Coordination of lanthanide cation to an Anderson type polyoxometalate anion leads to isomorphous metal-oxide based one-dimensional inorganic solids: Synthesis, crystal structure and spectroscopy

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Abstract. One-dimensional isomorphous inorganic polymers containing Anderson type heteropoly anion as a basic building unit, namely $[La(H_2O)_7Cr(OH)_6Mo_6O_{18}]_n \cdot 4nH_2O$ (**1**), $[Gd(H_2O)_7Cr(OH)_6Mo_6O_{18}]_n \cdot 4nH_2O$ (**2**), $[Gd(H_2O)_7Al(OH)_6Mo_6O_{18}]_n \cdot 4nH_2O$ (**3**), and $[Eu(H_2O)_7Al(OH)_6Mo_6O_{18}]_n \cdot 4nH_2O$ (**4**) have been synthesized and studied by the powdered X–ray diffraction, TGA, IR, electronic and ESR spectroscopy, and unambiguously by single crystal X-ray crystallography. Isomorphous compounds **1**-**4** are crystallized in orthorhombic system with $Pca2_1$ space group. The crystal structure analysis reveals a one-dimensional extended chain in which the Anderson type heteropolyanion, acting as the building unit, is linked by rare earth metal ions in a zig-zag fashion. In the crystal structure, all types of oxygens of the heteropolyanion, lattice waters, lanthanum coordinated waters are extensively involved in O—H···O hydrogen bonding interactions. Compounds are additionally characterized by UV-visible and ESR spectroscopy.

Keywords. Anderson type polyoxometalates; lanthanides; one-dimensional inorganic polymers; isomorphous solids; spectroscopy.

1. Introduction

Polyoxometalates (POMs), in addition to their importance in catalysis, biochemical separation and in medicinal chemistry,[1] play an important role in the design of new class of materials with interesting electronic, magnetic and topological properties.[2–5] The POM clusters were reported as discrete entities a century back and recently various synthetic techniques including hydrothermal methods, that have provided multidimensional POM clusters, have been reported. The polyoxoanions consist of nucleophilic oxo groups (hard donors) on their metal skeletal surface by which they are ready to form solid-state materials with lanthanides (hard acids). The resulting POM based metal-oxide materials, that have been used for various applications,[3] were reported by several groups.[6–13] We have been working on an Anderson type POM heteropolyanion $[X(OH)_6Mo_6O_{18}]$ (X = Al^{3+}, Cr^{3+}) for a while. We and others[14–18] have reported the extended structures (1D, 2D and 3D) based on Anderson–type heteropolyanions that are mainly inked by the metal complexes, and

lanthanide cations. In 2002, we reported a preliminary result[14] on "a polyoxometalate chain formed from heteropolyanion building blocks and rare earth metal ion linkers: $[La(H_2O)_7Al(OH)_6Mo6O_{18}]n \cdot 4nH_2O$", in which we mentioned that "this material provides an opportunity to synthesize a new class of 1D materials simply by replacing La^{3+} ions with other rare earth metal ions, Sm^{3+}, Eu^{3+}, Gd^{3+}, etc., and replacing Al^{3+} ion by Cr^{3+} ion". Almost at the same time, compound $[Sm(H_2O)_7Al(OH)_6Mo_6O_{18}]_n \cdot 4nH_2O$ was synthesized and structurally characterized.[19,20] Few years later, Chen and co-workers reported the syntheses and crystal structures of three compounds of this series, namely $[Ln(H_2O)_7Cr(OH)_6Mo_6O_{18}]_n \cdot 4nH_2O$ (Ln = Ce^{3+}, Sm^{3+} and Eu^{3+}).[21] We are now reporting four more compounds of this series, that are formulated as $[La(H_2O)_7Cr(OH)_6Mo_6O_{18}]_n \cdot 4nH_2O$ (**1**), $[Gd(H_2O)_7Cr(OH)_6Mo_6O_{18}]_n \cdot 4nH_2O$ (**2**), $[Gd(H_2O)_7 Al(OH)_6 Mo_6O_{18}]_n \cdot 4nH_2O$ (**3**), and $[Eu(H_2O)_7Al(OH)_6 Mo_6O_{18}]_n \cdot 4nH_2O$ (**4**). Even though, synthesis and PXRD studies of compounds **3** and **4** had been described earlier, their crystal structures were not reported.[20] Compounds **1**-**4** have been obtained in one-pot aqueous synthesis and characterized by IR-, UV-visible, ESR-spectral techniques, TGA analysis,

powdered XRD studies and unambiguously by single crystal X-ray structure determinations.

2. Experimental

2.1 *Materials and methods*

All chemicals were purchased from commercial sources and used without further purification. Infrared spectra were obtained as KBr pellets using a JASACO FT/IR-5300 spectrometer in the region of 400–4000 cm^{-1}. UV-visible spectra were recorded using a 3101PC/UV-VIS-NIR Philips spectrophotometer equipped with a diffuse reflectance accessory. The X-band polycrystalline powder EPR spectrum was measured at 110K on a (JEOL) JESFA200 ESR spectrometer. Powder X-ray diffraction data were collected on a Phillips PW 3710 diffractometer. TGA analyses of title compounds were performed on a Mettler Toledo Star System thermal analyzer under nitrogen atmosphere at a scan rate of 10° C min^{-1}.

2.2 *Synthesis of [La(H$_2$O)$_7$Cr(OH)$_6$Mo$_6$O$_{18}$]· 4nH$_2$O (1)*

Compound **1** was synthesized by dissolving La(NO$_3$)$_3$· 6H$_2$O (1.0 g, 2.31 mmol) in water (100 mL) followed by the addition of glacial acetic acid (15mL, 100%). To this solution Na$_2$MoO$_4$·2H$_2$O (3.5 g. 14.46 mmol) and CrCl$_3$ (1.0 g, 6.31 mmol) were added. The pH of the resultant reaction mixture was adjusted to 2.60 with nitric acid. This mixture was boiled at 80–85°C for about 10 min; it was then filtered into a 250 mL conical flask, which was subsequently covered/closed with aluminum foil. Pinkish crystals were obtained within 4–5 days which were filtered through suction and washed with distilled water and dried at room temperature. Yield: 1.4g. (42.90% based on Mo). IR (solid KBr cm^{-1}): 559(m), 659(m), 895(s), 949(s), 1591(vs), 1624(vs), and 3458(vs-br).

2.3 *Synthesis of [Gd(H$_2$O)$_7$Cr(OH)$_6$Mo$_6$O$_{18}$]· 4nH$_2$O (2)*

Compound **2** was prepared by dissolving Gd(NO$_3$)$_3$· 6H$_2$O (1.0 g, 2.21 mmol) in distilled water (75 mL) followed by the addition of glacial acetic acid (15 mL), Na$_2$MoO$_4$· 6H$_2$O (3.5 g. 14.46 mmol) and CrCl$_3$ (1.0 g, 6.31 mmol). The resultant reaction mixture was adjusted to pH of 2.60 with nitric acid and it was then boiled for 10 min at 80–85°C. This was then filtered into a 250 mL beaker and the filtrate was kept closed with aluminum foil at room temperature. The pinkish

crystals, that were obtained within 4–5 days, were filtered through suction, washed with water and dried at room temperature. Yield: 0.55 g (16.7% based on Mo). IR (KBr solid, pellet cm^{-1}): 574(w), 646(m), 895(s), 951(s), 1601(s), and 3165(vs-br).

2.4 *Synthesis of [Gd(H$_2$O)$_7$Al(OH)$_6$Mo$_6$O$_{18}$]· 4nH$_2$O (3)*

The compound **3** was synthesized by dissolving Gd(NO$_3$)$_3$·6H$_2$O (1.0 g, 2.21 mmol) in water (100 mL), acidified with 15 mL of glacial acetic acid (100%) followed by the addition of Na$_2$MoO$_4$· 2H$_2$O (3.5 g. 14.46 mmol) and AlCl$_3$·6H$_2$O (1.5 g, 6.21 mmol). The pH of the resulting reaction mixture was adjusted to 2.60 with the nitric acid and the filtered solution was kept in an open flask at room temperature for two weeks, after which time the solution afforded white block-shaped crystals of **3**. Yield: 0.932 g (25% based on Mo). IR (solid KBr pellet cm^{-1}): 441(s), 574(w), 667(m), 895(s), 951(s), 1601(s) and 3275(vs-br).

2.5 *Synthesis of [Eu(H$_2$O)$_7$Al(OH)$_6$Mo$_6$O$_{18}$]· 4nH$_2$O (4)*

The compound **4** was synthesized by dissolving Eu(NO$_3$)$_3$·6H$_2$O (1.0 g, 2.24 mmol) in water (100 mL) followed by the addition of glacial acetic acid (15 mL, 100%), Na$_2$MoO$_4$·2H$_2$O (3.5 g. 14.46 mmol) and AlCl$_3$·6H$_2$O (1.5 g, 6.21 mmol). The pH of the resulting solution was adjusted to 2.60 with the nitric acid and the filtered solution (filtrate) was kept in an open flask at room temperature for five days, during which time the solution afforded white block-shaped crystals of **4**. IR (solid KBr pellet cm^{-1}): 684(m), 898(s), 947(s), 1618(s), and 3410(vs-br).

2.6 *X-ray crystallography*

The crystal data of compounds **1**, **2**, **3** and **4** were measured at 298(2) K on a Bruker SMART APEX CCD area detector system [λ(Mo-Kα) = 0.71073] with graphite monochromator. 2400 frames were recorded with an ω scan width of 0.3°, each for 8 s, with crystal detector-detector system 60 mm and collimator 0.5 mm. An empirical absorption correction using equivalent reflections was performed with the program SADABS.[22] Data reduction was performed by SAINTPLUS (Software for the CCD Detector System, Bruker Analytical X-Ray Systems Inc., Madison, WI, 1998); structure solution was done using SHELXS-97[23] and the structures were refined using

SHELXL-97[24] (G. M. Sheldrick, Program for crystal structure analysis, University of Göttingen, Germany 1997). All non-hydrogen atoms were refined anisotropically. A summary of crystallographic data and structural determinations for complexes **1–3** and **4** are provided in tables 1 and 2 respectively. Further details of the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (Fax : (49) 7247-808-666; e-mail: crysdata@fiz.karlsruhe.de) on quoting the depository numbers CSD-418345 (compound **1**), CSD-418349 (compound **2**), CSD-418348 (compound **3**) and CSD-418350 (compound **4**).

3. Results and Discussion

3.1 *Synthesis*

Compound $[Sm(H_2O)_7Al(OH)_6Mo_6O_{18}]_n \cdot 4nH_2O$ was synthesized[19,20] from lanthanide salt and the ammonium salt of Anderson cluster anion $(NH_4)_3[Cr(OH)_6 Mo_6O_{18}] \cdot nH_2O$, which was first prepared by boiling ammonium chrom-alum $(NH_4)_2Cr_2(SO_4)_4$ with ammonium paramolybdate followed by recrystallization from hot water.[25] The other three compounds $[Ln(H_2O)_7Cr(OH)_6Mo_6O_{18}]_n \cdot 4nH_2O$ (Ln = Ce^{3+}, Sm^{3+} and Eu^{3+}),[21] relevant to present study, were synthesized from the lanthanide salt and sodium salt of Anderson cluster anion $Na_3[CrMo_6H_6O_{24}] \cdot 8H_2O$, which had to be prepared from an aqueous reaction

mixture of sodium molybdate, chromic nitrate, nitric acid at pH 4.5.[16] Thus, these two synthetic procedures, described above for the syntheses of four relevant compounds, consist of two major steps, wherein, the first step is an isolation of NH_4^+/Na^+ salt of Anderson anion and the second step is the reaction between NH_4^+/Na^+ salt of Anderson anion and lanthanide salts. On the contrary, we have prepared compounds **1-4** (present work) in an one-pot synthesis involving $CrCl_3/AlCl_3$, Na_2MoO_4 and $Ln(NO_3)_3$, in which the Anderson cluster anion $[X(OH)_6Mo_6O_{18}]^{3-}$ (X = Al^{3+} and Cr^{3+}) is formed in situ followed by its linking with Ln^{3+} ion. Thefore the one-pot synthetic procedure, in the present work, is superior to the syntheses of earlier reported compounds of this series. The requirement of temperature in the synthesis in case of chromium analogues (compounds **1** and **2**) is logical due to the inertness of the chromium(III) salt.

3.2 *Description of the crystal structure*

Compounds **1-4** are isomorphous to each other as shown from unit cell parameters (tables 1 and 2) and PXRD patterns (figure S5). Structural details of compound $[Eu(H_2O)_7Al(OH)_6Mo_6O_{18}]_n \cdot 4nH_2O$ (**4**) have been described throughout this article including figures and tables. The molecular structures of **1-4** consist of basic Anderson type heteropolyanion as building unit $[X(OH)_6Mo_6O_{18}]^{3-}$ (X = Al^{3+} and Cr^{3+}, in the present work) forming the polymeric chain by

Table 1. Crystal data and structure refinement parameters for compounds **1-3**.

	1	**2**	**3**
Formula	$H_{28}CrLaMo_6O_{35}$	$H_{28}CrGdMo_6O_{35}$	$H_{28}AlGdMo_6O_{35}$
Fw	1354.77	1373.11	1348.09
Temp (K)	298(2)	298(2)	298(2)
Wavelength (λ)	0.71073	0.71073	0.71073
Crystal System	orthorhombic	orthorhombic	orthorhombic
Space Group	$Pca2_1$	$Pca2_1$	$Pca2_1$
a (Å)	11.8875 (10)	11.8318 (11)	11.7899 (7)
b (Å)	10.0349 (10)	10.9732 (5)	10.9495 (6)
c (Å)	22.7070 (19)	22.4254 (16)	22.3468 (13)
V (Å^3), Z	2708.7 (4), 4	2911.6 (2), 4	2884.8 (3), 4
Density (Mg/m^3)	3.322	3.133	3.104
Abs. Coeff. mm^{-1}	4.745	5.225	4.948
Final R indices:			
R ($I > 2\sigma(I)$)	$R_1 = 0.0351$, $wR_2 = 0.0901$	$R_1 = 0.0327$, $wR_2 = 0.0819$	$R_1 = 0.0262$, $wR_2 = 0.0657$
R (all data)	$R_1 = 0.0366$, $wR_2 = 0.0911$	$R_1 = 0.0343$, $wR_2 = 0.0829$	$R_1 = 0.0277$, $wR_2 = 0.0663$
Largest diff peak & hole (e.A^{-3})	2.166 & −2.944	1.069 & −2.934	0.807 & −1.163

$R_1 = \Sigma \, \|Fo| - |F_c \, \|/\Sigma \mid Fo|$; $wR_2 = [\Sigma[w(Fo^2–Fc^2)^2]/\Sigma \, [w(Fo^2)^2]]^{1/2}$.

Table 2. Crystal data and structure refinement parameters for compound **4**.

	4
Formula	$H_{28}AlEuMo_6O_{35}$
Fw	1342.80
Temp (K)	298(2)
Wavelength (λ)	0.71073
Crystal System	orthorhombic
Space Group	$Pca2_1$
a (Å)	11.7932(8)
b (Å)	10.9493(7)
c (Å)	22.3690(15)
V (Å^3), Z	2888.4(3), 4
Density (Mg/m^3)	3.088
Abs. Coeff. mm^{-1}	4.817
Final R indices:	
R ($I > 2\sigma(I)$)	$R_1 = 0.0258$, $wR_2 = 0.0651$
R (all data)	$R_1 = 0.0274$, $wR_2 = 0.0658$
Largest diff peak & hole (e.A^{-3})	0.797 & −1.164

$R_1 = \Sigma \, \|Fo| - |F_c \, \|/\Sigma \mid Fo|$; $wR_2 = [\Sigma[w(Fo^2 – Fc^2)^2]/\Sigma [w(Fo^2)^2]]^{1/2}$.

getting linked with the lanthanide ions, such as La^{3+}, Gd^{3+} and Eu^{3+}. The crystal structure of the Anderson anion $[X(OH)_6Mo_6O_{18}]^{3-}$ is similar to that, reported for other Anderson anion (figure 1), which consists of six edge shared Mo$_6$-distorted octahedra arranged hexagonally around the central heterometal octahedron.[14,15] The molybdenum oxygen distances in the Anderson anion, as expected, can be divided into four groups. The molybdenum-terminal oxygens (Mo–O$_t$) distances are in the range of 1.665–1.734 Å with
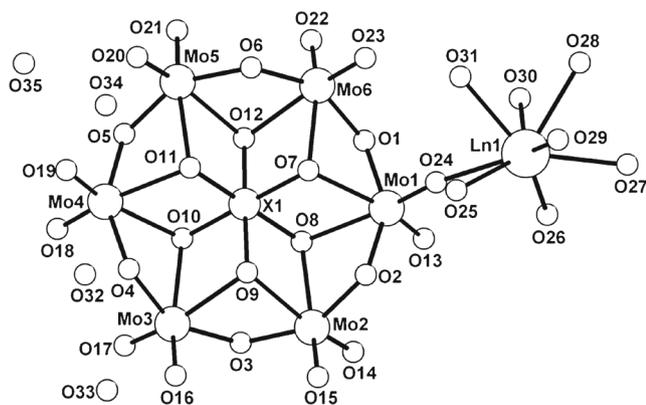

Figure 1. Molecular structure of the compound [Eu(H$_2$O)$_7$Al(OH)$_6$Mo$_6$O$_{18}$]$_n$·4nH$_2$O (**4**) (in the figure 1, X1 = Al^{3+} ion and Ln1 = Eu^{3+} ion).

molybdenum-bridging oxygens, (Mo–O$_b$) 1.887–1.991 Å, molybdenum-central oxygens (Mo–O$_c$) 2.264–2.349 Å, and molybdenum-oxygen linked to lanthanum Mo–O$_{t(La)}$ 1.722 Å.

The lanthanum cations get linked from both sides of the Anderson cluster through terminal oxygen atom of the heteropolyanion resulting in a one-dimensional chainlike structure as shown in figure 2. The coordination geometry of lanthanide ion in this chain is tri-capped trigonal prism that is filled by the coordination of seven water molecules and two terminal oxygen atoms of the two adjacent Anderson anions (figure 2).

The linking patterns of this cluster anion with lanthanide cation, so far known in one dimensional space, can be represented as shown in scheme 1. In one case, one Anderson anion is included between two lanthanide cations and in the other case, two Anderson anions are inserted between two cations along the chain. The chain, observed, in the present study belongs to the former type (scheme 1a and figure 2). Interestingly, an extensive hydrogen bonding network is observed in the crystal structures of title compounds **1-4**. This intricate H-bonding network is contributed by the lanthanum coordinated water molecules, central hydroxyl ions of the Al(OH)$_6$ moiety of the Anderson anion, terminal oxygen atoms of the Anderson anion and four crystal water molecules. The hydroxyl oxygens O7, O8, O9, O10, O11 and O12 of the central aluminum ion of the Anderson anion (figure 1) are involved in non-covalent weak interactions with the surrounding Anderson anions. The relevant O−H···O hydrogen bonding distances are presented as O···O separations in tables 3 and 4. The lattice water molecules, O34 and O35 connect two adjacent Anderson polyanions within the polymeric chains as shown in figure 3. The two adjacent layers of Anderson anions of the chainlike coordination polymer are connected by O34 water molecule (upper layer, figure 3) and O35 water molecule (lower layer, figure 3).

The lattice water molecules O32 and O33 are hydrogen bonded to each other forming a suparamolecular water dimer (a water dimer, formed exclusively from crystal water molecules) as shown in figure 4a. O33 water molecule of the water dimer is further hydrogen bonded to terminal oxygen O15, bridging oxygen O3 (of the Anderson anion) and lanthanide coordinated water molecule O30 with distances of 2.799, 2.743 and 2.701 Å respectively. The other water molecule O32 of the water dimer is hydrogen bonded to O17 (terminal oxygen atom of the Anderson anion) and O29 (lanthanide coordinated water molecule) with distances of 2.874 and 2.672 Å respectively. The hydrogen
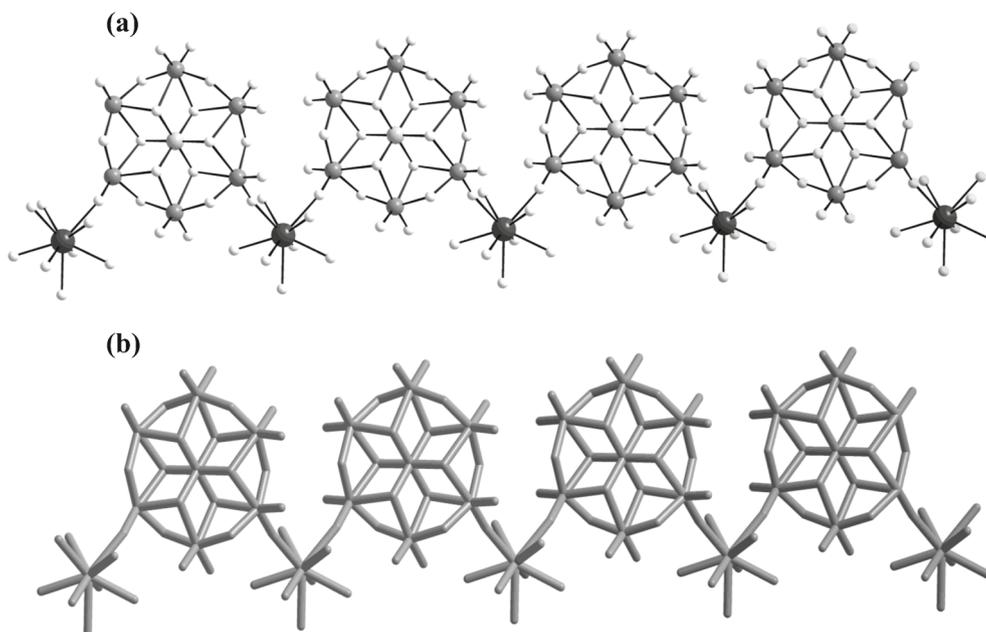
Figure 2. (a) Ball-and-stick representation of the chain, formed from Anderson heteropolyanion and lanthanide cation, the geometry around which is trigonal tricapped prism involving seven water ligands and two terminal oxo groups from two adjacent Anderson anion and (b) corresponding wire-frame representation.

bonding interactions between OH groups of an Anderson anion and terminal oxygen atoms of the adjacent Anderson anion results in formation of supramolecular chainlike arrangement (figure 4b), in which two adjacent Anderson cluster anions are almost perpendicular to each other. This hydrogen bond scheme indicates that the polymeric chains (coordination polymers), formed by the lanthanide linkers and Anderson anions, running parallel to the crystallographic *b* axis (figure 2) are intersected by the planes (containing O34 and O35 lattice waters and associated hydrogen bonds) parallel to the crystallographic *ac* plane (figure 3).
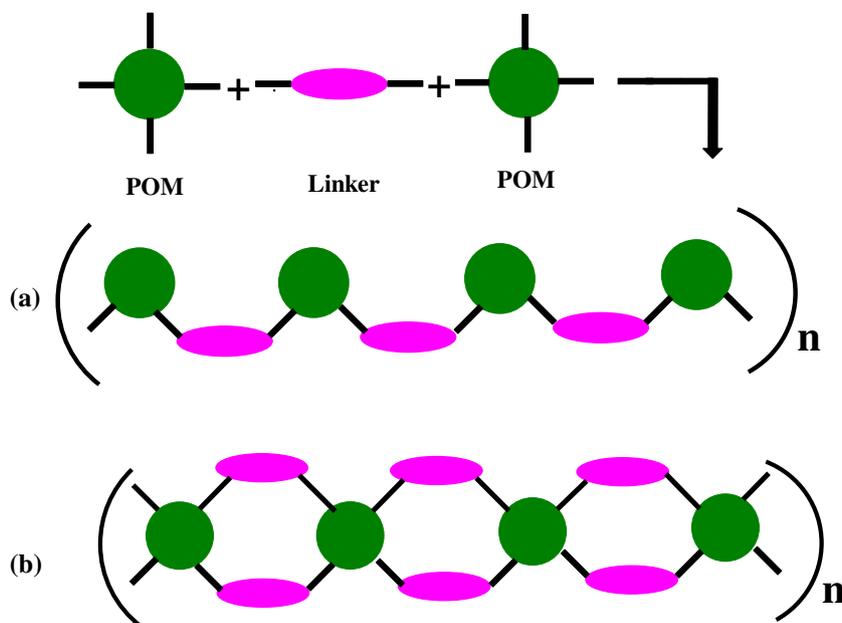
Scheme 1. Possible linking patterns of the lanthanide cation with Anderson anion in one dimension. The red ellipsoid = Anderson anion; green sphere = lanthanide cation.

Table 3. Hydrogen bonding interactions consisting of hydroxyl ions of Anderson anion and lanthanum coordinated water molecules in compound **4**.

O2$\cdots$O35#1	2.758(6)	O15$\cdots$O33#3	2.798(8)
O4$\cdots$O28#2	2.886(7)	O19$\cdots$O10#5	2.864(6)
O6$\cdots$O26#4	2.738(7)	O20$\cdots$O12#5	2.781(7)
O7$\cdots$O13#4	2.754(6)	O24$\cdots$O25#4	2.687(7)
O9$\cdots$O14#4	2.692(7)		

Symmetric transformations used to generate equivalent atoms
#1, −0.5+x, −y, z; #2, 1−x, −y, 0.5+z; #3, 0.5−x, −1+y, 0.5+z; #4, 0.5+x, −y, z; #5, 0.5+x, 1−y, z.

3.3 *Spectrosocpy*

3.3.1 *IR spectroscopy*

IR spectra of compounds **1**-**4** have been recorded in the region of 400–1000 cm^{-1} (figure S1). Expectedly, all IR spectra are similar in pattern, suggesting that an Anderson anion unit is common to all seven compounds. The symmetric and asymmetric stretching of the different modes of Mo-O bonds are observed at 950–440 cm^{-1}. The υ_{sym} Mo-O$_t$ stretching frequency is observed in the range of 947–951 cm^{-1}. The broad peaks at 3100–3460 cm^{-1} and the absorptions in the range of 1590–1650 cm^{-1} are the characteristics of water molecules. The peaks in the range of 640–540 cm^{-1} correspond to the υ(Mo-O-X) moiety (X= Al or Cr in the present series) and the peaks at 400–450 cm^{-1} correspond to the δ (Mo-O$_t$) bending.

3.3.2 *UV-visible spectroscopy*

The solid state (diffuse reflectance) electronic absorption spectra of these compounds were taken. Solid powders of the compounds were spread over a glass plate, and the diffuse reflectance spectra, obtained, were then Kubelka-Munk corrected with grease (on a glass plate) background. Figure 5 shows representative diffuse reflectance spectra of two compounds (**1** and **2**), recorded at room temperature. For both compounds [La(H$_2$O)$_7$Cr(OH)$_6$Mo$_6$O$_{18}$]$_n$·4nH$_2$O (**1**) and [Gd(H$_2$O)$_7$Cr(OH)$_6$Mo$_6$O$_{18}$]$_n$·4nH$_2$O (**2**), the absorption maxima at ∼400 nm can be assigned to the intramolecular charge transfer transition and the absorption maxima at ∼540 nm are attributed to the d-d transition for Cr^{3+} ion in their electronic absorption spectra.

3.3.3 *EPR spectroscopy*

The EPR spectra of polycrystalline powders of compound [La(H$_2$O)$_7$Cr(OH)$_6$Mo$_6$O$_{18}$]$_n$·4nH$_2$O (**1**) and [Gd(H$_2$O)$_7$Al(OH)$_6$Mo6O$_{18}$]$_n$ · 4nH$_2$O (**3**), measured at 110 K, are shown in figure 6. The EPR spectrum of compound **1** that contain Cr^{3+} as a central atom of the Anderson cluster reveals a zero field splitting, related to local symmetry of the Cr^{3+} ion in the octahedral site (3d^3, ^{4}F, L = 3, S = 3/2) of Anderson anion. Thus the chromium centre in compound **1** shows an anisotropic signal as shown in figure 6a. Similar EPR spectrum with zero field splitting (figure 6a) has been reported for the compound Na$_3$[Cr^{III}(OH)$_6$Mo$_6$O$_{18}$]· 6(CH$_3$)$_2$SO that contains Anderson type heteropolyanion having similar central octahedral Cr(III) ion.[26] For compound **3**, the free Gd^{3+} ion has the eightfold degeneracy with spin of 7/2. This can be split into four doubly degenerate energy levels in the presence of strong crystal field and

Table 4. Hydrogen bonding interactions involving crystal / lattice water molecules, oxygen atoms from Anderson cluster anion and lanthanum coordinated water molecules in compound **4** (see also figure S3, Supporting Information).

|			
O32$\cdots$O29#4	2.671(8)	O34$\cdots$O2#7	2.894(6)
O32$\cdots$O33#5	2.820(9)	O34$\cdots$O5#5	2.851(6)
O32$\cdots$O17#6	2.872(9)	O34$\cdots$O11	2.662(6)
O33$\cdots$O3#2	2.744(8)	O35$\cdots$O8#8	2.682(5)
O33$\cdots$O32#1	2.820(9)	O35$\cdots$O2#7	2.758(6)
O33$\cdots$O30#4	2.706(9)	O35$\cdots$O25#7	2.839(9)
O33$\cdots$O15#3	2.798(8)		

Symmetric transformations used to generate equivalent atoms
#1, −0.5+x, 1−y, z; #2, −x, 1−y, −0.5+z; #3, 0.5−x, 1+y, −0.5+z; #4, x, 1+y, z; #5, 0.5+x, 1−y, z; #6, 0.5−x, y, −0.5+z; #7, 0.5+x, −y, z; #8, 1+x, y, z
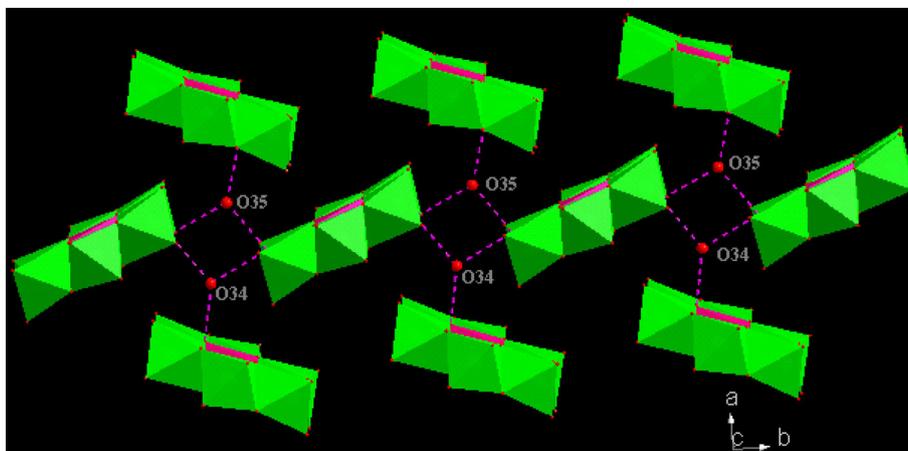
Figure 3. Supramolecular assembly of Andersion anions (polyhedral representation) in a "head to tail" fashion *via* solvent water molecules O(34) and O(35), viewed down to the the crystallographic *c* axis (in the crystal structure of compound **4**).

(a)   **(b)**
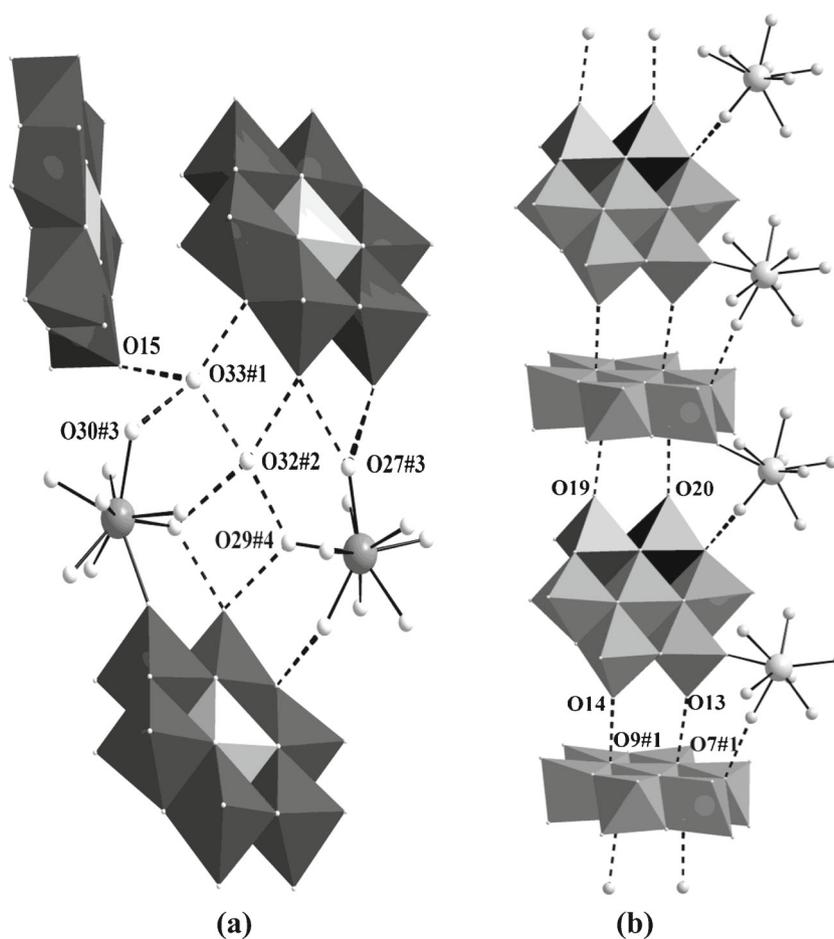
Figure 4. (a) Suprmolecular water dimer (O32 and O33 oxygen atoms are forming the water dimer) and its immediate environment in compound **4**. Symmetric transformations used to generate equivalent atoms: #1, 0.5−x, −1+y, 0.5+z; #2, 1−x, −y, 0.5+z; #3, 0.5−x, y, 0.5+z; #4, 1−x, −1−y, 0.5+z. (b) The terminal oxygens (O13 and O14) of Anderson anion and central heteroatom coordinated OH groups (O7 and O9) of the adjacent Anderson anions are involved in hydrogen bonding interactions; the concerned Anderson anions (shown in polyhedral representation) are near perpendicular to each other. Symmetric transformations used to generate equivalent atoms: .#1, 0.5+x, −y, z.
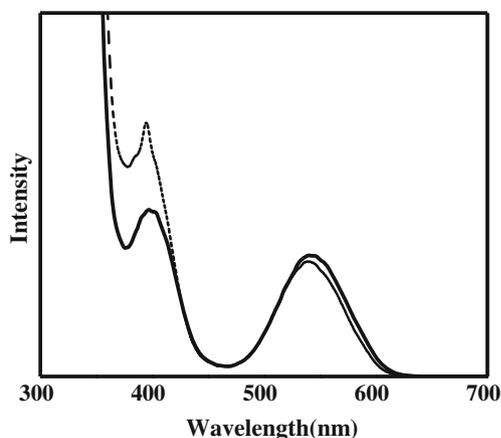
Figure 5. Solid state electronic absorption spectra of compounds $[La(H_2O)_7Cr(OH)_6Mo_6O_{18}]_n \cdot 4nH_2O$ (**1**) (solid line) and $[Gd(H_2O)_7Cr(OH)_6Mo_6O_{18}]_n \cdot 4nH_2O$ (**2**) (dotted line).

that degeneracy can be removed by the Zeeman field resulting in the transitions of unpaired electrons into the degeneracy levels that give additional lines with g > 2 or g < 2. Thus, these additional peaks indicate the presence of a strong crystal field. The peaks, observed at g > 2 and g < 2 (figure 6b) in the EPR spectrum of compound **3**, indicates the presence of a strong crystal field, contributed by seven water molecules and two terminal oxygen atoms that are coordinated to the Gd^{3+} ion.

3.4 *Thermogravimetry*

The TGA curves for the compounds **1-4** exhibit similar type of weight losses (representative TGA curves for **1**, **3** and **4** are shown in figure S3). First weight loss of 11–12.7% for all compounds occurring in the temperature range of 50–120° C corresponds to the loss of lanthanide coordinated seven water molecules and two crystal water molecules. The second weight loss of 4.5–6% (in the temperature range of 150–320° C) is ascribed to the loss of rest two crystal waters (described as a water dimer) and three hydroxyl ions attached to the central aluminium of Anderson anions. The total weight loss found is 18.8–19.2%, which is in good agreement with the calculated values of weight loss (18–19.5%).

3.5 *Powder X-ray diffraction studies*

Powder X-ray diffraction (PXRD) patterns of the compounds **1**–**4** have been recorded and the relevant diagrams/plots are presented in figure S5. The identical features of these PXRD patterns confirm that compounds **1**–**4** are isomorphous, which is also evidenced from their crystal structure parameters (tables 1 and 2).
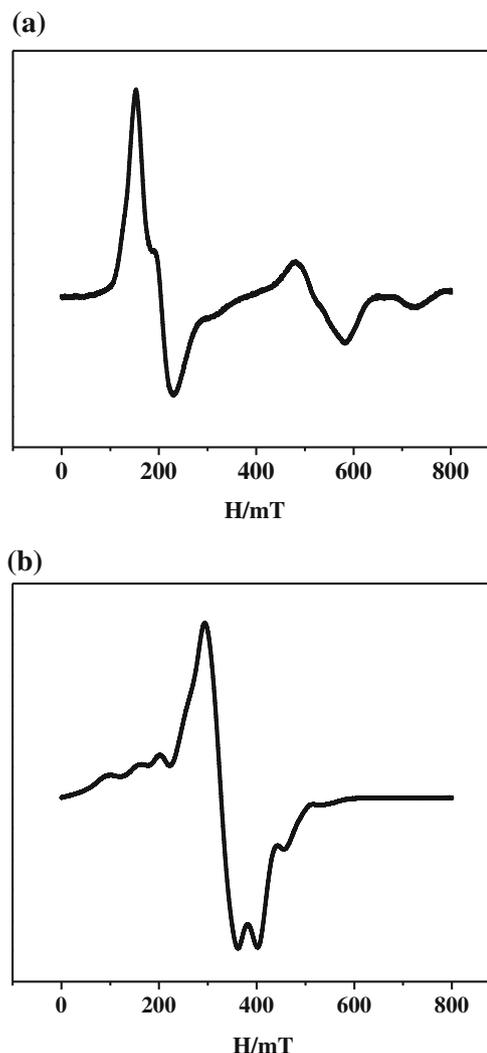
Figure 6. (a) ESR spectrum of $[La(H_2O)_7Cr(OH)_6Mo_6O_{18}]_n \cdot 4nH_2O$ (**1**) at 110K. (b) ESR spectrum of $[Gd(H_2O)_7Al(OH)_6Mo_6O_{18}]_n \cdot 4nH_2O$ (**4**) at 110K.

4. Conclusion

One-dimensional metal-oxide based inorganic solids **1**-**4** have been synthesized, in which the Anderson anion type polyoxometalate anions act as basic building units and the lanthanide cations as cationic linkers. Along the chain, the Anderson anion functions as a bidentate ligand, connecting the two lanthanides on either side of the cluster forming an infinite one-dimensional chain. We have described a unique one-pot synthesis, by which this series of compounds can effortlessly be isolated in contrast to the earlier two-step hectic procedures for the synthesis of same series of other compounds.[19–21] All four compounds have been characterized by powdered X-ray diffraction studies, IR, UV-visible spectroscopy, TGA analysis and unambiguously by single crystal X-ray crystallography. The crystal waters, metal

coordinated waters and hydroxyl groups of the central hetero-metal are involved in an extensive hydrogen bonding interactions resulting in the formation of 3D supramolecular network. In the present work, 1D structure is stabilized because, the ratio of cation to anion is 1:1 (each Anderson cluster has -3 charges that are counterbalanced by +3 charges of each lanthanide).

Supplementary Information

FT-IR spectra and powder X-ray diffraction patterns for compounds **1-4**, TGA plots for compounds **1**, **3** and **4** and some figures related to the crystal structures are available at www.ias.ac.in/chemsci.

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References

1. (a) Pope M T 1983 In *Heteropoly and isopoly oxometalates*, (Berlin: Springer-Verlag); (b) Pope MT and Müller A 1991 *Angew. Chem. Int. Ed. Engl.* **30** 34; (c) Okumara T Mizuno N and Misono M 1996 *Adv. Catal.* **41** 113; (d) Hill C L and Prosser-McCartha C M 1995 *Coord. Chem. Rev.* **143** 407; (e) Arumuganathan T, Rao A S, Vijaykumar T and Das S K 2008 *J. Chem. Sci.* **120** 95

2. Müller A, Peters F, Pope M T and Gatteschi D 1998 *Chem. Rev.* **98** 239

3. Yamase T 1998 *Chem. Rev.* **98** 307

4. Howell R C, Perez F G, Jain S, Horrocks W D and Francesconi L C 2001 *Angew. Chem. Int. Ed. Engl.* **41** 4031

5. (a) Yamase T and Tomita K 1990 *Inorg. Chim. Acta* **169** 147; (b) Yamase T and Sugeta M 1993 *J. Chem. Soc. Dalton Trans.* 759; (c) Khenkin A M and Neumann R 2002 *Adv. Synth. Catal.* **344** 1017

6. (a) Peacock R D and Weakly T J R 1971 *J. Chem. Soc (A)* 1836; (b) Molchanov V N, Tatjanina I V, Torchenkova E A and Kazansky L P 1981 *J. Chem. Soc. Chem. Comm.* 93; (c) Yamase T, Naruke H and Sasaki Y 1990 *J. Chem. Soc., Dalton Trans.* 1687

7. Wassermann K and Pope M T 2001 *Inorg. Chem.* **40** 2763

8. Wu C-D, Lu C-Z, Zhuang H–H and Huang J–S 2002 *J. Am. Chem. Soc.* **124** 3836

9. Wang X, Guo Y, Li Y, Wang E, Hu C and Hu N 2003 *Inorg. Chem.* **42** 4135

10. Gaunt A J, May I, Sarsfield M J, Collision D, Helliwell M and Dennis I S 2003 *J. Chem. Soc., Dalton Trans.* 2767

11. Fukaya K and Yamase T 2003 *Angew. Chem., Int. Ed. Engl.* **42** 654

12. (a) Naruke H, Ozeki T and Yamase T 1991 *Acta. Crystallogr.* **C47** 489; (b) Cronin L, Beugholt C, Krickemeyer E, Schmidtmann M, Bögge H, Kögerler P, Kim K, Luong K and Müller A 2002 *Angew. Chem. Int. Ed.* **41** 2805

13. Sadkane M, Dickman M H and Pope M T 2000 *Angew. Chem., Int. Ed.* **39** 2914

14. Shivaiah V, Reddy P V N and Das S K 2002 *J. Chem. Soc. Dalton Trans.* 3781

15. (a) Manikumari S, Shivaiah V and Das S K 2002 *Inorg. Chem.* **41** 6953; (b) Shivaiah V Nagaraju M, Das S K 2003 *Inorg. Chem.* **42** 6604; (c) Shivaiah V and Das S K 2005 *J. Chem. Sci.* **117** 227

16. Perloff A 1970 *Inorg. Chem.* **9** 2228

17. (a) Drewes D, Limanski E M and Krebs B 2004 *J. Chem. Soc., Dalton Trans.* 2087; (b) An H, Xiao D, Wang E, Sun C and Xu L 2005 *Eur. J. Inorg.* 854; (c) An H, Xiao D, Wang E and Xu L 2005 *New J. Chem.* **29** 667; (d) An H, Lan Y, Wang E, Hao N, Xiao D, Duan L and Xu L 2004 *Inorg. Chem. Commun.* **7** 356; (e) Drewes D and Krebs B 2005 *Z. Anorg. Allg. Chem.* **631** 2591; (f) Liu F-X, Marchal-Roch C, Dambournet D, Acker A, Marrot J and Sécheresse F 2008 *Eur. J. Inorg. Chem.* 2191; (g) Li S, Ma P, Wang J, Guo Y, Niu H, Zhao J and Niu J 2010 *Cryst. Eng. Comm.* **12** 1718; (h) Tan R-K, Liu S-X, Zhang W, Li S-J and Zhang Y-Y 2011 *Inorg. Chem. Commun.* **14** 384; (i) Singh M, Lofland S E, Ramanujachary K V and Ramanan A 2010 *Cryst. Growth Des.* **10** 5105

18. (a) An H, Xiao D, Wang E, Sun C and Lin X 2005 *J. Mol. Structure* **743** 117; (b) An H, Han Z, Xu T, Meng, C and Wang E 2008 *Inorg. Chem. Commun.* **11** 914; (c) Wang Y, Xiao D, Qi Y, Wang E and Liu J 2008 *J. Clust. Sci.* **19** 367; (d) Li J, Zhang L-C, Sun Z-G, Tian C-H, Zhu Z-M, Zhao Y, Zhu Y-Y, Zhang J, Zhang N, Liu L and Lu X 2008 *Z. Anorg. Allg. Chem.* **634** 1173; (e) Yang, Y, Xu L, Li F and Qu X 2013 *Inorg. Chem. Commun.* **33** 142

19. Andreev G B, Fedoseev A M, Budantseva N A and Antipin M Yu 2002 *Crystallography Reports* **47** 394

20. Fedoseev A M, Budantseva N A, Andreev G B, Yusov A B, and Shirokova I B 2002 *Russ. J. Coord. Chem.* **28** 279

21. Shi D-M, Ma F-X, Zhang C-J, Lu S and Chen Y-G 2008 *Z. Anorg. Allg. Chem.* **634** 758

22. Sheldrick G M 1996 *SADABS, A program for absorption correction with the Siemens SMART area-detector system* (Germany: University of Göttingen)

23. Sheldrick G M 1997 *SHELXS-97, A program for solution of crystal structures* (Germany: University of Göttingen)

24. Sheldrick G M 1997 *SHELXL-97, A program for solution and refinement of crystal structures* (Germany: University of Göttingen)

25. Hall R D 1907 *J. Am. Chem. Soc.* **29** 692

26. (a) Golhen S, Ouahab L, Grandjean D and Molinie P 1998 *Inorg. Chem.* **37** 1499; (b) Ouahab L, Golhen S, Yoshida Y and Saito G 2003 *J. Cluster Sci.* **14** 193