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Journal Name

ARTICLE

Lanthanide-based coordination polymers as the promising heterogeneous catalysts for ring-opening reactions

Gulshan Kumar,^a Girijesh Kumar^{a†} and Rajeev Gupta^{a*}Received 00th January 20xx,
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This work presents the synthesis and structural characterization of Eu³⁺- and Tb³⁺-based coordination polymers starting from a Co³⁺-based metalloligand offering appended arylcarboxylic acid groups. Both coordination polymers function as the reusable heterogeneous catalysts for the ring-opening reactions utilizing amines, alcohols, thiols, and azides as the nucleophiles. The catalytic results illustrate an excellent control over the regioselectivity whereas filtration test and mechanistic studies substantiate a Lewis – acid catalyzed activation of the epoxide during the reaction.

Introduction

Over the past few decades, extensive research has been devoted to develop coordination polymers (CPs) not only due to their structural diversity and fascinating molecular topologies¹ but also for their potential applications as a new class of materials in the field of sorption,² separation,³ ion-exchange,⁴ proton conduction,⁵ magnetism,⁶ luminescence,⁷ and catalysis.^{8,9} In particular, their emergence as the crystalline heterogeneous catalysts, having well-defined pores and channels, has opened novel avenues towards size- and shape-selective catalysis unprecedented from other polymeric materials including pillared clays and zeolites.¹⁰

The earlier synthetic protocols for the preparation of CPs were limited to mixing a suitable ligand and a desirable metal ion under the solvothermal conditions while leaving the structural diversity to a fair amount of serendipity.¹¹ The recent approaches are relying more and more on the directional bonding concept utilizing custom-made organic as well as metal-based precursors towards a rational approach for the synthesis of CPs.^{1,12} In this context, utilization of a well-defined metalloligand as the molecular building blocks offers several advantages over the conventional synthesis.^{1a,13} A metalloligand provides structural rigidity while offering the secondary binding sites; while the former structural feature induces elements of rational design,^{12a-c} the latter aspect ensures the viability of generating extended architectures. Our group has introduced a variety of metalloligands offering hydrogen bonding (H-bonding)¹⁴ as well as coordination bonding sensitive functional groups.¹⁵⁻¹⁸ The latter metalloligands have provided one- (1D), two- (2D), as well as three-dimensional (3D) CPs in a more rational manner.¹⁶⁻¹⁸ A few important characteristics offered by

such CPs were highly crystalline nature; robust architectures; presence of catalytically relevant secondary metal ions; and ubiquitous occurrence of labile water molecules on the catalytically-active sites. Several such features of our earlier crystalline CPs have allowed their utilization as the heterogeneous catalysts in various organic transformation reactions.¹⁶⁻¹⁸ Herein, we present the synthesis and characterization of two novel Eu³⁺ (**1-Eu**) and Tb³⁺ based (**1-Tb**) coordination polymers prepared using an arylcarboxylate appended Co³⁺-based metalloligand (**1**). Both CPs function as the reusable heterogeneous catalysts in ring-opening reactions utilizing assorted nucleophiles. In particular, we show remarkable catalytic applications of **1-Eu** and **1-Tb** in aminolysis, alcoholysis, thialysis, and azidolysis reactions.

Experimental section

Materials and Reagents

The solvents were purified as per as the standard literature method.¹⁹ Ligand H₂L and metalloligand Et₄N[Co(L)₂] (**1**) was synthesized according to our earlier report.^{18a}

Synthesis of [({1}Eu(OH₂)₅·8H₂O)_n (1-Eu). **1-Eu** was synthesized by layering a solution of metalloligand **1** (100 mg, 0.1004 mmol) in CH₃OH (4 mL) over Eu(CF₃SO₃)₃ (132 mg, 0.2209 mmol) dissolved in water (2 mL) with an intermediate layer of *tert*-butanol. After a period of 3–4 days, light green crystalline material resulted that was filtered and dried under vacuum. Yield: 208 mg (83 %). C₄₂H₅₀CoEuN₆O₂₅ (1250.137): calcd. C 40.36, H 4.03, N 6.72; found C 40.19, H 3.85, N 6.80. FTIR spectrum (Zn-Se ATR, selected peaks): (ν/cm⁻¹) = 3400 (OH), 1603, 1565 (C=O).

[({1}Tb(OH₂)₅·12H₂O)_n (1-Tb). **1-Tb** was synthesized by layering a CH₃OH solution of **1** (100 mg, 0.1004 mmol) over an aqueous solution (2 mL) of Tb(CF₃SO₃)₃ (133.4 mg, 0.2209 mmol) with an intermediate layer of *tert*-butanol. A pale green crystalline product was resulted at the interface of two solutions within 2 days that was filtered and dried under vacuum. Yield: 215 mg (86 %). C₄₂H₅₈CoTbN₆O₂₉ (1328.183): calcd. C 37.96, H 4.40, N 6.32; found: C 38.11, H 4.56, N 6.23. FTIR spectrum (Zn-Se ATR, selected peaks): (ν/cm⁻¹) = 3400 (OH), 1593, 1556 (C=O).

^a Department of Chemistry, University of Delhi, Delhi-110007, India.

E-mail: rgupta@chemistry.du.ac.in

Phone: +91-11-27666646; Fax: +91 - 11 - 2766 6605

Web: <http://people.du.ac.in/~rgupta/>

[†] Present Address: Department of Chemistry, Panjab University – Chandigarh, India.

Electronic Supplementary Information (ESI) available: [Figures for FTIR and diffuse-reflectance absorption spectra; TGA and DSC plots; PXRD plots; crystal structure; ¹H and ¹³C NMR spectra of organic products; and tables for the H-bonding distances]. CCDC No. 1439280 and 1439281. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/x0xx00000x.

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Physical measurements

The elemental analysis data were obtained with an Elementar Analysen Systeme GmbH Vario EL-III instrument. The NMR spectroscopic measurements were carried out with a Jeol 400 MHz spectrometer. The FTIR spectra were recorded with a Perkin-Elmer Spectrum-Two spectrometer having Zn-Se ATR. Gas chromatography (GC) and GC-MS studies were performed either with a Perkin Elmer Clarus 580 or Shimadzu QP 2010 instrument, with RTX-5SIL-MS column. Thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed with DTG 60 Shimadzu and TA-DSC Q200 instruments, respectively, at 5 °C min⁻¹ heating rate under nitrogen. The X-ray powder diffraction studies were performed either with an X'Pert Pro from PANalytical or a Bruker AXS D8 Discover instrument (Cu-K α radiation, λ = 1.54184 Å). The samples were ground and subjected to the range of θ = 5–35° with a scan rate of 1° per minute at room temperature.

Crystallography

Single-crystal X-ray diffraction data for **1-Eu** and **1-Tb** were collected on an Oxford XCalibur CCD diffractometer equipped with graphite monochromatic MoK α radiation (λ = 0.71073 Å).²⁰ For both CPs, frames were collected at 173(2) K. An empirical absorption correction was applied using spherical harmonics implemented in SCALE3 ABSPACK scaling algorithm.²⁰ The structures were solved by the direct methods using SIR-97²¹ and refined by the full-matrix least-squares refinement techniques on F^2 using the program SHELXL-97²² incorporated in the WINGX 1.8.05 crystallographic collective package.²³ The hydrogen atoms were fixed at the calculated position with isotropic thermal parameters except for C38 and C40 for **1-Tb**, whereas non-hydrogen atoms were refined anisotropically except for O11W for **1-Eu** and O6W1, O6W2, O8W1 and O8W2 for **1-Tb**. The lattice water molecules O6W, O9W and O10W in **1-Eu** and O6W and O8W in **1-Tb** were found to be positionally disordered and were solved using the PART command. For **1-Eu**, their positions were refined anisotropically with the site occupancy factors of 0.2730 (O6W), 0.7270 (O6W1), 0.2730 (O9W), 0.7270 (O9W1), 0.2730 (O10W) and 0.7270 (O14). However, for **1-Tb** their positions were refined isotropically with the site occupancy factors of 0.6900 (O6W1), 0.3100 (O6W2), 0.7700 (O8W1) and 0.2300 (O8W2). The hydrogen atoms on the carboxylic acid groups were added with fixed Uiso (1.2 of the parent atoms) using HFIX 83. Furthermore, hydrogen atoms of the coordinated as well as uncoordinated water molecules (except for O12W and O17W of **1-Tb**) could not be located from the Fourier map; however their contributions are included in the empirical formulae. Details of the crystallographic data collection and structural solution parameter are provided in Table 1.

Table 1 Crystallographic data collection and structural refinement parameters for **1-Eu** and **1-Tb**.

	1-Eu	1-Tb
Empirical formula	C ₄₂ H ₅₀ CoEuN ₆ O ₂₅	C ₈₄ H ₈₂ Co ₂ N ₁₂ O ₅₈ Tb ₂
Formula weight	1249.77	2623.32
T(K)	173(2)	173(2)

	Monoclinic	Triclinic
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$	$P-1$
a(Å)	20.9010(8)	11.4727(12)
b(Å)	9.7122(4)	15.695(2)
c(Å)	25.5412(16)	17.302(2)
α (°)	90	63.875(13)
β (°)	99.292(5)	79.754(10)
γ (°)	90	82.500(10)
V (Å ³)	5116.7(4)	2747.9(6)
Z	4	1
d [g cm ⁻³]	1.588	1.567
μ [mm ⁻¹]	1.629	1.672
$F(000)$	2432	1288
R (int.)	0.0546	0.1175
Final R indices ^a	$R_1 = 0.0442$	$R_1 = 0.0783$
[$>2\sigma(I)$]	$wR_2 = 0.1093$	$wR_2 = 0.1372$
R indices	$R_1 = 0.0537$	$R_1 = 0.1473$
(All data)	$wR_2 = 0.1142$	$wR_2 = 0.1667$
GOF on F^2	1.063	0.958
CCDC No.	1439280	1439281

$$^a R_1 = \sum ||F_o| - |F_c| | / \sum |F_o|; wR_2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [wF_o^4] \}^{1/2}$$

General Procedure for the Catalytic Reactions

Ring-opening reactions of the epoxides were carried out in oven-dried glassware. In a typical reaction, 1 equiv. of an epoxide was treated with 1.1 – 1.2 equiv. of the required nucleophile in presence of 2-mol% catalyst. The reaction mixture was stirred under ambient conditions for 4 h while progress of the reaction was monitored either by thin-layer chromatography (TLC) or GC. Subsequently, catalyst was filtered off after the addition of ethyl acetate. The organic layer was separated, washed with water (3–4 times), dried over anhydrous Na₂SO₄, followed by the removal of solvent under the reduced pressure. The organic product(s) were analyzed by the GC, GC-MS, and/or NMR techniques as and when required. The characterization data for a few representative products is provided below whereas their ¹H and ¹³C NMR spectra are included in Figure S16 – S31 in the Electronic Supporting Information.

Characterization Data for a Few Representative Products.

2-((4-Ethylphenyl)amino)cyclohexanol. ¹H NMR spectrum (400 MHz, CDCl₃): δ 7.00 (d, J = 8.4 Hz, 2H), 6.65 (d, J = 8.4 Hz, 2H), 3.34

(m, 1H), 3.11-3.05 (m, 1H), 2.8(brs, 2H), 2.56 (q, $J = 7.6$ Hz, 2H), 2.11-2.07 (m, 2H), 1.77-1.67 (m, 2H), 1.39-1.25 (m, 3H), 1.77 (t, $J = 7.6$, 3H), 1.06-0.95 (m, 1H). ^{13}C NMR spectrum (100 MHz, CDCl_3): δ 145.5, 134.4, 128.6, 114.6, 74.41, 60.5, 33.0, 31.5, 27.8, 25.0, 24.2, 15.9. HRMS (ESI): $[\text{M}+\text{H}]^+$ Calcd. for $[\text{C}_{14}\text{H}_{21}\text{NO}]$ 219.1623, found 220.2688.

2-Phenyl-2-(phenylamino)ethanol. ^1H NMR spectrum (400 MHz, CDCl_3): δ 7.40-7.41 (m, 4H), 7.28-7.24 (m, 1H), 7.09 (t, $J = 7.64$ Hz, 2H), 6.67 (t, $J = 7.64$ Hz, 1H), 6.56 (d, $J = 8.4$ Hz, 2H), 4.49 (q, $J = 3.84$, 1H), 3.92 (dd, $J = 4.56$ Hz and 11.4 Hz, 1H), 3.75-7.71 (m, 1H). ^{13}C NMR spectrum (100 MHz, CDCl_3): δ 147.2, 140.0, 129.1, 128.8, 127.6, 126.7, 117.8, 113.8, 67.3, 59.8. HRMS (ESI): $[\text{M}+\text{H}]^+$ Calcd. for $[\text{C}_{14}\text{H}_{15}\text{NO}]$ 213.11, found 214.2248.

2-Butoxy-2-phenylethanol. ^1H NMR spectrum (400 MHz, CDCl_3): δ 7.32 (d, $J = 3.2$ Hz, 4H), 7.28-7.24 (m, 1H), 3.97-3.94 (m, 1H), 3.84 (s, 2H), 2.46-2.44 (m, 2H), 2.04 (brs, 1H), 1.40-1.16 (m, 7H). ^{13}C NMR spectrum (100 MHz, CDCl_3): δ 139.7, 128.7, 128.0, 127.6, 65.5, 52.6, 25.1, 14.7. HRMS (ESI): $[\text{M}+\text{H}]^+$ Calcd. for $[\text{C}_{12}\text{H}_{18}\text{O}_2]$ 194.1307, found 194.1873.

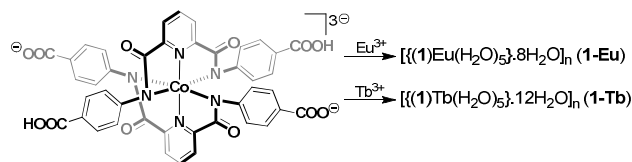
2-(tert-Butoxy)-2-phenylethanol. ^1H NMR spectrum (400 MHz, CDCl_3): δ 7.35-7.29 (m, 4H), 7.26-7.24 (m, 1H), 4.62-4.59 (m, 1H), 3.51-3.44 (m, 2H), 1.72 (brs, 1H), 1.16 (s, 9H). ^{13}C NMR spectrum (100 MHz, CDCl_3): δ 142.2, 128.2, 127.3, 126.3, 75.1, 74.9, 67.8, 28.8. HRMS (ESI): $[\text{M}+\text{H}]^+$ Calcd. for $[\text{C}_{12}\text{H}_{18}\text{O}_2]$ 194.1307, found 194.1873.

2-(Benzylthio)-2-phenylethanol. ^1H NMR spectrum (400 MHz, CDCl_3): δ 7.37-7.27 (m, 8H), 7.25-7.19 (m, 2H), 3.86-3.80 (m, 3H), 3.69-3.65 (m, 1H), 3.56-3.53 (m, 1H), 1.99 (brs, 1H). ^{13}C NMR spectrum (100 MHz, CDCl_3): δ 139.3, 137.8, 128.9, 128.7, 128.5, 128.2, 127.7, 127.1, 65.6, 51.9, 35.3. HRMS (ESI): $[\text{M}+\text{H}]^+$ Calcd. for $[\text{C}_{15}\text{H}_{16}\text{O}_1\text{S}_1]$ 244.0922, found 245.0753.

2-(Ethylthio)-2-phenylethanol. ^1H NMR spectrum (400 MHz, CDCl_3): δ 7.32-7.24 (m, 5H), 4.11-4.09 (m, 1H), 3.97-3.94 (m, 1H), 3.84-3.80 (m, 2H), 2.45-2.39 (q, $J = 6.1$, 2H), 1.24-1.16 (t, $J = 7.6$, 3H). ^{13}C NMR spectrum (100 MHz, CDCl_3): δ 139.7, 128.5, 127.9, 127.4, 65.5, 29.5, 25.0, 14.8. HRMS (ESI): $[\text{M}+\text{H}]^+$ Calcd. for $[\text{C}_{10}\text{H}_{14}\text{OS}]$ 182.0765, found 182.1831.

2-Azido-2-phenylethanol. ^1H NMR spectrum (400 MHz, CDCl_3): δ 7.33-7.25 (m, 5H), 4.60 (s, 3H), 2.1 (brs, 1H). ^{13}C NMR spectrum (100 MHz, CDCl_3): δ 140.8, 128.5, 127.6, 126.9, 65.2139.3, 137.8, 128.9, 128.7, 128.5, 128.2, 127.7, 127.1, 65.6, 51.9, 35.3.

3-Chloro-2-(phenylamino)propan-1-ol. ^1H NMR spectrum (400 MHz, CDCl_3): δ 7.19 (t, $J = 7.6$ Hz, 2H), 6.75 (t, $J = 7.6$ Hz, 1H), 6.65 (d, $J = 8.3$ Hz, 2H), 4.07-4.02 (m, 1H), 3.67-3.58 (m, 2H), 3.35 (dd, $J = 12.9$ Hz, 1H), 3.20 (dd, $J = 13.7$ Hz, 1H). ^{13}C NMR spectrum (100 MHz, CDCl_3): δ 129.4, 118.4, 114.1, 112.7, 68.8, 57.9, 47.3.



Scheme 1. Synthetic route for the preparation of coordination polymers **1-Eu** and **1-Tb**.

Results and discussion

Synthesis and characterization of CPs **1-Eu** and **1-Tb**

CPs **1-Eu** and **1-Tb** were synthesized by layering a solution of metalloligand **1** in CH_3OH over a solution of $\text{Ln}(\text{OTf})_3$ in H_2O with an intermediate layer of *tert*-butanol. Both CPs were isolated as pale green crystalline material in high yield. FTIR spectra (Fig. S1 and S2 in ESI) of both CPs show $\nu_{\text{O-H}}$ stretches between 3350 and 3410 cm^{-1} due to the presence of coordinated as well as lattice water molecules.²⁴ A strong band in 1560–1570 cm^{-1} region corresponds to amidic $\nu_{\text{C=O}}$ stretches.²⁴ TGA plots for CPs **1-Eu** and **1-Tb** support the presence of water molecules. For **1-Eu**, an observed weight loss of 18.12% fits nicely with the calculated value of 17.56% in the temperature range of 35–100 °C corresponding to the loss of five coordinated and seven lattice water molecules as observed crystallographically. Similarly, for **1-Tb**, a weight loss between 30 and 100 °C corresponded to the loss of 13 water molecules (obs. 17.99%; calcd. 17.64%). For both CPs, DSC studies display a broad exothermic feature for the loss of coordinated as well as lattice water molecules in the region of 30–150 °C (Fig. S3 and S4, ESI). Moreover, both TGA and DSC studies suggest thermal stability close to 370 °C for both CPs. The diffuse-reflectance absorption spectra of both CPs display signals at 470 and 635 nm (Fig. S5 and S6 in ESI). X-ray powder diffraction (XRPD) patterns were used to confirm the crystalline homogeneity and purity of the bulk products. The experimental XRPD patterns closely match the ones simulated from the single crystal diffraction data for both CPs (Fig. S7 and S8 in ESI), thereby indicating that a single crystalline phase has resulted during the bulk synthesis of the polymers.

Crystal structures

Both CPs, **1-Eu** and **1-Tb**, were crystallographically characterized and their structures are shown in Fig. 1 and 2 whereas tables 2 and 3 present the selected bonding parameters. The coordination polymer **1-Eu** crystallizes in monoclinic cell with $P2_1/n$ space group. The asymmetric unit cell of **1-Eu** consists of one Co^{3+} -based metalloligand, one Eu^{3+} ion, five coordinated and seven lattice water molecules. Similarly, **1-Tb** is found to crystallize in triclinic cell with $P-1$ space group and the asymmetric cell contains one metalloligand, one Tb^{3+} ion, five coordinated and twelve uncoordinated water molecules. In a metalloligand, two deprotonated tridentate ligands are arranged meridionally around the Co^{3+} ion maintaining a compressed octahedral geometry (Fig. 1a and 2a).¹⁸ The Co^{3+} ion is coordinated by four N_{amide} atoms in a distorted equatorial basal plane whereas two $\text{N}_{\text{pyridine}}$ atoms occupy the axial positions.¹⁸ The Eu^{3+} ion in **1-Eu** shows a nine-coordinate geometry wherein two bidentate arylcarboxylate groups stemming from two different metalloligands are present in *trans* manner whereas the remaining five sites are occupied by the water molecules (Fig. 1a). The Tb^{3+} ions in **1-Tb** are octa-coordinated by three $\text{O}_{\text{carboxylate}}$ atoms from two different metalloligands and five water molecules (Fig. 2a). Notably, in **1-Tb**, while one of the arylcarboxylate groups coordinates in a bidentate manner, the second one ligates in a monodentate form. In case of **1-Eu**, metalloligands coordinate to the europium ions and generate a 1D chain. Such parallel 1D chains are further connected to each other via an array of H-bonds involving amide, arylcarboxylate, and arylcarboxylic acid groups as well as coordinated and lattice water molecules (Fig. 1b). On the other hand, **1-Tb** exhibits the

coordination of two metalloligands to two Tb^{3+} ions resulting in the formation of a dimeric repeat unit (Fig. 2b). Such a bonding pattern has become possible due to the coordination of arylcarboxylate fragments on *syn* positions of the Tb^{3+} ion while originating from two different metalloligands. Subsequently, such dimeric repeat units extend via the operation of assorted H-bonds comprising of amide, arylcarboxylate, and arylcarboxylic acid groups as well as coordinated and lattice water molecules (Fig. 2c). In both polymers, a metalloligand provides three negative charge which is balanced by a Ln^{3+} ion. As a result, in both **1-Eu** and **1-Tb**, out of four, two arylcarboxylate groups remain protonated and therefore do not participate in coordinating the lanthanide metal ion. However, such arylcarboxylic acid groups participate in various H-bonding interactions and help in extending the structure to a 2D network (cf. Fig. 1c; Tables S1 and S2, ESI).

Fig. 1 and 2

Both **1-Eu** and **1-Tb** show several H-bonding interactions involving coordinated as well as lattice water molecules to that of metalloligands offering O_{amide} , arylcarboxylate, and arylcarboxylic acid groups. In **1-Eu**, one 1D chain is connected to the adjacent 1D chain via H-bonding of intervening water molecules (Fig. 1b and 1c). The O_{amide} atom O2 makes an H-bond with water molecule O8W which further connects to O11W which in turn is coordinated with O9 atom of arylcarboxylate group of another chain. The $O2 \cdots O8W$ and $O8W \cdots O11W$ separations were 2.786 Å and 2.836 Å, respectively. Similarly, O8 atom of arylcarboxylic acid shows H-bonding with O7W which is connected with O1W coordinated to the Eu^{3+} ion. The $O8 \cdots O7W$ and $O7W \cdots O1W$ separations were noted to be 2.852 Å and 2.812 Å, respectively. Additional H-bonding is provided by O1W of the Eu^{3+} centre of one 1D chain with O8W water molecule ($O1W \cdots O8W = 2.701$ Å) which further shows H-bonding with $O2_{amide}$ of the adjacent chain ($O8W \cdots O2 = 2.786$ Å).

Table 2 Selected bond lengths (Å) and bond angles (°) around the Co^{3+} ion in CPs **1-Eu** and **1-Tb**.

Bond	1-Eu	1-Tb
Co-N1	1.957(3)	1.945(7)
Co-N2	1.860(3)	1.862(6)
Co-N3	1.966(3)	1.934(7)
Co-N4	1.955(3)	1.953(7)
Co-N5	1.860(3)	1.853(6)
Co-N6	1.965(4)	1.949(7)
N1-Co1-N2	81.2(15)	81.6(3)
N1-Co1-N3	162.7(14)	163.4(3)
N1-Co1-N4	91.4(15)	92.2(3)
N1-Co1-N5	98.0(15)	97.1(3)
N1-Co1-N6	92.2(16)	89.8(3)
N2-Co1-N3	81.6(14)	81.7(3)
N2-Co1-N4	97.7(14)	97.6(3)
N2-Co1-N5	178.9(16)	178.5(3)
N2-Co1-N6	99.7(15)	98.2(3)
N3-Co1-N4	92.0(14)	90.0(3)
N3-Co1-N5	99.2(14)	99.5(3)
N3-Co1-N6	89.7(15)	92.5(3)
N4-Co1-N5	81.5(14)	81.6(3)
N4-Co1-N6	162.6(14)	164.2(3)
N5-Co1-N6	81.1(15)	82.6(3)

A somewhat similar H-bonding pattern is observed in case of CP **1-Tb** (Fig. 2b, 2c; and S9, ESI). The Tb^{3+} coordinated water molecule O1W in one chain shows H-bonding with O6 atom of the adjacent chain through intervening water molecules O10W, O15W and O16W ($O10 \cdots O1W = 2.709$ Å, $O6 \cdots O16W = 2.914$ Å). The $O3_{amide}$ of one chain shows H-bonding with $O2_{amide}$ of adjacent chain through the water molecule O14W in between them ($O3 \cdots O14W = 3.014$ Å and $O2 \cdots O14W = 2.826$ Å). The H-bonding is further extended by $O3_{amide}$ towards O8W ($O3 \cdots O8W = 2.762$ Å) which H-bonds to water molecule O10W while it further shows H-bonding with $O2_{amide}$ atom. The O_{amide} atom of one chain H-bonds to O6W which extends its H-bonding to O7 of an arylcarboxylate group of the next metalloligand within the same chain.

Table 3 Selected bond lengths (Å) and bond angles (°) around the lanthanide metal ion in CPs **1-Eu** and **1-Tb**. M stands for Eu and Tb in **1-Eu** and **1-Tb**, respectively.

Table 3: At the end

It is notable that a combination of such H-bonding interactions connects individual 1D chains to generate interesting H-bonded 2D architectures in both CPs. The H-bonding distances illustrate moderate to strong nature of the hydrogen bonding in both CPs (Tables S1 and S2, ESI). Such bonding features suggest a stable nature of H-bonded architectures in both CPs. In fact, TGA and DSC studies adequately display thermal stabilities of both CPs close to 370 °C. Therefore, both CPs highlight the importance of H-bonding in the construction of stable 2D architectures.

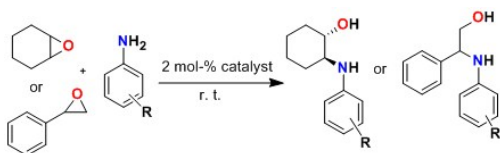
Catalytic applications of **1-Eu** and **1-Tb**

Both CPs offered several structural features that suggested their potential application in the catalysis: (i) 1D chain like structures of two CPs suggest the uncluttered access of substrates towards the lanthanide metals; (ii) presence of a large number of coordinated yet labile water molecules on both Eu^{3+} and Tb^{3+} ions point towards their facile replacement by the substrate(s); (iii) strong Lewis acidic nature of Eu^{3+} and Tb^{3+} ions; (iv) thermal stability of both CPs, close to ca. 370 °C, provide an option to carry out the reactions at elevated temperature; (v) existence of H-bonded network advocates the possibility of substrates and nucleophiles to have favorable interaction within the CPs; and (vi) insolubility of two CPs in common organic solvents provide an option to do the reactions heterogeneously.

Ring-opening reactions (RORs) of epoxides with various nucleophiles provide an easy access to a large number of intermediates widely desired in the synthesis of pharmaceutically and industrially important compounds.^{25–27} Importantly, RORs of epoxides can be accomplished with versatile nucleophiles such as amine, alcohol, thiol, cyanide, azide, etc. thus opening up the possibility to access assorted products. For example, azidolysis of epoxides produces 1,2-azidoalcohols which play crucial role as the precursors to vicinal amino alcohols.²⁸ Similarly, β -hydroxysulfide, the product of thialysis reaction, is a significant synthon for the synthesis of a number of biological and pharmacological relevant compounds.²⁹ In literature, RORs of epoxides with amine as the nucleophile (amilolysis) have been extensively studied; however, use of other nucleophiles such as alcohol, azide, and thiol has rarely been studied.^{16a,28,29} Further, activation of an epoxide ring has been

considered as a critical step during the RORs. Such an activation has been typically achieved using a suitable Lewis acidic metal ion although other chemicals, reagents, and even conditions have also been utilized.²⁵⁻²⁷ Out of various metal salts, lanthanide salts and in particular lanthanide triflate salts have been particularly successful.³⁰ Lately, there have been attempts to heterogenize the lanthanide-based catalysts considering their high Lewis acidic character.³¹ In this context, coordination polymers incorporating lanthanide metal ions are notable.^{16a,31} Keeping these points in perspective, we attempted to utilize the present Eu^{3+} and Tb^{3+} based coordination polymers, **1-Eu** and **1-Tb**, as the heterogeneous catalysts for the RORs.

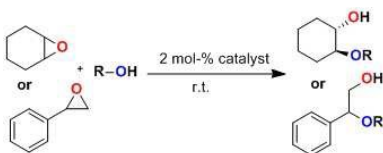
Table 4 Ring-opening reactions of cyclohexene oxide and styrene oxide with aniline and *para*-substituted anilines by using CPs **1-Eu** and **1-Tb**.



Entry	R-	Time(h)	Yield [%] ^a	
			1-Eu	1-Tb
1	H	4	98, 97, ^b 96 ^c	97, 95, ^b 95 ^c
2	C ₂ H ₅	4	98	97
3	CH ₃ O	4	99	98
4	Cl	4	96	97
5	F	4	98	98
6	NO ₂	6	96	95
7	H	4	92, 91, ^b 90 ^c	94, 93, ^b 92 ^c
8	C ₂ H ₅	4	88	92
9	CH ₃ O	4	90	91
10	Cl	4	96	95
11	F	4	79	80

^a The yields were calculated using the gas chromatograph. ^b Third run with the reused catalyst. ^c Fifth run with the reused catalyst.

Table 5 Ring-opening reactions of cyclohexene oxide and styrene oxide with various alcohols by using CPs **1-Eu** and **1-Tb**.



Entry	Epoxide ^a	R-OH	Product (R-)	Yield [%] ^b	
				1-Eu	1-Tb
1	C. O.	(CH ₃) ₃ COH	(CH ₃) ₃ C-	78	80
2	C. O.	CH ₃ CH ₂ CH(CH ₃)OH	CH ₃ CH ₂ CH(CH ₃)-	76	78
3	C. O.	(CH ₃) ₂ CHOH	(CH ₃) ₂ CH-	83	84
4	C. O.	C ₆ H ₅ CH ₂ OH	C ₆ H ₅ CH ₂ -	99	97
5	S. O.	(CH ₃) ₃ COH	(CH ₃) ₃ C-	99	98
6	S. O.	CH ₃ CH ₂ CH(CH ₃)OH	CH ₃ CH ₂ CH(CH ₃)-	98	96
7	S. O.	(CH ₃) ₂ CHOH	(CH ₃) ₂ CH-	99	97
8	S. O.	C ₆ H ₅ CH ₂ OH	C ₆ H ₅ CH ₂ -	92	96

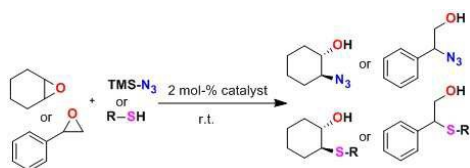
^a C.O. and S.O. stand for cyclohexene oxide and styrene oxide, respectively. ^b The yields were calculated using the gas chromatograph.

Thus, when an equimolar mixture of cyclohexene oxide and aniline was stirred in presence of 2-mol% of CPs **1-Eu** or **1-Tb** at room temperature under the solvent-free condition; a smooth reaction produced 2-(phenylamino)cyclohexanol in high yield (>97%; entry 1, Table 4). To evaluate the impact of electronic effect on the RORs, several *para*-substituted anilines containing assorted functional groups were employed (Entries 2–6; Table 4). Satisfyingly, high product yield was observed in all cases (95%–99%) irrespective of the nature of electronic substituent. Notably, the catalytic reaction did not proceed in absence of **1-Eu** and **1-Tb** thus supporting the probable Lewis acid catalyzed activity of both CPs. Moreover, in a control experiment using $\text{Eu}(\text{OTf})_3$ or $\text{Tb}(\text{OTf})_3$ as the catalyst, only 5 – 8% conversion was noted (data not shown). These experiments endorse that CPs **1-Eu** and **1-Tb** are responsible for the enhanced product yield. In order to avoid competition from the solvent molecules and greener reasons; all reactions were performed under the solvent-free conditions. However, use of solvents did not seem to improve the catalysis results (data not shown). Styrene oxide, an unsymmetrical epoxide, was selected to understand the regioselectivity. Thus, when styrene oxide was treated with assorted substituted anilines in presence of **1-Eu** and **1-Tb**; nucleophilic attack exclusively took place at the benzylic carbon atom of the epoxide (Entries 7–11; Table 4). The results suggest that the epoxide ring has potentially interacted with the lanthanide ion through the less-hindered side as noted before with our earlier heterogeneous catalysts.^{17,18}

We then extended the catalysis towards less common nucleophiles. Both CPs **1-Eu** and **1-Tb** worked effortlessly for the RORs of cyclohexene oxide as well as styrene oxide using a variety of alcohols as the nucleophiles (alcoholysis). Despite the poor nucleophilicity of alcohols, 80 to >99% product formation took place within 4 h as also noted for aminolysis (Table 5). In fact, nearly quantitative transformation was observed with various alcohols both with cyclohexene oxide and styrene oxide. In case of cyclohexene oxide, products were obtained as the single diastereoisomer with *trans* stereochemistry. On the other hand, styrene oxide again afforded a single regioisomer through the incorporation of alcohol at the phenyl-substituted carbon atom, as expected for a charge-controlled ring-opening process, irrespective of the nature of the alcohol.

Our next nucleophile was azide (azidolysis) and we selected trimethylsilyl azide for this purpose. Under the identical reaction conditions, both cyclohexene oxide and styrene oxide provided good to excellent conversion to the respective β -azido alcohols (Entries 1 and 4; Table 6). As noted for aminolysis and alcoholysis reactions; azidolysis of styrene oxide showed the regioselective product formation wherein azide preferentially attacked from the less hindered side of the epoxide that resulted in a single product.

Thialysis of cyclohexene oxide and styrene oxide afforded the corresponding products in 82 to 92% yield (Entries 2,3 and 5,6; Table 6). It may appear that thialysis reactions are slower in comparison to aminolysis, alcoholysis, and azidolysis reactions; but we did not increase the reaction time as well as temperature (25 °C) for a better comparison. The thialysis of cyclohexene oxide provided the stereo-selective *trans*- β -hydroxysulfide as the only product whereas styrene oxide afforded the exclusive regioselective products (Entries 5– 6; Table 6). It is important to mention that the use of azides (azidolysis) and thiols (thialysis) as the nucleophiles are far less common when compared to well-explored aminolysis and alcoholysis reactions.^{28,29}

Table 6 Ring-opening reactions of cyclohexene oxide and styrene oxide with trimethylsilyl azide (TMSN₃) and thiols by using CPs **1-Eu** and **1-Tb**.

Entry	Epoxide	Nucleophiles	Yield[%] ^a	
			1-Eu	1-Tb
1	C. O.	TMS-azide	99	99
2	C. O.	Benzyl thiol	89	90
3	C. O.	Ethane thiol	91	89
4	S. O.	TMS-azide	99	99
5	S. O.	Benzyl thiol	82	86
6	S. O.	Ethane thiol	86	84

^a The yields were calculated using the gas chromatograph.

Table 7 Ring-opening reactions of assorted epoxides with various nucleophiles by using CPs **1-Eu** and **1-Tb**.

Entry ^a	Substrate	Aniline		<i>tert</i> -Butyl phenol		<i>tert</i> -Butyl aniline	
		1-Eu / 1-Tb	1-Eu / 1-Tb	1-Eu / 1-Tb	1-Eu / 1-Tb	1-Eu / 1-Tb	
1		100/99	100/98	81/84	98/97		
2		80/82	70/76	79/82	100/99		
3		83/86	82/84	94/92	94/95		
4		100/98	100/99	83/85	97/99		
5		100/100	97/98	93/91	83/86		

^a The yields were calculated using the gas chromatograph.

To further establish the critical issue of regioselectivity, assorted unsymmetrical epoxides were investigated (Entries 1-4; Table 7).^{18b} Importantly, these substrates offer an epoxide ring in addition to intricately placed substituents. Moreover, various nucleophiles were used to understand their role in controlling the product regioselectivity (Table 7). Satisfyingly, in each case, a perfect regioselectivity was noticed in the form of a single product. Notably, in most cases, regioselectivity has not affected the product yield and high to excellent yield was noticed. These experiments confirm that the nucleophile has exclusively attacked on the less hindered side of the epoxide ring and the regioselectivity is controlled by the steric factor rather than resonance effect as a prevailing cause in a few substrates, such as styrene oxide.^{18b}

Leaching and Recyclability Experiments

To ascertain the true heterogeneous nature of catalysis and to make sure that the lanthanide metal ions are not leached out

during the catalysis, a filtration test was performed using **1-Eu** in the aminolysis reaction of styrene oxide with aniline (Fig. 3). In a typical reaction, **1-Eu** completes the ROR of styrene oxide with aniline within 4 h. However, taking the advantage of heterogeneous catalysis, if solid **1-Eu** is filtered off after 2 h and the reaction is allowed to continue; as shown in Fig. 3, there was practically no catalysis. Subsequently, re-addition of recovered **1-Eu** after a gap of 1.5 h immediately started the ROR. An overall profile illustrates that the removal of **1-Eu** ceases the ROR whereas its re-addition to the reaction restarts the ROR. This simple test establishes the *true* heterogeneous catalytic behavior of **1-Eu** and asserts that the lanthanide metal ions are not leached out from the CPs.

Both solid CPs, **1-Eu** and **1-Tb**, can easily be separated from the heterogeneous reaction mixture by simple filtration; a feature unique to the heterogeneous and solid immobilized catalysts.^{18b,c} Such a fact conveniently allows studying the recyclability of the heterogeneous catalysts. Importantly, both CPs can be easily recovered by filtration after the reaction and reused several times. We tested both CPs for five consecutive times (Entries 1 and 7, Table 4) and observed comparable catalytic activity with less than 2% drop in yield in the fifth run. The FTIR spectra of the recovered polymers exactly match to that of pristine samples (Fig. S10 and S11, ESI) whereas a comparison of PXRD patterns of the as-synthesized samples to that of recovered CPs authenticate that the crystallinity as well as the structural integrity of both polymers is preserved during the catalysis (Fig. S12 and S13, ESI).

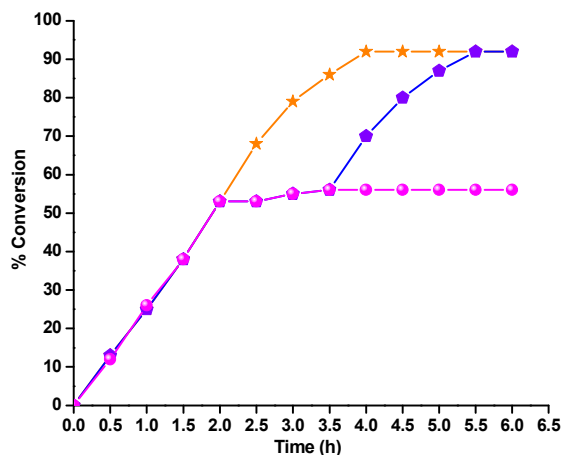


Fig. 3 (a) Ring-opening reaction of styrene oxide with aniline in presence of coordination polymer **1-Eu** (★); (b) catalyst **1-Eu** was filtered after 2 h leading to termination of reaction (●); (c) Catalyst **1-Eu** was re-added after 1.5 h causing commencement of the reaction (●) and leading to completeness.

Mechanistic insight

Our catalysis results primarily rely on the fact that the coordinated water molecules present on the lanthanide metals are labile and are easily replaceable. Such a critical step allows a substrate to interact with the lanthanide metal ion before its activation followed by reaction with the nucleophile. Therefore, in order to strengthen the suggested mechanistic proposal; it became essential to evaluate that the coordinated water molecules are indeed labile in nature

and the substrates and/or reagents are able to replace them; solvent exchange studies were performed. For such an experiment, powdered samples of both CPs were first heated at 150 °C under vacuum to remove lattice as well as coordinated water molecules followed by allowing the sample to equilibrate in a sealed environment of D₂O vapors. Such an experiment resulted in clean exchange of H₂O by D₂O and the $\nu_{\text{O-D}}$ stretches were observed at ca. 2500 cm⁻¹ with a shift of ca. 1000 cm⁻¹ from $\nu_{\text{O-H}}$ stretches (Fig. S14 and S15, ESI). It is important to mention that such a D₂O-exchange led to nearly complete replacement of both coordinated and lattice water molecules, therefore, firmly establishing the labile nature of the coordinated water molecules. We therefore suggest that a substrate could easily replace the coordinated water molecule(s) followed by its activation by the Lewis acidic lanthanide metal ion before a nucleophile attacks to produce the desired product.

Conclusions

This work has shown the synthesis and characterization of Eu- and Tb-based coordination polymers that were synthesized using a Co-based metalloligand offering appended arylcarboxylate groups. Both coordination polymers displayed the generation of 2D architectures due to the involvement of various intermolecular H-bonds whereas thermal studies illustrated the stable nature of the 2D architecture. Both coordination polymers functioned as the heterogeneous catalysts for the ring-opening reactions of assorted epoxides utilizing several nucleophiles. The illustration of regio-selective ring-opening reactions; solvent-free catalytic conditions; and reusability of both catalysts depicted the importance of lanthanide-based coordination polymers in the heterogeneous catalysis.

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Notes and references

- (a) G. Kumar and R. Gupta, *Chem. Soc. Rev.*, 2013, **42**, 9403; (b) G. Ferey, *Chem. Soc. Rev.*, 2008, **37**, 191; (c) M. Eddaoudi, D. B. Moler, H. Li, B. Chen, T. M. Reineke, M. O'Keeffe and O. M. Yaghi, *Acc. Chem. Res.*, 2001, **34**, 319; (d) M. O'Keeffe and O. M. Yaghi, *J. Solid State Chem.*, 2005, **178**, 5; (e) R. Sessoli and A. K. Powell, *Coord. Chem. Rev.*, 2009, **253**, 2328; (f) M. Kurmoo, *Chem. Soc. Rev.*, 2009, **38**, 1353; (g) R. J. Kuppler, D. J. Timmons, Q.-R. Fang, J.-R. Li, T. A. Makal, M. D. Young, D. Yuan, D. Zhao, W. Zhuang and H.-C. Zhou, *Coord. Chem. Rev.*, 2009, **253**, 3042.
- (a) L. Pan, D. H. Olson, L. R. Ciemnomolonski, R. Heddy and J. Li, *Angew. Chem., Int. Ed.*, 2006, **45**, 616; (b) J. R. Li, R. J. Kuppler and H. C. Zhou, *Chem. Soc. Rev.*, 2009, **38**, 1477.
- (a) M. O'Keeffe and O. M. Yaghi, *Chem. Rev.*, 2012, **112**, 675; (b) D. J. Tranchemontagne, J. L. Mendoza-Cortes's, M. O'Keeffe and O. M. Yaghi, *Chem. Soc. Rev.*, 2009, **38**, 1257.
- (a) C. K. Brozek and M. Dinca, *Chem. Soc. Rev.*, 2014, **43**, 5456; (b) P. Ramaswamy, N. E. Wong and G. K. H. Shimizu, *Chem. Soc. Rev.*, 2014, **43**, 5913.
- (a) S. Sen, N. N. Nair, T. Yamada, H. Kitagawa and P. K. Bharadwaj, *J. Am. Chem. Soc.*, 2012, **134**, 19432; (b) M. Sadakiyo, T. Yamada and H. Kitagawa, *J. Am. Chem. Soc.*, 2014, **136**, 13166; (c) M. Sadakiyo, T. Yamada and H. Kitagawa, *J. Am. Chem. Soc.*, 2009, **131**, 9906.
- (a) X. N. Cheng, W. X. Zhang, Y. Y. Lin, Y. Z. Zheng and X. M. Chen, *Adv. Mater.*, 2007, **19**, 1494; (b) X. Y. Wang, Z. M. Wang and S. Gao, *Chem. Commun.*, 2008, 281.
- (a) J. H. Deng, X. L. Yuan and G. Q. Mei, *Inorg. Chem. Commun.*, 2010, **13**, 1585; (b) Q. Y. Yang, K. Li, J. Luo, M. Pan and C. Y. Su, *Chem. Commun.*, 2011, **47**, 4234.
- (a) L. Q. Ma, C. Abney and W. B. Lin, *Chem. Soc. Rev.*, 2009, **38**, 1248; (b) J. Liu, L. Chen, H. Cui, J. Zhang, L. Zhang and C.-Y. Su, *Chem. Soc. Rev.*, 2014, **43**, 6011; (c) A. Dhakshinamoorthy and H. Garcia, *Chem. Soc. Rev.*, 2014, **43**, 5750; (d) A. Corma, H. Garcia and F. X. L. I. Xamena, *Chem. Rev.*, 2010, **110**, 4606; (e) J. Y. Lee, O. K. Farha, J. Roberts, K. A. Scheidt, S. B. T. Nguyen and J. T. Hupp, *Chem. Soc. Rev.*, 2009, **38**, 1450.
- (a) M. Fujita, Y. J. Kwon, S. Washizu and K. Ogura, *J. Am. Chem. Soc.*, 1994, **116**, 1151; (b) D. Jiang, T. Mallat, F. Krumeich and A. Baiker, *J. Catal.*, 2008, **257**, 390; (c) M. J. Ingleson, J. P. Barrio, J. Bacsá, C. Dickinson, H. Park and M. J. Rosseinsky, *Chem. Commun.*, 2008, 1287; (d) B. Xiao, H. Hou and Y. Fan, *J. Organomet. Chem.*, 2007, **692**, 2014; (e) L. Alaerts, E. Séguin, H. Poelman, F. Thibault-Starzyk, P. A. Jacobs and D. E. D. Vos, *Chem.-Eur. J.*, 2006, **12**, 7353.
- (a) T. J. Pinnavaia, *Science*, 1983, **220**, 365; (b) M. E. Davis, *Acc. Chem. Res.*, 1993, **26**, 111; (c) J. T. Hupp and K. R. Poeppelmeier, *Science*, 2005, **309**, 2008; (d) A. Gil, L. M. Gandia and M. A. Vicente, *Catal. Rev.*, 2000, **42**, 145; (e) F. Bedioui, *Coord. Chem. Rev.*, 1995, **144**, 39.
- (a) B. F. Abrahams, A. Hawley, M. G. Haywood, T. A. Hudson, R. Robson and D. A. Slizys, *J. Am. Chem. Soc.* 2004, **126**, 2894; (b) R. Robson, *J. Chem. Soc., Dalton Trans.*, 2000, 3735; (c) R. W. Saalfrank, H. Maid and A. Scheurer, *Angew. Chem. Int. Ed.* 2008, **47**, 8794.
- (a) T. R. Cook, Y.-R. Zheng and P. J. Stang, *Chem. Rev.*, 2013, **113**, 734; (b) R. Chakrabarty, P. S. Mukherjee and P. J. Stang, *Chem. Rev.*, 2011, **111**, 6810; (c) S. Leininger, B. Olenyuk and P. J. Stang, *Chem. Rev.*, 2000, **100**, 853; (d) J. W. Colson and W. R. Dichtel, *Nat. Chem.* 2013, **5**, 453; (e) M. Kondracka and U. Englert, *Inorg. Chem.* 2008, **47**, 10246; (f) S.-I. Noro, *Phys. Chem. Chem. Phys.*, 2010, **12**, 2519; (g) C. Marchal, Y. Filinchuk, D. Imbert, J.-C. G. Bunzli and M. Mazzanti, *Inorg. Chem.* 2007, **46**, 6242.
- (a) Y. Huang, T. Liu, J. Lin, J. Lu, Z. Lin and R. Cao, *Inorg. Chem.* 2011, **50**, 2191; (b) S. Kitagawa, S. Noro, T. Nakamura, *Chem. Commun.* 2006, 701; (c) P. Chaudhuri, V. Kataev, B. Buchner, H.-H. Klaus, B. Kersting and F. Meyer, *Coord. Chem. Rev.* 2009, **253**, 2261; (d) M. C. Das, S. Xiang, Z. Zhang and B. Chen, *Angew. Chem. Int. Ed.* 2011, **50**, 10510; (e) L. Carlucci, G. Ciani, S. Maggini, D. M. Proserpio and M. Visconti, *Chem. Eur. J.* 2010, **16**, 12328; (f) S. R. Halper, L. Do, J. R. Stork and S. M. Cohen, *J. Am. Chem. Soc.* 2006, **128**, 15255.
- (a) A. Ali, G. Hundal and R. Gupta, *Cryst. Growth Des.* 2012, **12**, 1308; (b) G. Kumar, H. Aggarwal and R. Gupta, *Cryst. Growth Des.* 2013, **13**, 74; (c) S. Srivastava, H. Aggarwal and R. Gupta, *Cryst. Growth Des.* 2015, **15**, 4110; (d) A. Ali, D. Bansal and R. Gupta, *J. Chem. Sci.* 2014, **126**, 1535.
- (a) A. Mishra, A. Ali, S. Upreti and R. Gupta, *Inorg. Chem.* 2008, **47**, 154; (b) A. Mishra, A. Ali, S. Upreti, M. S. Whittingham and R. Gupta, *Inorg. Chem.* 2009, **48**, 5234; (c) A. P. Singh and R. Gupta, *Eur. J. Inorg. Chem.* 2010, 4546. (d)

- S. Srivastava, A. Ali, A. Tyagi, and R. Gupta, *Eur. J. Inorg. Chem.* 2014, 2113; (e) S. Srivastava, M. S. Dagur, A. Ali and R. Gupta, *Dalton Trans.*, 2015, **44**, 17453.
- 16 (a) G. Kumar, A. P. Singh and R. Gupta, *Eur. J. Inorg. Chem.* 2010, 5103; (b) A. P. Singh, A. Ali and R. Gupta, *Dalton Trans.* 2010, **39**, 8135; (c) A. P. Singh, G. Kumar and R. Gupta, *Dalton Trans.* 2011, **40**, 12454; (d) S. Srivastava, M. S. Dagur and R. Gupta, *Eur. J. Inorg. Chem.* 2014, 4966; (e) G. Kumar and R. Gupta, *Inorg. Chem. Commun.* 2012, **23**, 103; (f) G. Kumar, G. Kumar and R. Gupta, *Inorg. Chim. Acta*, 2015, **425**, 260.
- 17 (a) D. Bansal, G. Hundal and R. Gupta, *Eur. J. Inorg. Chem.* 2015, 1022; (b) D. Bansal, S. Pandey, G. Hundal and R. Gupta, *New J. Chem.*, 2015, **39**, 9772.
- 18 (a) G. Kumar and R. Gupta, *Inorg. Chem.* 2012, **51**, 5497; (b) G. Kumar and R. Gupta, *Inorg. Chem.* 2013, **52**, 10773; (c) G. Kumar, G. Kumar and R. Gupta, *Inorg. Chem.* 2015, **54**, 2603.
- 19 D. D. Perrin, W. L. F. Armarego and D. R. Perrin, *Purification of Laboratory Chemicals*; Pergamon Press: Oxford, 1980.
- 20 CrysAlisPro, version 1.171.33.49b; Oxford Diffraction Ltd.: Abingdon, UK, 2009.
- 21 A. Altomare, G. Cascarano, C. Giacovazzo and A. J. Guagliardi, *Appl. Crystallogr.* 1993, **26**, 343.
- 22 G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2008, **64**, 112.
- 23 L. J. Farrugia, *WinGX-Version 1.80.05 - An Integrated System of Windows Programs for the Solution, Refinement and Analysis of Single Crystal X-Ray Diffraction Data*, (1997-2009) Dept. of Chemistry, University of Glasgow; L. J. Farrugia, *J. Appl. Crystallogr.*, 1999, **32**, 837.
- 24 (a) K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, John Wiley & Sons, 1986.
- 25 (a) M. E. Connolly, F. Kersting and C. T. Dollery, *Prog. CardioVasc. Dis.* 1976, **19**, 203; (b) D. J. Triggle, in *Burger's Medicinal Chemistry*, 4th ed. (Ed.: M. S. Wolff), Wiley-Interscience, New York, 1981, p. 225.
- 26 (a) J. De Cree, H. Geukens, J. Leempoels and H. Verhaegen, *Drug Dev. Res.* 1986, **8**, 109; (b) R. R. Young, J. H. Gowen and B. T. Shahani, *N. Engl. J. Med.* 1975, **293**, 950; (c) J. Joossens, P. Vander-Veken, A. M. Lambeir, K. Augustyns and A. Haemers, *J. Med. Chem.* 2004, **47**, 2411.
- 27 (a) D. M. Hodgson, A. R. Gibbs and G. P. Lee, *Tetrahedron* 1996, **52**, 14361; (b) E. N. Jacobsen and M. H. Wu, in *Comprehensive Asymmetric Catalysis* (Eds.: E. N. Jacobsen, A. Pfaltz, H. Yamamoto), Springer, New York, 1999, chapter 35.
- 28 (a) *The Chemistry of the Azido Group*; S. Patai, Ed.; Wiley: New York, 1971; (b) E. F. V. Scriven and K. Turnbull, *Chem. Rev.* 1988, **88**, 297; (c) D. M. Coe, P. L. Myers, D. M. Parry, S. M. Roberts and R. J. Storer, *Chem. Soc., Chem. Commun.* 1990, 151; (d) G. A. Jacobs, J. A. Tino and R. Zahler, *Tetrahedron Lett.* 1989, **30**, 6955; (e) J. H. L. Spelberg, J. E. T. V. H. Vlieg, L. Tang, D. B. Janssen and R. M. Kellogg, *Org. Lett.*, 2001, **3**, 41.
- 29 (a) M. Sander, *Chem. Rev.* 1966, **66**, 297; (b) Q. Dong, X. Fang, J. D. Schroeder and D. S. Garvey, *Synthesis* 1999, 1106; (c) M. S. Reddy, K. Surendra, S. Krishnaveni, M. Narender and K. Rama Rao, *Helv. Chim. Acta* 2007, **90**, 337; (d) H. Takeuchi, Y. Nakajima, *J. Chem. Soc., Perkin Trans. 2* 1998, 2441.
- 30 (a) S. Kobayashi, M. Sugiura, H. Kitagawa and W. W.-L. Lam, *Chem. Rev.* 2002, **102**, 2227; (b) M. Shibusaki and N. Yoshikawa, *Chem. Rev.* 2002, **102**, 2187; (c) S. Kobayashi, *Synlett* 1994, 689; (d) R. W. Marshman, *Aldrichimica Acta* 1995, **28**, 77; (e) S. Kobayashi, *Eur. J. Org. Chem.* 1950, **15**, 5; (f) S. Kobayashi, *Chem. Lett.* 1991, 2187.
- 31 T. M. Reineke, M. Eddaoudi, M. O'Keeffe and O. M. Yaghi, *Angew. Chem. Int. Ed.* 1999, **38**, 2590.

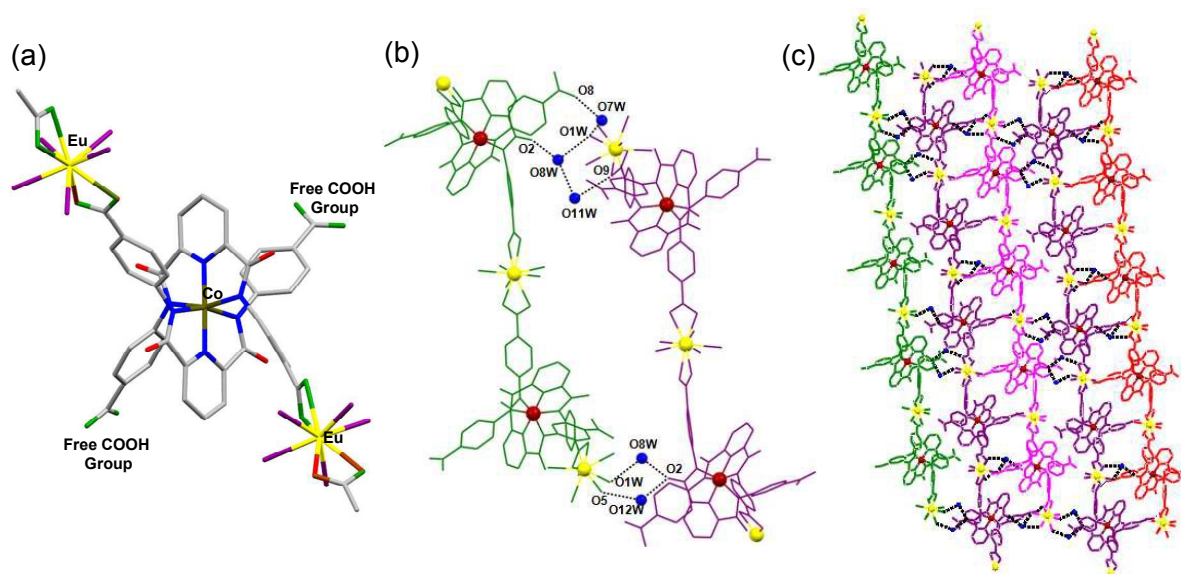


Fig. 1 (a) Partial crystal structure of **1-Eu** showing the coordination environment around the Eu^{3+} center and its bonding with the metalloligand; hydrogen atoms and solvent molecules have been omitted for clarity. (b) A section of crystal structure of **1-Eu** displaying arrangements of metalloligands and Eu^{3+} ions generating 1D chains (shown in green and magenta colours). Lattice water molecules, shown as blue balls, help in connecting two 1D chains to a double chain. (c) A view of 2D network created due to various H-bonding interactions involving free arylcarboxylic acid groups, O_{amide} groups, and coordinated as well as lattice water molecules connecting various 1D chains (shown in green, magenta, pink, and red colours). See text for details.

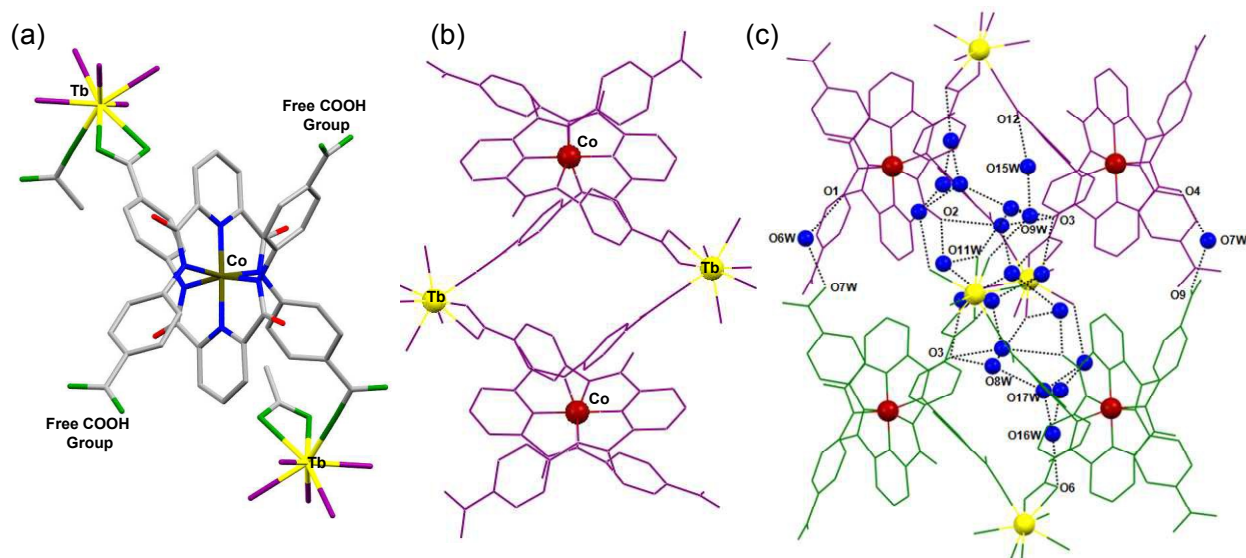


Fig. 2 (a) Partial crystal structure of **1-Tb** showing the coordination environment around the Tb^{3+} center and its bonding with the metalloligand; hydrogen atoms and solvent molecules have been omitted for clarity. (b) A section of crystal structure of **1-Tb** exhibiting coordination of Tb^{3+} ions to that of metalloligands generating 1D zig-zag chains. (c) Lattice water molecules, shown in blue balls, help in connecting 1D chains (shown in green and magenta colours) involving various weak interactions. See text for details.

Table 3 Selected bond lengths (Å) and bond angles (°) around the lanthanide metal ion in CPs **1-Eu** and **1-Tb**. M stands for Eu and Tb in **1-Eu** and **1-Tb**, respectively.

Bond	1-Eu	1-Tb	Bond	1-Eu	1-Tb
M-O5	2.444(3)	2.420(5)	^{2#} O6-M-O5W	87.05(14)	76.9(2)
M-O6	2.426(3)	2.431(6)	O9-M-O1W	77.99(11)	-----
M-O9	2.473(3)	-----	O9-M-O2W	77.81(12)	-----
M-O10	2.498(3)	-----	O9-M-O3W	69.43(12)	-----
M-O11	-----	2.271(5)	O9-M-O4W	96.25(12)	-----
M-O1W	2.457(3)	2.395(5)	O9-M-O5W	127.47(11)	-----
M-O2W	2.454(4)	2.414(6)	O10- M-O1W	71.43(11)	-----
M-O3W	2.477(4)	2.403(5)	O10-M-O2W	124.31(11)	-----
M-O4W	2.464(4)	2.420(6)	O10-M-O3W	104.99(12)	-----
M-O5W	2.488(3)	2.409(6)	O10-M-O4W	72.83(11)	-----
^{2#} O5-M-O6 ^{#2}	53.30(11)	53.5(2)	O10-M-O5W	75.93(11)	-----
^{2#} O5-M-O9	143.30(11)	-----	O11-M-O1W	-----	144.3(2)
^{2#} O5-M-O10	137.40(11)	-----	O11- M-O2W	-----	143.0(2)
O5-M-O11	-----	85.7(2)	O11- M-O3W	-----	101.8(2)
^{2#} O6-M-O9	142.46(12)	-----	O11-M-O4W	-----	75.0(2)
^{2#} O6-M-O10	150.50(12)	-----	O11- M-O5W	-----	75.9(19)
O6-M-O11	-----	80.2(2)	O1W-M-O2W	76.24(13)	72.2(2)
O9-M-O10	52.11(10)	-----	O1W-M-O3W	138.81(13)	84.5(19)
^{2#} O5-M-O1W	75.91(11)	103.3(2)	O1W-M-O4W	138.39(13)	139.4(2)
^{2#} O5-M-O2W	71.26(12)	76.1(2)	O1W-M-O5W	78.81(12)	71.8(2)
^{2#} O5-M-O3W	117.60(12)	155.3(2)	O2W-M-O3W	72.88(15)	84.3(2)
^{2#} O5-M-O4W	120.37(12)	85.5(2)	O2W-M-O4W	143.50(14)	71.7(2)
^{2#} O5- M-O5W	71.49(11)	129.5(2)	O2W-M-O5W	139.05(13)	139.9(19)
^{2#} O6-M-O1W	129.12(11)	78.0(2)	O3W-M-O4W	71.38(15)	74.1(19)
^{2#} O6-M-O2W	84.16(14)	111.9(2)	O3W-M-O5W	141.55(14)	75.2(2)
^{2#} O6-M-O3W	73.89(12)	150.57(19)	O4W-M-O5W	72.43(13)	131.7(2)
^{2#} O6-M-O4W	79.18(13)	133.39(19)			

Symmetry transformations used to generate equivalent atoms: for **1-Eu**; #2 x+1/2,-y-1/2,z+1/2

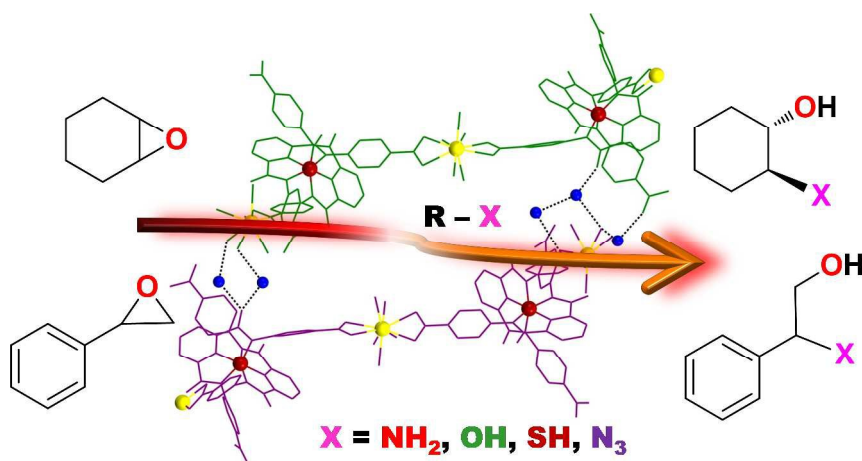
Graphical Abstract

Lanthanide-based coordination polymers as the promising heterogeneous catalysts for ring-opening reactions

*Gulshan Kumar, Girijesh Kumar and Rajeev Gupta**

Department of Chemistry, University of Delhi, Delhi – 110 007 (India)

Artwork:



Synopsis: Eu and Tb based coordination polymers function as the reusable heterogeneous catalysts for the ring-opening reactions with amines, alcohols, thiols, and azides as the nucleophiles.