## Heterogeneous Catalytic Epoxidation of Olefins Over Hydrothermally Synthesized Lanthanide Containing Framework Compounds

Rupam Sen,<sup>[a]</sup> Subratanath Koner,<sup>\*[a]</sup> Dipak K. Hazra,<sup>[b]</sup> Madeleine Helliwell,<sup>[c]</sup> and Monika Mukherjee<sup>[b]</sup>

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A series of novel complexes  $[Ln_2(N_3)(nic)_2(OH)_3(Hnic) (H_2O)]_n$  (Ln = Y<sup>III</sup> 1 and Gd<sup>III</sup> 2; Hnic = nicotinic acid) and  $[Sm_4(N_3)_2(nic)_4(OH)_6(Hnic)_2(H_2O)_2]_n$  (3) have been hydrothermally synthesized and structurally characterized by single-crystal X-ray analysis. Complexes 1, 2 and 3 have similar structures and consist of [Ln<sub>2</sub>(N<sub>3</sub>)(nic)<sub>2</sub>(OH)<sub>3</sub>(Hnic)(H<sub>2</sub>O)] units that are linked to neighboring units through end-on azido,  $\mu_2$  and  $\mu_3$  hydroxo, and bridging carboxylato groups to form 1D infinite chains. In all the complexes the 1D chains

### propagate parallel to crystallographic *a*-axis to give rise to a ribbon-like chain structure. All the compounds exhibit excellent catalytic performance in olefin epoxidation reactions, which is reflected in high turnover numbers. Good expoxide selectivity was obtained in the cases of cyclooctene and 1hexene. The possibility of easy recycling makes these catalysts highly promising candidates for addressing industrial needs and environmental concerns.

## Introduction

Research in the area metal-organic framework (MOFs) fabrication continues to be of interest because of the unique topology and tunable properties of these materials.<sup>[1]</sup> Interest in lanthanide compounds is very much focused on the preparation of homogeneous catalysis.<sup>[2]</sup> molecule-based magnetic materials,<sup>[3]</sup> artificial nucleases for the hydrolytic cleavage of DNA and RNA,<sup>[4]</sup> contrast agents for magnetic resonance imaging,<sup>[5]</sup> and fixation media for atmospheric gases.[6]

Lanthanide salts are used extensively in the synthesis of organic compounds and for several organic transformations.<sup>[7]</sup> The oxidation of alkenes is catalyzed by lanthanide salts in homogeneous reaction media.<sup>[8]</sup> Oxidative transformations,<sup>[9]</sup> and especially the epoxidation of alkenes, are key chemical processes in synthetic organic chemistry, in the chemical industry,<sup>[10]</sup> and in biology.<sup>[11]</sup> Considerable advances have been made in the development of atom-efficient heterogeneous catalytic oxidation methods employing tBuOOH.<sup>[12]</sup> There is ever-growing interest in the application of reusable catalysis in the synthesis of fine chemicals, including enantioselective reactions,<sup>[13]</sup> which could reduce the large amounts of waste products formed in noncatalytic organic synthesis methods. Combinatorial chemistry, currently used in the pharmaceutical industry for the synthesis of drugs, has recently been employed in the field of catalysis.<sup>[14]</sup> The performance of transition metal complexes in homogeneous catalysis is well established.<sup>[15]</sup> Polynuclear metal complexes, especially MOF solids, are receiving great attention in the field of heterogeneous catalysis.<sup>[16]</sup> A variety of reactions involving MOF catalysts have been studied. The catalytic activity observed for these materials is directly related to their metallic components, which may be isolated metal centers, clusters<sup>[17a,17b]</sup> (dimers,<sup>[17c]</sup> trimers,<sup>[17d]</sup> tetramers,<sup>[17e]</sup> etc.), chains,<sup>[17f]</sup> or sheets,<sup>[17g,17h]</sup> that are connected by organic linkers. Kitagawa et al. reported the preparation of a pillared copper-containing layered MOF,  $[Cu_2(pzdc)_2(pz)]$  (pzdc = pyrazine-2,3-dicarboxylate, pz = pyrazine). The complex, [Cu<sub>2</sub>(pzdc)<sub>2</sub>(pz)], catalyzes the polymerization of alkynes, which was possible because of the marked Lewis basicity of the carboxylate groups.<sup>[18]</sup> Hupp et al. performed the oxidation of olefins that was catalyzed by a bimetallic mixed ligand MOF under heterogeneous conditions with a substituted iodosylbenzene oxidant.<sup>[16f]</sup> In this catalytic compound the active center is a Schiff base Mn<sup>III</sup> moiety, which is stacked in between paddle-wheel carboxylate Zn<sub>2</sub> dimers and 4,4'-biphenyldicarboxylate ligands to form square planar layers. The iron(III)-based MOF containing benzene 1,3,5-tricarboxylate, Fe<sup>III</sup>-MIL100, which has a zeotype architecture has been synthesized hydrothermally.<sup>[16c]</sup> The Friedel-Crafts reaction of benzene with benzyl chloride was catalyzed by Fe<sup>III</sup>-MIL100 at 343 K and showed excellent selectivity for diphenylmethane. Ravon et al. have successfully used zinc dicarboxylate MOF solids as heterogeneous catalysts for the

<sup>[</sup>a] Department of Chemistry, Jadavpur University, Kolkata 700 032, India

E-mail: snkoner@chemistry.jdvu.ac.in

<sup>[</sup>b] Department of Solid State Physics, Indian Association for the Cultivation of Science, Jadavpur, Kolkata 700 032, India

<sup>[</sup>c] Department of Chemistry, University of Manchester, Oxford Road, Manchester, M13 9PL, UK

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alkylation of aromatics.<sup>[19]</sup> Alkylation of toluene with *t*Bu chloride selectively affords the corresponding *para*-substituted product. The same reaction catalyzed by AlCl<sub>3</sub> or the acidic zeolite beta gives mixtures of *ortho-* and *para*-substituted compounds and dialkylated products. Recently, we successfully used layered metal carboxylates and hydrogen phosphate to catalyze olefin epoxidation reactions under heterogeneous conditions.<sup>[16e,16g]</sup> Lanthanide-based MOFs are being used in for the catalytic oxidation of organic sulfur compounds as well as alkanes.<sup>[2d,2e]</sup> However, to the best of our knowledge no attempts have been made so far to use lanthanide carboxylate complexes for the catalytic epoxidation of olefins in heterogeneous media.

Herein we report the synthesis and crystal structures of three novel 1D lanthanide carboxylate complexes 1-3 that show good activity towards olefin epoxidation in heterogeneous media.

## **Results and Discussion**

### Crystal Structures of Compounds 1, 2 and 3

Single crystal XRD analysis revealed that complexes 1 and 2 have similar structures and crystallized in the centrosymmetric space group  $P\bar{1}$  with Z = 2. Selected bond lengths and angles are collated in Table 1. Since both of the compounds have similar structures, complex 1 has been selected to be the representative example for the following structure description. The asymmetric unit of 1 contains two Y<sup>III</sup> cations, one azide ligand, and three nicotinate anions (Figure 1), and each Y<sup>III</sup> ion is eight coordinate, and has *anti*-prismatic geometry. The coordination environment of the metal center Y(1) in 1 is achieved by one nitrogen atom [Y(1)–N(1)<sup>#2</sup> 2.420(10) Å (#2: x + 1, y, z)] from an azide group, three oxygen atoms [Y(1)–O(1) 2.328(9) Å, Y(1)–O(3) 2.307(8) Å and Y(1)–O(5) 2.326(9) Å] from three nicotinic acid groups, one  $\mu_2$  hydroxy group [Y(1)–O(8) 2.504(8) Å], and three  $\mu_3$  hydroxy groups [Y(1)–O(9)<sup>#1</sup> 2.362(8) Å, Y(1)–O(10) 2.388(7) Å, and Y(1)–O(10)<sup>#1</sup>



Figure 1. ORTEP diagram of compound 1 with ellipsoids at the 40% probability level.

Table 1. Selected bond lengths [Å] and angles [°] for complexes 1, 2 and 3.<sup>[a]</sup>

1	-	2		3	
Y(1)-O(1)	2.328(9)	Gd(1)-O(1)	2.442(7)	Sm(1)–O(1)	2.421(4)
Y(1)-O(3)	2.307(8)	Gd(1)–O(3)	2.264(6)	Sm(3)–O(1)	2.436(4)
Y(2)–O(4)	2.330(8)	Gd(1)–O(4)	2.378(7)	Sm(4) - O(1)	2.404(4)
Y(1)-O(5)	2.326(9)	Gd(2)–O(3)	2.382(7)	Sm(1)–O(2)	2.406(4)
Y(2)–O(6)	2.301(8)	Gd(2)–O(4)	2.290(6)	Sm(2)–O(2)	2.387(4)
Y(2)-O(7)	2.368(8)	Gd(2)–O(5)	2.503(6)	Sm(4)–O(2)	2.426(4)
Y(1)-O(8)	2.504(8)	Gd(2)–O(7)	2.380(7)	Sm(1)–O(3)	2.381(4)
Y(2)-O(8)#4	2.531(8)	Gd(2)–O(9)	2.471(7)	Sm(2)–O(3)	2.390(4)
Y(2)–O(9)	2.354(8)	Gd(2)–O(10)	2.579(7)	Sm(2)–O(10)	2.595(4)
Y(2)-O(9)#3	2.293(8)	Gd(2) - N(4)	2.403(8)	Sm(4)–O(10)	2.569(4)
Y(1)-O(9) <sup>#1</sup>	2.362(8)			Sm(1)-N(1)	2.549(5)
Y(1)-O(10)	2.388(7)			Sm(2) - N(4)	2.530(5)
Y(1)-O(10) <sup>#1</sup>	2.342(8)			Sm(4)–N(4)	2.497(5)
Y(2)-O(10)	2.366(7)				
$Y(1)-N(1)^{#2}$	2.420(10)				
Y(2)-N(1)	2.484(10)				
$O(1)-Y(1)-O(10)^{\#1}$	108.1(3)	$O(6)^{\#1}-Gd(1)-O(4)$	79.6(2)	O(3)–Sm(1)–O(2)	72.05(13)
O(5)-Y(1)-O(10) <sup>#1</sup>	82.0(3)	O(3)-Gd(1)-O(1)	78.1(2)	O(3)-Sm(1)-O(1)	113.2(12)
O(3)-Y(1)-O(8)	72.4(3)	O(4)-Gd(1)-O(1)	109.4(2)	O(2)-Sm(1)-O(4)	131.4(12)
O(1)-Y(1)-O(8)	78.3(3)	$O(8)^{\#1}$ - $Gd(1)$ - $O(4)^{\#1}$	81.1(2)	N(1)-Sm(1)-O(4)	64.48(14)
O(1)-Y(1)-O(10)	71.0(3)	$O(1)-Gd(1)-O(4)^{\#1}$	66.3(2)	O(3) - Sm(1) - O(4)	69.13(12)
$O(9)^{#3}-Y(2)-O(6)$	137.0(3)	$O(4)-Gd(1)-O(10)^{#2}$	137.2(2)	O(1)-Sm(1)-O(4)	152.5(13)
$O(9)^{#3}-Y(2)-O(4)$	140.7(3)	$O(3)-Gd(1)-N(4)^{#2}$	69.0(2)	O(2)-Sm(2)-O(3)	72.20(13)
O(6) - Y(2) - O(4)	75.5(3)	$O(4)-Gd(1)-N(4)^{#2}$	83.1(2)	O(2)-Sm(2)-O(9)	142.3(13)
$O(9)^{#3}-Y(2)-O(10)$	112.0(3)	$O(6)^{\#1}-Gd(1)-N(4)^{\#2}$	71.5(2)	O(3)–Sm(2)–O(9)	145.4(13)
O(6)-Y(2)-O(10)	83.9(3)	O(1)-Gd(1)-O(10) <sup>#2</sup>	80.7(2)	O(3)–Sm(2)–O(5)	71.37(13)
O(9)-Y(2)-O(10)	71.4(3)	$O(4)-Gd(1)-O(4)^{\#1}$	75.3(2)	O(3)-Sm(2)-N(4)	77.20(14)
O(4)–Y(2)–O(7)	75.2(3)			O(5)-Sm(2)-N(4)	146.1(14)

[a] Symmetry codes, #1: -x + 1, -y + 2, -z + 1; #2: x + 1, y, z; #3: -x, -y + 2, -z + 1; #4: x - 1, y, z.

2.342(8) Å (#1 = -x + 1, -y + 2, -z + 1)]. Whereas Y(2) is coordinated to an azide nitrogen atom [Y(2)-N(1)]2.484(10) Å], and two oxygen atoms [Y(2)–O(4) 2.330(8) Å, Y(2)–O(6) 2.301(8) Å] from two nicotinic acid groups, one  $\mu_2$  hydroxy group [Y(2)–O(8)<sup>#4</sup> 2.531(8) Å (#4: x - 1, y, z)] and three  $\mu_3$  hydroxy groups [Y(2)–O(9) 2.354(8) Å, Y(2)–  $O(9)^{#3}$  2.293(8) Å (#3: -x, -y + 2, -z + 1) and Y(2)–O(10) 2.366(7) Å], and a water molecule [Y(2)–O(7) 2.368(8) Å]. As the nicotinic acid ring atoms are disordered, the subsequent discussion of the structural parameters in 1 is limited to atoms that do not display any disorder. As shown in Figure 2, complex 1 forms a 1D chain with the azide ligands in end-on (EO) bridging mode, while the nicotinic ligands and hydroxy groups bind in two modes: bidentate  $\mu_2$ -(*syn*-*syn*) and monodentate for the nicotinic groups, and  $\mu_2$  and  $\mu_3$  modes for the hydroxy groups. The 1D chains propagate parallel to the crystallographic a-axis. The skeleton of the ID chain has a wave-like ladder structure (Fig-



Figure 2. Propagation of the 1D chain in compound 1 parallel to crystallographic *a*-axis.

Table 2. Intermolecular contacts for complexes 1, 2 and 3 [Å, °].



Figure 3. Skeleton of the 1D wave-like ladder (only  $\mu_3$ -O atoms are shown) in 1.

ure 3) constructed from Y cations and  $\mu_3$  hydroxy ligands, and is reinforced between adjacent Y<sup>III</sup> cations in two ways: (i) by being bonded to two carboxylate groups of the nico-tinic ligand in *syn-syn* mode; (ii) by being bonded to both an  $\mu_2$  hydroxy and  $\mu_{1,1}$  azide group.

The overall structure of compound **3**, including the coordination environment around the central metal ion, is the same as that of **1** and **2**. Compound **3** also crystallizes in the centrosymmetric space group  $P\overline{1}$  with Z = 2. However, the crystallographic asymmetric unit of complex **3** contains four Sm<sup>III</sup> cations (see Supporting Information, Figure S2). Selected bond lengths and angles for **3** are listed in Table 1.

The crystal packing of compounds **1**, **2** and **3** is stabilized by a combination of intermolecular C–H···O hydrogen bonds (Table 2). In addition to the van der Waals interactions, the molecular packing in **1** is influenced by strong hydrogen bonding involving a nicotinic acid group C atom and a water molecule, where the C(nicotinic)···O distance is 2.795(16) Å. The atom C4 of the nicotinic acid group in the molecule at (x, y, z) acts as a hydrogen bond donor for the water molecule O7 atom in the molecule at (1 - x, 2 - y, -z), forming a centrosymmetric  $R_2^2(22)$  ring that is propagated along the [001] direction (Figure 4), while in **2** a combination of strong intermolecular C4–H4···O9 (–1 + x, y, –1 + z) and C17–H17···O9 (3 – x, 2 – y, 2 – z) hydrogen bonds

D–H···A	<i>d</i> (D–H)	<i>d</i> (H···A)	<i>d</i> (D····A)	<(DHA)	Symmetry transformation
C(4)–H(4)•••O(7) <sup>[a]</sup>	0.93	1.89	2.795(16)	165	1 - x, 2 - y, -z
$C(4) - H(4) \cdots O(9)^{[b]}$	0.95	2.03	2.937(13)	160	-1 + x, y, -1 + z
C(17)–H(17)····O(9) <sup>[b]</sup>	0.95	1.87	2.784(13)	160	3-x, 2-y, 2-z
$C(4) - H(4) - O(8)^{[c]}$	0.93	2.40	3.304(8)	164	2 - x, -y, 1 - z
$C(5) - H(5) - O(16)^{[c]}$	0.93	1.89	2.787(8)	161	1 - x, -y, 1 - z
$C(12) - H(12) - O(20)^{[c]}$	0.93	1.86	2.774(8)	166	-x, 1-y, -z
$C(19) - H(19) - O(16)^{[c]}$	0.93	1.85	2.757(7)	163	1-x, 1-y, 1-z
$C(26) - H(26) - O(10)^{[c]}$	0.93	1.86	2.761(7)	163	x, -1 + y, z
$C(32) - H(32) - O(6)^{[c]}$	0.93	2.59	3.281(7)	132	-1 + x, $1 + y$ , z
$C(33) - H(33) - O(4)^{[c]}$	0.93	1.82	2.740(7)	169	x, 1 + y, z
$C(40) - H(40) - O(20)^{[c]}$	0.93	1.92	2.793(8)	154	1-x, -y, -z

[a] Complex 1. [b] Complex 2. [c] Complex 3.



Figure 4. Hydrogen bonding in 1 forming a centrosymmetric  $R_2^2(22)$  ring that is propagated along the [001] direction.

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inter link the molecules to form a supramolecular framework (Figure 5). In **3**, a pair of C(5)–H(5)···O(16) hydrogen bonds, with the C5 atom in the molecule at (x, y, z) acting as a donor to the O16 atom in the molecule at (1 - x, -y, 1 - z), generates a centrosymmetric  $R_2^2(18)$  dimeric ring (A). Similarly, a pair of intermolecular C(12)–H(12)···O(20) hydrogen bonds produce another  $R_2^2(18)$  dimeric ring (B). The two  $R_2^2(18)$  rings are alternately linked into an infinite 1D ABABAB chain that propagates along the [001] direction (Figure 6). Additional reinforcement within the chain is achieved by other C–H···O hydrogen bonds that give rise to the supramolecular network in **3**.



Figure 5. Formation through interlinking hydrogen bonds of the supramolecular framework in **2**.



Figure 6.  $R_2^2(18)$  rings alternately linked into an infinite 1D ABABAB chain that propagates along the [001] direction in compound **3**.

#### **Catalytic Epoxidation Reactions**

Olefin epoxidation reactions catalyzed by lanthanide containing catalysts under homogeneous conditions are well documented.<sup>[20]</sup> However, homogeneous catalysts suffer from the problems of separation of catalyst from the reaction mixture and recycling of the catalyst. Catalyst recycling is a task of great economic and environmental importance in the chemical and pharmaceutical industries, especially when expensive and/or toxic heavy metal complexes are employed. To this end many attempts have been made to resolve this problem such as intercalating or encapsulating the metal complex into layered compounds or within the cavities of a porous solid (e.g., zeolites),<sup>[21]</sup> binding the metal complex into a polymeric matrix,<sup>[22]</sup> and employing steric hindrance<sup>[23]</sup> to design recyclable catalysts. Polymer supported lanthanide-binol systems and Ln(O-iPr)3 systems have been used extensively in the catalytic oxidation of olefinic substrates.<sup>[24]</sup> At variance with the above, the lanthanide carboxylate compounds reported herein do not require

any support to act as recyclable heterogeneous catalysts for olefin epoxidation. Aromatic and aliphatic alkenes react with tBuOOH to produce epoxides with remarkable selectivity and in good yields with compounds 1, 2, and 3, acting as heterogeneous catalyst in acetonitrile, a result which is reflected by the high turnover numbers for all the olefinic substrates in this study (Table 3). Alkyl-hydroperoxides are used on a large scale for industrial epoxidation reactions, for example in Halcon-Arco and Sumitomo processes.<sup>[25a–25c]</sup> The recycling of co-products e.g. *t*BuOH has been realized in the Sumitomo process. The results of the catalytic epoxidation of different substrates are summarized in Table 3 and Figures 7, 8 and 9. The oxidation of cyclooctene proceeded smoothly, showing conversion (86%, 41% and 40% for 1, 2 and 3, respectively) to cyclooctene oxide with 100% selectivity. Oxidation of styrene occurred with 81-92% conversion, while epoxide yields were 41-47%; along with styrene oxide, benzaldehyde was also formed. In fact, in the epoxidation of styrene with tBuOOH over transition metal immobilized zeolites, or molecular sieve catalysts, the epoxide yields seldom exceed 40%.<sup>[26,27]</sup> We recently succeeded in improving the yield of styrene epoxide to ca. 70% using layered metal carboxylate catalysts.<sup>[16e]</sup> The substituted styrene was converted (99%) successfully to the oxide with up to 60% selectivity, the remaining conversion product was the corresponding aldehyde. However, in

Table 3. Epoxidation of olefins catalyzed by 1, 2 and 3.<sup>[a]</sup>

Substrate	Reaction time [h]	Conversion [wt%]	% Yield of products		TON <sup>[f]</sup>
			Epoxide	Others	
		a) 86	100	-	2532
ſ	24	b) 41	100	_	1464
$\bigcirc$		c) 40	100	-	1406
//	24	a) 92	41	51 <sup>[b]</sup>	2886
		b) 81	46	35 <sup>[b]</sup>	3061
$\square$		c) 87	47	40 <sup>[b]</sup>	3237
//	24	a) 79	49	30 <sup>[c]</sup>	2166
		b) 65	37	28 <sup>[c]</sup>	2147
$\square$		c) 81	46	35 <sup>[c]</sup>	2114
	24	a) 99	55	45 <sup>[d]</sup>	2715
ſ		b) 95	60	25 <sup>[d]</sup>	3139
$\square$		c) 99	56	43 <sup>[d]</sup>	3220
	24	a) 95	85	$10^{[e]}$	3688
		b) 90	90	0	4210
$\sim\sim$		c) 96	96	0	4221

[a] (a), (b), (c) corresponds to the catalytic performance of compounds 1, 2 and 3, respectively. Reaction conditions: alkenes (1 g); catalyst (2 mg); *t*BuOOH (2 mL); acetonitrile (8 mL); T = 68-70 °C. The products of the epoxidation reactions were collected at different time intervals and were identified and quantified with a Varian CP3800 gas chromatograph equipped with an FID detector and a CP-Sil 8 CB capillary column. [b] Benzaldehyde. [c] 4-Meth-ylbenzaldehyde. [d] 3-Methylbenzaldehyde. [e] 1-Hexanol. [f] Turn over number (TON) is the ratio of (mol converted):(mol of active site).

the case of linear alkenes, 1-hexene was converted to the corresponding oxide in a high yield of 85-96%. The formation of side products was minimal in this reaction. Notably, in the epoxidation of 1-hexene catalyzed by **2** and **3** no side products were formed.



Figure 7. Kinetic profile for the conversion of olefins catalyzed by compound 1.



Figure 8. Kinetic profile for the conversion of olefins catalyzed by compound **2**.



Figure 9. Kinetic profile for the conversion of olefins catalyzed by compound **3**.

The catalytic reactions were performed with a variety of oxidants to study the catalytic efficacy of 1, 2 and 3. The best catalytic performance was observed with *t*BuOOH in acetonitrile. Hydrogen peroxide and sodium hypochlorite solution completely failed to activate the catalysts. We also undertook a few control experiments; all of these reactions

were performed with a simple carboxylate  $Gd(OAc)_3$  salt acting as the heterogeneous catalyst. The performance of Gd(OAc)<sub>3</sub> in heterogeneous catalytic epoxidation reactions is summarized in Table 4. The results clearly indicate that the reactions with lanthanide chain compounds are more selective and the yields are much better than when simple gadolinium carboxylate is the catalyst. Further comparison of catalytic efficiency of 1, 2 and 3 with the corresponding lanthanide oxides, clearly indicates that the 1D lanthanide carboxylates perform better as catalysts than the metal oxides (Table 5).<sup>[25d]</sup> The temperature dependence of the catalytic performance of compounds 1, 2 and 3 has been studied. While the catalysts showed almost no conversion at room temperature, they did exhibit the desired conversion at 70 °C, which demonstrates the vital role of temperature for the activation of the catalyst (see Supporting Information, Figure S3). Notably, the amount of catalyst in the reaction mixture has no influence on the progress of reaction. No induction period was observed for all the reactions.

Table 4. Epoxidation of olefins catalyzed by Gd(OAc)<sub>3</sub>.<sup>[a]</sup>

Substrate	Reaction time [h]	Conversion [wt%]	% Yield of products		TON <sup>[e]</sup>
			Epoxide	Others	
$\bigcirc$	24	22	100	-	333
	24	54	31	23 <sup>[b]</sup>	867
Ś	24	69	15	54 <sup>[c]</sup>	968
	24	84	25	59 <sup>[d]</sup>	1178
~~~/	24	65	65	0	1291

[a] Reaction conditions were the same as given in the footnote of Table 3. [b] Benzaldehyde. [c] 4-Methylbenzaldehyde. [d] 3-methylbenzaldehyde. [e] Turn over number (TON) is the ratio of (mol converted):(mol of active site).

Table 5. Epoxidation of styrene with *t*BuOOH catalyzed by a variety of Ln-based catalysts.<sup>[a]</sup>

Catalyst	Conversion	% Yield of product		TON <sup>[b]</sup>	References
	[%0]	oxide	others		
1	92	41	51	2886	this work
2	81	46	35	3061	this work
3	87	47	40	2337	this work
$Y_2O_3$	82	30	52	887	this work
Gd <sub>2</sub> O <sub>3</sub>	15.7	60	39.8	74	[28d]
$Sm_2O_3$	9.8	48.6	51.3	38	[28d]
Gd(OAc) <sub>3</sub>	54	31	23	867	this work

[a] Reaction conditions were the same as given in footnote of Table 3. [b] Turn over number (TON) is the ratio of (mol converted):(mol of active site).

### Separation, Catalyst Reuse and Heterogeneity Test

The major advantage of the use of heterogeneous catalysts is the possible recovery of the catalyst from the reaction mixtures and its possible reuse. To test if metal is leached out from the solid catalyst during reaction, the liquid phase of the reaction mixture was collected by filtration, at the reaction temperature, after 30% of the epoxidation reaction was complete, and the residual activity of the supernatant solution after separation of the catalysts was studied. To test for leaching, the organic phase of a first run was separated from the catalyst and new reagents were added to the clear filtrate, and then the composition of the reaction mixture was determined by gas chromatography. This homogeneous reaction mixture was then treated as a standard catalytic experiment. After 6 h, the composition was of the mixture was redetermined, and no reaction products were observed, which excludes the presence of an active catalytic species in the solution. These experiments clearly demonstrate that metal is not leaching out of the solid catalyst during the epoxidation reactions. In order to check the stability of the catalysts, we have characterized them after the completion of the reactions in which they were involved. After the catalytic reactions were complete, the solid catalyst was recovered by centrifugation and washed with fresh acetonitrile several times and dried in an air oven. The recovered catalyst was then subjected to IR and powder XRD analysis. Comparison of the IR spectra and XRD patterns of the pristine complexes and recovered catalysts convincingly demonstrated that the structural integrity of complexes 1, 2 and 3 remains unaltered during the epoxidation reactions (see Supporting Information, Figures S4-S9). Notably the recovered catalyst can be reused several times for epoxidation reactions with no considerable loss of activity (Table 6). The kinetic profiles for the epoxidation reaction of 1-hexene with fresh and recovered catalysts are virtually the same (see Supporting Information, Figures S10–S12).

Table 6. Catalytic efficacy towards 1-hexene epoxidation of the recovered complexes 1, 2 and 3 over successive runs.<sup>[a]</sup>

	Cycles	Conversion (wt%)	Yield of product (wt%)	TON
1	first reuse	95	85	3688
	second reuse	93	84	3572
2	first reuse	90	90	4210
	second reuse	88	88	4116
3	first reuse	96	96	4221
	second reuse	95	95	4375

[a] Reaction conditions were the same as given in the footnote of Table 3.

### Conclusions

In summary we have successfully prepared three new 1D lanthanide compounds via a hydrothermal route. Metal centers in these compounds are bridged through end-on azido,  $\mu_2$  and  $\mu_3$  hydroxo, and carboxylato ligands to form ribbon-like structures. Notably, compounds 1, 2 and 3 exhi-

bit excellent catalytic performance in heterogeneous olefinic epoxidation reactions. As there are no pores in the compounds, epoxidation reactions clearly take place on the surface of the catalysts. This study affords new vistas for the design of lanthanide compounds that can be used as recyclable heterogeneous epoxidation catalysts. Further investigations employing this type of catalyst in other reactions are currently in progress.

## **Experimental Section**

Materials and Physical Measurements: Gadolinium nitrate hexahydrate, samarium nitrate hexahydrate, yttrium nitrate hexahydrate, nicotinic acid, sodium azide, cyclooctene, styrene, 4-methylstyrene, 3-methylstyrene, 1-hexene, and *tert*-butyl hydroperoxide (70 wt.-% aqueous) were purchased from Aldrich and were used as received. Solvents were purchased from Merck (India). The solvents were distilled and dried before use. Fourier transform infrared spectra of KBr pellets were measured on a Shimadzu S-8400 FTIR spectrometer. The powder XRD patterns of the samples were recorded with a Scintag XDS-2000 diffractometer with Cu- $K_{\alpha}$  radiation. The products of the catalytic reactions were identified and quantified with a Varian *CP*3800 gas chromatograph with a CP-Sil 8 CB capillary column. Other instruments used in this study were the same as reported earlier.<sup>[16e]</sup>

Synthesis and Preliminary Characterization of the Compounds: Compounds 1, 2 and 3 were prepared by a hydrothermal process. To obtained the desired product, Ln(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O, sodium azide and nicotinic acid were mixed in a 1:3:2 ratio, and maintained at 170 °C for 3 d at autogenously developed pressure in a teflon lined reaction bomb. After cooling to room temperature colorless needle shaped crystals were isolated in high yield by filtration [Yield ca. 85%, 87% and 91% (based on metal) for 1, 2 and 3 respectively], washed with water and dried in a desiccator. For preliminary characterization of the compounds, elemental analysis and IR spectroscopic studies were undertaken. 1: calcd. C 33.12, H 2.14, N 12.88; found C 33.05, H 2.10, N 13.0. Selected IR peaks (KBr disk):  $\tilde{v}$  = 1617, 1549 [v<sub>as</sub> (CO<sub>2</sub><sup>-</sup>)], 1412 [v<sub>s</sub> (CO<sub>2</sub><sup>-</sup>)], 1230, 1063 [v<sub>s</sub> (C-O)], 3600-3200 [s. br., v (O-H)] cm<sup>-1</sup>. 2: calcd. C 27.38, H 1.78, N 10.64; found C 27.28, H 1.72, N 10.60. Selected IR peaks (KBr disk): v = 1623, 1577  $[\upsilon_{as} (CO_2^{-})]$ , 1406  $[\upsilon_s (CO_2^{-})]$ , 1284, 1176  $[\upsilon_s (C-O)]$ , 3600–3200 [s. br., υ (O–H)] cm<sup>-1</sup>. 3: calcd C 27.94, H 1.81, N 10.86; found C 27.86, H 1.77, N 10.78. Selected IR peaks (KBr disk): v = 1669, 1573  $[\upsilon_{as} (CO_2^{-})]$ , 1449  $[\upsilon_s (CO_2^{-})]$ , 1284, 1178  $[\upsilon_s (C-O)]$ , 3600-3200 [s.br., υ (O-H)].

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 with graphite-monochromated Mo- $K_a$  radiation ( $\lambda$ = 0.71073 Å). Determination of integrated intensities and cell refinement were performed with the SAINT<sup>[28]</sup> software package with a narrow-frame integration algorithm. An empirical absorption correction (SADABS)<sup>[29]</sup> was applied to the data. All the structures were solved by direct methods and refined using full-matrix least-squares technique against  $F^2$  with anisotropic displacement parameters for all non-hydrogen atoms with the programs SHELXS97 and SHELXL97.<sup>[30]</sup> Since the nicotinic acid ring atoms in 1 and 2 are disordered over two positions, anisotropic refinement of these atoms was restrained with the DELU, SIMU and ISOR options in SHELXL. Hydrogen atoms were placed at calculated positions with suitable riding models and isotropic displacement parameters derived from their carrier atoms. In the final difference Fourier maps there were no remarkable peaks except ghost peaks surrounding the metal centers. A summary of crystal data and relevant refinement parameters for complexes 1, 2 and 3 are given in Table 7.

Table 7. Crystal data and structure refinement details for complexes 1, 2 and 3.

Compound	1	2	3
Formula	C <sub>18</sub> H <sub>14</sub> N <sub>6</sub> O <sub>10</sub> Y <sub>2</sub>	C <sub>18</sub> H <sub>12</sub> N <sub>6</sub> O <sub>10</sub> Gd <sub>2</sub>	C <sub>36</sub> H <sub>24</sub> N <sub>12</sub> O <sub>20</sub> Sm <sub>4</sub>
Formula weight	652.17	786.84	1546.07
Temperature [K]	100(2)	100(2)	100(2)
Wavelength [Å]	0.71073	0.71073	0.71073
Crystal system	triclinic	triclinic	triclinic
Space group	ΡĪ	ΡĪ	PĪ
<i>a</i> [Å]	7.925(4)	8.050(2)	8.1462(4)
<i>b</i> [Å]	12.502(6)	12.523(3)	12.5647(6)
c [Å]	12.474(6)	12.581(3)	23.0020(11)
a [°]	108.191(7)	108.011(5)	99.207(1)
$\beta$ [°]	103.893(7)	98.218(5)	90.245(1)
γ [°]	98.026(7)	104.173(6)	98.283(1)
Volume [Å <sup>3</sup> ]	1108.5(8)	1136.1(5)	2298.9(2)
Z	2	2	2
Calculated density	1.966	2.300	2.234
[Mg/m <sup>3</sup> ]			
Absorption	5.280	5.855	5.125
coefficient [mm <sup>-1</sup> ]			
F(000)	652	740	1464
$\theta$ range for	2.72-21.97	1.75-25.03	0.90-25.00
data collection [°]			
Reflections col-	5884/2699	5768/3927	26793/8061
lected /unique			
R(int)	0.0594	0.0313	0.0249
$R1 [I > 2\sigma(I)]$	0.0746,	0.0512,	0.0366,
$wR2 [I > 2\sigma(I)]$	0.1812	0.1141	0.0965
R1 (all data)	0.1085,	0.0647,	0.0392,
wR2 (all data)	0.2010	0.1210	0.0985
Goodness of fit on $F^2$	1.028	1.063	1.067
Largest diff. peak [eÅ <sup>-3</sup> ]	2.942,	1.592,	1.643,
Largest diff. hole [e Å <sup>-3</sup> ]	-1.087	-1.660	-2.172

CCDC-791076 (for 1), -791077 (for 2), and -791078 (for 3) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif.

Catalytic Reactions: The catalytic reactions were carried out in a glass batch reactor. The substrate, solvent and catalysts were mixed, and the mixture then equilibrated to 70 °C in an oil bath. After addition of tBuOOH, 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.

Supporting Information (see also the footnote on the first page of this article): ORTEP structures of 2 and 3, temperature dependence of the catalytic performance of compounds 1, 2 and 3, powder Xray patterns, IR spectra and kinetic profiles of the recovered catalysts.

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- [1] a) R. E. Morris, P. S. Wheatley, Angew. Chem. Int. Ed. 2008, 47, 4966; b) H. Furukawa, J. Kim, N. W. Ockwig, M. O'Keeffe, O. M. Yaghi, J. Am. Chem. Soc. 2008, 130, 11650; c) S. Horike, M. Dinca, K. Tamaki, J. R. Long, J. Am. Chem. Soc. 2008, 130, 5854; d) D. Maspoch, D. Ruiz-Molina, J. Veciana, Chem. Soc. Rev. 2007, 36, 770; e) Y. Goto, H. Sato, S. Shinkai, K. Sada, J. Am. Chem. Soc. 2008, 130, 14354; f) C. N. R. Rao, S. Natarajan, R. Vaidhanathan, Angew. Chem. Int. Ed. 2004, 43, 1466; g) M. Eddaoudi, J. Kim, D. Vodak, A. Sudik, J. Wachter, M. O'Keefe, O. M. Yaghi, Proc. Natl. Acad. Sci. USA 2002, 99, 4900; h) S. Kitawaga, R. Kitaura, S. Noro, Angew. Chem. Int. Ed. 2004, 43, 2334; i) X. Gu, D. Xue, Inorg. Chem. 2007, 46, 3212; j) G. Férey, C. M. Draznieks, C. Serre, F. Millange, J. Dutour, S. Surble, I. Margiolaki, Science 2005, 309, 2040; k) X.-J. Kong, L.-S. Long, L.-S. Zheng, R. Wang, Z. Zheng, Inorg. Chem. 2009, 48, 3268.
- [2] a) J. Perles, M. Iglesias, C. Ruiz-Valero, N. Snejko, J. Mater. Chem. 2004, 14, 2683; b) S. G. Podkolzin, E. E. Stangland, M. E. Jones, E. Peringer, J. A. Lercher, J. Am. Chem. Soc. 2007, 129, 2569; c) S. Liu, P. Poplaukhin, E. Ding, C. E. Plecnik, X. Chena, M. A. Keane, S. G. Shore, J. Alloys Compd. 2006, 418, 21; d) F. Gándara, E. G. Puebla, M. Iglesias, D. M. Proserpio, N. Snejko, M. A. Monge, Chem. Mater. 2009, 21, 655; e) F. Gándara, A. García-Cortés, C. Cascales, B. Gómez-Lor, E. Gutiérrez-Puebla, M. Iglesias, A. Monge, N. Snejko, Inorg. Chem. 2007, 46, 3475.
- [3] L. E. Sweet, L. E. Roy, F. Meng, T. Hughbanks, J. Am. Chem. Soc. 2006, 128, 10193.
- [4] a) M. Komiyama, N. Takeda, H. Shigekawa, Chem. Commun. 1999, 1443; b) K. Nwe, C. M. Andolina, C.-H. Huang, J. R. Morrow, Bioconjugate Chem. 2009, 20, 1375; c) K. Nwe, M. C. Andolina, J. R. Morrow, J. Am. Chem. Soc. 2008, 130, 14861.
- [5] a) L. Messerle, D. Nolting, L. Bolinger, A. H. Stolpen, B. F. Mullan, D. Swenson, M. Madsen, Acad. Radiol. 2005, 12, S46; b) C.-H. Huang, J. R. Morrow, Inorg. Chem. 2009, 48, 7237.
- [6] a) T. Devic, C. Serre, N. Audebrand, J. Marrot, G. Férey, J. Am. Chem. Soc. 2005, 127, 12788; b) L. Pan, K. M. Adams, H. E. Hernandez, X. Wang, C. Zheng, Y. Hattori, K. Kaneko, J. Am. Chem. Soc. 2003, 125, 3062; c) J. Luo, H. Xu, Y. Liu, Y. Zhao, L. L. Daemen, C. Brown, T. V. Timofeeva, S. Ma, H.-C. Zhou, J. Am. Chem. Soc. 2008, 130, 9626 and references cited therein.
- [7] a) S. Y. Seo, T. J. Marks, Org. Lett. 2008, 10, 317; b) J. Li, F. Xu, Y. Zhang, Q. Shen, J. Org. Chem. 2009, 74, 2575; c) H. C. Aspinall, Chem. Rev. 2002, 102, 1807.
- [8] a) D. Díez, M. G. Núñez, A. B. Antón, P. García, R. F. Moro, N. M. Garrido, I. S. Marcos, P. Basabe, J. G. Urones, Curr. Org. Synth. 2008, 5, 186; b) M. Bougauchi, S. Watanabe, T. Arai, H. Sasai, M. Shibasaki, J. Am. Chem. Soc. 1997, 119, 2329.
- J.-E. Bäckvall (Ed.), Modern Oxidation Methods, Wiley-VCH, [9] Weinheim, Germany, 2004.
- [10] a) B. S. Lane, K. Burgess, Chem. Rev. 2003, 103, 2457; b) R. A. Sheldon, J. K. Kochi, Metal-Catalyzed Oxidations of Organic Compounds, Academic Press, New York, 1981; c) J. Brinksma, J. W. de Boer, R. Hage, B. L. Feringa, in Modern Oxidation Methods (Eds.: J.-E. Bäckvall), Wiley-VCH, Weinheim, Germany, 2004, chapter 10, p. 295 ff; d) R. Noyori, M. Aoki, K. Sato, Chem. Commun. 2003, 1977; e) T. Katsuki, Chem. Soc. Rev. 2004, 33, 437; f) T. Punnivamurthy, S. Velusamy, J. Igbal, Chem. Rev. 2005, 105, 2329; g) D. W. Nelson, A. Gypser, P. T. Ho, H. C. Kolb, T. Kondo, H.-L. Kwong, D. V. McGrath, A. E. Rubin, P.-O. Norrby, K. P. Gable, K. B. Sharpless, J. Am. Chem. Soc. 1997, 119, 1840; h) T. Katsuki, K. B. Sharpless, J.

*Am. Chem. Soc.* **1980**, *102*, 5974; i) K. Sato, M. Aoki, M. Ogawa, T. Hashimoto, R. Noyori, *J. Org. Chem.* **1996**, *61*, 8310; j) W. A. Herrmann, R. W. Fischer, D. W. Marz, *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1638.

- [11] A. J. Wu, J. E. Penner-Hahn, V. L. Pecoraro, *Chem. Rev.* 2004, *104*, 903.
- [12] J.-M. Brégeault, Dalton Trans. 2003, 3289.
- [13] a) H. U. Blaser, B. Pugin, *Chiral Reactions in Heterogeneous Catalysis* (Eds.: G. Jannes, V. Dubois), Plenum, New York, **1995**, pp 33; b) A. Baiker, H. U. Blaser, *Handbook of Heterogeneous Catalysis*, vol. 5 (Eds.: G. Ertl, H. Knözinger, J. Weitkamp), VCH, Weinheim, **1997**, p. 2432 ff.
- [14] W. Gerhartz, Y. S. Yamamoto, L. Kandy, J. F. Rounsaville, G. Schulz, Ullmann's Encyclopedia of Industrial Chemistry, 5th ed., Verlag Chemie, Weinheim, Germany, 1987, vol. A9, p. 531 ff.
- [15] S. Bhaduri, D. Mukesh, *Homogeneous Catalysis*, John Wiley & Sons, Inc., New York, **2000**.
- [16] a) D. Farrusseng, S. Aguado, C. Pinel, Angew. Chem. Int. Ed.
  2009, 48, 7502; b) A. Corma, H. García, F. X. L. I. Xamena, Chem. Rev. 2010, 110, 4606; c) P. Horcajada, S. Surblé, C.
  Serre, D.-Y. Hong, Y.-K. Seo, J.-S. Chang, J.-M. Grenèche, I.
  Margiolakid, G. Férey, Chem. Commun. 2007, 2820; d) C. Janiak, Dalton Trans. 2003, 2781; e) R. Sen, S. Bhunia, D. Mal, S.
  Koner, Y. Miyashita, K.-I. Okamoto, Langmuir 2009, 25, 13667; f) S.-H. Cho, B. Ma, S. T. Nguyen, J. T. Hupp, T. E.
  Albrecht-Schmitt, Chem. Commun. 2006, 2563; g) R. Sen, R.
  Bera, A. Bhattacharjee, P. Gütlich, S. Ghosh, A. K. Mukherjee, S. Koner, Langmuir 2008, 24, 5970.
- [17] a) D. J. Tranchemontagne, J. L. Mendoza-Cortés, M. O'Keeffe, O. M. Yaghi, Chem. Soc. Rev. 2009, 38, 1257; b) C. Chizallet, S. Lazare, D. Bazer-Bachi, F. Bonnier, V. Lecocq, E. Soyer, A. Quoineaud, N. Bats, J. Am. Chem. Soc. 2010, 132, 12365; c) S. S. Y. Chui, S. M. F. Lo, J. P. H. Charmant, A. G. Orpen, I. D. Williams, Science 1999, 283, 1148; d) J. S. Seo, D. Whang, H. Lee, S. I. Jun, J. Oh, Y. J. Jeon, K. Kim, Nature 2000, 404, 982; e) H. Li, M. Eddaoudi, M. O'Keeffe, O. M. Yaghi, Nature 1999, 402, 276; f) D. N. Dybtsev, A. L. Nuzhdin, H. Chun, K. P. Bryliakov, E. P. Talsi, V. P. Fedin, K. Kim, Angew. Chem. Int. Ed. 2006, 45, 916; g) B. Gomez-Lor, E. Gutierrez-Puebla, M. Iglesias, M. A. Monge, C. Ruiz-Valero, N. Snejko, Inorg. Chem. 2002, 41, 2429; h) K. Barthelet, K. Adil, F. Millange, C. Serre, D. Riou, G. Férey, J. Mater. Chem. 2003, 13, 2208.
- [18] R. Matsuda, R. Kitaura, S. Kitagawa, Y. Kubota, R. V. Belosludov, T. C. Kobayashi, H. Sakamoto, T. Chiba, M. Takata, Y. Kawazoe, Y. Mita, *Nature* 2005, 436, 238.

- [19] U. Ravon, M. E. Domine, C. Gaudillere, A. Desmartin-Chomel, D. Farrusseng, New J. Chem. 2008, 32, 937.
- [20] a) Q.-H. Xia, H.-Q. Ge, C.-P. Ye, Z.-M. Liu, K.-X. Su, *Chem. Rev.* 2005, 105, 1603; b) T. Nemoto, H. Kakei, V. Gnanadesi-kan, S.-Y. Tosaki, T. Ohshima, M. Shibasaki, *J. Am. Chem. Soc.* 2002, 124, 14544; c) H. Kakei, R. Tsuji, T. Ohshima, M. Shibasaki, *J. Am. Chem. Soc.* 2005, 127, 8962; d) M. Bougauchi, S. Watanabe, T. Arai, H. Sasai, M. Shibasaki, *J. Am. Chem. Soc.* 1997, 119, 2329.
- [21] J. C. Medina, N. Gabriunas, E. Paez-Mozo, J. Mol. Catal. A 1997, 115, 233.
- [22] P. Anzenbacher Jr., V. Kral, K. Jursikova, J. Gunterova, A. Kasal, J. Mol. Catal. A 1997, 118, 63.
- [23] a) P. Bhyrappa, J. K. Young, J. S. Moore, K. S. Suslick, J. Mol. Catal. A 1996, 113, 109; b) P. Bhyrappa, J. K. Young, J. S. Moore, K. S. Suslick, J. Am. Chem. Soc. 1996, 118, 5708.
- [24] a) H. Sasai, T. Suzuki, S. Arai, T. Arai, M. Shibasaki, J. Am. Chem. Soc. 1992, 114, 4418; b) H. Sasai, T. Suzuki, N. Itoh, K. Tanaka, T. Date, K. Okamura, M. Shibasaki, J. Am. Chem. Soc. 1993, 115, 10372; c) R. F. Chen, C. T. Qian, J. G. de Vries, Tetrahedron 2001, 57, 9837.
- [25] a) M. N. Sheng, G. J. Zajaczek, ARCO, U. K. Patent 1136923,
   1968; b) Halcon Kollar, J. U. S. Patent 3350422, 1967; c) J. Kollar, Halcon, US Patent 3351635, 1967; d) V. R. Choudhary, R. Jha, P. Jana, *Green Chem.* 2006, *8*, 689.
- [26] D. E. De Vos, M. Dams, B. F. Sels, P. A. Jacobs, Chem. Rev. 2002, 102, 3615.
- [27] a) V. R. Choudhary, R. Jha, P. Jana, *Catal. Commun.* 2008, 10, 205; b) H. Sohrabi, M. Esmafeli, F. Farzaneh, M. Ghandi, J. *Inclusion Phenom. Macrocyclic Chem.* 2006, 54, 23; c) Q. Zhang, Y. Wang, S. Itsuki, T. Shishido, K. Takehira, J. Mol. Catal. 2002, A188, 189; d) R. Malakooti, F. Farzaneh, M. Ghandi, J. Sci. I. R. Iran 2006, 17, 43.
- [28] APEX 2, SAINT, XPREP, Bruker AXS Inc., Madison, Wisconsin, USA, 2007.
- [29] SADABS, Bruker AXS Inc., Madison, Wisconsin, USA, 2001.
- [30] G. M. Sheldrick, SHELXS97 and SHELXL97: Programs for Crystal Structure Solution and Refinement, University of Göttingen, Germany, 1997.

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