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Hydrothermal synthesis of dimeric lanthanide compounds: X-ray structure, magnetic study and heterogeneous catalytic epoxidation of olefins

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ABSTRACT

A series of dimeric lanthanide carboxylato complexes $[La(5-Br-NIC)_3(H_2O)_2]_2 \cdot H_2O$ (1); $[Gd(5-Br-NIC)_3(H_2O)_2]_2$ (2), [5-Br-NIC = 5-bromonicotinate] and $[Sm(NIC)_3(H_2O)_2]_2$ (3) [NIC = nicotinate], have been hydrothermally synthesized and structurally characterized by single crystal X-ray analysis. Complexes 1, 2 and 3 are of similar structure and consist of a basic unit $[La(carboxylato)_3(H_2O)_2]_2$. In compound 1 lanthanide cation is surrounded by one chelating 5-bromo-nicotinato ligand, two bridging oxygen atoms from 5-bromo-nicotinato and two water molecules, in which each La(III) ion is nine coordinated in a tricapped prismatic geometry. However, in compounds 2 and 3 four carboxylate groups link a pair of lanthanide atoms in the 0,0'-bridging mode to generate a paddle-wheel-like centrosymmetric dimer. All the compounds exhibit excellent catalytic performance in olefin epoxidation reaction. The variable temperature magnetic susceptibility measurements showed that the magnetic interaction in $[Gd(5-Br-NIC)_3(H_2O)_2]_2$ (2), is antiferromagnetic ($J = -0.048 \text{ cm}^{-1}$), while compound $[Sm(NIC)_3(H_2O)_2]_2$ (3), showed a complicated low-temperature magnetic property.

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1. Introduction

In the last decade lanthanide compounds attract a large share of interest with their versatile properties and application. Especially, the carboxylate bridged lanthanide frameworks have been studied extensively due to their different linking modes to the metal centers. In most of these compounds the metal ions are bridged by carboxylate groups to produce dimers [1,2], 1D chains [3], 2D-layer [4] and 3D structures [5]. There is growing interest of lanthanide compounds in catalysis [6], molecule-based magnetic materials [7], artificial nucleases for the hydrolytic cleavage of DNA and RNA [8], contrast agents for magnetic resonance imaging [9], and fixation media for atmospheric gases [10]. It is noteworthy that magnetic interaction in most of the di-and poly-nuclear lanthanide complexes are very weak, often show no interaction at all. However, in some cases strong interaction is associated with both d and f orbitals [11]. It is noticeable that there are difficulties in obtaining pure and well-characterized (f-f or f-f') complexes and in analyzing their magnetic interaction because of the orbital contribution of most of the f orbital is much shielded. The substantial

intra-atomic exchange energy involving electrons in the valence 5d/6s and core like 4f orbitals in Ln atoms provides an interaction for coupling the 4f orbitals moments on two or more lanthanide atoms via electrons in the bonding orbitals. Since the 4f orbitals are highly contracted, their direct involvement in Ln-ligand bonding is very limited, and magnetic coupling via Ln–ligand–Ln super-exchange is very small. However, if there are unpaired electrons with significant 5d/6s character delocalized over lanthanide centers, electrons localized in the 4f orbitals can couple strongly. Maximum interaction can be achieved by the reduction of lanthanide ions to lower oxidation state. Previous studies furnish very limited structural exploration of homopolynuclear Ln(III) complexes with magnetic analysis [12,13].

On the other hand lanthanide salts are extensively used in the organic synthesis for developing new methodology and also for organic transformation study [14]. Lanthanide compounds have been used for catalytic transformation of alkene to its oxide in homogeneous media [15,16]. Oxidation of alkane and sulfur compounds have been studied using lanthanide compounds in heterogeneous condition [6]. Nevertheless olefin epoxidation reactions catalyzed by lanthanide carboxylates are rarely reported [14]. Oxidative transformations [16] and especially epoxidation of alkenes is key chemical processes in biology [17], synthetic organic chemistry,



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and the chemical industry [18–20]. In recent years, considerable advances have been made in the development of atom-efficient and benign heterogeneous catalytic methods employing *tert*-BuOOH [21]. There is an ever-growing interest in the application of reusable catalysis for synthesis of fine chemicals, including enantioselective reactions [22,23], this could reduce the large amounts of waste products formed in non-catalytic organic synthesis. Great efforts are being put to develop new catalytic systems for a given reaction, and/or to improve the existing catalytic systems. Combinatorial chemistry, used currently in the synthesis of drugs in the pharmaceutical industrial, has recently entered in the field of catalysis [24]. To our knowledge attempts to use lanthanide carboxylate in catalytic olefin epoxidation have been made only scarcely.

We report here the hydrothermal synthesis and structural characterization of three dimeric lanthanide carboxylates [La(5-Br-NI-C)₃(H₂O)₂]₂ H₂O (**1**), [Gd(5-Br-NIC)₃(H₂O)₂]₂ (**2**), [5-Br-NIC = 5bromonicotinate] and [Sm(NIC)₃(H₂O)₂]₂ (**3**) [NIC = nicotinate]. Compounds **1–3** act as efficient heterogeneous catalyst in olefin epoxidation reactions. The magnetic property of compounds **2** and **3** were studied by SQUID in the temperature range 4–300 K and both the compounds are antiferromagnetically coupled below transition temperature.

2. Experimental

2.1. Materials and physical measurements

Lanthanum nitrate heptahydrate, gadolinium nitrate hexahydrate, samarium nitrate hexahydrate, 5-bromo-nicotinic acid, nicotinic acid, cyclooctene, styrene, 4-methyl styrene, 3-methyl styrene, 1-hexene, and *tert*-butylhydroperoxide (70 wt% aqueous) were purchased from Aldrich and were used as received. Sodium hydroxide and solvents were purchased from Merck (India). Fourier transformed infrared spectra of KBr pellets were measured on a Shimadzu S-8400 FTIR spectrometer. The products of the catalytic reactions were identified and quantified by a Varian CP-3800 gas chromatograph using a CP-Sil 8 CB capillary column. Magnetic measurements were carried out with Quantum Design's MPMS XL SQUID magnetometer. Diamagnetic corrections were estimated from the Pascal constants. Other instruments used in this study were the same as reported earlier [25].

2.2. Synthesis and preliminary characterization

To prepare the complexes we followed the routine hydrothermal process. To obtained the desired product, $Ln(NO_3)_3$ hydrate, sodium hydroxide and nicotinic acid/5-bromo-nicotinic acid were mixed in a 1:2:2 ratio, and kept in a reaction bomb at 160 °C for 2 days in autogenously created pressure. After cooling to room temperature colorless needle shaped crystals with high yield were obtained. Yield ca. 75%, 80% and 82% (based on metal) for 1, 2 and 3 respectively. The crystals were collected by filtration, washed thoroughly with water and dried in ambient condition. Compound ${\bf 2}$ has been synthesized previously to study its luminescence properties. However, its structure was not solved by single crystal X-ray structure analysis [2]. For preliminary characterization of the compounds elemental analysis and IR spectroscopic study were undertaken. Anal. Calc. for 1: C, 27.47; H, 1.79; N, 5.34. Found: C, 27.3; H, 1.6; N, 5.4%. Selected IR peaks (KBr disk, v, cm⁻¹): 1617, 1558 [v_{as} (CO₂⁻)], 1403 [v_s (CO₂⁻)], 1306, 1195 [v_s (C-O)], and 3600-3200 s.br [v (O–H)]. Anal. Calc. for 2: C, 27.15; H, 1.65; N, 5.28. Found: C, 27.2; H, 1.6; N, 5.2%. Selected IR peaks (KBr disk, v, cm⁻¹): 1687, 1626, 1572 $[v_{as} (CO_2^{-})]$, 1428 $[v_s (CO_2^{-})]$, 1321, 1161 $[v_s$ (C-O)], and 3600-3200 s.br [v (O-H)]. Anal. Calc. for 3: C, 39.12;

H, 2.92; N, 7.60. Found: C, 38.8; H, 2.6; N, 7.7%. Selected IR peaks (KBr disk, v, cm⁻¹): 1641, 1588 [v_{as} (CO₂⁻)], 1397 [v_s (CCO₂⁻)], 1199, 1023 [v_s (C-O)], and 3600–3200 s.br [v (O–H)].

2.3. X-ray crystallography

X-ray diffraction data for 1, 2 and 3 were collected at 100(2) K on a Bruker SMART APEX CCD X-ray diffractometer using graphite-monochromated Mo K α radiation (λ = 0.7107 Å). Determination of integrated intensities and cell refinement were performed with the SAINT [26] software package using a narrow-frame integration algorithm. An empirical absorption correction (sADABS) [27] was applied. All the structures were solved by direct methods and refined using full-matrix least-squares technique against F^2 with anisotropic displacement parameters for non-hydrogen atoms with the programs SHELXS97 and SHELXL97 [28]. All hydrogen atoms were located from difference Fourier map and treated as a suitable riding models with isotropic displacement parameters derived from their carrier atoms, except the hydrogen atoms of water molecules were refined with isotropic thermal parameters. A summary of crystal data and relevant refinement parameters for complexes 1, 2 and 3 is provided in Table 1.

2.4. Catalytic reactions

The catalytic reactions were carried out in a glass batch reactor according to following procedure. Substrate, solvent and catalysts were first mixed. The mixture was then equilibrated to $70 \,^{\circ}$ C in an oil bath. After addition of *tert*-BuOOH, the reaction mixture was stirred continuously for 24 h. The products of the epoxidation reactions were collected at different time intervals and were identified and quantified by gas chromatography.

3. Results and discussion

3.1. Crystal structure of $[La(5-Br-NIC)_3(H_2O)_2]_2 H_2O(1)$

The dimeric unit of 1 is shown in Fig. 1, consists of [La(5-Br-NI- $C_{3}(H_{2}O_{2})_{2}$ along with a water of crystallization. The dimer is build up around an inversion centre followed by a translation along the z-direction. The unique lanthanide cation is surrounded by one chelating 5-Br-nicotinato unit, two bridging 5-Br-nicotinato oxygen atoms and two water molecules, in which each La(III) ion is nine coordinated in a tricapped prismatic geometry. One of the oxygen atoms (O1) from the chelating nicotinato groups acts in a bridging mode linked with both cations to form a dimer through a central (La-O)₂ rectangular loop (pink in Fig. 1) leading to a La–La distance of 3.8267(6) Å. Other two oxygen atoms (05, 06) of carboxylate groups acts also bridging in a bidentate-(µ2-carboxylato- $k^{1}O:k^{1}O'$) mode. Apart from bridging carboxylato ligands, there are monodentate carboxylato groups in this compound. The combination of bridging oxygen atoms (μ_2 -carboxylato- $k^1 O: k^1 O'$), bridged sharing oxygen atoms, chelating carboxylate oxygen atoms and water molecules produce a pair of LaO₉ tricapped prismatic polyhedral with La-O distances in the range 2.481(2)-3.004(2) Å (Table 2). These are connected to each other through a central loop.

The crystal packing in **1** is stabilized by intermolecular hydrogen bonds (Table 3). A combination of intermolecular O9– H60···O7 (-x+1, -y+1, -z+1) and O7–H20···O9 (x, y-1, z) hydrogen bonds generated by water molecules forming almost square motif inter link the dimeric units running along [1 0 0] direction (Fig. 2). Additional reinforcement within the motif is achieved by O9–H50···N1 (x+1/2, y+1/2, -z+3/2) and O8– H30···O9 (x, y-1, z) hydrogen bonds. In addition, the crystal

Table 1		
Crystal data and structure refinement parameters	for complexes	1, 2 and 3.

	1	2	3
Formula	C ₃₆ H ₃₀ Br ₆ La ₂ N ₆ O ₁₈	$C_{36}H_{26}Br_{6}Gd_{2}N_{6}O_{16}$	$C_{36}H_{32}N_6O_{16}Sm_2$
Formula weight	1591.94	1592.59	1105.38
Т (К)	100(2)	100(2)	100(2)
λ (Å)	0.71073	0.71073	0.71073
Crystal system	monoclinic	triclinic	monoclinic
Space group	P21/n	ΡĪ	P21/c
a (Å)	11.601(2)	9.5962(6)	9.636(2)
b (Å)	16.893(3)	11.4731(8)	11.760(1)
<i>c</i> (Å)	12.222(2)	11.7305(8)	17.428(3)
α (°)	90	85.711(1)	90
β (°)	105.985(2)	66.490(1)	93.077(5)
γ (°)	90	75.955(1)	90
V (Å ³)	2302.7(6)	1148.6(1)	1972.1(6)
Ζ	2	2	2
D_{calc} (Mg/m ³)	2.296	2.303	1.862
Absorption coefficient (mm ⁻¹)	7.116	8.155	3.029
F(0 0 0)	1512	750	1084
θ Range for data collection (°)	2.11-26.39	1.83-25.03	2.09-25.00
Reflections collected/unique (R_{int})	18133/4694 (0.033)	8338/4032 (0.022)	17805/3461 (0.035)
Completeness to 2θ (%)	99.7	99.2	100.0
Refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F ²
Data/restraints/parameters	4694/0/331	4032 / 4 / 314	3461/4/288
Final R indices $[I > 2\sigma(I)]$	0.0245, 0.0502	0.0248, 0.0594	0.0172, 0.0436
R indices (all data)	0.0298, 0.0517	0.0283, 0.0610	0.0195, 0.0444
Goodness-of-fit on F ²	1.090	1.057	1.057
Largest difference in peak and hole ($e Å^{-3}$)	0.565 and -0.604	2.144 and -1.341	0.559 and -0.496



Fig. 1. Dimeric structure of [La(5-Br-NIC)₃(H₂O)₂]₂·H₂O (1).

packing is influenced by other intermolecular hydrogen bonds to complete a three-dimensional supramolecular framework (Fig. 3).

3.2. Crystal structure of $[Gd(5-Br-NIC)_3(H_2O)_2]_2$ (2) and $[Sm(NIC)_3(H_2O)_2]_2$ (3)

The X-ray crystallography analyses revealed that **2** and **3** are having similar structure including coordination geometry around metal. In this report we will describe the molecular structure of **2**. Compound **3** was structurally characterized by X-ray in previous studies [29,30]. In this study we have synthesized the complex through hydrothermal route and we got phase pure crystalline product in high yield. We have redetermined the structure of **3** and got better refinement than the previous cases. The molecular

structure of **2** is shown in Fig. 4. The molecular entity comprises a center-related dinuclear $[Gd_2(CO_2)_4]$ unit. Four carboxylate groups link a pair of Gd atoms in the O,O'-bridging mode to generate a paddle-wheel-like [12] centrosymmetric dimer $[Gd_2-(carboxylate-O,O')_4]$ with Gd...Gd distances of 4.4033(4) Å. The octacoordination of metal center in **2** is achieved by four O atoms from four bridging 5-Br-nicotinate ligand, two O atoms from one chelating 5-Br-nicotinate unit and two coordinated water molecules. The geometry around Gd atom is distorted square antiprism. One of the quadrangular faces is described by two oxygen atoms (O5, O6, O7, and O8) with the r.m.s. deviation of the least-squares plane through the equatorial atoms is 0.047 Å; the other one is defined by four oxygen atoms from four bridging

Table 2	
Selected bond lengths (Å) and angles (°) for complexes $\textbf{1},\textbf{2}$ and	3.

1		2		3	
La(1) - O(1)	2.481(2)	Gd(1) - O(1)	2.363(3)	Sm(1)-O(1)	2.525(2)
$La(1) - O(1)^{\#1}$	2.831(2)	$Gd(1)-O(2)^{\#2}$	2.335(3)	Sm(1)-O(2)	2.364(2)
$La(1)-O(2)^{\#1}$	2.531(2)	$Gd(1)^{#2}-O(2)$	2.335(3)	Sm(1)-O(3)	2.390(2)
$La(1)^{\#1}-O(2)$	2.531(2)	Gd(1)-O(3)	2.323(3)	Sm(1)-O(4)	2.367(2)
La(1)-O(3)	2.631(2)	$Gd(1)-O(4)^{#2}$	2.341(3)	Sm(1)-O(5)	2.545(2)
La(1)-O(4)	2.539(2)	$Gd(1)^{#2}-O(4)$	2.341(3)	Sm(1)-O(6)	2.447(2)
La(1)-O(5)	2.631(2)	Gd(1)-O(5)	2.524(3)	Sm(1)-O(7) ^{#3}	2.483(2)
La(1)-O(6)	3.004(2)	Gd(1)-O(6)	2.501(3)	Sm(1)-O(8) ^{#3}	2.370(2)
$La(1)^{\#1}-O(6)$	2.518(2)	Gd(1)-O(7)	2.434(3)	$Sm(1)^{#3}-O(7)$	2.483(2)
La(1)-O(7)	2.548(2)	Gd(1)-O(8)	2.438(3)	Sm(1) ^{#3} -O(8)	2.370(2)
La(1)-O(8)	2.508(2)				
O(1)-La(1)-O(8)	78.11(8)	O(2)-Gd(1)-O(1)	123.96(10)	O(2)-Sm(1)-O(4)	139.06(7)
O(1)-La(1)-O(6)	65.85(7)	O(3)-Gd(1)-O(2)	74.50(10)	O(2)-Sm(1)-O(8)	82.08(6)
O(8)-La(1)-O(6)	141.09(8)	O(4)-Gd(1)-O(1)	77.11(10)	O(4)-Sm(1)-O(8)	87.67(6)
O(8)-La(1)-O(2)	143.69(8)	O(2)-Gd(1)-O(4)	79.09(10)	O(2)-Sm(1)-O(3)	134.86(6)
O(6)-La(1)-O(2)	75.07(7)	O(3)-Gd(1)-O(6)	135.79(10)	O(4)-Sm(1)-O(3)	80.70(6)
O(2)-La(1)-O(7)	74.94(8)	O(7)-Gd(1)-O(6)	103.62(10)	O(2)-Sm(1)-O(6)	93.03(6)
O(4)-La(1)-O(7)	68.04(7)	O(8)-Gd(1)-O(6)	70.56(10)	O(8)-Sm(1)-O(6)	143.57(7)
O(4)-La(1)-O(3)	50.49(7)	O(1)-Gd(1)-O(5)	147.64(10)	O(4)-Sm(1)-O(7)	125.35(6)
O(7)-La(1)-O(3)	100.34(7)	O(6)-Gd(1)-O(5)	52.10(9)	O(6)-Sm(1)-O(7)	141.55(6)
O(6)-La(1)-O(5)	123.92(7)	O(1)-Gd(1)-O(6)	145.62(10)	O(8)-Sm(1)-O(5)	73.08(6)

 $x^{\#1}-x, -y, -z+1; x^{\#2}-x+1, -y+1, -z+2; x^{\#3}-x+1, -y+1, -z.$

Table 3

Intermolecular contacts for complex **1**, **2** and **3** (Å, °).

D−H····A	<i>d</i> (D–H)	$d(H \cdot \cdot \cdot A)$	$d(D \cdot \cdot \cdot A)$	<(DHA)	(Symmetry transform)
$O(7)-H(10)\cdots N(2)^{a}$	0.83(5)	1.93(5)	2.756(3)	171	-x + 1/2, $y - 1/2$, $-z + 1/2$
$O(7)-H(20)\cdots O(9)^a$	0.78(5)	1.98(5)	2.726(3)	162	x, y - 1, +z
O(8)-H(30)···O(9) ^a	0.84(4)	1.95(4)	2.760(3)	160	x, y - 1, +z
$O(8)-H(40)\cdots N(3)^{a}$	0.83(3)	1.95(3)	2.771(4)	176	-x + 1/2, $y + 1/2$, $-z + 3/2$
$O(9)-H(50)\cdots N(1)^a$	0.79(3)	2.01(3)	2.782(4)	164	-x + 1/2, $y + 1/2$, $-z + 3/2$
$O(9)-H(60)\cdots O(4)^a$	0.79(5)	2.43(5)	3.142(3)	151	-x + 1, -y + 1, -z + 1
$O(9)-H(60)\cdots O(7)^{a}$	0.79(5)	2.33(4)	2.913(3)	131	-x + 1, $-y + 1$, $-z + 1$
$O(7)-H(10)\cdots O(5)^{b}$	0.81(5)	1.96(6)	2.746(4)	163	-x, 1-y, -z
$O(7)-H(20)\cdots N(1)^{b}$	0.80(2)	2.22(3)	2.916(5)	146	-x, 1-y, 1-z
$O(8)-H(30)\cdots N(2)^{b}$	0.81(4)	2.03(4)	2.834(5)	174	-x, 1-y, -z
O(8)– $H(40)$ ··· $N(3)$ ^b	0.82(5)	2.09(4)	2.883(5)	163	-x, 2-y, -z
$O(5)-H(5A) \cdot \cdot \cdot O(2)^{c}$	0.81(3)	1.96(3)	2.767(3)	173	-x, 1-y, -z
$O(5)-H(5B)\cdots N(4)^{c}$	0.82(2)	1.98(2)	2.798(3)	174	x, $1/2 - y$, $1/2 + z$
$O(6)-H(6A) \cdot \cdot \cdot N(16)^{c}$	0.81(2)	1.92(2)	2.737(3)	167	x - 1, y, z
$O(6)-H(6B)\cdots N(11)^{c}$	0.81(2)	2.02(3)	2.776(3)	155	1 - x, $-1/2 + y$, $1/2 - z$

^a Complex 1.
^b Complex 2.
^c Complex 3.



Fig. 2. Hydrogen bonds in 1 generated by water molecules forming square motif interlinking the dimeric units.



Fig. 3. Hydrogen bonded three-dimensional supramolecular framework in 1.



Fig. 4. Dimeric structure of [Gd(5-Br-NIC)₃(H₂O)₂]₂ (2).

 $(\mu_2\text{-}carboxylato\text{-}k^1O\text{:}k^1O^\prime)$ 5-Br-nicotinate (O1, O2, O3, and O4) with r.m.s. deviation of 0.028 Å from the least-squares plane.

The distortion of metal coordination geometry from an ideal square antiprism arrangement is revealed by the dihedral angle

between the square faces is $5.81(7)^{\circ}$. The Gd–O bond distances fall in range of 2.323(3)–2.524(3)Å (Table 2), which are similar to those of the Gd analogue [1].

The crystal packing in 2 is stabilized by intermolecular hydrogen bonds (Table 3). In 2, the metal centre dimeric unit fused together by strong intermolecular O-H···N hydrogen bonds with coordinated water molecule O7 atom in the molecule at (x, y, y)z) acting as a donor to the nicotinic N1 atom in the molecule at (-x, 1-y, 1-z) generates a centrosymmetric $R_2^2(16)$ dimeric ring (A) running along [001] direction as shown in Fig. 5. The second $R_2^2(8)$ dimeric ring (B) running along [100] direction (Fig. 5) is also formed by a pair of intermolecular $O-H \cdots O(-x, x)$ 1 - y, -z) hydrogen bonds involving the oxygen (07) atom which acts as double accepter in the hydrogen bonding pattern. The combination of $R_2^2(16)$ and $R_2^2(8)$ synthons generate a two dimensional supramolecular sheet (Fig. 5). Finally, additional reinforcement within the sheet is achieved by other intermolecular O-H···N hydrogen bonds to complete the 3-D supramolecular architecture.

3.3. Epoxidation reactions

Lanthanide carboxylates have seldom been used as heterogeneous catalyst for the olefin epoxidation. Olefin epoxidation reactions catalyzed by other types of lanthanide complexes in homogeneous and heterogeneous medium are well documented [14,31]. In most of the cases homogeneous lanthanide complexes have been used for catalytic conversion. Homogeneous catalysis process has several disadvantages. In most of the cases the complex decomposes or dimerizes or often autoxidation takes place. To avoid the loss of catalyst and for its recovery many attempts have been taken, such as intercalating or encapsulating the metal complex into the layered compounds or within the cavities of a porous solid (e.g., zeolites) [32], binding the metal complex to a polymeric matrix [33] and employing the steric hindrance [34,35]. In the recent time, a lot of polymer supported lanthanide-binol systems and Ln(O-*i*Pr)₃ systems have been extensively studied and they are proved to be efficient catalyst for various olefinic systems [36,37]. In contrast to these systems it is interesting to use the lanthanide carboxylates as such as recyclable heterogeneous catalyst in olefin epoxidation reaction, instead of using any support. However, such reactions catalyzed by metalcarboxylates in heterogeneous medium have seldom been explored. Aromatic and aliphatic alkenes react with tert-BuOOH to produce epoxides with remarkable selectivity and in good yield with 1, 2, and 3, as heterogeneous catalyst in acetonitrile. Epoxides are very useful and versatile intermediates for the synthesis of many commodity and fine chemicals as well as pharmaceuticals and agrochemicals. Alkyl-hydroperoxides are used on a large scale in industrial epoxidation, for example, in Halcon-Arco and Sumitomo processes [38,39]. The recycling of co-products, e.g., *tert*-BuOH has been realized in the Sumitomo process. The results of the catalytic epoxidation of different substrates are summarized in Table 4 and Figs. 6-8. Oxidation of cyclooctene goes smoothly, showing the conversion (65%, 45% and 40% for 1, 2 and 3, respectively) to form cyclooctene oxide with 100% selectivity. Oxidation of styrene showed 70-92% conversion while epoxide yields were 45-70%. The substituted styrene was also converted successfully in 99% with oxide selectivity up to 68%. In case of linear alkenes, 1-hexene was converted to its oxide with good yield with 100% selectivity. It is worth mentioning that, a lot of binol systems have been proven as highly reactive catalyst for the epoxidation of α , β -unsaturated ketones, amide and esters [36,37]. Some polymer supported lanthanide complexes have also been developed to introduced heterogeneity but it is of quite interest to introduce a lanthanide-carboxylate as a highly efficient heterogeneous epoxidation catalyst.

The overall catalytic efficacy of **1**, **2** and **3** in epoxidation reactions were remarkable which is reflected in the high turnover frequencies for all the olefinic substrates (Table 4). Besides, to ascertain the catalytic efficacy of compounds **1**, **2** and **3** we have also undertaken few control experiments. 1-hexene epoxidation reaction for the compounds was carried out using varied amount of catalysts. This study clearly indicates that the amount of catalyst



Fig. 5. Two dimensional supramolecular sheet in 2, produced by the combination of $R_2^2(16)$ and $R_2^2(8)$ synthons.

Table 4
Catalytic performance of compounds 1, 2 and 3 in epoxidation reaction of olefin

Substrate	Reaction time/h	Conversion (wt%)	% Yield of products		TOF ^e
			Epoxide	Others	
	24	(a) 65	100		241
í l		(b) 45	100		170
		(c) 40	100		151
//	24	(a) 92	70	22 ^b	366
Í		(b) 78	45	33 ^b	312
\checkmark		(c) 70	45	25 ^b	280
//	24	(a) 75	42	33°	262
		(b) 86	46	40 ^c	300
		(c) 85	43	42 ^c	297
11	24	(a) 99	68	32 ^d	358
(/		(b) 85	43	42 ^d	297
		(c) 94	51	43 ^d	328
$\sim \sim /$	24	(a) 86	100		425
		(b) 94	100		465
		(c) 89	100		440

Values in (a), (b) and (c) row correspond to the data for compounds 1, 2, and 3, respectively.

^a Reaction conditions: alkenes (1 g); catalyst (2 mg); *tert*-BuOOH (2 mL); acetonitrile (8 mL); temperature 68–70 °C. The products of the epoxidation reactions were collected at different time intervals and were identified and quantified by Varian CP-3800 gas chromatograph equipped with an FID detector and a CP-Sil 8 CB capillary column.

^b Benzaldehyde.

^c 3-Methyl benzaldehyde.

^d 4-Methyl benzaldehyde.

^e Turn over frequency (TOF) = moles converted/moles of active site per hour.



Fig. 6. Kinetic profile for the conversion of olefins catalyzed by compound 1.

has no influence on the progress of reactions. No induction period was observed in all the reactions.

3.4. Separation, catalyst reuse and heterogeneity test

The major advantage of the use of heterogeneous catalysts is to recover the catalyst from the reaction mixtures by simple filtration and recycle. To test if metal is leached out from the solid catalyst during reaction, the liquid phase of the reaction mixture is collected by filtration at the reaction temperature after 30% of the epoxidation reaction is completed and the residual activity of the



Fig. 7. Kinetic profile for the conversion of olefins catalyzed by compound 2.

supernatant solution after separation of the catalysts was studied. The impending leaching was premeditated as, the organic phase of a first run was separated from the catalyst and new reagents were added to the clear filtrate, and the composition of the reaction mixture was determined by GC. This homogeneous reaction mixture was treated as a standard catalytic experiment. After 6 h, the composition was determined, and no reaction was observed, which excludes the presence of active species in solution. These experiments clearly demonstrate that metal is not leaching out from the solid catalyst during epoxidation reactions. In order to check the stability of the catalysts, we have characterized the sol-



Fig. 8. Kinetic profile for the conversion of olefins catalyzed by compound 3.

 Table 5

 Catalytic efficacy of the recovered complexes 1, 2 and 3 in successive runs for 1-hexene epoxidation.^a

	Cycles	Conversion (wt%)	Yield of product (wt%)	TOF
1	First reuse	86	86	425
	Second reuse	85	85	420
2	First reuse	94	94	465
	Second reuse	92	92	455
3	First reuse	89	89	440
	Second reuse	86	86	425

^a Reaction conditions were the same as given in footnote of Table 1.

ids after the completion of reactions. After the catalytic reactions are over, solid catalyst was recovered by centrifugation and washed with fresh acetonitrile several times and dried in air oven. The recovered catalyst was then subjected for IR spectroscopic analysis. Comparison of IR spectra patterns of the pristine complexes and recovered catalysts convincingly demonstrate that the structural integrity of the complexes **1**, **2** and **3** is remained unaltered after the epoxidation reactions (Fig. S1–S3). Notably the recovered catalyst can be reused in epoxidation reactions for several times with no considerable loss of activity (Table 5).

3.5. Magnetic study

The temperature dependence of the molar magnetic susceptibility, χ_{M} , for complex **2** was measured in the 4–300 K temperature range with a Quantum Design's MPMS XL SQUID magnetometer, under magnetic fields of 10 kOe Fig. 9. The $\chi_{M}T$ product at 300 K, 17.61 cm³ mol⁻¹ K for complex **2**, little higher than the magnetically isolated two non-interacting spin carrier Gd(III) ions, with S = 7/2 ($\chi_{M}T = 15.8$ cm³ mol⁻¹ K for g = 2.00). Upon cooling, the $\chi_{M}T$ value remains almost unchanged until *ca*. 80 K, then decreases rapidly and reaches a minimum value of 15.02 cm³ mol⁻¹ K at 4.0 K, indicating that weak but predominantly antiferromagnetic interaction exists in the complex. The analytical expression that relates χ_{M} with the coupling for a Gd (III) dimer system is available in the literature [1].

$$\chi_m^{(ir)} = \frac{N_A \mu_B^2 g^2}{k_B T} \\ \times \frac{e^{2x} + 5e^{6x} + 14e^{12x} + 30e^{20x} + 55e^{30x} + 91e^{42x} + 140e^{56x}}{1 + 3e^{2x} + 5e^{6x} + 7e^{12x} + 9e^{20x} + 11e^{30x} + 13e^{42x} + 15e^{56x}}$$



Fig. 9. χ_M vs. $T(\bigcirc)$ and $\chi_M T$ vs. $T(\Box)$ plots for complex $[Gd(5-Br-NIC)_3(H_2O)_2]_2$ (**2**). The solid lines represent the best fit of the data with the model described in the text.



Fig. 10. μ_{eff} vs. $T(\bigcirc)$ plots for complex $[Sm(NIC)_3(H_2O)_2]_2$ (**3**).

with $x = J/k_{\rm B}T$, where $N_{\rm A}$ is the Avogadro constant, $\mu_{\rm B}$ the Bohr magneton, g the Landé-factor, $k_{\rm B}$ the Boltzmann constant, T the absolute temperature and J the coupling constant. The best fit parameters were $J = -0.048(1) \, {\rm cm}^{-1}$ and g = 2.0(1) with an agreement factor $R = 2.1 \times 10^{-5}$. The results of J and g values are consistent with the previously reported polynuclear Gd(III) systems, with several bridging ligands [40]. In general, as reported earlier by Andruh et al. [41], the magnitude of J values in all polynuclear Gd(III) complexes is very small, clearly because of weak interaction between metal centers. As regards the magnetic property of compound **3**, Sm(III) ion features an effective magnetic moment of $0.93(3)\mu_{\rm B}$, which is close to the theoretical $0.84\mu_{\rm B}$ for the free-ion ground state (${}^{6}H_{5/2}$) of Sm(III) with five localized unpaired f-electrons (Fig. 10). Often Sm(III) compounds feature such type of complicated low-temperature magnetic property [11,42].

4. Conclusion

In summary we have successfully prepared lanthanide carboxylate dimers by facile hydrothermal methods. Magnetic interaction between metal centers in $[Gd(5-Br-NIC)_3(H_2O)_2]_2$ (2), is antiferromagnetic ($J = -0.048 \text{ cm}^{-1}$), while low-temperature magnetic property of $[Sm(NIC)_3(H_2O)_2]_2$ (3), could not be explicable on the basis of dimeric structure. Compounds are highly stable and insoluble in various solvent media that facilitates to carry out catalytic epoxidation reaction in heterogeneous condition. Notably, compounds **1**, **2** and **3** exhibit excellent catalytic performance in heterogeneous olefinic epoxidation reaction. This study affords new vistas of designing of new lanthanide complexes based heterogeneous epoxidation catalyst.

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Appendix A. Supplementary data

CCDC 775943, 775944 and 775945 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2010.08.033.

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