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Self-assembly of 1D coordination polymers of two rare-earth complexes with carboxylate linkages: Synthesis, crystal structure and DFT studies

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Two new lanthanide carboxylato complexes $[Ln(3,5\text{-}DNBA)_3(H_2O)_2]_n$, ($Ln = La^{III}$ in **1** and Gd^{III} in **2**, DNBA = dinitrobenzoic acid) have been synthesized hydrothermally and characterized structurally by single crystal X-ray analysis. Alternate $(\mu\text{-}\eta^1:\eta^1)_4$ and $(\mu\text{-}\eta^1:\eta^1)_2$ type bridging modes by carboxylate ligands provide eightfold coordination around the Ln center in both complexes, which result in two different Ln···Ln distances, with polymeric chains propagating along the [1 0 0] direction. Intermolecular O–H···O hydrogen bonds and π–π stacking interactions form $R_2^2(20)$, $R_4^4(40)$ rings, thus generating three-dimensional supramolecular frameworks in **1** and **2**. Density functional theory (DFT) calculations were carried out using the hybrid exchange–correlation functional, PBE. The HOMO–LUMO energy gap of 2.63 eV in **1** is found to be greater than that of 1.86 eV in **2**.

1. Introduction

The rational design of functional rare-earth (RE) coordination complexes with various N- and/or O-donor ligands has attracted considerable attention in recent years due to their fascinating structural diversities and potential applications as optical, electronic and catalytic materials, and molecular-based magnets [1–5]. As a consequence of the unpredictable coordination geometries of the 4f series metal complexes, structural studies of this class of compounds have been a field of rapid growth in material chemistry [6–11]. The synthesis of such complexes can be accomplished by the appropriate choice of organic ligands. Of the approaches that have been widely recognized as a rational strategy for the preparation of metal–organic hybrid networks, organic ligands with versatile functions as bridges or terminal groups (building blocks) with metal ions or metal clusters as nodes are highly effective [12–14]. Metal ions with diverse coordination behavior have also been utilized [8,15,16]. The Ln^{III} ions, with potentially high and variable coordination numbers, have a strong affinity for hard bases containing neutral and negatively charged oxygen atoms [17–19]. Among the ligands, benzoic acid and its derivatives have been widely used in the coordination polymers of lanthanides due to its oxophilic nature [8,20]. Since each carboxyl oxygen atom can be monodentate or bidentate, the benzoate group binding mode to metal ions is versatile, leading to various kinds of polynuclear or multidimensional polymers [21–24]. In most of these compounds, the metal ions are bridged by carboxylate groups to produce dimers [25,26], 1D chains [27], 2D-layers [28] and 3D structures [29]. Beside the covalent linkages between the building blocks, non-covalent interactions, i.e. hydrogen bonds, C–H···π and π–π stacking interactions, facilitate the formation of self-assembled structures of variable dimensions [30]. In continuation to our ongoing studies [31,32] on the synthesis and structural characterization of rare earth complexes, we report here the synthesis, spectroscopic characterization and crystal structure determination of two lanthanum and gadolinium complexes with 3,5-dinitrobenzoic acid, along with DFT calculations to investigate the electronic structures.

2. Experimental

2.1. Synthesis and preliminary characterization

Compounds **1** and **2** were prepared by following a hydrothermal process. To obtain the desired product, $Ln(NO_3)_3{\cdot}6H_2O$, sodium hydroxide and 3,5-dinitrobenzoic acid were mixed in a 1:2:2 ratio, and maintained at 160 °C for 3 days at autogenously developed pressure in a Teflon lined reaction bomb. After cooling to room temperature, yellow rectangular crystals were isolated by filtration in high yield [Yield *ca.* 75% and 77% (based on metal) for **1** and **2** respectively], washed with water and dried in a desiccator. For

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Table 1
Crystal data and structure refinement parameters for **1** and **2**.

Empirical formula	$C_{21}H_{13}N_6O_{20}La$	$C_{21}H_{13}N_6O_{20}Gd$
Formula weight	808.28	826.62
Temperature (K)	100(2)	100(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a (Å)	9.462(2)	9.469(2)
b (Å)	12.040(3)	12.051(2)
c (Å)	14.117(4)	14.127(2)
α (°)	114.609(4)	114.127(2)
β (°)	102.385(4)	102.431(3)
γ (°)	97.378(4)	97.334(3)
Volume (Å^3)	1384.5(6)	1388.0(4)
Z	2	2
D_{calc} (mg/m^3)	1.939	1.978
Absorption coefficient (mm^{-1})	1.649	2.495
F(0 0 0)	796	810
θ Range for data collection (°)	1.88–26.37	1.92–25.03
Limiting indices	$-11 \leqslant h \leqslant 11$ $-14 \leqslant k \leqslant 15$ $-17 \leqslant l \leqslant 17$	$-11 \leqslant h \leqslant 11$ $-14 \leqslant k \leqslant 14$ $-16 \leqslant l \leqslant 16$
Reflections collected/unique	10904/5542 [R_{int} = 0.0428]	10107/4878 [R_{int} = 0.0317]
Completeness to 2θ (%)	98.0	99.2
Refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
Data/restraints/parameters	5542/7/449	4878/402/445
Final R indices [$I > 2\sigma(I)$]	0.0433, 0.1234	0.0470, 0.1185
R indices (all data)	0.0448, 0.1249	0.0508, 0.1205
Goodness-of-fit on F^2	1.095	1.097
Largest difference in peak and hole (e Å^{-3})	3.593 and −1.853	1.318 and −1.036

Table 2
Selected bond lengths [Å] and angles (°) with esd's in parentheses for **1** and **2**.

Bond lengths		
	1 (Ln = La)	**2** (Ln = Gd)
Ln–O1	2.545(3)	2.542(4)
Ln–O7	2.447(3)	2.448(4)
Ln–O13	2.449(3)	2.440(4)
Ln–O19	2.599(3)	2.605(4)
Ln–O20	2.674(3)	2.678(4)
Ln–O2[b]	2.472(3)	2.481(4)
Ln–O8[b]	2.501(3)	2.504(4)
Ln–O14[a]	2.424(3)	2.429(4)

[a] $-x+2, -y+2, -z+1$.
[b] $-x+1, -y+2, -z+1$.

preliminary characterization of the compounds, elemental analysis and an IR spectroscopic study were undertaken. *Anal.* Calc. for [La(3,5-DNBA)$_3$(H$_2$O)$_2$] (**1**): C, 30.51; H, 1.59; N, 10.17. Found: C, 29.87; H, 1.50; N, 9.9%. Selected IR peaks (KBr disk, v, cm^{-1}): 1611, 1572 [v_{as}(COO$^-$)], 1403 [v_s(COO$^-$)], 1306, 1195 [v_s(C–O)], 1558 [v_{as}(NO$_2$)], 1412 [v_s(NO$_2$)], 3600–3200 s.br [v(O–H)]. *Anal.* Calc. for [Gd(3,5-DNBA)$_3$(H$_2$O)$_2$] (**2**): C, 31.21; H, 1.62; N, 10.40. Found: C, 30.56; H, 1.53; N, 10.10%. Selected IR peaks (KBr disk, v, cm^{-1}): 1626, 1576 [v_{as}(COO$^-$)], 1428 [v_s(COO$^-$)], 1321, 1161 [v_s(C–O)], 1538 [v_{as}(NO$_2$)], 1410 [v_s(NO$_2$)] and 3600–3200 s.br [v(O–H)].

2.2. X-ray crystallography

X-ray diffraction data for **1** and **2** were collected at 100(2) K on a Bruker SMART APEX CCD X-ray diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.7107 Å). Determination of integrated intensities and cell refinement were performed with the SAINT [33] software package using a narrow-frame integration algorithm. An empirical absorption correction was applied (SADABS) [34]. Both structures were solved by direct methods and refined using the full-matrix least-squares technique against F^2 and anisotropic displacement parameters for non-hydrogen atoms with the programs SHELXS97 and SHELXL97 [35]. All hydrogen atoms in **1** and **2** were located from difference Fourier maps and treated with suitable riding models, having isotropic displacement parameters derived from their carrier atoms, except the hydrogen atoms of water molecules which were refined with isotropic thermal parameters. In the final difference Fourier maps there were no remarkable peaks, except the ghost peaks surrounding the metal centers. A summary of the crystal data and relevant refinement parameters for complexes **1** and **2** is provided in Table 1.

2.3. Computational

Geometry-optimized, spin-unrestricted, density functional theory (DFT) calculations have been performed using DMol^3 code [36] of the Materials Studio of System of programs in the framework of a generalized-gradient approximation (GGA) [37]. The starting atomic coordinates of both complexes were taken from the final X-ray refinement cycles. The geometry of the molecule was fully optimized using the hybrid exchange–correlation functional PBE [37] and a double numeric plus polarization (DNP) basis set. The electronic structures were also calculated at the same level. No constraints to bonds, angles or dihedral angles were applied in the calculations, and all atoms were free to optimize. Convergence in the calculations was assumed to be reached when the total energy change between two consecutive self-consistent field (SCF) cycles was less than 1×10^{-5} a.u.

3. Results and discussion

3.1. Crystal structures of [Ln(3,5-DNBA)$_3$(H$_2$O)$_2$]$_n$, (Ln = La^{III} in **1** and Gd^{III} in **2**)

Single crystal structure analysis revealed that the complexes **1** and **2** are isomorphous and crystallized in the space group $P\bar{1}$ with Z = 2. Selected bond distances around the metal centers are listed in Table 2. The asymmetric unit of complexes **1** and **2** consists of discrete [Ln(3,5-DNBA)$_3$(H$_2$O)$_2$], (Ln = La^{III} in **1** and Gd^{III} in **2**, DNBA = dinitrobenzoic acid), which are shown in Figs. 1 and 2, [38] respectively. The close similarity between the crystallographic parameters, e.g., unit cell dimensions, space group, atomic coordinates, crystal packing of **1** and **2**, indicates that the complexes are isostructural and subsequent discussions relating to complex **1** are also applicable to complex **2**. Superposition of the molecules of **1** (red-colored lines) and **2** (blue-colored lines) (Fig. 3) obtained from the X-ray analysis with a r.m.s deviation of 0.009 reveal a high degree of isostructurality between the complexes. The coordination geometry around the Ln center can be best described as distorted square-face bicapped trigonal prism. One of the quadrangular faces is described by four oxygen atoms from four carboxylate ligands (O1, O2, O7, and O8) with a r.m.s. deviation of the least-squares plane through the equatorial atoms of 0.1454 Å in **1** and 0.1428 Å in **2**.

The molecular entity comprises of symmetry-related basic building blocks, which are connected through two/four carboxyl groups along the [1 0 0] direction to give rise to a one-dimensional (1D) polymeric chain –Ln–O–C–O–Ln– (Fig. 4). The carboxylate groups link a pair of Ln centers in the O,O′-bridging mode to generate a paddle-wheel-like [39] polymeric chain of [Ln$_2$-(carboxylate-O,O′)$_n$] units. As can be seen from Fig. 5, the Ln ions are bridged alternately in (μ-η^1:η^1)$_4$ and (μ-η^1:η^1)$_2$ modes by four