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Solvothermal synthesis, structure, and luminescent properties of a series of 3D lanthanide carbonate frameworks

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Abstract

A series of three-dimensional (3D) lanthanide carbonate coordination polymers [Ln(μ_5-CO_3)(μ_2-OH)], Ln^{III} = Pr (**1Pr**), Nd (**2Nd**), Sm (**3Sm**), Eu (**4Eu**), Gd (**5Gd**), Tb (**6Tb**) and Dy (**7Dy**), has been synthesized using solvothermal conditions and characterized by spectroscopic methods. Structures of compounds **1Pr**-**3Sm** were solved from single crystal X-ray diffraction (SCXRD) data, whereas microcrystals of compounds **4Eu**-**7Dy** were not of sufficient quality for SCXRD analysis. Therefore, conventional powder X-ray diffraction (PXRD) and elemental analysis have been used to verify the phase purity. SCXRD analysis revealed that compounds **1Pr**-**3Sm** are isostructural and crystallize in the orthorhombic space group *Pnma* with four formula units per unit cell. In the crystal structure, each Ln^{III} cation is bridged by five μ_5-η^2:η^2:η^2:η^1:η^1-CO_3^{2-} and two μ_2-OH^- ligands forming a neutral 3D framework. The luminescence properties of compounds **4Eu** and **6Tb** were investigated in the solid state at room temperature.

Keywords: *carbonate, crystallography, crystal structure, lanthanide, luminescence, solvothermal synthesis*

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1. Introduction

Over the past several years, the design and synthesis of lanthanide coordination polymers have attracted significant attention due to the rich diversity of their topological structures as well as their luminescent properties, which allow potential applications in luminescent devices, sensors, and lasers (Bünzli & Piguet, 2005; McMahon, Mauer, McCoy, Lee, & Gunnlaugsson, 2009). In general, the luminescent properties of lanthanide complexes are derived from their 4f-4f transitions and coordination geometries (Mishra, Wernsdorfer, Abboud, & Christou, 2004; Zhao et al., 2004; Miyato et al., 2011; Matthes et al., 2013). It should be noted that the trivalent f-block metal ions possess large coordination numbers and flexible coordination geometries (Sastri, Bünzli, Rao, Rayudu, & Perumareddi, 2003). Furthermore, the nature and structural characteristics, as well as the ligand field strength, are the key factors that can affect the coordination number (Long, Blake, Champness, Wilson, & Schröder, 2001 & 2002; Han & Hill, 2007). These factors make it more difficult to control or predict the formation of structures and properties of trivalent lanthanide compounds. In addition, lanthanide contraction may also influence the coordination numbers and properties (Mu et al., 2015; Hutchings, Habib, Holmberg, Korobkov, & Murugesu, 2014; Regueiro-Figueroa, Esteban-Gómez, de Blas, Rodríguez-Blas, & Platas-Iglesias, 2014). Thus, achieving controlled synthesis of desired structures with satisfactory luminescent properties remains a fundamental scientific challenge.

One design strategy for the development of novel lanthanide functional materials is the use of carboxylic acids as bridging ligands. These ligands can provide structural scaffolding, charge balance, act as luminescent sensitizers, and lead to significant magnetic interactions between the Ln^{III} ions, allowing for the generation of a wide range of such materials with interesting topologies and properties (Martínez-Calvo et al., 2015; Guo et al., 2015; Long et al., 2015; Nakai et al., 2014; Zheng et al., 2014; Gu et al., 2013; Dang, Zhang, Sun, & Zhang, 2012; Marchal, Filinchuk, Chen, Imbert, & Mazzanti, 2009). Among the numerous new rare earth compounds, some of the most intriguing are luminescent and magnetic lanthanide coordination polymers containing a small anion with trigonal planar geometry such as carbonate (Zhang et al., 2015; Hooper et al., 2014; Chesman et al., 2012; Langley, Moubaraki, & Murray, 2012; Bag et al., 2012; Gass, Moubaraki, Langley, Batten, & Murray, 2012; Gunanathan, Diskin-Posner, & Milstein, 2010; Andrews et al., 2007; Fang, Anderson, Neiwert, & Hill, 2003) or nitrate (Langley et al., 2015; Langley et al., 2014; Langley, Chilton, Moubaraki, & Murray, 2013; Xu et al., 2013; Ma et al., 2012; Seidel, Lorbeer, Cybińska, Mudring, & Ruschewitz, 2012; Yan et al., 2011; Calvez, Daiguebonne, & Guillou, 2011). These anions possess oxygen electron-donating atoms and can exhibit versatile coordination modes with the metal ion centers. The bonding modes range from μ_1- to μ_6, with the μ_5- and μ_6-bridging modes appearing only rarely in the literature.

Inspired by these versatilities in the chemistry of lanthanide complexes with small molecule anions, we report the solvothermal syntheses of seven three-dimensional (3D) lanthanide frameworks in which the CO_3^{2-} bridge to the Ln^{III} ions in the μ_5-$\eta^2{:}\eta^1{:}\eta^1{:}\eta^1{:}\eta^1$ bonding mode: [Ln(μ_5-CO_3)(μ_2-OH)], Ln^{III} = Pr (**1Pr**), Nd (**2Nd**), Sm (**3Sm**), Eu (**4Eu**), Gd (**5Gd**), Tb (**6Tb**) and Dy (**7Dy**). These compounds have been characterized by elemental analysis, powder X-ray diffraction, and single crystal X-ray diffraction. The luminescent properties of compounds **4Eu** and **6Tb** have been investigated in solid state at room temperature. It should be noted that the crystal structure of the Sm^{III} compound has been previously reported (Xu, Ding, Feng, Zhou, & Liu, 2006). Also, the structure and phase transitions of the Gd^{III} compound have recently been studied by synchrotron powder X-ray diffraction (Sheu, Shih, Chuang, Li, & Yeh, 2010).

2. Objectives

The main aim of the present study is to synthesize lanthanide coordination polymers containing a small anion with the trigonal planar geometry and to study the correlation between the crystal structure and luminescent properties.

3. Experimental section

3.1 Materials and methods

All chemicals used in the present study were reagent grade and were used without further purification. All compounds were synthesized under an autogenous pressure in a 23 ml Teflon-lined autoclave. Elemental analysis of carbon and hydrogen were determined with a LECO CHNS 932 elemental analyzer. Powder X-ray diffraction (PXRD) patterns of the samples were collected on a Bruker D8 Advance X-ray diffractometer with graphite-monochromatized Cu K_α radiation (λ = 1.5418 Å) and 2θ ranging from 5 to 70° with scanning rate of 0.025° per second. The luminescence spectra were measured at room temperature using a Horiba Scientific FluoroMax-4 spectrofluorometer.

3.2 Synthesis of lanthanide complexes

[Pr((μ_5-CO_3)(μ_2-OH)] (1Pr): A mixture of $Pr(NO_3)_3{\cdot}6H_2O$ (217 mg, 0.5 mmol), Na_2CO_3 (60 mg, 0.5 mmol) and $LiOH{\cdot}H_2O$ (82 mg, 2 mmol) in H_2O/DMF (2 ml, 1:1 v/v) was placed in a Teflon lined reactor, stirred at room temperature for 10 min, sealed in a 23 ml stainless steel autoclave, placed in an oven, and heated to 170 °C under autogenous pressure for 2 days. The reaction mixture was cooled to room temperature. The pale green plate crystals of **1Pr** were separated from a residual uncharacterized white powder by hand under an optical microscope, and were washed with distilled H_2O. Yield: 62% (135 mg) based on Pr^{III} source. Anal. Calcd for $CHPrO_4$: C, 5.51; H, 0.46. Found: C, 5.55; H, 0.49%.

[Nd(μ_5-CO_3)(μ_2-OH)] (2Nd): The reaction was carried out using procedure similar to that for **1Pr**, starting from $Nd(NO_3)_3{\cdot}6H_2O$ (220 mg, 0.5 mmol) instead of $Pr(NO_3)_3{\cdot}6H_2O$. The pale violet plate crystals of **2Nd** were separated from a residual uncharacterized blue powder by hand under an optical microscope, and were washed with distilled H_2O. Yield: 48% (106 mg) based on Nd^{III} source. Anal. Calcd for $CHNdO_4$: C, 5.43; H, 0.46%. Found: C, 5.40; H, 0.41%.

[Sm(μ_5-CO_3)(μ_2-OH)] (3Sm): The reaction was carried out using a procedure similar to that for **1Pr**, starting from $Sm(NO_3)_3{\cdot}6H_2O$ (224 mg, 0.5 mmol) instead of $Pr(NO_3)_3{\cdot}6H_2O$. The light yellow plate crystals of **3Sm** were separated from a residual uncharacterized yellow powder by hand under an optical microscope, and were washed with distilled H_2O. Yield: 60% (134 mg) based on Sm^{III} source. Anal. Calcd for CHO_4Sm: C, 5.28; H, 0.44%. Found: C, 5.30; H, 0.48%.

[Eu(μ_5-CO_3)(μ_2-OH)] (4Eu): The reaction was carried out using a procedure similar to that for **1Pr**, starting from $EuCl_3{\cdot}6H_2O$ (184 mg, 0.5 mmol) instead of $Pr(NO_3)_3{\cdot}6H_2O$. The colorless plate microcrystals of **4Eu** were separated from a residual uncharacterized white powder by hand under an optical microscope, and were washed with distilled H_2O. Yield: 49% (90 mg) based on Eu^{III} source. Anal. Calcd for $CHEuO_4$: C, 5.25; H, 0.44%. Found: C, 5.24; H, 0.40%.

[Gd(μ_5-CO$_3$)(μ_2-OH)] (5Gd): The reaction was carried out using a procedure similar to that for **1Pr**, starting from $Gd(NO_3)_3{\cdot}6H_2O$ (203 mg, 0.5 mmol) instead of $Pr(NO_3)_3{\cdot}6H_2O$. The colorless plate microcrystals of **5Gd** were separated from a residual uncharacterized white powder by hand under an optical microscope, and were washed with distilled H_2O. Yield: 56% (114 mg) based on Gd^{III} source.

[Tb(μ_5-CO$_3$)(μ_2-OH)] (6Tb): The reaction was carried out using a procedure similar to that for **1Pr**, starting from $TbCl_3{\cdot}6H_2O$ (187 mg, 0.5 mmol) instead of $Pr(NO_3)_3{\cdot}6H_2O$. The colorless plate microcrystals of **6Tb** were separated from a residual uncharacterized white powder by hand under an optical microscope, and were washed with distilled H_2O. Yield: 52% (97 mg) based on Tb^{III} source. Anal. Calcd for CHO_4Tb: C, 5.09; H, 0.43%. Found: C, 5.07; H, 0.47%.

[Dy(μ_5-CO$_3$)(μ_2-OH)] (7Dy): The reaction was carried out using a procedure similar to that for **1Pr**, starting from $Dy(NO_3)_3{\cdot}6H_2O$ (217 mg, 0.5 mmol) instead of $Pr(NO_3)_3{\cdot}6H_2O$. The colorless plate microcrystals of **7Dy** were separated from a residual uncharacterized white powder by hand under an optical microscope, and were washed with distilled H_2O. Yield: 52% (113 mg) based on Dy^{III} source. Anal. Calcd for CHO_4Tb: C, 5.01; H, 0.42%. Found: C, 5.05; H, 0.42%.

3.3 X-ray crystallography

Single cry were measured stals of all the title compounds were mounted to the end of a hollow glass fiber. X-ray intensity data at 296(2) K on a Bruker D8 QUEST CMOS diffractometer with graphite-monochromatic Mo K_α radiation (λ = 0.71073 Å). Data reductions and absorption corrections were performed with the SAINT and SADABS software packages (Bruker, 2014), respectively. The structures were solved using SHELXT and refined on F^2 using SHELXL (Sheldrick, 2015). Crystallographic figures were prepared using OLEX2 (Dolomanov, Bourhis, Gildea, Howard, & Puschmann, 2009). All non-hydrogen atoms were refined anisotropically. The hydroxide H atom was located in a difference Fourier map and positional parameters were refined with $U_{iso}(H) = 1.5U_{eq}(O)$. For compounds **4Eu**-**7Dy**, the crystals were of poor quality, often twinned, and did not diffract significantly at high 2θ angles (collected with a scan width of 0.3º in omega and phi and an exposure time of 45 seconds/frame), only unit cell parameters of these compounds were determined. Crystallographic data and selected structural refinement results for compounds **1Pr-7Dy** are summarized in Table 1. Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-1063235 (**1Pr**), CCDC-1063236 (**2Nd**) and CCDC-1063237 (**3Sm**) (E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

4. Results and discussion

4.1 Synthesis and phase purity

The solvothermal reaction between nitrate or chloride salts of Ln^{III} and Na_2CO_3 in the presence of LiOH using a mixed solvent system, H_2O and DMF (1:1, v/v) at 170 °C resulted in the formation of two products. The first product is the major crystalline form of the title compounds isolated in moderate yields (48-62%). Additionally, a residual unknown powder has been formed. The reaction time has been extended from two to five days in an attempt to improve the product yield. However, this increase in reaction time did not have the intended result. On the other hand, if the reaction medium was a pure common solvent such as H_2O, DMF, MeOH and EtOH, while other conditions were kept constant, only unknown powders could be isolated. In this study, the temperature of the reaction is of crucial importance for the crystallization of the final products. Although, suitable single crystals for X-ray structure determination can be prepared by maintaining the reaction temperature between 170 and 180 °C, good quality crystalline products of **1Pr-3Sm** could only be prepared at the reaction temperatures close to 170 °C. Despite many attempts to regrow the crystals of **4Eu**-**7Dy**, only the colorless plates like microcrystals were always obtained. These were always small, often twinned, and of poor quality. However, the unit cell parameters (*a*, *b*, *c* and *α*, *β*, *γ*) and the space group of these compounds determined by single crystal X-ray diffraction were very similar to those of compounds **1Pr**-**3Sm** (Table 1). Furthermore, the phase purity of all compounds was established using powder X-ray diffraction and microelemental analysis. As shown in Figure 1, PXRD patterns of bulk materials of all compounds correspond well in position with the simulated ones constructed on the basis of the single crystal data, indicating the phase purity of the synthesized sample.

Table 1 Summary of crystallographic data for compounds **1Pr-7Dy**

	1Pr	**2Nd**	**3Sm**	
Empirical formula	$CHPrO_4$	$CHNdO_4$	CHO_4Sm	
Formula weight	217.93	221.26	227.37	
Temperature /K	296(2)	296(2)	296(2)	
Colour/Habit	Pale green /plate	Pale violet /plate	Light yellow /plate	
Crystal size (mm)	0.10 × 0.10 × 0.16	0.06 × 0.06 × 0.10	0.08 × 0.10 × 0.10	
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	
Space group	*Pnma*	*Pnma*	*Pnma*	
a /Å	7.2679(3)	7.2221(2)	7.1366(3)	
b /Å	4.9866(2)	4.9582(2)	4.9154(2)	
c /Å	8.5171(3)	8.4808(3)	8.4584(3)	
V /Å^3	308.68(2)	303.69(2)	296.71(2)	
Z	4	4	4	
D_{calc} /g·cm^{-3}	4.689	4.839	5.090	
μ /mm^{-1}	15.61	16.91	19.60	
F(000)	392	396	404	
Collected reflections	8100	15784	4383	
Unique data	730	422	785	
Data [$I > 2\sigma(I)$]	730	410	785	
R_{int}	0.037	0.036	0.036	
GOF (F^2)	1.06	1.19	1.18	
$R_1$$^{a)}$ [$I > 2\sigma(I)$]	0.015	0.010	0.016	
$wR_2$$^{b)}$ [$I > 2\sigma(I)$]	0.027	0.022	0.033	
$\Delta\rho_{\max}$ /$\Delta\rho_{\min}$ /e Å^{-3}	0.89, −0.96	0.44, −0.53	0.99, −1.06	
	4Eu	**5Gd**	**6Tb**	**7Dy**
Temperature /K	296(2)	296(2)	296(2)	296(2)
Colour/Habit	Colorless /plate	Colorless /plate	Colorless /plate	Colorless /plate
Crystal size (mm)	0.08 × 0.10 × 0.14	0.10 × 0.18 × 0.22	0.08 × 0.12 × 0.16	0.06 × 0.06 × 0.08
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic
Space group	*Pnma*	*Pnma*	*Pnma*	*Pnma*
a /Å	7.1000(5)	7.0704(8)	7.0261(1)	6.9866(3)
b /Å	4.8927(3)	4.8692(6)	4.8578(1)	4.8342(2)
c /Å	8.4473(6)	8.4375(10)	8.4622(2)	8.4527(4)
V /Å^3	293.44(3)	290.48(6)	288.83(1)	285.49(2)

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

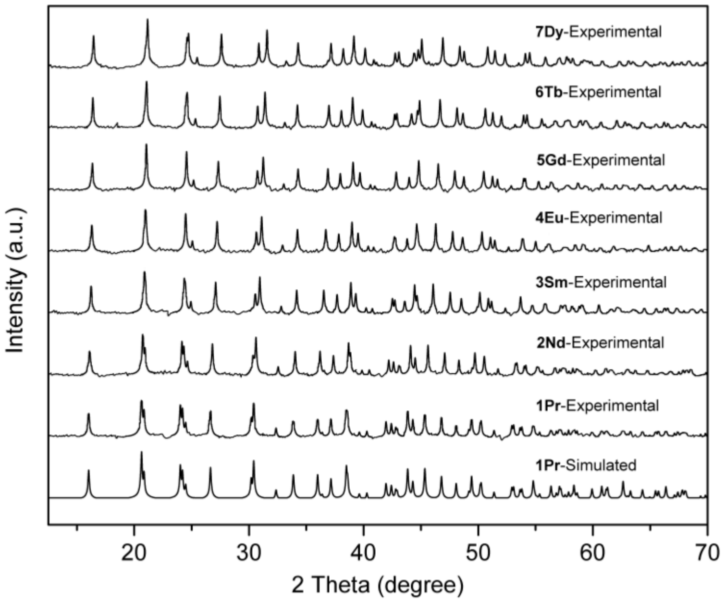
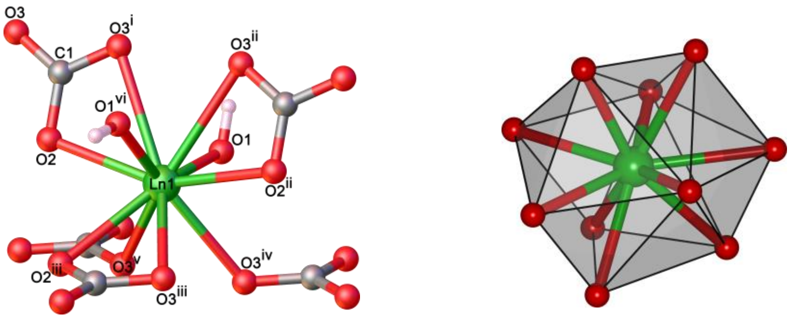


Figure 1 Comparison of the experimental powder XRD patterns of all compounds with the results simulated on the basis of the single-crystal structures

4.2 Crystal structure description

Single crystal X-ray diffraction analysis reveals that all seven compounds are isostructural and isomorphous with the [$LnONO_3$] analogues, *i.e.* Ln^{III} = La (Sun, Kyotani, & Tomita, 1986) and Nd (Li, Jin, Li, & Zhang, 2008). All of the title compounds crystallize in the orthorhombic space group *Pnma* (No. 62) with four formula units per unit cell and feature neutral 3D frameworks. The asymmetric unit contains half Ln^{III} ion, half CO_3^{2-} anion and half OH^- anion, each of which lie on a crystallographic mirror plane. As shown in Figure 2, the Ln^{III} ion is ten-coordinated with eight oxygen atoms from five CO_3^{2-} molecules and two oxygen atoms from two OH^- group in an irregular {LnO_{10}} coordination geometry. The Ln−$O_{carbonate}$ bond lengths in the title compounds are longer than the corresponding Ln−$O_{hydroxide}$ bond lengths, Table 2, which corresponds to previous reports (Chesman et al., 2012). As illustrated in Figure 3, due to the effect of the lanthanide contraction, the unit cell volumes decrease consecutively with increasing lanthanide atomic numbers from **1Pr** to **7Dy**. These trends are similar to those found in lanthanide coordination polymers containing carbonate groups and oxygen donor ligands (Xu et al., 2013; Yan et al., 2011).



(a) (b)

Figure 2 The coordination environment (a) and polyhedron of Ln^{III} ion in the title compounds. Symmetry codes: (i) x, $0.5-y$, z; (ii) x, $1+y$, z; (iii) $-0.5-x$, $0.5+y$, $0.5+z$; (iv) $0.5+x$, $1+y$, $1.5-z$; (v) $0.5+x$, $0.5-y$, $1.5-z$; (vi) $-0.5+x$, $1.5-y$, $1.5-z$

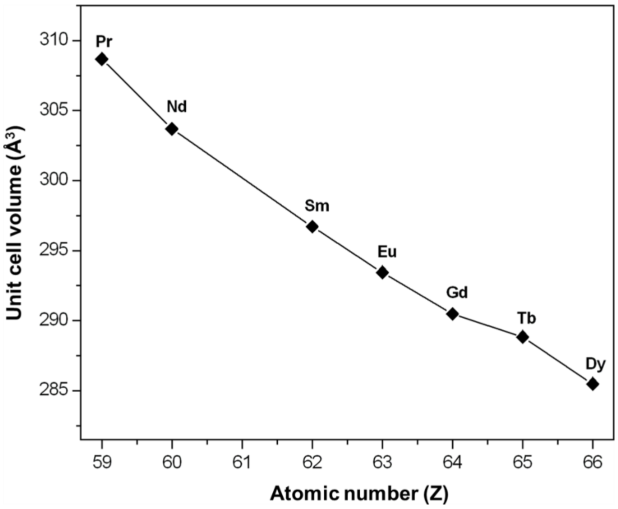


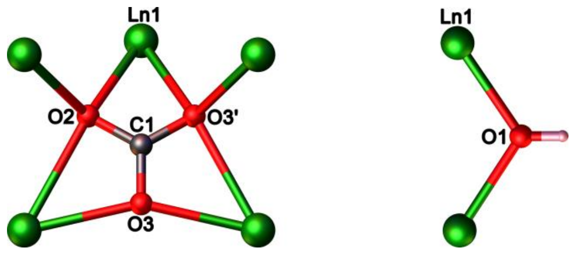
Figure 3 The dependence of the unit cell volume V (Å^3) on the atomic number Z of the lanthanide in the title compounds

Table 2 Selected bond lengths (Å) for compounds **1Pr-3Sm**

	1Pr	**2Nd**	**3Sm**
Ln1−O1	2.364(2)	2.356(2)	2.315(2)
Ln1−O1^{i}	2.366(2)	2.346(2)	2.323(2)
Ln1−O2^{ii}	2.547(4)	2.532(6)	2.512(6)
Ln1−O3^{iii}	2.756(1)	2.745(2)	2.747(2)
Ln1−O3^{iv}	2.635(2)	2.617(2)	2.587(2)
Ln1−O3^{v}	2.599(1)	2.580(1)	2.542(2)

Symmetry codes: (i) – 0.5 + *x*, 1.5 – *y*, 1.5 – *z*; (ii) *x*, 1 + *y*, *z*; (iii) *x*, 0.5 – *y*, *z*; (iv) – 0.5 – *x*, 0.5 + *y*, 0.5 + *z*; (v) 0.5 + *x*, 1 + *y*, 1.5 – *z*

Coordination modes of the CO_3^{2-} and OH^- groups found in the title compounds **1Pr-3Sm** are shown in Figure 4. The most striking structural feature is that the CO_3^{2-} anion exhibits a μ_5-$\eta^2:\eta^2:\eta^2:\eta^1:\eta^1$ coordination mode. Namely, the CO_3^{2-} group coordinates to five Ln^{III} atoms $\{\mu_5\}$. Three of these Ln^{III} ions are connected to two oxygen atoms of the CO_3^{2-} group $\{\eta^2$(O2,O3):η^2(O2,O3'):η^2(O3,O3')$\}$ and the remaining two Ln^{III} ions are connected one oxygen atom of the CO_3^{2-} group (η^1(O2):η^1(O3')). On the other hand, the OH^- bridging mode present in the title compounds **1Pr-3Sm** is quite common. The hydroxide binds in a μ_2-coordination mode connecting two adjacent Ln^{III} ions. As a result, an overall neutral 3D framework structure is achieved as shown in Figure 5. The Ln^{III}···Ln^{III} distances bound through the carbonate and hydroxide bridging anions for compounds **1Pr-3Sm** are listed in Table 3. These distances steadily decrease from Pr^{III} to Sm^{III} following the lanthanide contraction.



(a) (b)

Figure 4 Coordination modes of CO_3^{2-} (a) and OH^- (b) observed in the title compounds **1Pr-3Sm**

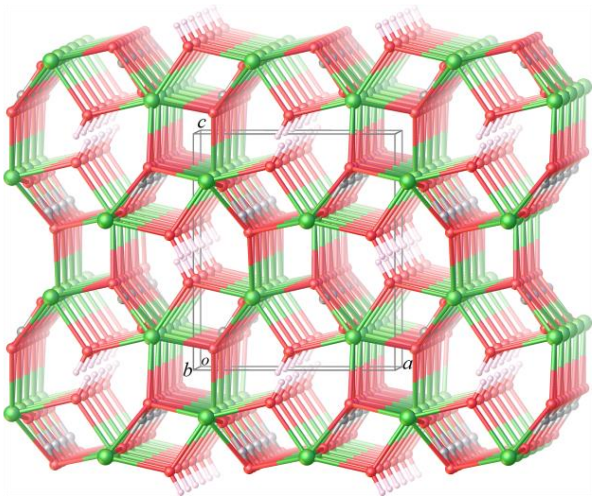


Figure 5 Prospective view of the 3D framework of the title compounds **1Pr-3Sm** running approximately along the *a* axis

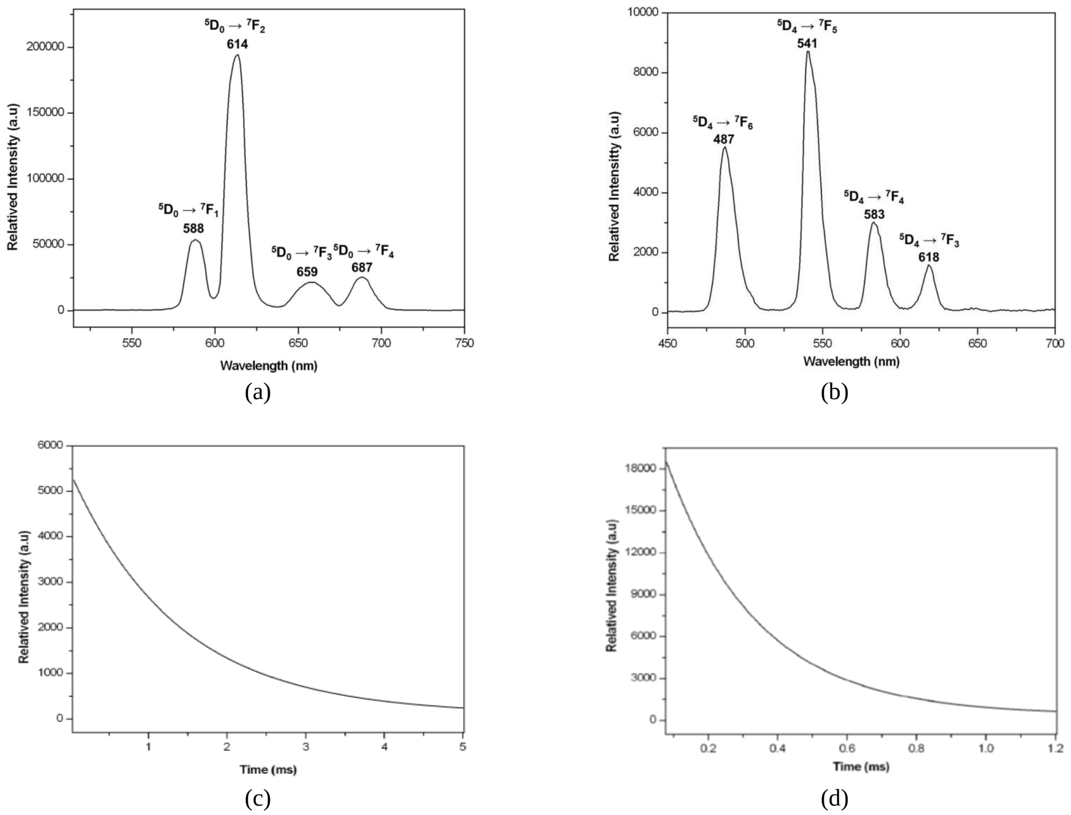
Table 4 The $Ln^{III}\cdots Ln^{III}$ distances bound through the carbonate and hydroxide bridging anions for compounds **1Pr-7Dy**

	1Pr	**2Nd**	**3Sm**
Hydroxide bridged			
$Ln\cdots Ln^{i}$	3.9009(2)	3.8799(2)	3.8433(2)
Carbonate bridged			
$Ln\cdots Ln^{ii}$	4.3234(2)	4.2960(2)	4.2385(2)
$Ln\cdots Ln^{iii}$	4.9866(2)	4.9582(2)	4.9154(2)
$Ln\cdots Ln^{iv}$	5.1678(2)	5.1433(2)	5.1310(2)

Symmetry codes: (i) $-0.5 + x, 1.5 - y, 1.5 - z$; (ii) $-x, 0.5 + y, 2 - z$; (iii) $0.5 - x, 1 - y, 0.5 + z$; (iv) $x, 1 + y, z$

4.3 Luminescent properties

The luminescent properties and the emission lifetimes of compounds **4Eu** and **6Tb** were investigated in solid state at room temperature, and are shown in Figure 6. The emission spectra of the two compounds were obtained with excitation at 330 nm for **4Eu** and 247 nm for **6Tb**. The spectra exhibit the characteristic emission peaks of Eu^{III} and Tb^{III} based on the f– f transitions in these species (Sivakumar, Reddy, Cowley, & Butorac, 2011; Li et al., 2010; Lu, Jiang, & Lu, 2010; Wang et al., 2009). Compound **4Eu** exhibits four characteristic peaks at 588, 614, 659 and 687 nm, respectively, corresponding to the transitions from $^5D_0 \rightarrow {}^7F_J$ (J = 1, 2, 3, 4). Among these transitions, $^5D_0 \rightarrow {}^7F_2$ (614 nm) is the strongest, which implies that the emitted light is red (Xu et al., 2013). Compound **6Tb** also shows four emission peaks at 487, 541, 583 and 618 nm, which correspond to the characteristic $^5D_4 \rightarrow {}^7F_J$ (J = 6, 5, 4, 3). The most intense green emission $^5D_4 \rightarrow {}^7F_5$ (541 nm) was observed in the spectra (Calvez, et al., 2011). The emission decay lifetimes of **4Eu** at 614 nm ($^5D_0 \rightarrow {}^7F_2$) and **6Tb** at 541 nm ($^5D_4 \rightarrow {}^7F_6$) are 1.37 and 0.26 ms, respectively.



(a) (b)

(c) (d)

Figure 6 Room temperature solid state photoluminescence spectra of **4Eu** excited at 361 nm (a) **6Tb** excited at 366 nm (b) and the emission intensity decays of **4Eu** (c) and **6Tb** (d)

5. Conclusion

In summary, a series of seven 3D lanthanide coordination polymers based on carbonate and hydroxide has been successfully synthesized by solvothermal reactions and structural characterized by spectroscopic methods. In crystal structure, the CO_3^{2-} adopts the interesting μ_5-η^2:η^2:η^2:η^1:η^1 coordination mode. Compounds **4Eu** and **6Tb** emit intense red and green luminescence in the visible region, which may make these compounds good candidates for red- or green-light emitting diode devices.

6. Acknowledgements

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7. References

Andrews, P. C., Beck, T., Forsyth, C. M., Fraser, B. H., Junk, P. C., Massi, M., & Roesky, P. W. (2007). Templated assembly of a μ_6-CO_3^{2-} dodecanuclear lanthanum dibenzoylmethanide hydroxido cluster with concomitant formation of phenylglyoxylate. *Dalton Transactions*, Issue 48, 5651-5654. DOI: 10.1039/B710534G

Bag, P., Dutta, S., Biswas, P., Maji, S. K., Flörke, U., & Nag, K. (2012). Fixation of carbon dioxide by macrocyclic lanthanide(III) complexes under neutral conditions producing self-assembled trimeric carbonato-bridged compounds with μ_3-η^2:η^2:η^2 bonding. *Dalton Transactions*, Issue 41, 3414-3423. DOI: 10.1039/C2DT12221A

Bruker (2014). *APEX2*, *SAINT*, *XPREP and SADABS*. Madison, Wisconsin, USA: Bruker AXS Inc.

Bünzli, J.-C. G., & Piguet, C. (2005). Taking advantage of luminescent lanthanide ions. *Chemical Society Reviews, 34,* 1048-1077. DOI: 10.1039/B406082M

Calvez, G., Daiguebonne, C., & Guillou, O. (2011). Unprecedented lanthanide-containing coordination polymers constructed from hexanuclear molecular building blocks: $\{[Ln_6O(OH)_8](NO_3)_2(bdc)(Hbdc)_2{\cdot}2NO_3{\cdot}H_2bdc\}_\infty$. *Inorganic Chemistry*, *50*(7), 2851-2858. DOI: 10.1021/ic102036q

Chesman, A. S. R., Turner, D. R., Moubaraki, B., Murray, K. S., Deacon, G. B., & Batten, S. R. (2012). Tetradecanuclear polycarbonatolanthanoid clusters: diverse coordination modes of carbonate providing access to novel core geometries. *Dalton Transactions*, Issue 41, 10903-10909. DOI: 10.1039/C2DT31101A

Dang, S., Zhang, J. H., Sun, Z. M., & Zhang, H. (2012). Luminescent lanthanide metal-organic frameworks with a large SHG response. *Chemical Communications*, *48*(90), 11139-11141. DOI: 10.1039/C2CC35432B

Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K., & Puschmann, H. (2009). OLEX2: a complete structure solution, refinement and analysis program. *Journal of Applied Crystallography*, *42*(2), 339-341. DOI: 10.1107/S0021889808042726

Fang, X., Anderson, T. M., Neiwert, W. A., & Hill, C. L. (2003). Yttrium polyoxometalates: synthesis and characterization of a carbonate-encapsulated sandwich-type complex. *Inorganic Chemistry*, *42*(26), 8600-8602. DOI: 10.1021/ic0350842

Gass, I. A., Moubaraki, B., Langley, S. K., Batten, S. R., & Murray, K. S. (2012). A π–π 3D network of tetranuclear μ_2/μ_3-carbonato Dy(III) bis-pyrazolylpyridine clusters showing single molecule magnetism features. *Chemical Communications*, *48*(15), 2089-2091. DOI: 10.1039/C2CC16946K

Gu, J. Z., Wu, J., Lv, D. Y., Tang, Y., Zhu, K., & Wu, J. (2013). Lanthanide coordination polymers based on 5-(2′-carboxylphenyl) nicotinate: syntheses, structure diversity, dehydration/hydration, luminescence and magnetic properties. *Dalton Transactions*, Issue 42, 4822-4830. DOI: 10.1039/C2DT32674D

Gunanathan, C., Diskin-Posner, Y., &Milstein, D. (2010). Lanthanide-organic framework of a rigid bis-Gd complex: composed by carbonate ions spacers. *Crystal Growth and Design*, *10*(10), 4235-4239. DOI: 10.1021/cg100843k

Guo, Z., Song, X., Lei, H., Wang, H., Su, S., Xu, H., . . . Chen, B. (2015). A ketone functionalized luminescent terbium metal-organic framework for sensing of small molecules. *Chemical Communications*, *51*, 376-379. DOI: 10.1039/C4CC06729K

Han, J. W., & Hill, C. L. (2007). A coordination network that catalyzes O_2-based oxidations. *Journal of the American Chemical Society*, *129*(49), 15094-15095. DOI: 10.1021/ja069319v

Hooper, T. N., Inglis, R., Palacios, M. A., Nichol, G. S., Pitak, M. B., Coles, S. J., . . . Brechin, E. K. (2014). CO_2 as a reaction ingredient for the construction of metal cages: a carbonate-panelled [Gd_6Cu_3] tridiminished icosahedron. *Chemical Communications*, *50*(26), 3498-3500. DOI: 10.1039/C4CC00141A

Hutchings, A.-J., Habib, F., Holmberg, R. J., Korobkov, I., & Murugesu, M. (2014). Structural rearrangement through lanthanide contraction in dinuclear complexes. *Inorganic Chemistry*, *53*(4), 2102-2112. DOI: 10.1021/ic402682r

Langley, S. K., Moubaraki, B., & Murray, K. S. (2012). Magnetic properties of hexanuclear lanthanide(III) clusters incorporating a central μ_6-carbonate ligand derived from atmospheric CO_2 fixation. *Inorganic Chemistry*, *51*(7), 3947-3949. DOI: 10.1021/ic3002724

Langley, S. K., Chilton, N. F., Moubaraki, B., & Murray, K. S. (2013). Anisotropy barrier enhancement *via* ligand substitution in tetranuclear $\{Co^{III}_2Ln^{III}_2\}$ single molecule magnets. *Chemical Communications*, *49*(62), 6965-6967. DOI: 10.1039/C3CC44037K

Langley, S. K., Wielechowski, D. P., Vieru, V., Chilton, N. F., Moubaraki, B., Chibotaru, L. F., & Murray, K. S. (2014). Modulation of slow magnetic relaxation by tuning magnetic exchange in $\{Cr_2Dy_2\}$ single molecule magnets. *Chemical Science*, *5*, 3246-3256. DOI: 10.1039/C4SC01239A

Langley, S. K., Wielechowski, D. P., Vieru, V., Chilton, N. F., Moubaraki, B., Chibotaru, L. F., & Murray, K. S. (2015). The first 4d/4f single-molecule magnet containing a $\{Ru^{III}_2Dy^{III}_2\}$ core. *Chemical Communications*, *51*, 2044-2047. DOI: 10.1039/C4CC08811E

Li, Y. F., Jin, L., Li, D. P., & Zhang, L. (2008). $NdO(NO_3)$. Acta Crystallographica Section E: Structure Reports Online, E64, i81. DOI: 10.1107/S1600536808036295

Li, Q. Y., Yang, G. W., Tang, X. Y., Ma, Y. S., Yao, W., Zhou, F., . . . Zhou, H. (2010). Constructions of a set of new lanthanide-based coordination polymers with Hatza Ligands (Hatza = 5-aminotetrazole-1-acetic acid). *Crystal Growth and Design*, *10*(1), 165-170. DOI: 10.1021/cg900807t

Long, D. L., Blake, A. J., Champness, N. R., Wilson, C., & Schröder, M. (2001). Unprecedented seven- and eight-connected lanthanide coordination networks. *Angewandte Chemie International Edition*, *40*(13), 2443-2447. DOI: 10.1002/1521-3773(20010702)40:13<2443::AID-ANIE2443>3.0.CO;2-C

Long, D. L., Blake, A. J., Champness, N. R., Wilson, C., & Schröder, M. (2002). Constructing terbium coordination polymers of 4,4′-bipyridine-*N*,*N*′-dioxide by means of diffusion solvent mixtures. *Chemistry – A European Journal*, *8*(9), 2026-2033. DOI: 10.1002/1521-3765(20020503)8:9<2026::AID-CHEM2026>3.0.CO;2-8

Long, J., Rouquette, J., Thibaud, J. M., Ferreira, R. A. S., Carlos, L. D., Donnadieu, B., . . . Larionova, J. (2015). A high-temperature molecular ferroelectric Zn/Dy complex exhibiting single-ion-magnet behavior and lanthanide luminescence. *Angewandte Chemie International Edition*, *127*(7), 2236-2240. DOI: 10.1002/ange.201410523

Lu, W. G., Jiang, L., & Lu, T. B. (2010). Lanthanide contraction and temperature-dependent structures of lanthanide coordination polymers with imidazole-4,5-dicarboxylate and oxalate. *Crystal Growth and Design*, *10*(10), 4310-4318. DOI: 10.1021/cg100196j

Ma, X., Li, X., Cha, Y. E., & Jin, L. P. (2012). Highly thermostable one-dimensional lanthanide(III) coordination polymers constructed from benzimidazole-5,6-dicarboxylic acid and 1,10-phenanthroline: synthesis, structure, and tunable white-light emission. *Crystal Growth and Design*, *12*(11), 5227-5232. DOI: 10.1021/cg300932a

Marchal, C., Filinchuk, Y., Chen, X. Y., Imbert, D., & Mazzanti, M. (2009). Lanthanide-based coordination polymers assembled by a flexible multidentate linker: design, structure, photophysical properties, and dynamic solid-state behavior. *Chemistry – A European Journal*, *15*(21), 5273-5288. DOI: 10.1002/chem.200802589

Martínez-Calvo, M., Kotova, O., Möbius, M. E., Bell, A. P., McCabe, T., Boland, J. J., & Gunnlaugsson, T. (2015). Healable luminescent self-assembly supramolecular metallogels possessing lanthanide (Eu/Tb) dependent rheological and morphological properties. *Journal of the American Chemical Society*, *137*(5), 1983-1992. DOI: 10.1021/ja511799n

Matthes, P. R., Nitsch, J., Kuzmanoski, A., Feldmann, C., Steffen, A., Marder, T. B., & Müller-Buschbaum, K. (2013). The series of rare earth complexes [$Ln_2Cl_6(\mu$-4,4′-bipy)$(py)_6$], Ln=Y, Pr, Nd, Sm-Yb: A molecular model system for luminescence properties in MOFs based on $LnCl_3$ and 4,4′ bipyridine. *Chemistry – A European Journal*, *19*(51), 17369-17378. DOI: 10.1002/chem.201302504

Mcmahon, B., Mauer, P., Mccoy, C. P., Lee, T C., & Gunnlaugsson, T. (2009). Selective imaging of damaged bone structure (microcracks) using a targeting supramolecular Eu(III) complex as a lanthanide luminescent contrast agent. *Journal of the American Chemical Society*, *131*(48), 17542-17543. DOI: 10.1021/ja908006r

Mishra, A., Wernsdorfer, W., Abboud, K. A., & Christou, G. (2004). Initial observation of magnetization hysteresis and quantum tunneling in mixed manganese-lanthanide single-molecule magnets. *Journal of the American Chemical Society*, *126*(48), 15648-15649. DOI: 10.1021/ja0452727

Mu, W., Huang, X., Zhong, R., Xia, W., Liu, J., & Zou, R. (2015). Lanthanide contraction effects on the structures, thermostabilities, and CO_2 adsorption and separation behaviors of isostructural lanthanide-organic frameworks. *CrystEngCommunity*, *17*(7), 1637-1645. DOI: 10.1039/C4CE02073A

Nakai, H., Goto, T., Kitagawa, K., Nonaka, K., Matsumoto, T., & Ogo, S. (2014). A highly luminescent and highly oxygen-sensitive Tb(III) complex with a tris-aryloxide functionalised 1,4,7 triazacyclononane ligand. *Chemical Communications*, *50*, 15737-15739. DOI: 10.1039/C4CC07717B

Okamoto, Y. (2002). Organo lanthanide metal complexes for electroluminescent materials. *Chemical Reviews*, *102*(6), 2357-2368. DOI: 10.1021/cr010448y

Regueiro-Figueroa, M., Esteban-Gómez, D., de Blas, A., Rodríguez-Blas, T., & Platas-Iglesias, C. (2014). Understanding stability trends along the lanthanide series. *Chemistry – A European Journal*, 20(14), 3974-3981. DOI: 10.1002/chem.201304469

Sastri, V. S., Bünzli, J.-C. G., Rao, V. R., Rayudu, G. V. S., & Perumareddi, J. R. (2003). *In Modern Aspects of Rare Earth and Their Complexes*. New York, USA: Elsevier.

Seidel, C., Lorbeer, C., Cybińska, J., Mudring, A. V., & Ruschewitz, U. (2012). Lanthanide coordination polymers with tetrafluoroterephthalate as a bridging ligand: thermal and optical properties. *Inorganic Chemistry*, *51*(8), 4679-4688. DOI: 10.1021/ic202655d

Sheldrick, G. M. (2015). Crystal structure refinement with SHELXL. *Acta Crystallographica Section C: Crystal Structure Communications*, *C71*, 3-8. DOI:10.1107/S2053229614024218

Sheu, H. S., Shih, W. J., Chuang, W. T., Li, I. F., & Yeh, C. S. (2010). Crystal structure and phase transitions of $Gd(CO_3)OH$ studied by synchrotron powder diffraction. *Journal of the Chinese Chemical Society*, *57*(4B), 938-945. DOI: 10.1002/jccs.201000130

Sivakumar, S., Reddy, M. L. P., Cowley, A. H., & Butorac, R. R. (2011). Lanthanide-based coordination polymers assembled from derivatives of 3,5-dihydroxy benzoates:

syntheses, crystal structures, and photophysical properties. *Inorganic Chemistry*, *50*(11), 4882-4891. DOI: 10.1021/ic2001249

Sun, J., Kyotani, T., & Tomita, A. (1986). Preparation and characterization of lanthanum carbonate hydroxide. *Journal of Solid State Chemistry*, *65*(1), 94-99. DOI: 10.1016/0022-4596(86)90093-9

Wang, C. G., Xing, Y. H., Li, Z. P., Li, J., Zeng, X. Q., Ge, M. F., & Niu, S. Y. (2009). A series of three-dimensional lanthanide-rigid-flexible frameworks: synthesis, structure, and luminescent properties of coordination polymers with 2,5-pyridine dicarboxylic acid and adipic acid. *Crystal Growth and Design*, *9*(3), 1525-1530. DOI: 10.1021/cg801157k

Xu, Y., Ding, S. H., Feng, W. J., Zhou, G. P., & Liu, Y. G. (2006). Samarium(III) carbonate hydroxide. *Acta Crystallographica Section E: Structure Reports Online*, *E62*, i147-i149. DOI: 10.1107/S1600536806022665

Xu, W., Zhou, Y., Huang, D., Xiong, W., Su, M., Wang, K., Han, S., & Hong, M. (2013). Crystal structure, multiplex photoluminescence, and magnetic properties of a series of lanthanide coordination polymers based on quinoline carboxylate ligand. *Crystal Growth and Design*, 13(13), 5420-5432. DOI: 10.1021/cg401391b

Yan, X., Li, Y., Wang, Q., Huang, X., Zhang, Y., Gao, C., . . . Shao, Y. (2011). Two- to one-dimensional: radii-dependent self-assembly crystal structures and luminescent properties of lanthanide coordination polymers with an amide type semirigid bridging ligand. *Crystal Growth and Design*, *11*(9), 4205-4212. DOI: 10.1021/cg200816f

Zhang, J., Zheng, B., Zhao, T., Li, G., Huo, Q., & Liu, Y. (2014). Topological diversities and luminescent properties of lanthanide metal-organic frameworks based on a tetracarboxylate ligand. *Crystal Growth and Design*, *14*(5), 2394-2400. DOI: 10.1021/cg500114k

Zhang, Y., Huang, L., Miao, H., Wan, H. X., Mei, H., Liu, Y., & Xu, Y. (2015). Hydrothermal synthesis, structure, and optical properties of two nanosized $Ln_{26}@CO_3$ (Ln = Dy and Tb) cluster-based lanthanide-transition-metal-organic frameworks (Ln MOFs). *Chemistry – A European Journal*, *21*(8), 3234-3241. DOI: 10.1002/chem.201405178

Zhao, B., Chen, X. Y., Cheng, P., Liao, D. Z., Yan, S. P., & Jiang, Z. H. (2004). Coordination polymers containing 1D channels as selective luminescent probes. *Journal of the American Chemical Society*, *126*(47), 15394-15395. DOI: 10.1021/ja047141b