A lanthanum pyromellitate coordination polymer with three-dimensional structure

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Abstract. A new three-dimensional metal–organic coordination polymer, $[La_2(H_2O)_2(H_2BTEC)(BTEC)]$, **1**, was hydrothermally synthesized and characterized by single crystal X-ray diffraction. The three-dimensional framework is built up from La_2O_{16} dimers connected by carboxylate anions. The polymer exhibits strong photoluminescence at room temperature with the main emission band at 390 nm ($\lambda_{ex} = 338$ nm). Crystal data: triclinic, space group $P(-1)$, $a = 6.4486(3)$, $b = 9.4525(5)$, $c = 9.6238(5)$ Å, $\alpha = 88.24(1)$, $\beta = 74.67(2)$, $\gamma = 76.76(1)°$, $V = 550.45(5)$.

1. Introduction

Research in the area of inorganic coordination polymers has developed rapidly in recent years. The variety of molecular topologies and crystal packing motifs observed in many of these compounds, along with their potential applications, appears to be the driving force for many studies.[1–4] Structures based on *d*-block transition elements dominate the area of coordination polymers and work is beginning to emerge on the use of *f*-block lanthanide elements. One of the reasons for this, probably, is the predictability in the coordination number and geometry of the transition elements compared to that of the lanthanides. The fascinating variety in the coordination geometry along with special properties (*f–f* electronic transitions) of the lanthanides has attracted the attention of researchers, resulting in many new compounds.[5–10]

Among the many coordination polymeric compounds of the lanthanides, those formed using 1,2,4,5-benzenetetracarboxylic acid (H₄BTEC) appear to be rare.[11–16] One of the reasons for the lack of study using H₄BTEC acid could be the steric consideration as all the four carboxylic groups are unlikely to participate in the coordination of the metal. On the other hand, H₄BTEC with uncoordinated carboxylic acid groups could provide many interesting features. We have been interested in the study of lanthanide coordination polymers using a variety of benzene carboxylic acids.[17,18] Presently we have prepared a new three-dimensional lanthanum coordination polymer, $[La_2(H_2O)_2(H_2BTEC)(BTEC)]$, **1**, employing hydrothermal methods. In this paper, we present the synthesis, structure and characterization of this polymer.

2. Experimental

The title compound was prepared employing hydrothermal techniques. In a typical synthesis, 0·105 g of $La(NO_3)_3·6H_2O$ was dissolved in 10 ml of water. To this, 0·0616 g of benzenetetracaroxylic acid (BTEC) and 0·0208 g of piperazine (PIP) were added and the mixture was homogenized at room temperature for 30 min. The mixture with the composition, $La(NO_3)_3·6H_2O : BTEC : PIP : 2220H_2O$, and a pH of ~2 was transferred to a 23 ml PTFE-lined stainless-steel autoclave and heated at 150°C for 3 days. The pH of the mixture did not show any change after the reaction. The resulting product, contained large quantities of slightly brown rectangular single crystals (yield = ~70%), was filtered and dried at ambient temperature. We have also been able to prepare the same

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compound using other salts of La as well as by replacing the piperazine by NaOH and other inorganic bases, though the quality of the single crystals obtained using NaOH are not good.

The compound was characterized by powder XRD, IR, TGA and photoluminescence studies. Powder XRD revealed the compound to be crystalline and new. The XRD pattern matched well with that simulated from single crystal studies. The powder XRD pattern along with the simulated one is shown in figure 1a. Infrared (IR) spectroscopic studies have been carried out in the mid-IR region as a KBr pellet. The results indicate characteristic sharp lines. The observed bands are: $3481(s)$ cm^{-1} – ν_{as}OH, $2891(w)$ cm^{-1} – ν_s(C–H)$_{aromatic}$, $1671(m)$ cm^{-1} – ν_s(C–OH), 1612–$1493(s)$ – (C–C)$_{skeletal}$, $1388(s)$ cm^{-1} – ν_s(COO), 1294–$1124(s)$ cm^{-1}, – δ(CH$_{aromatic}$)$_{in-plane}$, 918–$789(s)$ cm^{-1} – δ(CH$_{aromatic}$)$_{out-of-plane}$.

Thermogravimetric analysis (TGA) has been carried out in oxygen atmosphere (flow rate = 50 ml/min) in the temperature range 25 to 700°C (heating rate = 10°C/min). The studies show that weight loss occurs in one continuous stretch in the temperature region 350–500°C with a sharp drop at 475°C. This, probably indicates that the sample is stable up to 350°C. The total observed weight loss of 66·1% corresponds to the loss of bound water molecule and the loss of the carboxylate groups (65·8%). The calcined sample was crystalline and the powder XRD lines match well with the corresponding pure lanthanum oxide.

A suitable single crystal was carefully selected under a polarizing microscope and glued to a thin glass fibre. Crystal structure determination by X-ray diffraction was performed on a Siemen's Smart-CCD diffractometer equipped with a normal focus, 2.4 kW sealed tube X-ray source (MoKα radiation, $\lambda = 0{\cdot}71073$ Å) operating at 40 kV and 40 mA. An empirical absorption correction based on symmetry equivalent reflections was applied using the SADABS programs.[19] The structure was solved and refined using the SHELXTL-PLUS suite of programs.[20] All the hydrogen atoms of the carboxylic acids were initially located in the difference Fourier maps and for the final refinement the hydrogen atoms were placed geometrically and held in the riding mode. The hydrogen atoms of the water molecules were not located in the difference Fourier maps. Final refinement included atomic positions for all the atoms, anisotropic thermal parameters for all the non-hydrogen atoms and isotropic thermal parameters for all the hydrogen atoms. Full-matrix least-squares refinement against $|F^2|$ was carried out using the SHELXTL-PLUS suite of programs.[20] Details of the structure solution and final refinements are given in table 1 and the selected bond distances in table 2.

3. Results and discussion

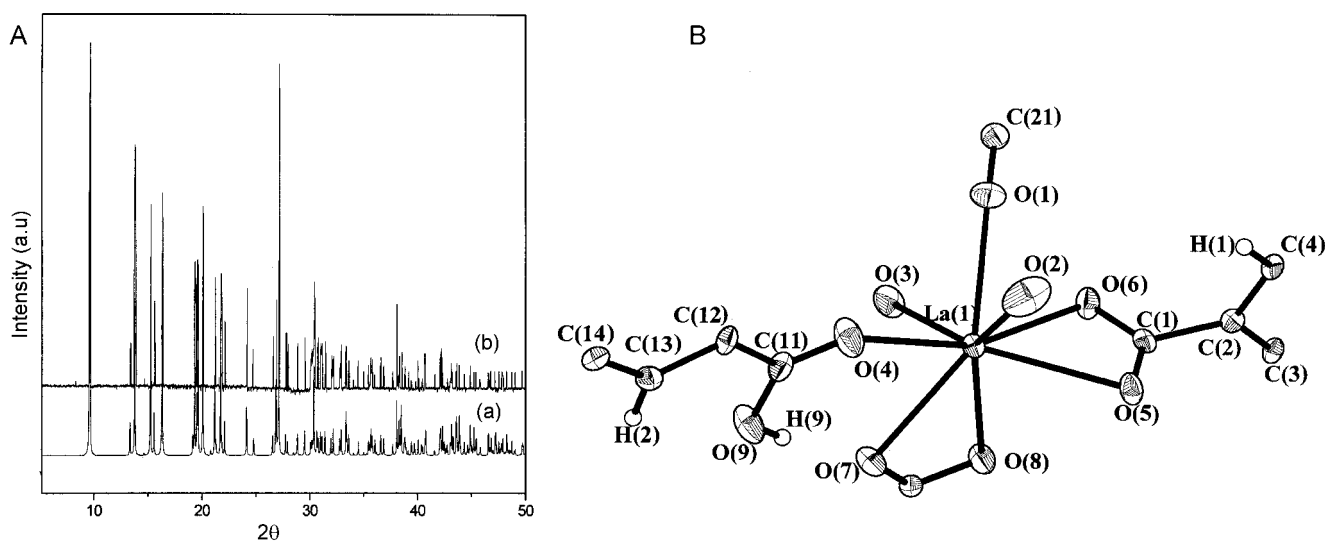The asymmetric unit consists of 20 non-hydrogen atoms (figure 1b). The La atoms are coordinated to

Figure 1. (**A**) Powder XRD pattern (CuKα) of **1**, [La$_2$(H$_2$O)$_2$(H$_2$BTEC)(BTEC)], (a) simulated and (b) experimental. (**B**) ORTEP plot of **1**, [La$_2$(H$_2$O)$_2$(H$_2$BTEC)(BTEC)], showing the connectivity. Thermal ellipsoids are given at 50% probability.
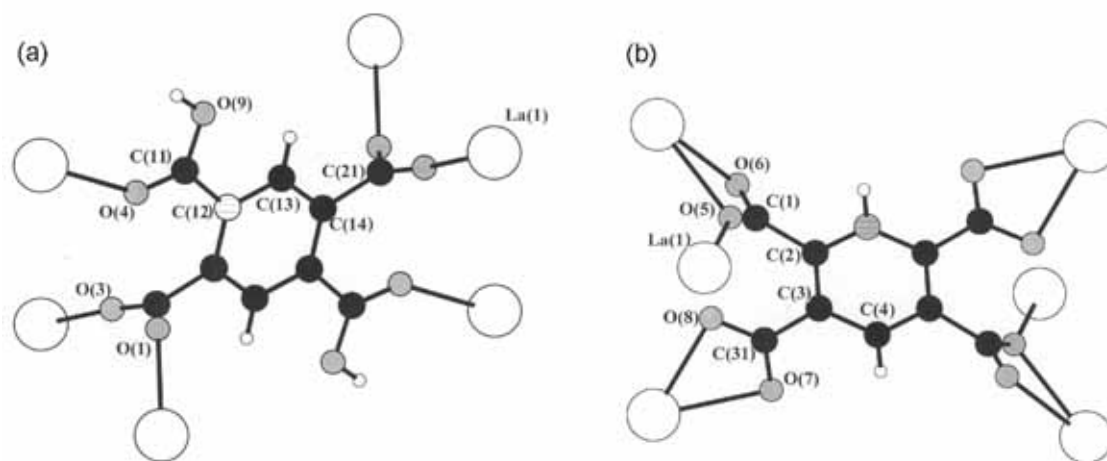
Figure 2. The connectivity of the BTEC in **1**, [La$_2$(H$_2$O)$_2$(H$_2$BTEC)(BTEC)]. (**a**) The [H$_2$BTEC] and (**b**) BTEC acid.

Table 1. Crystal data and structure refinement for **1**, [La$_2$(H$_2$O)$_2$(H$_2$BTEC)(BTEC)].

Empirical formula	C$_{10}$H$_3$LaO$_9$
Formula weight	406·03
Crystal system	Triclinic
Space group	P-1
Crystal size (mm)	0·40 × 0·32 × 0·28
a (Å)	6·4486 (2)
b (Å)	9·4525 (5)
c (Å)	9·6238 (5)
α (°)	88·240 (1)
β (°)	74·675 (2)
γ (°)	76·760 (1)
Volume (Å^3)	550·45 (5)
Z	2
ρ_{calc} (mgm^{-3})	2·450
μ (mm^{-1})	3·927
θ range	2·20–23·27
Total data collected	2369
Unique data	1575
Refinement method	Full-matrix least-squares on $|F^2|$
R_{merg}	0·0236
R indices [$I > 2\sigma(I)$]	$R_1 = 0.0338$,[a] $wR_2 = 0.0842$[b]
R indices (all data)	$R_1 = 0.0371$, $wR_2 = 0.0861$
Goodness of fit (S_{obs})	1·129
No. of variables	384
Largest difference map hole and peak (eÅ^{-3})	1·030 and –1·520

[a]$R_1 = \Sigma ||F_0| - |F_c|| / \Sigma |F_0|$; [b]$wR_2 = \{\Sigma[w(F_0^2 - F_c^2)^2]/\Sigma[w(F_0^2)^2]\}^{1/2}$. $w = 1/[\sigma^2(F_0)^2 + (aP)^2 + bP]$, $P = [\max.(F_0^2, 0) + 2(F_c)^2]/3$, where $a = 0.0525$ and $b = 0.0$.

Figure 3. Figure shows the connectivity in *bc* plane showing the arrangement of the La$_2$ dimer and the BTEC acid.

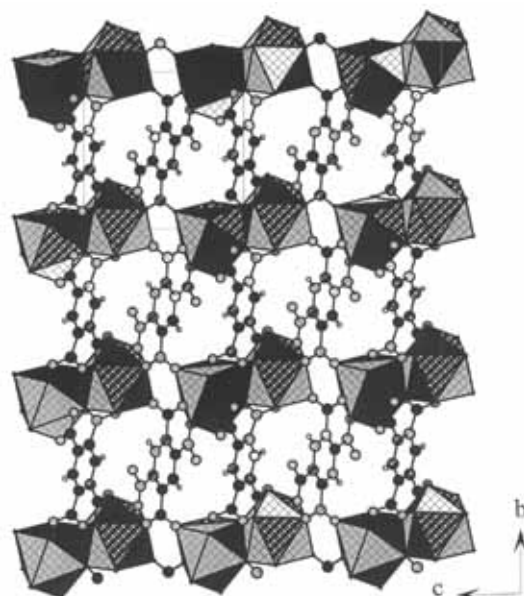nine nearest neighbour oxygen atoms and have a distorted tri-capped trigonal prismatic arrangement. The oxygen atoms, in turn, are connected to the car-bon atoms of the carboxylate group, except O(2), which is a terminal water molecule. The La–O dis-tances are in the range 2·439(5)–2·667(4) Å (av. 2·559 Å). There are two types of BTEC acids in the structure, the benzene rings of both of them lie in the inversion centre. Both the acids are connected to six La^{3+} ions as shown in figure 2. Acid-1, H$_2$BTEC, is coordinated to six La^{3+} ions through monodendate coordination, while acid-2, BTEC, has predomi-
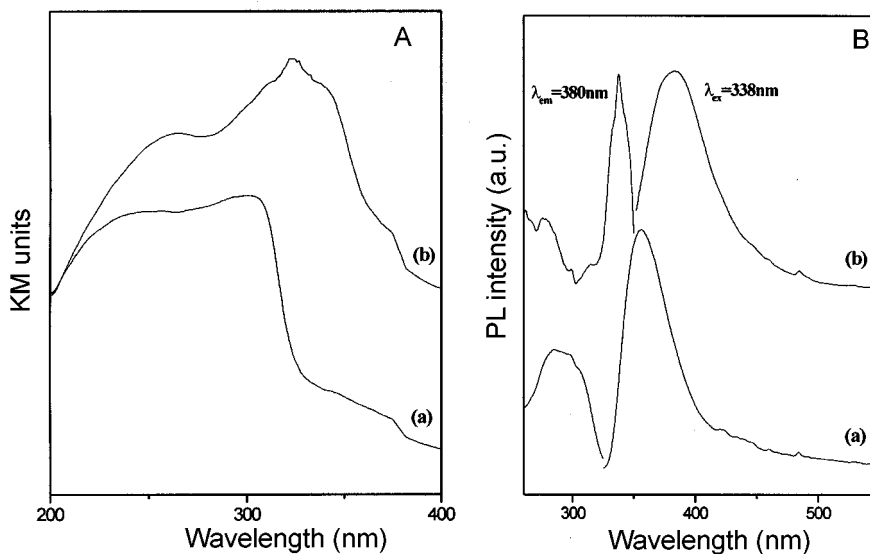
Figure 4. (**A**) The diffuse-reflectance solid-state UV-Vis spectra (**B**) photo-luminescence spectra for (a) the BTEC acid and (b) the polymer.

Table 2. Selected bond distances in **1**, $[La_2(H_2O)_2(H_2BTEC)(BTEC)]$.

Bond	Distance (Å)	Bond	Distance (Å)
La(1)–O(1)	2·493(5)	O(1)–C(21)	1·243(8)
La(1)–O(2)	2·526(5)	O(3)–C(21)	1·258(8)
La(1)–O(3)	2·439(5)	O(4)–C(11)	1·220(8)
La(1)–O(4)	2·572(5)	O(5)–C(1)	1·264(8)
La(1)–O(5)	2·565(4)	O(6)–C(1)	1·249(8)
La(1)–O(6)	2·569(4)	O(7)–C(31)	1·263(7)
La(1)–O(7)	2·601(5)	O(8)–C(31)	1·268(8)
La(1)–O(8)	2·603(4)	O(9)–C(11)	1·312(9)
La(1)–O(5)#1	2·667(4)		

Symmetry transformations used to generate equivalent atoms: #1 $-x + 1, -y + 2, -z$

nantly *bis*-bidentate coordination through all the four carboxylate groups. In addition, acid-2 is also connected to two additional La^{3+} ions through the three-coordinate oxygen atom [O(5)]. The torsion angles suspended by this connectivity between the acid and La^{3+} are as follows: for acid-1 – La(1)–O(1)–C(21)–C(14) = $-110°$, La(1)–O(3)–C(21)–C(14) = $-48·6°$, La(1)–O(4)–C(11)–C(12) = $180°$, and for acid-2 – La(1)–O(5)–C(1)–C(2) = $-31·3°$, La(1)–O(6)–C(1)–C(2) = $-165°$, La(1)–O(8)–C(31)–C(3) = $169·2°$, La(1)–O(7)–C(31)–C(3) = $-169°$ respectively. The La^{3+} ions are connected by three acid-1 and five acid-2 moieties and possess one terminal oxygen atom. The carbon atoms also posses one

terminal C–O linkage, C(11)–O(9) with a distance of $1·312(9)$ Å, which is a C–OH group. The presence of protonated carboxylic acid group is also observed in the IR spectrum with an absorption peak at 1671 cm^{-1}. The other distances and angles observed are in the range expected for this type of bonding and agree well with those reported in the literature for other similar compounds.[5–18]

The structure of **1** consists of a network of La^{3+} ions and carboxylate anions giving rise to a three-dimensional structure. The La^{3+} ions are connected together through the three-coordinated oxygen atom, O(5), to form a dimer, La_2O_{16}. These dimers are connected through the carboxylate anions forming a one-dimensional chain. The chains are further connected in both the directions giving rise to a layer and the three-dimensional structure (figure 3). This structure, in a way, can be described as one-dimensional oxidic chains cross-linked by the benzene carboxylate.

Optical properties of lanthanide benzene carboxylates in general are investigated, since they involve the $4f$ orbitals, which are generally well shielded from their chemical environments by $5s^2$ and $5p^6$ electrons. The *f–f* transitions are parity forbidden, which leads to unfavourable excitation of the lanthanide ions. In the present compound the La^{3+} possess empty $4f$ orbitals, which can be perturbed by exciting the benzene carboxylate ligands. We have carried out experiments to probe this nature of La^{3+} ions.

The diffuse reflectance UV-Vis spectra for H_4BTEC and the as-synthesized polymer show different absorption features (figure 4A). There are essentially two bands for the acid, and the longer and shorter wavelength absorptions correspond to the intraligand $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions respectively.[21] The bands for the polymer, on the other hand, appear to be different with the shorter wavelength appearing at the same energy and the longer wavelength shifting to higher energy. This shift may be related to the $n \rightarrow \pi^*$ transition with the n orbitals (HOMO located on the O atoms of the carboxylate group) being perturbed by the La^{3+} ions of the polymer. Both the BTEC acid and the polymer show photoluminescence (figure 4b). The main emission peak for the acid is located at 370 nm. This may be attributable to the $\pi^* \rightarrow n$ transition. Interestingly, the emission spectrum for the lanthanum coordination polymer shows the main peak at ~ 390 nm. This peak corresponds to the intra-ligand fluorescent emission. The strongest excitation peak for the polymer is at 340 nm, a higher energy than that for the H_4BTEC excitation peaks. The excitation peak of the polymer is coincident, in peak position, with the threshold of the UV-Vis absorption band of the polymer.

In conclusion, a new three-dimensional coordination polymer between La and BTEC has been prepared by employing hydrothermal methods. The strong photoluminescence behaviour of the polymer indicates that it is profitable to explore other similar compounds. Further work is currently in progress.

Acknowledgments

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