# Robust 1D open rack-like architecture in coordination polymers of Anderson POMs [ $\{Na_4(H_2O)_{14}\}$ {Cu(gly)}<sub>2</sub>][TeMo<sub>6</sub>O<sub>24</sub>] and [ $\{Cu(en)_2\}_3$ {TeW<sub>6</sub>O<sub>24</sub>}]: synthesis, characterization and heterogeneous catalytic epoxidation of olefines<sup>†</sup>

Daipayan Dutta,<sup>a</sup> Atish D. Jana,<sup>b</sup> Mainak Debnath,<sup>a</sup> Asim Bhaumik,<sup>c</sup> Jaromir Marek<sup>d</sup> and Mahammad Ali\*<sup>a</sup>

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Two novel organic-inorganic hybrid tungsto- and molybdo- telurates having formula  $[\{Na_4(H_2O)_{14}\} \{Cu(gly)\}_2]$  [TeMo<sub>6</sub>O<sub>24</sub>] (1){gly = glycine} and [{Cu(en)\_2}\_3 \{TeW\_6O\_{24}\}] \cdot 6H\_2O \{en = 0\} ethyline-diamine {(2) based on Anderson type heteropolyoxometalates (POMs) have been synthesized and characterized by X-ray crystallography. Common structural feature of both 1 and 2 is the presence of a unique 1D open rack-like architecture, where the disc shaped Anderson POMs act as steps and cationic Cu-organic complexes act as handles of the rack. In 1 the independent structural unit is a 1D coordination polymer with the above mentioned rack type architecture, while in 2, these independent rack-like architectures are further extended to a 2D coordination polymer. Heterogeneous catalysis for the epoxidation of cyclohexene and styrene by complexes 1 and 2 showed very good catalytic efficiency resulting epoxides of  $\sim 60\%$  yield, with dialcohol formed by the hydrolysis of epoxides, as the other major product (~28%). Cyclic voltammetric studies of  $[\{Na_4(H_2O)_{14}\} \{Cu(gly)\}_2]$ [TeMo<sub>6</sub>O<sub>24</sub>] (1) in aqueous KCl solution indicates that the redox changes occur only on the copper centers and supported by carrying out parallel experiments on the precursors like  $([Cu(gly)_2]^{2+})^{2+}$  and  $[TeMo_6O_{24}]^{6-}$ , under the identical experimental conditions. The  $E_{1/2} = 0.662$ , -0.142 and -0.332 V(vs. SCE) correspond to Cu(III)  $\rightarrow$  Cu(II), Cu(II)  $\rightarrow$  Cu(I) and Cu(I)  $\rightarrow$  Cu(0) reductions, respectively. Thermal analyses reveal identical phase transition reactions with an exothermic peak in the DTA curve at 380 °C for 1 and an endothermic peak appears at comparatively higher temperature (408 °C) for 2 manifesting the higher stability of tungstane based POM over the molybdenum ones. EPR as well as magnetic moment results indicate that both the complexes 1 and 2 are paramagnetic with one unpaired electron per copper(II) ion.

# Introduction

Framing and generation of metal-oxide based new materials with value added properties is a challenging task in modern inorganic chemistry. Polyoxometalates (POMs), metal-oxide based materials, are gaining more and more interest due to their unlimited structural varieties and widespread applications in numerous fields like catalysis, biochemical separations and medicinal chemistry.<sup>1</sup> They play an important role for the design of new materials with novel electronic, magnetic and topological properties.<sup>2</sup> Up until now, various organic/metallo-organic/inorganic linkers have been utilized to construct extended metal-oxide based materials of the type Keggin,<sup>3</sup> Wells-Dawson,<sup>4</sup> Lindquist<sup>5</sup> polyoxoanions, and isopoly anions; <sup>6-8</sup> but in contrast, the use of Anderson-

POM is very rare.11

Although POMs are regarded as promising candidates as green catalysts,<sup>19-21</sup> their application as heterogeneous catalysts is very limited due to their inherent tendency to conglomerate resulting deactivation of the POMs.<sup>22</sup> Efforts have been taken to overcome such limitations through the incorporation of the

type polyoxoanions as inorganic building block is only in its infancy.<sup>9</sup> Anderson type POMs being inherently planar, act as

promising templates for the organization of layered structures.<sup>10</sup>

Only very recently, some Anderson-type heteropolyanions based

on molybdenum oxide cluster linked to metal complexes including

transition metals and lanthanides have been reported<sup>9</sup> but in

contrast the use of corresponding tungsten oxide based Anderson

In general, most of the POMs form 1D chain like architecture

with transition metal ions and especially with lanthanides as

linkers.<sup>12</sup> On the other hand, Keggin type POMs and only in few

cases Anderson POMs were found to form 2D and 3D frameworks

in presence of Na<sup>+</sup> or Na<sup>+</sup> and transition metal or lanthanide

ions as linkers.<sup>13-15</sup> Recently, Das *et al.* reported an extended polymer  $[La(H_2O)_7Al(OH)_6Mo_6O_{18}]_n.4H_2O$  with rare earth cation

as linkers.16 They also reported a spiral-shaped inorganic-organic

hybrid chain  $[Cu(2,2'-bipy)(H_2O)_2-Al(OH)_6Mo_6O_{18}]_n^{n-.17}$  On the

<sup>&</sup>lt;sup>a</sup>Department of Chemistry, Jadavpur University, Kolkata, 700 032, India. E-mail: mali@chemistry.jdvu.ac.in

<sup>&</sup>lt;sup>b</sup>Department of Physics, Sripat Singh College, Jiaganj, Murshidabad, W.B., 742123, India

<sup>&</sup>lt;sup>e</sup>Department of Materials Science, Indian Association for the Cultivation of Science, Jadavpur, Kolkata, 700 032, India

<sup>&</sup>lt;sup>d</sup>Laboratory of Functional Genomics and Proteomics, Institute of Experimental Biology, Faculty of Science, Masaryk University, Kamenice 5/A2, CZ-625 00, Brno, Czech Republic

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POMs into the metal–organic frameworks (MOFs).<sup>23–28</sup> Though, a great variety of POM-based coordination polymers in the MOFs have successfully been assembled,<sup>23–28</sup> their application as catalysts remains practically unexplored;<sup>29–30</sup> particularly the Anderson-POM based materials are totally absent from this scenario.

Very recently, we have reported a crystal structure where due to the templating action of the Anderson POMs, the tris-chelated  $[Cu(phen)_3]^{2+}$  units are organized in a layer with honeycomb network topology<sup>10</sup> instead of their preferred tendency to organize through multifold embrace motifs<sup>31</sup> In our continuing effort to synthesize Anderson POM based novel materials we further envisaged that a suitable design strategy can lead to rational construction of Anderson based 1D and 2D polymeric frameworks. In contrast to the spherical or oval shape of other type of POMs, Anderson POMs have disk-shaped structure and has the potentiality to give rise to ladder topology, if these discs could be connected by linear spacers (Scheme 1). An obvious design strategy in this regard is to use transition metal complexes with octahedral coordination where the terminal oxygen atoms of Anderson POM units can satisfy the axial sites and the equatorial sites have to be blocked by suitable chelating ligands. Here, we report the successful employment of this strategy to generate rack type architecture of Anderson based POMs, for the first time, in two complexes  $[{Na_4(H_2O)_{14}}{Cu(gly)}_2][TeMo_6O_{24}]$  (1) and  $[Cu(en)_2]_3$  [TeW<sub>6</sub>O<sub>24</sub>]<sub>2</sub> (2). This also comprises the first report where Anderson POMs based MOFs have been found to be efficient heterogeneous catalyst for the liquid phase partial oxidation of olefins.



Scheme 1 Framing of Racks from Anderson POM and transition metal complexes

# Experimental

# Materials and methods

Sodium molybdate (Merck, Germany), Sodium tungstate (Merck, Germany), copper chloride (A. R. Loba, India), copper nitrate (Merck, Germany), glycine (Merck, Germany), ethylenediamine (Merck, Germany), telluric acid (Alfa Aesar, Germany) and hydrochloric acid were of reagent grade and used as received. De-ionised water was used as the solvent.

# Synthesis of the complexes: $[\{Na_4(H_2O)_{14}\}\{Cu(gly)\}_2][TeMo_6O_{24}]$ (1)

A mixture of  $H_6$ TeO<sub>6</sub> (0.08 g, 0.35 mmol), Na<sub>2</sub>MoO<sub>4</sub>·2H<sub>2</sub>O (0.508 g, 2.1 mmol), CuCl<sub>2</sub>·2H<sub>2</sub>O (0.060 g, 0.35 mmol), glycine (0.053 g, 0.7 mmol), 4(M) HCl (8–10 drops) and H<sub>2</sub>O (25 mL) were taken together in a 100 mL beaker. The *p*H of the resultant solution was maintained at 5.50 by the addition of 4.0 (M) HCl solution. Then, the mixture was stirred with heating at ~ 80° C for 1 h to get a blue solution. It was cooled to room temperature and filtered. The resultant sea-blue filtrate was kept in open air for slow evaporation, which resulted to blue, rhombic single crystals in 10 days. The crystals were filtered off, washed with distilled water, and dried in a desiccator at room temperature to give an yield of 50% based on Mo. Anal. Calcd for 1, C<sub>4</sub>H<sub>36</sub>Na<sub>4</sub>O<sub>42</sub>Cu<sub>2</sub>Mo<sub>6</sub>TeN<sub>2</sub> (M.W. 1706.2): C, 2.81; H, 2.11; N, 1.64%. Found: C, 2.78; H, 2.07; N, 1.62%.

#### Synthesis of the complex [Cu(en)<sub>2</sub>]<sub>3</sub>[TeW<sub>6</sub>O<sub>24</sub>]·6H<sub>2</sub>O (2)

The synthetic procedure is similar to that of **1**, except  $Na_2WO_4 \cdot 2H_2O$  (0.693 g, 2.1 mmol),  $Cu(NO_3)_2 \cdot 4H_2O$  (0.242 g, 1.0 mmol) and ethylenediamine (0.18 g, 3.0 mmol) were added instead of  $Na_2MoO_4 \cdot 2H_2O$ ,  $CuCl_2 \cdot 2H_2O$  and glycine, respectively. The violet rectangular crystals, formed within few days, were filtered off, washed with distilled water, and dried in a desiccator at room temperature to give an yield of 40% based on W. Anal. Calcd for 2,  $C_{12}H_{48}Cu_3N_{12}O_{24}TeW_6$  (M. W. 2261.92) : C, 6.37; H, 2.12; N, 7.43%. Found: C, 6.08; H, 2.28; N, 7.34%

#### Physical measurements

Elemental analyses were carried out using a Perkin-Elmer 240 elemental analyzer. Room temperature magnetic susceptibility was recorded on a PAR vibrating sample magnetometer using [Hg{Co(NCS)<sub>4</sub>}] as the calibrant. EPR was recorded from Bruker EMX-220 digital X-Band (v = 9.43 GHz) spectrophotometer. TGA and DTA study were carried out using a Perkin-Elmer Pyris Diamond TGA/DTA Analyser. Catalysis were carried out using an Agilent 6890A, FID GC. Electrochemical measurements were carried out using a computer controlled AUTOLAB (model: 263A VERSASTAT) electrochemical system with glassy carbon as working electrode, Pt-wire as counter electrode and saturated calomel as reference electrode. Cyclic voltammograms were recorded at 25 °C in deionized water from Millipore - Milli-Q Water Purification Systems under pure N<sub>2</sub> atmosphere with 0.10 M KCl as supporting electrolyte.

#### Crystal data collection and refinement

Intensity data for complexes **1** and **2** were collected on a fourcircle diffractometer Kuma KM-4 equipped with a CCD detector and an Oxford Cryostream Cooler. The  $\omega$ -scan technique with different  $\kappa$  and  $\varphi$  offsets for covering the whole independent part of reflections in the 2 < 2 $\theta$  < 25° for monochromated (monochromator Enhance, Oxford Diffraction) Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å) was performed. Data collection, cell parameter refinement and data reduction were carried out using a CrysAlis program package.<sup>32</sup> The cell parameters were refined from all strong reflections. During data reduction of less absorbing

#### Table 1 Crystal data and refinement parameters

	1	2
Formula	$C_4H_{36}Na_4O_{42}Cu_2Mo_6TeN_2$	$C_{12}H_{48}Cu_3N_{12}O_{24}TeW_6 \cdot 6(H_2O)$
Formula weight	1706.6	2274.04
Wavelength (Å)	0.71073	0.71073
Crystal system	Triclinic	Triclinic
Space group	<i>P</i> 1(No.2)	<i>P</i> 1(No.2)
a, b, c (Å)	7.1526 (5)	8.5534(3)
	10.6481(6)	11.5294(4)
	14.2288 (9)	13.1841(5)
$\alpha, \beta, \gamma$ (°)	73.573(5),	67.382(4)
	78.822(5)	85.597(3)
	78.197(5)	72.689(3)
$V(Å^3)$	1006.74(11)	1144.75(8)
Z	1	1
$D(calc) [g cm^{-3}]$	2.808	3.299
$\mu$ (Mo-K $\alpha$ ) [1/mm]	3.720	16.932
<i>F</i> (000)	812	1039
Crystal Size/mm	$0.10 \times 0.30 \times 0.30$	$0.30 \times 0.34 \times 0.44$
T/K	120(2)	100(2)
Mo-Kα[Å]	0.71073	0.71073
$\theta_{\rm Min},  \theta_{\rm Max}  [^{\circ}]$	3.8, 25.0	3.0, 25.0
Dataset	-8: 8; -12: 12; -16: 15	-10: 9; -10: 13; -12: 15
Tot., Uniq. Data, <i>R</i> <sub>int</sub>	6905, 3549, 0.016	5959, 4013, 0.019
Observed data $[I > 2.0 \sigma(I)]$	3348	3947
Nref, Npar	3549, 323	4013, 310
$R, WR_2, S$	0.0246, 0.0635, 0.90	0.0289, 0.0786, 1.26
Max. and Av. Shift/Error	0.00, 0.00	0.00, 0.00

complex 1 an empirical absorption correction using spherical harmonics was applied,<sup>32</sup> while an analytical numeric absorption correction using a multifaceted crystal model<sup>33</sup> has been applied on heavily absorbing complex 2. The both structures were determined by direct methods (SHELXS-97)<sup>34</sup> and refined anisotropically on  $F^2$  using full matrix least-squares procedure by SHELXL-97<sup>34</sup> All C and N bonded hydrogen atoms in 1 and 2 were placed in their geometrically calculated positions, while positions for O-bonded H-atoms were localized in difference electron density maps and refined with restrained the O–H distances. An only exception is the terminal oxygen atom attached to Na2 in complex 1: this atom is disordered over two positions (O24a and O24b) and hydrogen atoms attached to these oxygen positions could not be located. Table 1 Comprises the detail of crystallographic data collection and refinement parameters for complexes 1 and 2.

# Catalysis

The catalytic epoxidation reactions of cyclohexene and styrene by Tert-butylhydroperoxide (TBHP) were carried out heterogeneously in MeCN using 0.02 g of complex 1 or complex 2, 0.5 g substrate, 5 ml acetonitrile under stirring in a two-neck roundbottom flask fitted with a water condenser and placed in an oil bath at 333 K, 70 wt% aqueous TBHP, equimolar with respect to the substrate, was added immediately before the start of the reaction. Aliquots of the reaction mixture were withdrawn at various time intervals to study the progress of the reaction. In a typical operation, 0.5 mL solution was taken out with the help of a micropipette and the solution was subjected to multiple ether extraction and the extract was concentrated. From this, 1 µL solution was withdrawn with the help of a gas tight syringe and injected to the GC port (Agilent 6890A, FID). For the identification of products the GC retention times of different reaction products were compared with those of commercial standards.

# **Results and discussion**

#### Solid state structure

Complexes 1 and 2 were prepared by simple one-pot reaction between  $[TeM_6O_{24}]^{6-}$  (H<sub>6</sub>TeO<sub>6</sub> + Na<sub>2</sub>MO<sub>4</sub>) (M = Mo or W)  $Cu^{2+}$  and appropriate ligand in aqueous media at pH 5.50. The main intention was to generate open shelf-like architecture with Anderson POM as base and copper(II) complexes as linker as shown in Scheme 1. Single crystal X-ray structure of compound 1 reveals that it consists of one dimensional polymeric chains having open rack-like architecture (Fig. 1a). It is formed by Anderson type [TeMo<sub>6</sub>O<sub>24</sub>]<sup>6-</sup> polyoxoanion<sup>10</sup> and  $[\{Na_4(H_2O)_{14}\}\{Cu(gly)\}_2]^{6+}$  cationic complexes (Fig. 1c). The structure of  $[TeMo_6O_{24}]^{6-}$  in 1 is similar to the structures reported for other Anderson type anions. This consists of six coplanar MoO<sub>6</sub> octahedra which are arranged in a ring sharing edges leaving an octahedral pocket at the center of the ring for the heteroatom, Te6+, in the present case, which occupies a center of inversion (Fig. 1b). The Mo-O bond lengths are as follows: Mo-O<sub>t</sub>(terminal oxygens), 1.703(3)–1.955(3) Å; Mo-O<sub>b</sub>(bridging oxygens), 2.257(3)-2.300(3) Å and that for Te-O ranges between 1.922(3) and 1.934(3) Å.

The  $[TeMo_6O_{24}]^{6-}$  anions act as steps of the rack-like assembly which are joined on both sides by a complex of two sodium atoms and a Cu atom. The Cu atom (Cu1) and the sodium atoms (Na1 and Na2) each possesses octahedral coordination environment. Among four equatorial sites of the Cu(II) octahedron, two are occupied by water oxygen atoms (O4 and O5) and the rest two are contributed by a glycine molecule which acts as a chelating agent for the Cu(II) center by binding it through the carboxylate O atom (O1) and amine N atom (N3). The *trans* axial sites of the two Cu(II) octahedra are occupied by O6 oxygen atoms that are contributed by two  $[TeMo_6O_{24}]^{6-}$  units from opposite sides. In the



**Fig. 1** (a) The rack-like architecture of compound 1. (b) Structure of X-Te metal cluster (X = Mo for compound 1 and X = W for compound 2. (c) The ORTEP diagram of 1 (30% ellipsoidal probability) with atom numbering scheme. (i) = -1+x,y,z; (ii) = 1-x, 1-y, 1-z.

equatorial plane the Cu(II) octahedron shares an edge with the adjacent Na1 octahedron; as oxygen atoms O5 of water and O1 of glycine occupy two of the equatorial cis-positions of the Na1 octahedron. Two other equatorial sites of the Na1 octahedron are occupied by water oxygen atoms (O21 and O22). The trans axial sites of the Na1 octahedron are constituted by oxygen atoms (O11) of two [TeMo<sub>6</sub>O<sub>24</sub>]<sup>6-</sup> units from opposite directions. Thus both Cu1 and Na1 take part in joining successive steps  $[TeMo_6O_{24}]^{6-1}$ of the rack on both sides due to centrosymmetric arrangement of the system to give rise to an open rack-like architecture of the complex. Na1 atom is further connected to Na2 atom. They share O21 and O22 water oxygen atoms in the equatorial plane of their respective octahedral coordination environments. Two terminal water oxygen atoms, (O23) and a disorder water oxygen atom over two sites (O24a and O24b) satisfy the other two equatorial coordination sites of the Na2 octahedron. The trans axial sites of the Na2 octahedron are occupied by a water molecule (O20) and the glycine O2 atoms from an adjacent chain. The Na2-O2 distance is rather larger 2.886(4) Å as compared to 2.290(3) Å for Na2–O20. There is no unusual bonding geometry for the Cu1 and Na1 coordination and the bond distances and angles are described in Table 2. The inter ladder Cu ··· Cu separation is 7.153 Å. These anion chains are arranged to form layers along the *ab* plane, with the inter-chain distance of about 10.171 Å (in the same layer). Individual polymeric chains pack (Fig. 2) in a compact fashion due to hydrogen bonding interaction between adjacent polymers.



**Fig. 2** The packing diagram of individual ladders of **1** viewed down the *a*-axis.

Table 3 displays selective bond distances and bond angles of complex 2. Crystal structure of 2 contains  $[TeW_6O_{24}]^{6-}$  heteropoly anions and  $[Cu(en)_2]^{2+}$  cations. Te atom and one of the Cu (Cu2) atoms occupy the center of inversion.

The architecture of the complex is a 2D polymeric sheet (Fig. 3) in which  $[TeW_6O_{24}]^{6-}$  ions are bridged doubly (along

Bond distances (Å) Na1-O21 2.372(4)3.2703(4) Te-Mo1 Na1-O22 2.318(3)Te-Mo2 3.2674(4) Nal-Ol2 a 2.346(3) 2.334(4)Te-Mo3 3.3051(4) Na1-O1 Te-O10 1.930(2)Na2-O20 2.290(3) 1.934(3) Te-O14 Na2-O21 2.382(3)Te-O15 1.922(3) Na2-O22 2.458(5) Na2-O23 Mol-O6 1.718(3) 2.369(5) Mol-O7 1.703(3) Na2-O24A 2.355(8) 1.955(3) Na2–O24B Mo1-08 2.31(2)Mo1-09 1.940(3) Cu-O1 1.967(3) Mo1-O10 2.257(3) Cu-O4 1.993(3) Mo1-015 2.307(3)Cu-O5 2.006(3) Mo2-O8 1.931(2)Cu-O6 2.346(3)Na1-05 2.476(3)Cu-N3 1.969(3)Na1-011 2.347(3)Cu-O8 a 2.405(3)Bond angles (°) O1-Cu-N3 O6-Mo1-O7 107.87(15) 83.45(12) O6-Mo1-O8 99.42(12) O1-Cu-O8 a 89.58(11) 06-Mo1-09 96.77(13) O20-Na2-O21 172.69(16) O6-Mo1O10 157.69(13) O20-Na2-O22 99.60(13) O6-Mo1O15 88.45(13) O20-Na2-O23 87.25(15) O1-Cu-O4 178.21(13) O20-Na2-O24A 86.0(3) O1-Cu-O5 90.87(12) O20-Na2-O24B 87.2(10) 01-Cu-06 92.42(11)

 Table 2
 Selected bond distances (Å) and bond angles (°) of compound 1

Symmetry a = -1+x, y, z; c = 1-x, 1-y, 1-z.

Table 3Selected bond distances (Å) and bond angles (°) of 2

Bond distances (Å)						
W1-O1	1.744(6)	Te1-O10_b	1.932(6)			
W1-O2	1.749(6)	Cu1-O12	2.409(6)			
W1-O3	1.933(6)	Cu1–N1	2.031(8)			
W1-O4	2.268(6)	Cu1–N2	2.009(8)			
W1-O5	2.271(6)	Cu1–N3	2.009(7)			
W1–O6	1.936(5)	Cu1–N4	2.015(8)			
Te1–O4	1.920(5)	Cu1–O1 a	2.848(6)			
Te1-O5	1.929(6)	Cu2–O7	2.521(6)			
Te1-O10	1.932(6)	Cu2–N5	2.008(8)			
Te1-O4_b	1.920(5)	Cu2–N6	2.031(7)			
Te1-O5_b	1.929(6)					
Bond angles (°)						
O1-W1-O2	104.8(3)	N2-Cu1-N4	170.9(3)			
O1-W1-O3	97.2(3)	O1_a-Cu1-N2	80.7(2)			
O1-W1-O4	157.7(2)	N3-Cu1-N4	84.2(3)			
O1-W1-O5	89.4(3)	O7-Cu2-N5	85.1(3)			
O1-W1-O6	99.9(3)	O7-Cu2-N6	93.8(3)			
O12-Cu1-N1	88.5(3)	O7-Cu2-O7_c	180			
O12-Cu1-N2	90.3(3)	O7-Cu2-N5_c	94.9(3)			
O12-Cu1-N3	89.6(2)	O7-Cu2-N6_c	86.2(3)			
O12-Cu1-N4	97.9(3)	N5-Cu2-N6	85.3(3)			
O1_a-Cu1-O12	161.59(19)	O7_c-Cu2-N5	94.9(3)			
N1-Cu1-N2	83.8(3)	N5-Cu2-N5_c	180.00			
N1–Cu1–N3	175.9(3)	O5–Te1–O5_b	180			
N1-Cu1-N4	92.4(3)	O5-Te1-O10_b	85.5(3)			
a = -1-x, -y, 1-z; b = -x, -y, 1-z; c = -x, -y, 2-z.						

crystallographic *a*-axis) and singly by  $[Cu(en)_2]^{2+}$  cations (along crystallographic *b*-axis). Due to double bridging along *a*-axis the  $[TeW_6O_{24}]^{6-}$  units give rise to rack-like architecture (Fig. 3(i)) which are joined side by side along *c*-axis by  $[Cu(en)_2]^{2+}$  units giving rise to the 2D polymeric sheet. Successive polymeric sheets are stacked along crystallographic *b* axis giving rise to *T*shaped supramolecular channels which accommodate solvent water molecules (Fig. 4).

![](_page_4_Figure_7.jpeg)

Fig. 3 The 2D polymeric sheet (ii) of the complex 2 which is the result of joining of successive ladders (shown in [i]) that running along crystallographic *a*-axis by  $[Cu(en)_2]^{2+}$  units.

![](_page_4_Figure_9.jpeg)

**Fig. 4** Packing of successive polymeric sheets of **2** that give rise to intra layer channels that accommodate solvent water molecules.

#### Catalysis

Typically, the oxidation reactions were carried out using 0.02 g of complex 1 or complex 2, 0.5 g substrate, 5 mL acetonitrile at 333 K with TBHP, 70 wt% aqueous, equimolar with respect to the substrate as oxidant. Identification of products were carried out by comparing the GC retention times of different reaction products with those of commercial standards.

In Table 4 results of the catalytic activity as well as TON (Turn Over Number) for selected catalytic runs are given for complexes 1 and 2. Acetonitrile has been used as the solvent in all these liquid phase reactions. The major products for the partial oxidation of both styrene and cyclohexene were their respective epoxides. It is clear from the Fig. 5 that the selectivity of the epoxide for both the substrates was high at the initial stage of the reaction. However, with time as the conversion reaches the respective maxima, epoxide selectivities go down to some extent.

Cat.	Olefin	Time/h	Conv. (%)	Epoxide (%)	Diol (%)	Others (%)	TON
1	Styrene	12	78.5	59.8	27.9	12.3	15.8
2 Sty	Styrene	12	82.4 89.8	59.2	27.5 29.6	11.2	20.9
	Cyclohexene	12	80.2	62.1	28.4	9.5	24.4

 Table 4
 Catalytic activity of 1 and 2 in liquid phase partial oxidation of olefins in the presence of TBHP oxidant

![](_page_5_Figure_3.jpeg)

**Fig. 5** % Conversions of styrene (red diamond) and cyclohexene (blue circle) at different reaction hours in liquid phase partial oxidation by **2**. Corresponding selectivity of styrene oxide (cyan, diamond) and cyclohexene oxide (green circle) are at the right hand axis.

This could be attributed to the hydrolysis of the epoxides to the respective diols (Scheme 2), which is quite common for the liquid phase partial oxidation of olefin over a heterogeneous catalyst,<sup>35</sup> as water generated in the oxidation process promote the epoxide ring opening. From Table 2, it is clear that TON for cyclohexene conversion was relatively more than that for styrene. Nevertheless high TON for the oxidation of styrene and cyclohexene suggests the high catalytic efficiency for the Cu-hydroperoxo species that could form at the active sites in the presence of TBHP oxidant.<sup>35</sup> For both the substrates, corresponding diols are the other major products. Control experiments for the epoxidation reactions were carried out, *i.e.* using only TBHP without the catalysts and it was observed that about 2.6% and 0.7% epoxides were formed in the oxidation of styrene and cyclohexene respectively.

![](_page_5_Figure_6.jpeg)

Scheme 2 Liquid phase partial oxidation of olefins by TBHP to epoxides catalyzed by compounds 1 and 2.

To verify whether the observed catalysis is truly heterogeneous or not, the complex was removed from the reaction mixture by the filtration and the reaction was again carried out with the filtrate under the same conditions but with no epoxidation products indicating the fact that it is the complex **1** or **2** which are solely responsible for such catalytic process. Besides that there is no leaching of reactive species during the epoxidation process. The material separated by filtration showed more than 80% catalytic activity strongly suggesting the reusability of the catalyst.

# EPR study

EPR spectra were recorded from Bruker EMX-220 digital X-Band ( $\nu = 9.43$  GHz) spectrophotometer. Room temperature EPR spectra on the polycrystalline powdered samples of Cu(II) complexes 1 and 2 with one unpaired electron were recorded at the X-band frequency ( $\nu$ ) = 9.583 cm<sup>-1</sup> and for both the complexes low resolution EPR spectra were obtained having only  $\langle g_{eff} \rangle = 2.014$  and 1.995 respectively (Fig. 6 and 7).

![](_page_5_Figure_12.jpeg)

Fig. 6 Room temperature solid state EPR spectrum of 1.

#### TGA and DTA Studies

TGA and DTA studies were carried out using a Perkin-Elmer Pyris Diamond TGA/DTA Analyzer. TGA on **1** and **2** were performed at a rate of 5 °C min<sup>-1</sup> in the range of temperature 30-500 °C under N<sub>2</sub> gas flow. For **1**, successive weight losses (Fig. 8) of 4.22%, 8.44% and 2.11%, in the range of 40–70°, 80– 100° and 105–125 °C correspond to endothermic peaks at 70°, 98° and 120 °C, respectively in the DTA curve. These observed values are in accordance with the removal of four, eight and two water molecules respectively, (calcd. 4.16%, 8.35% and 2.07% respectively). Another weight loss of ~9.30% takes place in the range of 250–300 °C and corresponds to the decomposition of two glycine molecules (calcd. 8.67%). An exothermic peak corresponding to this change appears at ~290 °C in the DTA

![](_page_6_Figure_1.jpeg)

![](_page_6_Figure_2.jpeg)

Fig. 9 TGA/DTA thermogram of 2.

Fig. 7 Room temperature solid state EPR spectrum of 2.

![](_page_6_Figure_5.jpeg)

Fig. 8 TGA/DTA thermogram of 1.

curve. Another exothermic peak observed in the DTA curve at 380 °C may arise due to a phase transition, which possibly leads to the formation of telluric oxide (TeO<sub>3</sub>) along with CuMoO<sub>4</sub> and MoO<sub>3</sub> (Eqn. 1)<sup>36</sup>

 $Cu_3[TeM_6O_{24}] \rightarrow 3CuMO_4 + 3MO_3 + TeO_3 [M = Mo/W]. \quad (1)$ 

For the compound **2** an initial weight loss of ~5% (calculated 4.77%) in the range of 40–80 °C may arrise due to the loss of six water molecules loosely trapped in open channel of the framework. An endothermic peak at 77 °C in the DTA curve corresponds to this change. The second weight loss of ~ 16% takes place in the range 260–320 °C corresponds to the loss of six ethylenediamine molecules (calculated 15.92%) which corresponds to an endothermic peak 280 °C in the DTA curve (Fig. 9). Another endothermic peak was observed in the DTA curve at ~408 °C due to the phase transition leading to the formation of TeO<sub>3</sub> along with CuWO<sub>4</sub> and WO<sub>3</sub> according to Eqn. 1.

In 2 the third step at 408 °C in the DTA curve is endothermic in nature which is in contrary to the exothermic peak observed in 1. Not only that, this phase transition appears comparatively at higher temperature than that in its molybdenum analogue clearly demonstrating the higher stability of 2 over 1 and conforms to the previous observations.<sup>34</sup>

Magnetic study

Room temperature magnetic susceptibilities were recorded on a PAR vibrating sample magnetometer using  $[Hg{Co(NCS)_4}]$  as the calibrant. The magnetic moments for the two complexes 1 and 2 have been measured at room temperature with  $\mu_{eff}$  values 1.76 BM and 1.93 BM for 1 and 2 respectively, indicating that copper atom in both the complexes are paramagnetic with one unpaired electron.

### Electrochemical study of compound 1

It is interesting to envisage the electrochemical properties of a unique Anderson-type species, **1** as the probable redox behaviour would provide information for its further application in electrochemistry and catalytic studies. Cyclic voltammetric (CV) studies were carried out in aqueous 0.1 M KCl solution within the potential range from -1.0 to 1.0 V in order to avoid any complication from the redox processes of POM moiety. Fig. 10 shows the cyclic voltammogram of **1** in aqueous medium at a scan rate of 50 mV s<sup>-1</sup> with two reduction peaks located at +0.130 (C<sub>1</sub>') and -0.450 V (C<sub>2</sub>') and a not well resolved peak at -0.697 V (C<sub>3</sub>') with corresponding anodic peaks at 0.596 (A<sub>1</sub>'),

![](_page_6_Figure_15.jpeg)

Fig. 10 Cyclic voltammograms of complex 1 in  $H_2O$  using a platinum electrode and KCl (0.10 M) as supporting electrolyte at 50 mV s<sup>-1</sup> scan rate.

0.118 (A<sub>2</sub>') and 0.033 V (A<sub>3</sub>') (vs. SCE) corresponding  $E_{1/2}$  = 0.662, -0.142 and -0.332 V, respectively and correspond to the reduction of Cu(III)  $\rightarrow$  Cu(II), Cu(II)  $\rightarrow$  Cu(I) and Cu(I)  $\rightarrow$  Cu(0) respectively. The  $E_{1/2}$  corresponding to Cu(III)  $\rightarrow$  Cu(II) reduction at ~ 0.62 V is not uncommon and comparable to literature values.<sup>37</sup> The peak at  $-0.697 \text{ V}(\text{C}_3)$  becomes prominent when we run the experiment at lower scan rate in the potential range -1.0 to + 0.20 V (SUP Fig. 1) giving two cathodic peaks at -0.407 and -0.710 V and corresponding anodic peaks at -0.145 and -0.308 V, respectively. It is to be highlighted that the anodic peaks are shifted significantly towards more negative potentials while the cathodic peaks remain almost invariant on changing the scan rates from 50 to 10 mV s<sup>-1</sup> under identical experimental conditions and this kind of observations are not uncommon.<sup>38</sup> The redox processes are mainly copper centered and this is supported by carrying out CV studies on [Cu(gly)<sub>2</sub>] precursor under the identical experimental conditions.<sup>37</sup> In case of  $[Cu(gly)_2]$  two cathodic peaks appear at  $-0.398(C_2)$  and  $-0.501(C_3)$  V with corresponding anodic peaks at -0.165 (A<sub>2</sub>) and -0.232 (A<sub>3</sub>) V (vs. SCE) and can be assigned to  $Cu(II) \rightarrow Cu(I)$  and  $Cu(I) \rightarrow Cu(0)$  transformations, respectively and these are in conformity with the previous results.<sup>39</sup> These assignments of redox couples are further supported by carrying out the cyclic voltammetric studies on  $[TeMo_6O_{24}]^{6-}$  and  $H_6TeO_6$ precursors under the identical experimental conditions. In both the cases no characteristic peaks appeared for the  $Mo(VI) \rightarrow Mo(V)$ conversion. If we compare the CV profiles of complex 1 to that of  $[Cu(gly)_2]$  it is clear that both the  $Cu(II) \rightarrow Cu(I)$  and Cu(I) $\rightarrow$  Cu(0) of 1 are anodically shifted to lower potential values indicating that Cu(II) ion in [Na4(H2O)14][Cu(Gly)]6+ are more stable towards redox processes than in  $[Cu(gly)_2]$ , and it is justified in the sense that the former is in more restricted environment than in the later. Unfortunately, complex 2 is insoluble in any suitable solvents. Hence, Cyclic voltammetry (CV) curve of 2 could not be obtained.

# Conclusion

In summary, complexes 1 and 2 are unprecedented example of Anderson POMs  $[TeM_6O_{24}]^{6-}$  with two different addenda atoms (M = Mo for 1 and W for 2) giving rise to roboust 1D open rack-like architecture. The robustness is evident in the recurrence of ladder architecture, both in 1 and 2, though two different linker metal complexes have been employed. This suggests that, Anderson POMs can be further explored as a template for the generation of ladder architecture. Though, Keggin, Well-Dawson, Lindqvist type of POMs have been frequently utilized as green catalysts for heterogeneous catalysis with limited efficiency, compounds 1 and 2 are the first example where Anderson POM based metal-organic frameworks have been utilized for this purpose. Modifications of these parent compounds through the incorporation of transition metal ions or metal complexes may lead to their better catalytic efficiency. Here, we have been successful to generate and employ such materials as heterogeneous catalyst for the liquid-phase partial oxidation of olefines with moderately high catalytic efficiency. Cyclic voltammetric studies in 1 and its precursors hint that redox processes are mainly copper centered at neutral pH. TGA studies on 1 and 2 indicate that W-based POMs are more stable than it's Mo-analogue.

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