DOI: 10.1002/ejic.201100118

Gd_{26} Cluster Consisting of Distorted Cubane Cores: Synthesis, Structure and Heterogeneous Catalytic Epoxidation of Olefins

Rupam Sen,[a] Dipak K. Hazra,[b] Monika Mukherjee,[b] and Subratanath Koner*[a]

Keywords: Gadolinium / Cluster compounds / Hydrothermal synthesis / Epoxidation / Heterogeneous catalysis / Framework solids

A new Gd_{26} cluster based 3D framework, $\{[Gd_{26}(\mu_6\text{-}CO_3)_9(NIC)_{32}(\mu_3\text{-}OH)_{26}](NO_3)_2{\cdot}3(H_2O)\}_n$ (**1**) (NIC = nicotinato anion) has been prepared through hydrothermal synthesis and characterised by single-crystal X-ray diffraction. The Gd_{26} clusters are formed by the combination of five distorted cubane cores attached to each other through six Gd^{3+} ions. The Gd_{26} clusters are then connected to each other by organic linkers forming a 3D framework. The dimensions of the spherical cluster shell including the organic ligands is around 2.32(4) nm. The compound catalyses the heterogeneous epoxidation of olefinic substrates including α, β-unsaturated ketones.

Introduction

In the last few years, there has been tremendous interest in the preparation and properties of high-nuclearity metal clusters.[1–3] Many attempts to prepare new polynuclear clusters that demonstrate interesting properties have been successful.[4–8] A lot of transition metal clusters containing molybdenum,[9] silver,[10] manganese[11] and copper[12] etc. have been synthesised and characterised although reports of lanthanide clusters are limited. Controlled hydrolysis of the metal ions led to high-nuclearity lanthanide clusters producing tetra-,[13] penta-,[14] hexa-,[15] hepta-,[16] octa-,[17] nona-,[18] deca-,[19] dodeca-,[20] tetradeca-,[21] pentadecanuclear[22] and hexatriacontanuclear[23] lanthanide clusters. In this context, oxo, hydroxo and fluorido bridged lanthanide clusters are worthy of note.[24–31]

It has been well documented that lanthanide compounds have relevance to homogeneous catalysis,[32] molecule-based magnetic materials,[33] contrast agents for magnetic resonance imaging[34] and fixation media for essential atmospheric gases.[35] In the field of oxidative catalytic transformations,[36] epoxidation of alkenes is a key chemical process in biology,[37] synthetic organic chemistry and in chemical industry.[38–40] There is an ever-growing interest in the application of reusable catalysts for the synthesis of fine chemicals as well as enantioselective reactions[41] which could reduce the large amounts of waste products that are usually formed in noncatalytic organic synthesis. Lanthanide compounds have been used in several organic transformations[42] including the conversion of alkenes to their corresponding oxides in homogeneous media,[43] although rarely have they been used in epoxidation of olefins[44] or oxidation[45] of alkanes and sulfur compounds in heterogeneous media. The last decade witnessed an enormous effort to produce epoxides of electron deficient alkenes[46] and several approaches indicated that many lanthanide catalysts are reactive in epoxidation of α,β-unsaturated ketones, amides and esters. Recently we succeeded in catalytically activating layered transition metal carboxylato,[47a] hydrogenphosphato[47b] or lanthanide based metal-organic framework compounds[47c,47d] towards olefin epoxidation under heterogeneous conditions. Here we report a new Gd_{26}-cluster based 3D framework that catalyses epoxidation of various kinds of alkenes in heterogeneous media. To the best of our knowledge, this is the first example of a cluster-based 3D lanthanide framework.

Results and Discussion

Synthesis of $\{[Gd_{26}(\mu_6\text{-}CO_3)_9(NIC)_{32}(\mu_3\text{-}OH)_{26}](NO_3)_2{\cdot}3(H_2O)\}_n$ (1)

The synthesis of $\{[Gd_{26}(\mu_6\text{-}CO_3)_9(NIC)_{32}(\mu_3\text{-}OH)_{26}](NO_3)_2{\cdot}3(H_2O)\}_n$ (**1**) (NIC = nicotinato anion) is not a straight-forward process and, hence, it deserves a brief discussion. The azido ion plays an important role in isolating the cluster-based compound **1**. Mixing of the reactants viz., $Gd(NO_3)_3$, nicotinic acid and sodium azido in a 1:2:2 ratio resulted a 1D chain compound of gadolinium(III) ions and EO azido bridges.[47d] However, increasing the concentration of sodium azido to a molar ratio of 1:2:4 led to the formation of high nuclearity clusters, $\{[Gd_{26}(\mu_6\text{-}CO_3)_9(NIC)_{32}(\mu_3\text{-}OH)_{26}](NO_3)_2{\cdot}3(H_2O)\}_n$ (**1**). Interestingly, how-

[a] Department of Chemistry, Jadavpur University, Kolkata 700 032, India
E-mail: snkoner@chemistry.jdvu.ac.in
[b] Department of Solid State Physics, Indian Association for the Cultivation of Science, Jadavpur, Kolkata 700 032, India

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejic.200900xxx.

ever, the azido ion is absent in **1** but it is not possible to prepare compound **1** without NaN_3. The exact role of the azido ion is still unclear to us. With an assumption that the azido ion, upon hydrolysis, might facilitate the formation of the cluster by changing the pH of the medium, we tried several different weak bases. However, this does not lead to the formation of the high nuclearity cluster-based compound **1**. Further work regarding the synthesis this cluster and other similar systems are in progress.

X-ray Structure of $\{[Gd_{26}(\mu_6\text{-}CO_3)_9(NIC)_{32}(\mu_3\text{-}OH)_{26}](NO_3)_2{\cdot}3(H_2O)\}_n$ (1)

Single-crystal X-ray analysis revealed that the asymmetric unit of the framework compound consists of 26 Gd^{3+} ions, two NO_3^- and nine CO_3^{2-} anions, 32 nicotinic acid ligands, 26 μ_3-OH units and three molecules of water of crystallisation (Figure 1). The molecule exhibits a fascinating 3D polymeric arrangement connecting the building unit Gd_{26} clusters "CO_3@Gd_{26}" (Figure 2). The nicotinato anions act as a chelating ligand as well as a bridging ligand to link the clusters thus forming the 3D polymeric structure. The metal centres have three types of coordination environment: Gd(9), Gd(12), Gd(19) and Gd(25) are nine-coordinate, while the remaining Gd atoms are eight-coordinate surrounded by μ_3-OH, terminal water molecules, nicotinato anions and CO_3^{2-} ions. Four GdO_x polyhedra are connected to each other to form a secondary building unit, Gd_4, by sharing four μ_3-OH groups, consequently, giving rise to five distorted cubane cores having the face dimensions of c.a. 2.395(3) × 2.415(5) Å (Figure 3). Besides, three GdO_x polyhedra share a μ_3-OH unit to make another secondary building unit, Gd_3 (Figure 4). Five Gd_4 units connected by two Gd_3 rings form a Gd_{26} cage which is further connected by nine μ_6-CO_3^{2-} anions to generate a spherical cluster shell, CO_3@Gd_{26} (Figure 5). One free NO_3^{2-} anion is entrapped at the centre of the Gd_{26} cage, while another is outside the cage. The diameter of the spherical cluster shell including organic ligands is about 2.32(4) nm. The Gd_{26} cluster units are then connected to each other by the organic linker forming a 3D framework.

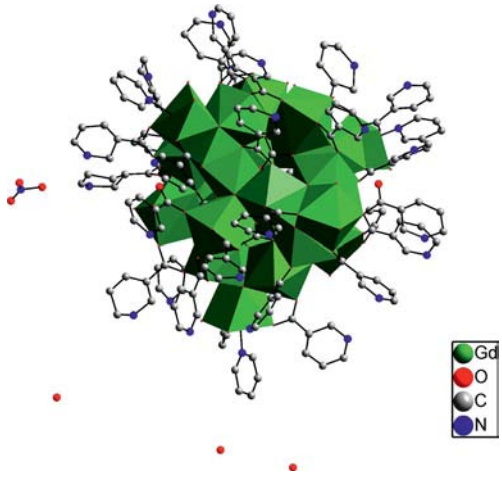


Figure 1. Polyhedral representation of the asymmetric unit of compound **1**.

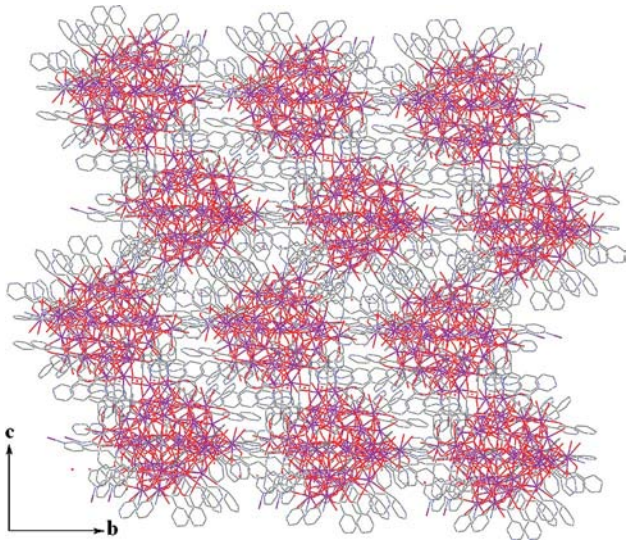


Figure 2. 3D packing of compound **1**.

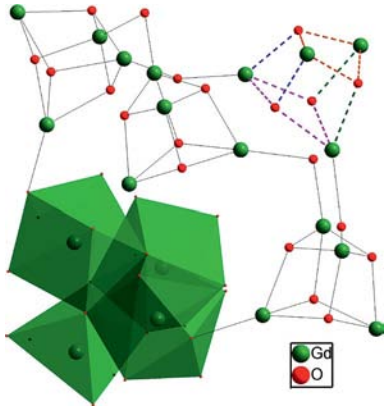


Figure 3. μ_3-OH-bridged five-cubane core with polyhedral presentation.

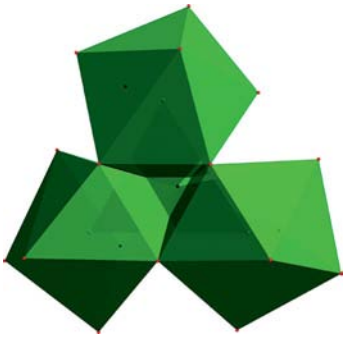


Figure 4. Polyhedral representation of μ_3-OH-bridged Gd_3 triad.

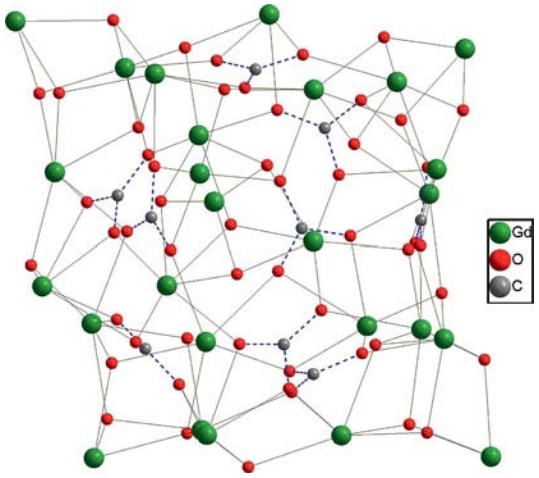
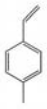
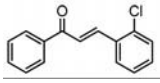


Figure 5. Cluster formation in **1** by the CO_3^{2-} anion shown in dotted lines.

Catalytic Epoxidation Reactions

Epoxides are very useful and versatile intermediates for the synthesis of many commodity and fine chemicals as well as pharmaceuticals and agrochemicals. Alkyl-hydroperoxido materials are used on a large scale in industrial epoxidation, for example in the Halcon–Arco and Sumitomo processes.[48] The recycling of coproducts, e.g., *t*BuOH has been realised in the Sumitomo process. Olefin epoxidation reactions catalysed by lanthanide-containing homogeneous catalysts are well documented.[43,46] However, there are several disadvantages in using homogeneous catalysts. In most of the cases the compound decomposes or dimerises and autoxidation frequently takes place during the catalytic reaction. Recycling of catalysts is a task of great economic and environmental importance in the chemical and pharmaceutical industries, especially when expensive and/or toxic heavy metal compounds are employed. Many attempts have been made such as intercalation or encapsulation of the metal compounds into the layered inert matrices or within the cavities of a porous solid (e.g. zeolites),[49] binding the metal compounds onto a polymeric matrix[50] and employing steric hindrance etc.[51] for easy recovery and reuse of the catalysts. This is to minimise the loss of catalyst after the reaction. To this end, polymer supported lanthanide-binol and $Ln(O\text{-}iPr)_3$ systems have been extensively used in catalytic epoxidation of olefins.[52] In contrast, in this study, a Gd_{26} cluster based framework solid has been used, without any support, as a recyclable heterogeneous catalyst in olefin epoxidation. Lanthanide compounds have rarely been explored as heterogeneous catalysts for olefin epoxidation.[47c,47d] Various olefinic substrates react with *t*BuOOH to produce epoxides with remarkable selectivity and in good yield using compound **1** as a heterogeneous catalyst in acetonitrile. The results of the catalytic epoxidation of different substrates are summarised in Table 1. The oxidation of cyclooctene proceeds smoothly, showing an excellent conversion of 71% to form cyclooctene oxide with 100% selectivity. Oxidation of styrene showed 80% conversion, however, epoxide yields were only 57%. The substituted styrene was also converted (95%) successfully with oxide selectivity of ca. 74%. It is noteworthy that in the case of styrene, epoxidation with such high selectivity has rarely been achieved with heterogeneous systems.[49b] In the case of linear alkenes, olefins with shorter chain lengths undergo epoxidation with higher selectivity than the long-chain olefins, for example 1-hexene was converted to 96% with 100% selectivity whereas the 1-octene oxide yield was 69% with a conversion of 76%. An electron-deficient system (2-chloro-chalcone) was also studied. The catalyst efficiently catalyses its epoxidation giving ca. 99% selectivity. The reactions profiles of the epoxidations of various alkenes are shown in Figure 6.

Table 1. Epoxidation of olefins catalysed by **1**.[a]

Substrate	Reaction time/h	Conversion [wt.-%]	% Yield of products epoxide	others	TON[d]
	24	71	100	–	29374
	24	80	57	23[b]	35018
	24	95	70	25[b]	36649
	24	96	100	–	52105
	24	76	69	7[c]	30903
	24	81	99	–	14909

[a] Reaction conditions: alkenes (1 g); catalyst (2 mg); *t*BuOOH (2 mL); acetonitrile (8 mL); temperature 68(±2) °C. The products of the epoxidation reactions were collected at different time intervals and were identified and quantified by using a Varian CP3-800 gas chromatograph equipped with an FID detector and a CP-Sil 8 CB capillary column. [b] Benzaldehyde and 4-methylbenzaldehyde. [c] 2-Octanone. [d] Turn over number (TON): mol converted/mol of active site.

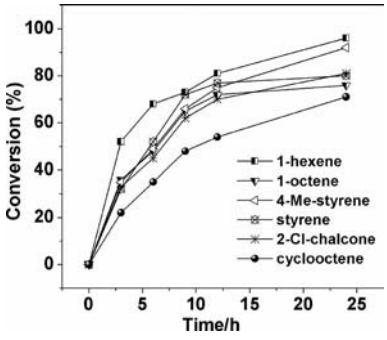


Figure 6. Reaction profile for the epoxidation of olefins with *t*BuOOH catalysed by compound **1** in acetonitrile media.

The overall catalytic efficacy of the Gd_{26} cluster-based catalyst in epoxidation reactions was impressive and this is reflected in the high turnover numbers for all the olefinic substrates (Table 1). Besides, to ascertain the catalytic effi-

cacy of compound **1** we also undertook a few control experiments. The epoxidation of 1-hexene was carried out using varied amounts of catalyst. This study clearly indicates that the amount of catalyst has no influence on the progress of the reactions. Epoxidation of 1-hexene was also studied using the catalyst but adding different amounts of *t*BuOOH. The optimum amount of *t*BuOOH needed for completion of the catalytic reaction was found to be ca. 1.5 molar equiv. (*t*BuOOH/substrate) for compound **1**. A comparison of the catalytic efficacy of compound **1** with that of a simple carboxylato, $Gd(OAc)_3$ acting as the heterogeneous catalyst (see Supporting Information; Table S1), clearly indicates that the reactions with the lanthanide cluster are more selective and yields are much better than the gadolinium acetato compound. Furthermore, comparison of the catalytic efficiency of **1** with the corresponding lanthanide oxide and carbonato also indicates that compound **1** performs better as a catalyst than the other gadolinium containing species (Table 2). To check if the particle size had any influence on the progress of the reactions or on conversion we carried out the reaction with crystals and with fine powder. The epoxidation reaction is a little slower if the crystals obtained from the hydrothermal reactor are used directly as a catalyst. However, the difference is not significant. For example, conversion of 4-methyl-styrene to its epoxide was 89% in 24 h when crystals were used as the catalyst while in case of powder, conversion was 95% for this substrate. Hence, we studied all the reactions by grinding the crystals to a fine powder. Since the reactions take place on the surface of the catalyst, the difference is not unexpected. Furthermore, no variation of activity was observed for the powder catalyst obtained from different batches in hydrothermal reactions. No induction period was observed in all the reactions.

Table 2. Epoxidation of styrene with *t*BuOOH catalysed by **1** and other Gd-containing catalysts.[a]

Catalyst	Conversion / %	Yield of product / %		References
		Epoxide	others	
1	80	57	23	this work
Gd_2O_3	15.7	9.4	6.3	[44]
$Gd(OAc)_3$	54	31	23	[47d]
$Gd_2(CO_3)_3$	17	12	5	this work

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

Separation, Catalyst Reuse and Heterogeneity Test

The major advantages of the use of heterogeneous catalysts are their recovery from reaction mixtures and possible reuse. To test if the metal leached out from the solid catalyst during the reaction, the liquid phase of the reaction mixture was collected by repeated centrifugation after ca. 30% of the epoxidation reaction was complete and the residual activity of the supernatant solution, after separation of the catalyst, was studied. The supernatant solution was kept at 70 °C in an oil bath for 6 h and the composition of the solution was determined by GC. No further progress of the reaction was observed during this period, which indicates the absence of active species in solution. These experiments clearly demonstrate that the metal does not leach out from the solid catalyst during epoxidation reactions. In order to check the stability of the catalyst, we characterised the solids after the completion of the reactions. When the catalytic reactions were over, the solid catalyst was recovered by centrifugation and washed with fresh acetonitrile several times and dried in air in an oven. The recovered catalyst was then subjected to IR spectroscopic analysis. A comparison of the IR spectra of the pristine complexes and the recovered catalysts convincingly demonstrates that the structural integrity of the compound remains unaltered after the epoxidation reactions; see Figure S1 in the Supporting Information. Notably, the recovered catalyst can be reused in further epoxidation reactions with no considerable loss of activity (Table 3).

Table 3. Catalytic efficacy of the recovered complex **1** in successive runs for cyclooctene epoxidation[a].

Cycles	Conversion / wt.-%	Selectivity / wt.-%	TON
First reuse	71	100	29374
Second reuse	70	100	28960

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

Conclusions

In summary, we have succeeded in preparing a new example of a high nuclearity, Gd_{26} lanthanide cluster-based compound by means of a hydrothermal route. The extension of the connectivity between Gd_{26} clusters through organic linkers results in a fascinating 3D framework compound, $\{[Gd_{26}(\mu_6\text{-}CO_3)_9(NIC)_{32}(\mu_3\text{-}OH)_{26}](NO_3)_2\cdot 3(H_2O)\}_n$. Importantly, the Gd_{26} cluster-based framework compound catalyses epoxidation reactions of a variety of olefinic substrates including α,β-unsaturated ketones in heterogeneous media. This study affords new scope for designing high-nuclearity lanthanide compound-based heterogeneous catalysts. Further investigations of the application of this type of catalyst in other organic reactions are currently in progress.

Experimental Section

Materials and Measurements: $Gd(NO_3)_3\cdot 6H_2O$, NaN_3, 1-hexene, 1-octene, cyclooctene, styrene, 4-methylstyrene, 2-chloro-chalcone and *t*BuOOH (70 wt.-% aq.) were purchased from Aldrich and were used as received. Solvents were purchased from Merck (India) and were distilled and dried before use. Fourier transform infrared spectra of KBr pellets were recorded on a Perkin–Elmer RX I FTIR spectrometer. The powder X-ray diffraction (XRD) patterns of the samples were recorded with a Scintag XDS-2000 diffractometer using Cu-K_α radiation. The products of the catalytic reactions were identified and quantified by using a Varian CP3-800 Gas Chromatograph using a CP-Sil 8 CB capillary column.

Synthesis and Characterisation of $\{[Gd_{26}(\mu_6\text{-}CO_3)_9(NIC)_{32}(\mu_3\text{-}OH)_{26}](NO_3)_2\cdot 3(H_2O)\}_n$ (1): We synthesised the compound hydro-

thermally as colourless block crystals. To prepare the compound, an aqueous solution of $Gd(NO_3)_3$, nicotinic acid and sodium azide was digested in a teflon-lined Parr acid digestion bomb at autogenously developed pressure at 170 °C for 3 d followed by slow cooling at 5 °C h^{-1} to room temperature. The colourless block crystals of compound **1** thus formed were collected by filtration, washed with water and a small amount of ethyl alcohol and dried in air; yield ca. 35% (based on metal). For characterisation of the compounds, elemental analysis and IR spectroscopic studies were undertaken. $\{[Gd_{26}(\mu_6\text{-}CO_3)_9(NIC)_{32}(\mu_3\text{-}OH)_{26}](NO_3)_2\cdot 3(H_2O)\}_n$ (**1**): calcd: C 26.45, H 1.38, N 5.22; found C 26.35, H 1.29, N 5.12. Selected IR peaks (KBr disk): $\tilde{\nu}$ = 1610, 1564 [υ_{as} (CO_2^-)], 1412 [υ_s (CO_2^-)], 1246, 1191 [υ_s (C–O)], 1481, 1404 [υ_s N–O], and 3500–3200 s (br. [υ, O–H)]) cm^{-1}.

X-ray Crystallographic Study: X-ray diffraction data for **1** were collected at 293(2) K on a Bruker SMART APEX CCD X-ray diffractometer using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). Determination of integrated intensities and cell refinement were performed with the SAINT[53] software package using a narrow-frame integration algorithm. An empirical absorption correction[54] (SADABS) was applied. The structure was solved by direct methods and refined using full-matrix least-squares techniques against F^2 with anisotropic displacement parameters for nonhydrogen atoms with the programs SHELXS97 and SHELXL97.[55] Some of the organic ligands were restrained using the ISOR option in SHELXL during anisotropic refinement. The hydrogen atoms of the organic moieties as well as in the water molecules were not included in the model. A summary of crystal data and relevant refinement parameters for compound **1** is given in Table 4.

Table 4. Crystal data and structure refinement parameters for **1**.

Empirical formula	$C_{402}Gd_{52}N_{68}O_{252}H_{252}$
Formula weight	18237
Temperature [K]	100(2)
Wavelength [Å]	0.71073
Crystal system	triclinic
Space group	$P\bar{1}$
a, b, c [Å]	21.2508(4), 21.9899(4), 29.6001(5)
α, β, γ [°]	93.477(1), 90.363(1), 95.571(1)
Volume [Å^3]	13740.5(4)
Z	1
Calculated density [Mg m^{-3}]	1.583
Absorption coefficient [mm^{-1}]	3.876
F(000)	6240
θ range for data collection [°]	0.93 to 27.58
Limiting indices	$-27 \le h \le 27$, $-27 \le k \le 28$, $-38 \le l \le 32$
Reflections collected / unique	218918 / 61566 [R_{int} = 0.0894]
Completeness to 2θ [%]	96.7
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	61566 / 2268 / 3401
Goodness-of-fit on F^2	1.050
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0697, wR_2 = 0.1908
R indices (all data)	R_1 = 0.1294, wR_2 = 0.2242
Extinction coefficient	0.00031(2)

CCDC-805728 contains 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 according to the following procedure: substrate, solvent and catalysts were first mixed and the mixture was then equilibrated to 70 °C in an oil bath. After addition of *t*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. The crystals of compound **1** were ground to a fine powder before using them in catalytic reactions.

Supporting Information (see footnote on the first page of this article): IR spectra of recovered catalyst, Table showing catalytic performance of compound **1** in comparison to other Gd-containing species.

Acknowledgments

We acknowledge the Department of Science and Technology (DST), Government of India, for funding a project (to S. K.) (SR/S1/IC-01/2009). We also thank DST for funding the Department of Chemistry under DST-FIST programme to procure a single-crystal X-ray diffractometer. R. S. thanks Council of Scientific and Industrial Research (CSIR) [grant number 09/096(0551)2k8-EMR-I] for a Senior Research Fellowship.

[1] L. M. C. Beltran, J. R. Long, *Acc. Chem. Res.* **2005**, *38*, 325–334.
[2] E. J. L. McInnes, S. Piligkos, G. A. Timco, R. E. P. Winpenny, *Coord. Chem. Rev.* **2005**, *249*, 2577–2590.
[3] M. W. Cooke, G. S. Hanan, *Chem. Soc. Rev.* **2007**, *36*, 1466–1476.
[4] J.-F. Bai, A. V. Virovets, M. Scheer, *Science* **2003**, *300*, 781–783.
[5] T. C. Stamatatos, K. A. Abboud, W. Wernsdorfer, G. Christou, *Angew. Chem. Int. Ed.* **2007**, *46*, 884–888.
[6] O. Cador, D. Gatteschi, R. Sessoli, F. K. Larsen, J. Overgaard, A.-L. Barra, S. J. Teat, G. A. Timco, R. E. P. Winpenny, *Angew. Chem. Int. Ed.* **2004**, *43*, 5196–5200.
[7] a) W.-G. Wang, A.-J. Zhou, W.-X. Zhang, M.-L. Tong, X.-M. Chen, M. Nakano, C. C. Beedle, D. N. Hendrickson, *J. Am. Chem. Soc.* **2007**, *129*, 1014–1015; b) Q.-R. Fang, G.-S. Zhu, Z. Jin, M. Xue, X. Wei, D.-J. Wang, S.-L. Qiu, *Angew. Chem. Int. Ed.* **2006**, *45*, 6126–6130; c) T. Liu, Y.-J. Zhang, Z.-M. Wang, S. Gao, *J. Am. Chem. Soc.* **2008**, *130*, 10500–10501; d) S. C. Xiang, S. M. Hu, T. L. Sheng, R. B. Fu, X. T. Wu, X. D. Zhang, *J. Am. Chem. Soc.* **2007**, *129*, 15144–15146.
[8] a) X.-J. Kong, Y.-P. Ren, W.-X. Chen, L.-S. Long, Z. Zheng, R.-B. Huang, L.-S. Zheng, *Angew. Chem. Int. Ed.* **2008**, *47*, 2398–2401; b) X.-J. Kong, Y.-P. Ren, L.-S. Long, Z. Zheng, R.-B. Huang, L.-S. Zheng, *J. Am. Chem. Soc.* **2007**, *129*, 7016–7017.
[9] a) A. Müller, S. Q. N. Shah, H. Bögge, M. Schmidtmann, *Nature* **1999**, *397*, 48–50; b) A. Müller, C. Serain, *Acc. Chem. Res.* **2000**, *33*, 2–10; c) A. Müller, E. Beckmann, H. Bögge, M. Schmidtmann, *Angew. Chem. Int. Ed.* **2002**, *41*, 1162–1167; d) A. Müller, *Science* **2003**, *300*, 749–750.
[10] a) D. Fenske, C. Persau, S. Dehnen, C. E. Anson, *Angew. Chem. Int. Ed.* **2004**, *43*, 305–309; b) D. Fenske, C. E. Anson, A. Eichhöfer, O. Fuhr, A. Ingendoh, C. Persau, C. Richert, *Angew. Chem. Int. Ed.* **2005**, *44*, 5242–5246.
[11] a) M. Soler, W. Wernsdorfer, K. Folting, M. Pink, G. Christou, *J. Am. Chem. Soc.* **2004**, *126*, 2156–2165; b) A. J. Tasiopoulos, A. Vinslava, W. Wernsdorfer, K. A. Abboud, G. Christou, *Angew. Chem. Int. Ed.* **2004**, *43*, 2117–2121.
[12] a) G. Mezei, P. Baran, R. G. Raptis, *Angew. Chem. Int. Ed.* **2004**, *43*, 574–577; b) M. Murugesu, R. Clérac, C. E. Anson, A. K. Powell, *Inorg. Chem.* **2004**, *43*, 7269–7271.
[13] B.-Q. Ma, D.-S. Zhang, S. Gao, T.-Z. Jin, C.-H. Yan, G.-X. Xu, *Angew. Chem. Int. Ed.* **2000**, *39*, 3644–3646.
[14] O. Poncelet, W. J. Sartain, L. G. Hubert-Pfalzgraf, K. Folting, K. G. Caulton, *Inorg. Chem.* **1989**, *28*, 263–267.

[15] a) D.-S. Zhang, B.-Q. Ma, T.-Z. Jin, S. Gao, C.-H. Yan, T. C. Mak, *New J. Chem.* **2000**, *24*, 61–62; b) R. Wang, M. D. Carducci, Z. Zheng, *Inorg. Chem.* **2000**, *39*, 1836–1837; c) N. Mahé, O. Guillou, C. Daiguebonne, Y. Gérault, A. Caneschi, C. Sangregorio, J. Y. Chane-Ching, P. E. Car, T. Roesnel, *Inorg. Chem.* **2005**, *44*, 7743–7750.

[16] X.-J. Zheng, L.-P. Jin, S. Gao, *Inorg. Chem.* **2004**, *43*, 1600–1602.

[17] a) T. Kajiwara, H. Wu, T. Ito, N. Iki, S. Miyano, *Angew. Chem. Int. Ed.* **2004**, *43*, 1832–1835; b) K. Norton, S. Banerjee, S. Das, L. Huebner, T. J. Emge, J. G. Brennan, *Dalton Trans.* **2010**, *39*, 6794–6800; c) C. G. Pernin, J. A. Ibers, *Inorg. Chem.* **1997**, *36*, 3802–3803.

[18] a) L. G. Hubert-Pfalzgraf, N. Miele-Pajot, R. Papiernik, J. Vaissermann, *J. Chem. Soc., Dalton Trans.* **1999**, 4127–4130; b) G. Xu, Z.-M. Wang, Z. He, Z. Lü, C.-S. Liao, C.-H. Yan, *Inorg. Chem.* **2002**, *41*, 6802–6807.

[19] a) L. G. Westin, M. Kritikos, A. Caneschi, *Chem. Commun.* **2003**, 1012–1013; b) A. Kornienko, T. J. Emge, G. Ajith Kumar, R. E. Riman, J. G. Brennan, *J. Am. Chem. Soc.* **2005**, *127*, 3501–3505.

[20] a) R. Wang, H. D. Selby, H. Liu, M. D. Carducci, T. Jin, Z. Zheng, J. W. Anthis, R. J. Staples, *Inorg. Chem.* **2002**, *41*, 278–286; b) S. Banerjee, G. A. Kumar, R. E. Riman, T. J. Emge, J. G. Brennan, *J. Am. Chem. Soc.* **2007**, *129*, 5923–5931.

[21] a) M. R. Bürgstein, M. T. Gamer, P. W. Roesky, *J. Am. Chem. Soc.* **2004**, *126*, 5213–5218; b) M. R. Bürgstein, P. W. Roesky, *Angew. Chem. Int. Ed.* **2000**, *39*, 549–551; c) R. Wang, D. Song, S. Wang, *Chem. Commun.* **2002**, 368–369.

[22] a) R. Wang, Z. Zheng, T. Jin, R. J. Staples, *Angew. Chem. Int. Ed.* **1999**, *38*, 1813–1815; b) R. Wang, H. D. Selby, H. Liu, M. D. Carducci, T. Jin, Z. Zheng, J. W. Anthis, R. J. Staples, *Inorg. Chem.* **2002**, *41*, 278–286.

[23] J.-W. Cheng, J. Zhang, S.-T. Zheng, M.-B. Zhang, G.-Y. Yang, *Angew. Chem. Int. Ed.* **2006**, *45*, 73–77.

[24] a) M. Romanelli, G. A. Kumar, T. J. Emge, R. E. Riman, J. G. Brennan, *Angew. Chem. Int. Ed.* **2008**, *47*, 6049–6051; b) B. F. Moore, G. A. Kumar, M.-C. Tan, J. Kohl, R. E. Riman, M. G. Brik, T. J. Emge, J. G. Brennan, *J. Am. Chem. Soc.* **2011**, *133*, 373–378.

[25] K. S. Jeong, Y. S. Kim, Y. J. Kim, E. Lee, J. H. Yoon, W. H. Park, Y. W. Park, S. J. Jeon, Z. H. Kim, J. Kim, N. Jeong, *Angew. Chem. Int. Ed.* **2006**, *45*, 8134–8138.

[26] a) J.-Y. Xu, B. Zhao, H.-D. Bian, W. Gu, S.-P. Yan, P. Cheng, D.-Z. Liao, P.-W. Shen, *Cryst. Growth Des.* **2007**, *7*, 1044–1048; b) X. J. Gu, D. F. Xue, *Inorg. Chem.* **2007**, *46*, 3212–3216.

[27] J. K. Tang, I. Hewitt, N. T. Madhu, G. Chastanet, W. Wernsdorfer, C. E. Anson, C. Benelli, R. Sessoli, A. K. Powell, *Angew. Chem. Int. Ed.* **2006**, *45*, 1729–1733.

[28] a) Z. Zheng, *Chem. Commun.* **2001**, 2521–2529; b) R. Wang, Z. Zheng, T. Z. Jin, R. J. Staples, *Angew. Chem. Int. Ed.* **1999**, *38*, 1813–1815; c) R. Wang, H. D. Selby, H. Liu, M. D. Carducci, T. Jin, Z. Zheng, J. W. Anthis, R. J. Staples, *Inorg. Chem.* **2002**, *41*, 278–286.

[29] N. Mahe, O. Guillou, C. Daiguebonne, Y. Gerault, A. Caneschi, C. Sangregorio, J. Y. Chane-Ching, P. E. Car, T. Roisnel, *Inorg. Chem.* **2005**, *44*, 7743–7750.

[30] P. C. Andrews, T. Beck, C. M. Forsyth, B. H. Fraser, P. C. Junk, M. Massi, P. W. Roesky, *Dalton Trans.* **2007**, 5651–5654.

[31] X.-J. Kong, Y. Wu, L.-S. Long, L.-S. Zheng, Z. Zheng, *J. Am. Chem. Soc.* **2009**, *131*, 6918–6919.

[32] F. Gándara, E. G. Puebla, M. Iglesias, D. M. Proserpio, N. Snejko, M. A. Monge, *Chem. Mater.* **2009**, *21*, 655–661.

[33] L. E. Sweet, L. E. Roy, F. Meng, T. Hughbanks, *J. Am. Chem. Soc.* **2006**, *128*, 10193–10201.

[34] L. Messerle, D. Nolting, L. Bolinger, A. H. Stolpen, B. F. Mullan, D. Swenson, M. Madsen, *Acad. Radiol.* **2005**, *12*, S46–56, and references cited therein.

[35] 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*, 9626–9627.

[36] J.-E. Bäckvall (Ed.), *Modern Oxidation Methods*, Wiley-VCH, Weinheim, Germany, **2004**.

[37] A. J. Wu, J. E. Penner-Hahn, V. L. Pecoraro, *Chem. Rev.* **2004**, *104*, 903–938.

[38] B. S. Lane, K. Burgess, *Chem. Rev.* **2003**, *103*, 2457–2474.

[39] T. Katsuki, *Chem. Soc. Rev.* **2004**, *33*, 437–444.

[40] T. Punniyamurthy, S. Velusamy, J. Iqbal, *Chem. Rev.* **2005**, *105*, 2329–2364.

[41] a) H. U. Blaser, B. Pugin, in: *Chiral Reactions in Heterogeneous Catalysis* (Eds.: G. Jannes, V. Dubois), Plenum, New York, **1995**; b) A. Baiker, H. U. Blaser, in: *Handbook of Heterogeneous* Catalysis (Eds.: G. Ertl, H. Knözinger, J. Weitkamp), vol. 5, Wiley-VCH, Weinheim, Germany, **1997**.

[42] a) S. Y. Seo, T. J. Marks, *Org. Lett.* **2008**, *10*, 317–319; b) J. Li, F. Xu, Y. Zhang, Q. Shen, *J. Org. Chem.* **2009**, *74*, 2575–2577; c) H. C. Aspinall, *Chem. Rev.* **2002**, *102*, 1807–1850.

[43] 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*, 186–216; b) M. Bougauchi, S. Watanabe, T. Arai, H. Sasai, M. Shibasaki, *J. Am. Chem. Soc.* **1997**, *119*, 2329–2330.

[44] V. R. Choudhary, R. Jha, P. Jana, *Green Chem.* **2006**, *8*, 689–690.

[45] a) F. Gándara, E. G. Puebla, M. Iglesias, D. M. Proserpio, N. Snejko, M. A. Monge, *Chem. Mater.* **2009**, *21*, 655–661; b) F. Gándara, A. García-Cortés, C. Cascales, B. Gómez-Lor, E. Gutiérrez-Puebla, M. Iglesias, A. Monge, N. Snejko, *Inorg. Chem.* **2007**, *46*, 3475–3485.

[46] a) H. Kakei, R. Tsuji, T. Ohshima, M. Shibasaki, *J. Am. Chem. Soc.* **2005**, *127*, 8962–8963; b) Q.-H. Xia, H.-Q. Ge, C.-P. Ye, Z.-M. Liu, K.-X. Su, *Chem. Rev.* **2005**, *105*, 1603–1662; c) T. Nemoto, H. Kakei, V. Gnanadesikan, S.-y. Tosaki, T. Ohshima, M. Shibasaki, *J. Am. Chem. Soc.* **2002**, *124*, 14544–14545.

[47] a) R. Sen, S. Bhunia, D. Mal, S. Koner, Y. Miyashita, K.-I. Okamoto, *Langmuir* **2009**, *25*, 13667–13672; b) R. Sen, R. Bera, A. Bhattacharjee, P. Gütlich, S. Ghosh, A. K. Mukherjee, S. Koner, *Langmuir* **2008**, *24*, 5970–5975; c) R. Sen, D. K. Hazra, S. Koner, M. Helliwell, M. Mukherjee, A. Bhattacharjee, *Polyhedron* **2010**, *29*, 3183–3191; d) R. Sen, D. K. Hazra, S. Koner, M. Helliwell, M. Mukherjee, *Eur. J. Inorg. Chem.* **2011**, 241–248.

[48] a) M. N. Sheng, G. J. Zajaczek, ARCO, U. K. Patent 1136923, **1968**; b) J. Halcon Kollar, U. S. Patent 3350422, **1967**.

[49] a) J. C. Medina, N. Gabriunas, E. Paez-Mozo, *J. Mol. Catal. A* **1997**, *115*, 233–239; b) D. E. De Vos, M. Dams, B. F. Sels, P. A. Jacobs, *Chem. Rev.* **2002**, *102*, 3615–3640.

[50] P. Anzenbacher Jr., V. Kral, K. Jursikova, J. Gunterova, A. Kasal, *J. Mol. Catal. A* **1997**, *118*, 63–68.

[51] P. Bhyrappa, J. K. Young, J. S. Moore, K. S. Suslick, *J. Mol. Catal. A* **1996**, *113*, 109–116.

[52] a) H. Sasai, T. Suzuki, S. Arai, T. Arai, M. Shibasaki, *J. Am. Chem. Soc.* **1992**, *114*, 4418–4420; b) H. Sasai, T. Suzuki, N. Itoh, K. Tanaka, T. Date, K. Okamura, M. Shibasaki, *J. Am. Chem. Soc.* **1993**, *115*, 10372–10373; c) R. F. Chen, C. T. Qian, J. G. de Vries, *Tetrahedron* **2001**, *57*, 9837–9842.

[53] *APEX 2*, *SAINT*, *XPREP*, Bruker AXS Inc., Madison, Wisconsin, USA, **2007**.

[54] *SADABS*, Bruker AXS Inc., Madison, Wisconsin, USA, **2001**.

[55] G. M. Sheldrick, *SHELXS97* and *SHELXL97: Programs for Crystal Structure Solution and Refinement*, University of Göttingen, Germany, **1997**.

Received: February 3, 2011
Published Online: May 13, 2011

