – z |
| N2-H2E-O5 | 120.46 | 3.069(5) | 1 – x, –½ + y, ½ – z |
| N2-H2F-O3 | 170.86 | 2.855(6) | 1 – x, 1 – y, 1 – z |
2.174(3)–2.318(3) Å, while the Yb-N distance is 2.576(5) Å and are comparable with those reported for similar compounds in the literature (Zabicky, 1970; Burwell and Thompson, 1991a,b; Tang et al., 2006a). The Yb(PMIDA) chelating units are connected by alternating bridging carboxylate and phosphonate groups along the [010] direction, forming chains with a corrugated pattern. The phosphonate oxygen O2, bridges the chains together along the [001] direction to build the layered material as shown in Figure 5.

The PMIDA$^{3-}$ anion is a heptadentate ligand, coordinating through three phosphonate oxygen atoms (O1, O2, O3), three carboxylate oxygen atoms (O4, O5, and O6) and the amino nitrogen (N1). The phosphonate group is tridentate and bridges with three equivalent Yb(PMIDA) chelating units, that is the three oxygen atoms of the PO$_3$ group are bonded to different ytterbium atoms, such that each is directly connected to only one ytterbium atom in a [111] connectivity (Massiot et al., 1997; Bauer et al., 2006; Tang et al., 2006a,b; Zhou et al., 2010). Both the Yb(III) and phosphonate group are 3-connectors in terms of topology giving the 2D layer a vertex symbol of 6 (Ayi et al., 2013), with two types of four-coordinate nodes. This kind of topology has also been observed in similar lanthanide(III) complexes, but with two types of three-coordinate nodes (Massiot et al., 1997; Bauer et al., 2006; Tang et al., 2006a,b; Zhou et al., 2010). The non-coordinating carboxylate oxygen O(7) points into the interlamellar space and interacts with the ammonium ions through hydrogen bonding (Table 2). The interlayer distance is 9.181(3) Å. Hydrogen bonding between the ammonium ions and the layers hold the layers together.

It is interesting to note that whereas the two reactions took place in aqueous solution, compound 1 has coordinated and lattice water, while compound 2 is an anhydrous complex. There is a change in coordination number from 9 in compound 1–7 in compound 2 attributed to the decrease in the size in going from La$^{3+}$ (103pm) to Yb$^{3+}$ (87pm) ions (Shannon, 1976; Ma et al., 2007) Similar hydrothermal reactions of H$_4$PMIDA with lanthanide(III) salts reported by Mao and coworkers gave lanthanide(III) carboxylate-phosphonates, which was formulated as Ln(HPMIDA)(H$_2$O)$_2$H$_2$O (Ln: Gd, Tb, Dy, Y, Er, Yb, Lu, Y) (Tang et al., 2006a). Their structures feature a three-dimensional network with helical tunnels. In this present investigation, compound 1 is formulated as (NH$_4$)$_2$[Ln(PMIDA)(H$_2$O)]·H$_2$O and compound 2 has the formula (NH$_4$)$_2$[Yb(PMIDA)]$_2$, both featuring a two-dimensional structure with extensive hydrogen bonding involving the ammonium ion. In the previously reported compounds, the phosphate group is singly protonated, whereas the compounds under present study shows complete deprotonation of the acidic oxygen atoms. The complete deprotonation is made possible by the addition of urea into the synthetic media, which resulted in the incorporation of ammonium ion in the present structure.

The infrared spectra of the compounds are particularly informative, providing supporting evidence for the structural differences existing between compounds 1 and 2. The free ligand shows absorption peaks in the spectral range between 1731 and 1216 cm$^{-1}$ arising from stretching and bending vibrational modes associated with C = O, C-O, and C-H bonds. While the band at 1731 cm$^{-1}$ is assigned to $v_{asym}(C = O)$, the one at 1473 cm$^{-1}$ is due to $v_{sym}(C = O)$. The bands at 1336, 1265, 1244, and 1216 cm$^{-1}$ are attributed to $v(C = O)$ whereas those at 1442 and 1423 cm$^{-1}$ are due to $v$ (C-H in –CH$_2$ –). In the infrared spectrum of 1, the broad band in the spectral region 3500–3360 cm$^{-1}$ (peaking at ca. 3436 cm$^{-1}$) is attributed to the $v$(O-H) of water molecules involved in hydrogen bonds. This feature is absent in compound 2. The broad absorption bands observed at ca. 3207 cm$^{-1}$ (1) and at ca. 3180 cm$^{-1}$ (2) are attributed to the $v$(N-H) vibrations involved in hydrogen bonding. The stretching mode of –CH$_2$ groups is markedly visible in the spectra, giving rise to peak around 2981 cm$^{-1}$ in 1 and 2948 cm$^{-1}$ in 2. The strong peaks observed at 1558 and 1399 cm$^{-1}$ in 1 (1593, and 1384 cm$^{-1}$ in 2) are due to the asymmetric and symmetric stretching mode of the CO$_2^-$ bonds of the carboxyl group. This is lower than the 1731 cm$^{-1}$ absorption peak seen in that of the free ligand. This down field shift in the absorption frequency is a clear indication that the carboxylate groups are involved in coordinating to the metal center (Zabicky, 1970; Nakamoto, 1978; Deacon and Phillips, 1980; Burwell and Thompson, 1991a,b; Drumel et al., 1995; Ai et al., 2011) in both 1 and 2. In the infrared spectrum of 2, the characteristic antisymmetric and symmetric stretching bands for the carboxylate ions are present with the corresponding $\Delta[v_{asym}(CO_2^-) - v_{sym}(CO_2^-)]$ values being 188
and 209 cm\(^{-1}\) indicating the presence of carboxylate groups in the anti-unidentate and bridging-\(\eta^2\)-anti,anti-chelate coordination modes, respectively (Nakamoto, 1978; Deacon and Phillips, 1980; Drumel et al., 1995). The vibrational modes of the phosphonate (PO\(^3\)) units are also noticeable in the infrared spectra of compounds 1 and 2. In 1, the asymmetric stretching vibrational band of P-O group is observed at 1018 cm\(^{-1}\) and at 1084 cm\(^{-1}\) for 2, while the symmetric stretching mode is at 981 cm\(^{-1}\) in 1 and at 1020 cm\(^{-1}\) in 2. The P-C stretching modes are observed around 787 cm\(^{-1}\) in both compounds.

In order to investigate the thermal stability of these materials, the TGA curves of compounds 1 and 2 were measured (Figure 6). Compound 1, releases the interlayer water molecule of crystallization in the temperature range 62–197\(^{\circ}\)C. The observed weight loss of 4.62\% is close to the calculated value (4.35\%). In the region 202–376\(^{\circ}\)C, there is a weight loss of 8.92\% (calc. 8.84\%) attributed to the loss of coordinated water molecule and NH\(_3\), as well as a loss of about 11.50\% due to the presence of little impurities in the bulk sample. However, the final weight loss of 42.29\% (calc. 43.78\%) corresponds to the decomposition of the organic part of the material to give LaPO\(_4\) (JCPDF card no. 01-084-0600) as the final product. Compound 2 is thermally stable up to 300\(^{\circ}\)C. The first weight loss of 28.82\% (calc. 28.25\%) is attributed to the loss of NH\(_3\), 2CO, and CO\(_2\). A plateau appears in the range 422–849\(^{\circ}\)C, above which a final weight loss of 35.9\% (calc. 35.28\%) occurs, corresponding to the decomposition of the organic part to give YbPO\(_4\) (JCPDF card no. 01-076-1643).
The photoluminescence properties of compound 2 were investigated in the solid state at room temperature (Figure 7). Under excitation of 330 nm, the compound shows a broad emission band at $\lambda_{\text{max}} = 460$ nm. This emission is essentially in the blue luminescent region, which corresponds to ligand centered fluorescence (Tang et al., 2006a; Zhou et al., 2010). Owing to the quenching effect of the luminescent state reported for complexes with coordinated water molecules, (Song et al., 2004; Sarkar et al., 2006; Deng et al., 2011) the solid state luminescence of 1 was not studied.

CONCLUSION

We have successfully synthesized hydrothermally, two new compounds based on $N$-(phosphonomethyl)iminodiacetic acid (H$_4$PMIDA), namely (NH$_4$La(PMIDA)(H$_2$O)$_1$, and (NH$_4$)Yb(PMIDA)$_2$. The presence of the ammonium ions serves to compensate the framework negative charge in both compounds and is crucial in the syntheses of the compounds under investigation as it stabilizes the structures through hydrogen bonding interactions. The change in the coordination number from 9 for compound 1–7 for compound 2 clearly shows that the size of the cation plays an important role in determining the coordination number. Thus, ion with larger radius favors a higher coordination number and a larger cavity to accommodate more water molecules (Shannon, 1976; Ma et al., 2007). Solid state photoluminescent studies of compound 2 at room temperature shows broad emission in the blue luminescent region, which is essentially attributed to ligand centered fluorescence. Efforts are under way to synthesize the complete series of the ammonium ion-templated lanthanide(III) complexes with this particular ligand with a view to elucidate their crystal structures, magnetic and luminescent properties.

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SUPPLEMENTAL MATERIAL

The Supplementary Material for this article can be found online at: http://www.frontiersin.org/journal/10.3389/fchem.2014.00094/abstract

Supporting Information Available: X-ray crystallographic files in CIF format (CCDC 847459) and (CCDC 847460) for compounds 1 and 2, respectively as well as simulated and experimental XRD powder patterns for compounds 1 and 2.

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