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Synthesis, structure, and magnetism of four polyoxomolybdate compounds containing yttrium and ytterbium

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Four new polyoxometalate compounds consisting of Anderson-type anions and trivalent rare earth (RE) cations, $[\text{RE}_2(\text{H}_2\text{O})_{14}\text{M}(\text{OH})_6\text{Mo}_6\text{O}_{18}][\text{M}(\text{OH})_6\text{Mo}_6\text{O}_{18}] \cdot 14\text{H}_2\text{O}$, RE = Y, M = Cr(1), Al(2); RE = Yb, M = Al(3), Cr(4), have been synthesized in aqueous solution and characterized by elemental analyses, infrared (IR) spectra, thermal gravimetric (TG) analyses, and single crystal X-ray diffraction. $[\text{M}(\text{OH})_6\text{Mo}_6\text{O}_{18}]^{3-}$ as a bidentate ligand coordinates to two RE^{3+} , forming a double-supported cation $[\text{RE}_2(\text{H}_2\text{O})_{14}\text{M}(\text{OH})_6\text{Mo}_6\text{O}_{18}]^{3+}$. The cations and other $[\text{M}(\text{OH})_6\text{Mo}_6\text{O}_{18}]^{3-}$ anions in the crystals are linked *via* hydrogen bonding interactions tightly, forming four supramolecular compounds. The magnetic properties of 1, 3, and 4 have been examined by measuring their magnetic susceptibilities from 2 to 300 K.

Keywords: Polyoxomolybdate; Rare earth element; Anderson-type anion; Supramolecular compound; Crystal structure; Magnetic property

1. Introduction

Polyoxometalates (POMs) which exhibit compositional diversity and structural versatility represent a class of nano-sized metal-oxo anions. POMs are remarkable not only in terms of molecular and electronic structural versatility but also because of their reactivity and application in photochemistry, analytical chemistry, clinical chemistry, magnetism, catalysis, biology, medicine, and materials science [1–9]. Several large nanostructure POM clusters have been reported [10–13] and many 1-D, 2-D, and 3-D POM-based polymers have also been synthesized [14–19]. In contrast, using Anderson-type polyoxoanions as inorganic building blocks to construct multi-dimensional frameworks is less explored. However, Anderson-type polyoxoanions exhibit attractive planar structure, and each Mo (or W) has two terminal oxygens which make them have high reactivity and readily integrate with transition metal

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centers [20–24]. Recently, Das *et al.* [25] reported an extended polymer $[\text{La}(\text{H}_2\text{O})_7\text{Al}(\text{OH})_6\text{Mo}_6\text{O}_{18}]_n \cdot 4\text{H}_2\text{O}$ with rare earth (RE) cation linkers. They also reported a spiral-shaped inorganic–organic hybrid chain $[\text{Cu}(2,2'\text{-bipy})(\text{H}_2\text{O})_2\text{-Al}(\text{OH})_6\text{Mo}_6\text{O}_{18}]_n^{3-}$ [20]. Meanwhile, Krebs *et al.* reported some compounds containing $[\text{TeMo}_6\text{O}_{24}]^{3-}$ and RE cations [26–28]. These have inspired our research interest and we have chosen $[\text{Cr}(\text{OH})_6\text{Mo}_6\text{O}_{18}]^{3-}$ and $[\text{Al}(\text{OH})_6\text{Mo}_6\text{O}_{18}]^{3-}$ polyoxoanions as building blocks in constructing multidimensional frameworks.

Some giant structures are known in which polyoxoanion building blocks are connected *via* lanthanide cations [12, 13, 29–31]. Because of their multiple coordination requirements and oxophilicity, lanthanide (Ln) cations are suitable for linking POMs together to form new classes of materials with extended metal–oxygen frameworks [29]. Several POM compounds containing Y and Yb have been reported [32–35]. However, example of Anderson-type POMs connected with Y^{3+} and Yb^{3+} cations/coordination complexes have never been reported. Therefore, it is of interest to design and synthesize new hybrid architectures based on Anderson-type POMs and Y^{3+} and Yb^{3+} cation/coordination complexes. In addition, spectroscopic and magnetic properties of lanthanides and their compounds have inspired our interest [13, 17, 18, 36–38].

In this article, we report the synthesis, crystal structure, and characterization of four new polyoxomolybdate compounds, $[\text{RE}_2(\text{H}_2\text{O})_{14}\text{M}(\text{OH})_6\text{Mo}_6\text{O}_{18}][\text{M}(\text{OH})_6\text{Mo}_6\text{O}_{18}] \cdot 14\text{H}_2\text{O}$, RE = Y, M = Cr(1), Al(2); RE = Yb, M = Al(3), Cr(4).

2. Experimental

2.1. General methods and materials

The $\text{Na}_3[\text{CrMo}_6\text{H}_6\text{O}_{24}] \cdot 8\text{H}_2\text{O}$ and $\text{Na}_3[\text{AlMo}_6\text{H}_6\text{O}_{24}] \cdot 8\text{H}_2\text{O}$ were prepared according to the literature [39]. $\text{RECl}_3 \cdot 6\text{H}_2\text{O}$ (RE = Y and Yb) were prepared by the addition of concentrated hydrochloric acid to RE_2O_3 then heated to dryness. All other reagents were used as purchased commercially. Elemental analyses (Y, Yb, Cr, Al, and Mo) were carried out on a Leaman inductively coupled plasma (ICP) spectrometer. IR spectra were obtained on a Magna-560 Fourier transform (FT)/IR spectrometer with KBr pellets from 400 to 4000 cm^{-1} . Magnetic susceptibilities were measured on crystalline samples with a Quantum Design MPMS-5SQUID magnetometer from 2 to 300 K at a fixed field of 0.1 T. Thermal gravimetric (TG) analyses were performed on a Perkin-Elmer TGA7 instrument in flowing N_2 with a heating rate of $10^\circ\text{C min}^{-1}$.

2.2. Synthesis

2.2.1. Synthesis of $[\text{Y}_2(\text{H}_2\text{O})_{14}\text{Cr}(\text{OH})_6\text{Mo}_6\text{O}_{18}][\text{Cr}(\text{OH})_6\text{Mo}_6\text{O}_{18}] \cdot 14\text{H}_2\text{O}$ (1). A mixture of $\text{YCl}_3 \cdot 6\text{H}_2\text{O}$ (0.0677 g, 0.2 mmol) and $\text{Na}_3[\text{CrMo}_6\text{H}_6\text{O}_{24}] \cdot 8\text{H}_2\text{O}$ (0.1231 g, 0.1 mmol) was dissolved in 25 mL of water in a 100 mL beaker fitted with a magnetic stirrer. The pH was adjusted to 2.46 by adding 1 mol L^{-1} HCl, was stirred for 2 h at 60°C , then filtered. Slow evaporation of this filtrate at room temperature resulted in pink block crystalline product after 2 weeks (Yield: *ca* 35% based on Mo). Anal. Calcd

for $\text{Cr}_2\text{H}_{68}\text{Mo}_{12}\text{O}_{76}\text{Y}_2$: Mo, 42.87; Y, 6.49; Cr, 3.79 (%). Found: Mo, 42.68; Y, 6.38; Cr, 3.70 (%).

2.2.2. Synthesis of $[\text{Y}_2(\text{H}_2\text{O})_{14}\text{Al}(\text{OH})_6\text{Mo}_6\text{O}_{18}][\text{Al}(\text{OH})_6\text{Mo}_6\text{O}_{18}] \cdot 14\text{H}_2\text{O}$ (2). Compound **2** was prepared using a method similar to that employed for the synthesis of **1**, with $\text{Na}_3[\text{AlMo}_6\text{H}_6\text{O}_{24}] \cdot 8\text{H}_2\text{O}$ in place of $\text{Na}_3[\text{CrMo}_6\text{H}_6\text{O}_{24}] \cdot 8\text{H}_2\text{O}$. Colorless block crystalline products were obtained (Yield: *ca* 32% based on Mo). Anal. Calcd for $\text{Al}_2\text{H}_{68}\text{Mo}_{12}\text{O}_{76}\text{Y}_2$: Mo, 43.66; Y, 6.61; Al, 2.01 (%). Found: Mo, 43.54; Y, 6.50; Al, 1.91 (%).

2.2.3. Synthesis of $[\text{Yb}_2(\text{H}_2\text{O})_{14}\text{Al}(\text{OH})_6\text{Mo}_6\text{O}_{18}][\text{Al}(\text{OH})_6\text{Mo}_6\text{O}_{18}] \cdot 14\text{H}_2\text{O}$ (3). Compound **3** was prepared using the method similar to that employed for the synthesis of **1**, with $\text{Na}_3[\text{AlMo}_6\text{H}_6\text{O}_{24}] \cdot 8\text{H}_2\text{O}$ and $\text{YbCl}_3 \cdot 6\text{H}_2\text{O}$ in place of $\text{Na}_3[\text{CrMo}_6\text{H}_6\text{O}_{24}] \cdot 8\text{H}_2\text{O}$ and $\text{YCl}_3 \cdot 6\text{H}_2\text{O}$, respectively. Colorless block crystalline products were obtained (Yield: *ca* 40% based on Mo). Anal. Calcd for $\text{Al}_2\text{H}_{68}\text{Mo}_{12}\text{O}_{76}\text{Yb}_2$: Mo, 41.07; Yb, 12.16; Al, 1.89 (%). Found: Mo, 39.91; Yb, 12.05; Al, 1.79 (%).

2.2.4. Synthesis of $[\text{Yb}_2(\text{H}_2\text{O})_{14}\text{Cr}(\text{OH})_6\text{Mo}_6\text{O}_{18}][\text{Cr}(\text{OH})_6\text{Mo}_6\text{O}_{18}] \cdot 14\text{H}_2\text{O}$ (4). Compound **4** was prepared using a method similar to that employed for synthesis of **1**, with $\text{YbCl}_3 \cdot 6\text{H}_2\text{O}$ in place of $\text{YCl}_3 \cdot 6\text{H}_2\text{O}$. Pink block crystalline products were obtained (Yield: *ca* 38% based on Mo). Anal. Calcd for $\text{Cr}_2\text{H}_{68}\text{Mo}_{12}\text{O}_{76}\text{Yb}_2$: Mo, 40.36; Yb, 11.95; Cr, 3.57 (%). Found: Mo, 40.27; Yb, 11.84; Cr, 3.48 (%).

2.3. X-ray crystallography

Diffraction intensity data for **1–4** were collected on a Bruker Smart CCD diffractometer equipped with a Mo anode and graphite monochromator ($\lambda = 0.071073 \text{ \AA}$) at 293 K using the ω -scan technique. An empirical absorption correction was applied. The structures of **1–4** were solved by direct methods and refined by full-matrix least squares on F^2 using *SHELXTL-97* software [40, 41]. The nonhydrogen atoms were refined anisotropically. Hydrogens on oxygen around Cr^{3+} and Al^{3+} and water were located in the difference Fourier maps for **1–4**. A summary of the crystallographic data and structure refinement for **1–4** is listed in table 1. Selected bond lengths and angles of **1** are listed in table S1.

3. Results and discussion

3.1. Crystal structures of compounds

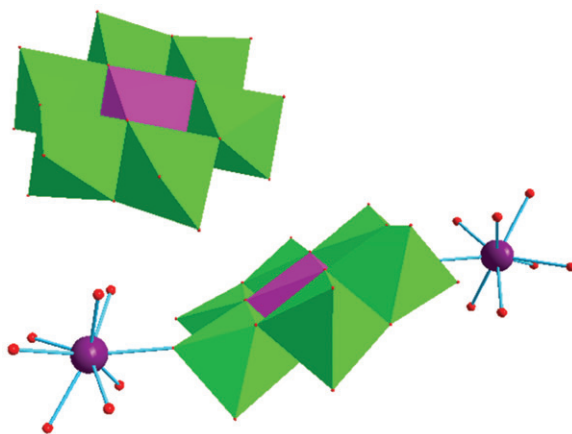
The single-crystal X-ray diffraction analysis reveals that **1–4** are isostructural, therefore we discuss the structure of **1** herein as representative.

Compound **1** consists of $[\text{Cr}(\text{OH})_6\text{Mo}_6\text{O}_{18}]^{3-}$, $[\text{Y}_2(\text{H}_2\text{O})_{14}\text{Cr}(\text{OH})_6\text{Mo}_6\text{O}_{18}]^{3+}$ and lattice water (figure 1). $[\text{Cr}(\text{OH})_6\text{Mo}_6\text{O}_{18}]^{3-}$ has *B*-type Anderson structure made up of seven edge-sharing octahedra, six $\{\text{MoO}_6\}$ octahedra are arranged hexagonally around

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

| Compound | 1 | 2 | 3 | 4 |
|--|--|---|--|--|
| Empirical formula | Cr ₂ Y ₂ Mo ₁₂ O ₇₆ H ₆₈ | Al ₂ Y ₂ Mo ₁₂ O ₇₆ H ₆₈ | Al ₂ Yb ₂ Mo ₁₂ O ₇₆ H ₆₈ | Cr ₂ Yb ₂ Mo ₁₂ O ₇₆ H ₆₈ |
| Mr | 2717.64 | 2667.60 | 2835.86 | 2885.90 |
| Color, habit | Pink, block | Colorless, block | Colorless, block | Pink, block |
| Crystal size (mm ³) | 0.050 × 0.045 × 0.033 | 0.040 × 0.35 × 0.033 | 0.060 × 0.055 × 0.053 | 0.050 × 0.045 × 0.033 |
| Crystal system | Triclinic | Triclinic | Triclinic | Triclinic |
| Space group | <i>P</i> $\bar{1}$ | <i>P</i> $\bar{1}$ | <i>P</i> $\bar{1}$ | <i>P</i> $\bar{1}$ |
| Unit cell dimensions (Å, °) | | | | |
| <i>a</i> | 11.0492(6) | 11.052(5) | 11.034(5) | 11.043(5) |
| <i>b</i> | 11.6488(6) | 11.620(5) | 11.604(5) | 11.655(5) |
| <i>c</i> | 13.9350(8) | 13.947(5) | 13.894(5) | 13.911(5) |
| α | 75.070(4) | 75.006(5) | 75.020(5) | 74.950(5) |
| β | 84.551(4) | 84.535(5) | 84.512(5) | 84.488(5) |
| γ | 89.536(4) | 89.582(5) | 89.539(5) | 89.446(5) |
| Volume (Å ³), <i>Z</i> | 1724.94(17), 1 | 1722.0(12), 1 | 1710.4(12), 1 | 1720.8(12), 1 |
| Calculated density (g cm ⁻³) | 2.616 | 2.572 | 2.753 | 2.785 |
| Absorption coefficient, μ (mm ⁻¹) | 4.190 | 3.924 | 4.984 | 5.223 |
| <i>F</i> (000) | 1306.0 | 1284 | 1346 | 1368.0 |
| Reflections measured | 18277 | 8748 | 8974 | 10635 |
| Reflections unique | 6617 | 6071 | 6556 | 8357 |
| Data/parameters | 6560/438 | 5971/360 | 6479/430 | 7634/417 |
| Goodness-of-fit on <i>F</i> ² | 1.034 | 1.087 | 1.034 | 1.008 |
| Final <i>R</i> indices [<i>I</i> ≥ 2σ(<i>I</i>)] | <i>R</i> ₁ ^a = 0.0332, <i>wR</i> ₂ ^b = 0.0913 | <i>R</i> ₁ = 0.0588, <i>wR</i> ₂ = 0.1606 | <i>R</i> ₁ = 0.0344, <i>wR</i> ₂ = 0.0836 | <i>R</i> ₁ = 0.0550, <i>wR</i> ₂ = 0.1343 |
| <i>R</i> indices (all data) | <i>R</i> ₁ = 0.0480, <i>wR</i> ₂ = 0.0951 | <i>R</i> ₁ = 0.0871, <i>wR</i> ₂ = 0.1757 | <i>R</i> ₁ = 0.0469, <i>wR</i> ₂ = 0.0860 | <i>R</i> ₁ = 0.0846, <i>wR</i> ₂ = 0.1506 |

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

Figure 1. Drawing of **1**. Hydrogens and free water molecules have been omitted for clarity.

the central {Cr(OH)₆} octahedron. The oxygens in the anion are divided into four kinds according to their coordination, terminal oxygens O_t, terminal oxygens coordinating to RE O_t', bridge oxygens O_b and central oxygens O_c. The Mo–O distances are divided into four groups: Mo–O_t 1.682(4)–1.713(4) Å, Mo–O_t' 1.730(4) Å, Mo–O_b

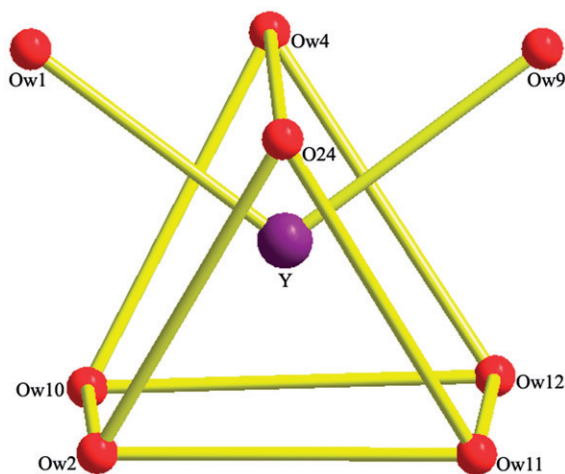


Figure 2. Coordination polyhedron around Y^{III} in **1**.

1.914(4)–1.950(4) Å, and Mo–O_c 2.267(4)–2.304(4) Å in **1**. The central Cr–O_c distances vary from 1.959(3) to 1.980(3) Å in **1**, which may be compared with the typical octahedral Cr³⁺–O distance of 1.98 ± 0.08 Å [42, 43]. The O–Cr–O bond angles in the anion deviate widely from the 90°, expected for an ideal octahedron (table S1), perhaps resulting from outward displacements of the Mo.

The crystallographically unique Y³⁺ is eight-coordinate with positions of oxygens approximating a bicapped-trigonal prism (figure 2). In addition to one terminal oxygen of anion coordinated to Y³⁺, water occupies the other seven positions. In the coordination polyhedron around Y³⁺, the O24, Ow11, and Ow2 form one trigonal plane, Ow10, Ow4, and Ow12 form the other trigonal plane, and Ow1 and Ow9 occupy the cap sites.

One [Cr(2)(OH)₆Mo₆O₁₈]³⁻ as a bidentate ligand coordinates to two [Y(H₂O)₇]³⁺ through the terminal oxygens of two opposite MoO₆ octahedra, forming a polyoxoanion-supported complex cation [Y₂(H₂O)₁₄Cr(OH)₆Mo₆O₁₈]³⁺, and the other [Cr(1)(OH)₆Mo₆O₁₈]³⁻ acts as the charge compensating anion.

The [Cr(OH)₆Mo₆O₁₈]³⁻ anions and [Y₂(H₂O)₁₄Cr(OH)₆Mo₆O₁₈]³⁺ cations join to form a 1-D infinite chain-like structure (figure S1) *via* hydrogen bonds (table 2). A 3-D supramolecular architecture is formed *via* strong hydrogen bonding interactions (table 2) which exist not only between adjacent anions and cations (figure 3), but also between water molecules and ions.

The bond valence sum calculations [44] indicate that Cr, Al, Y, and Yb are in the +3 oxidation state, and all Mo sites are +6. These results are consistent with the charge balance considerations.

3.2. FT-IR spectroscopy

IR spectra of **1–4** are similar (as shown in figure S2). In the low-wavenumber regions, they display the characteristic patterns of the Anderson structure [19–23]. The peaks

Table 2. Selected hydrogen-bond lengths (Å) and angles (°) for **1**.

| D-H...A | $d(\text{H}\cdots\text{A})$ | $\angle\text{DHA}$ | $d(\text{D}\cdots\text{A})$ | Symmetry transformation for A |
|------------------|-----------------------------|--------------------|-----------------------------|-------------------------------|
| 1-D | | | | |
| O12-H12B...O23 | 2.014 | 170.82 | 2.906 | $-x+1, -y-1, -z+3$ |
| O4W-H4A...O21 | 1.5441 | 92 | 2.971 | $-x+1, -y-1, -z+3$ |
| 2-D | | | | |
| O17-H17...O22 | 1.937 | 158.07 | 2.682 | $-x+1, -y-1, -z+2$ |
| O19-H19...O10 | 1.731 | 170.95 | 2.733 | $x-1, y+1, z$ |
| 3-D | | | | |
| O15-H15...O14 | 2.148 | 168.37 | 2.801 | $-x+1, -y, -z+2$ |
| O16-H16...O13 | 1.843 | 168.16 | 2.675 | $x, y-1, z$ |
| O13W-H13A...O1 | 1.851 | 158.68 | 2.709 | $-x+1, -y, -z+2$ |
| O13W-H13B...O2W | 2.018 | 125.83 | 2.647 | $x+1, y, z-1$ |
| O13W-H13B...O10W | 2.089 | 142.74 | 2.858 | $x+1, y, z-1$ |

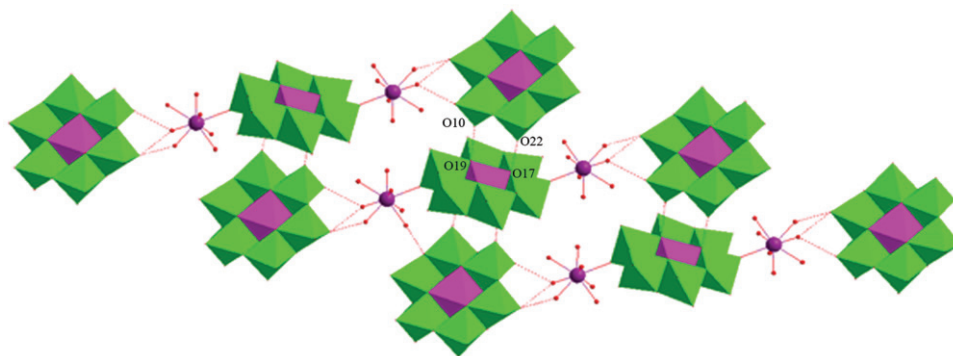


Figure 3. Hydrogen bonding interactions between adjacent anions and cations.

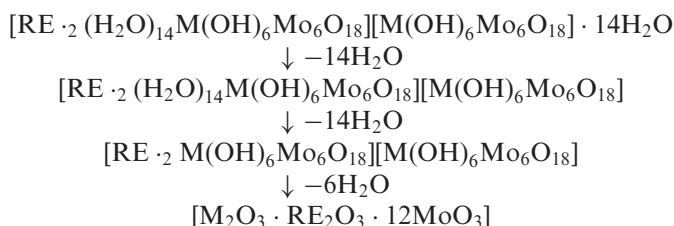
between 400 and 600 cm^{-1} are attributed to Mo–O_c stretching, those between 640 and 800 cm^{-1} to Mo–O_b stretch, and those between 890 and 960 cm^{-1} are assigned to Mo–O_t vibration. The absorptions at 410 cm^{-1} are attributed to RE–O (RE = Y and Yb) vibration; bands at 1600–1620 cm^{-1} are assigned to deformation vibrations of H–O–H owing to the existence of the crystallization and coordination water molecules. Absorptions at 3400 cm^{-1} are attributed to O–H bond stretch.

3.3. TG analyses

The TG curves (figure S3) recorded at 20–600°C reveal that there are three continuous weight loss stages for **1–4**. The total weight loss of 22.99%, 22.90%, 21.88%, and 21.43% of **1–4** are in agreement with the calculated value of 22.54%, 22.95%, 21.59%, and 21.23%, respectively. Because **1–4** are isostructural and have the same weight loss pattern, we discuss the thermal behavior of **1**.

The TG curve of **1** exhibits three weight loss steps. The first weight loss of 8.9% corresponds to the removal of lattice water molecules (Calcd 9.3%). The second weight loss of 9.6% at 89–170°C arises from coordination water molecules (Calcd 9.3%).

The third weight loss of 4.5% begins at 210°C and ends at 330°C arising from the backbone destruction of the polyanion (Calcd 4.0%). The thermal decomposition of the four compounds can be described as follows:



These results indicate that the water molecules in different coordination environments are lost in different temperatures and the compounds have low thermal stability. In order to prove the products from thermal gravimetric analysis are $[\text{M}_2\text{O}_3 \cdot \text{RE}_2\text{O}_3 \cdot 12 \text{MoO}_3]$, we carried out IR analysis of the product from heating **2** to 400°C for half an hour when its mass was constant. The IR spectrum is shown in figure S4, the peak around 880 cm^{-1} is attributed to the Mo–O characteristic vibration, the peak around 500 cm^{-1} is attributed to the Al–O and Y–O vibration, and the characteristic vibration peaks of Anderson anions disappear. So, the products are $[\text{M}_2\text{O}_3 \cdot \text{RE}_2\text{O}_3 \cdot 12 \text{MoO}_3]$.

3.4. Magnetic susceptibilities

The magnetic susceptibility data of **1** is shown in figure 4(a) as the χ_M^{-1} and $\chi_M T$ versus T plots. As the sample was cooled, the $\chi_M T$ values changed very little: increasing slightly from $3.72 \text{ cm}^3 \text{ K mol}^{-1}$ to $3.77 \text{ cm}^3 \text{ K mol}^{-1}$ from 300 to 125 K and then decreasing to $3.56 \text{ cm}^3 \text{ K mol}^{-1}$ at 2 K. The fitting to χ_M^{-1} versus T curve gives a small positive Weiss constant $\theta = 0.6191 \text{ K}$ and a Curie constant $C = 3.74 \text{ cm}^3 \text{ K mol}^{-1}$ in 2–300 K. The $\chi_M T$ value of $3.72 \text{ cm}^3 \text{ K mol}^{-1}$ at 300 K of **1** is very close to the expected spin-only value ($3.75 \text{ cm}^3 \text{ K mol}^{-1}$) of two Cr(III) ions, showing that the Cr^{3+} in **1** are isolated and **1** is basically simple paramagnetic.

The $\chi_M T$ value of $4.77 \text{ cm}^3 \text{ K mol}^{-1}$ at 300 K of **3** (figure 4b) is lower than the expected value of $5.14 \text{ cm}^3 \text{ K mol}^{-1}$ for two magnetic isolated Yb(III) ($J = 7/2$, $g = 8/7$). The plot of χ_M^{-1} versus T in the range of 300–28 K is well described by the Curie–Weiss law, giving a Curie constant $C = 5.40 \text{ cm}^3 \text{ K mol}^{-1}$ and a Weiss constant $\theta = -38.45 \text{ K}$, which suggests weak antiferromagnetic exchange interactions in **3** [45–47]. The small magnitude of the magnetic coupling in **3** is in agreement with its structure. In fact, the hydrogen-bonds linking yttrium(III) units in **3** provide the exchange pathway. Compound **3** has different magnetic behavior than $\text{K}_{13}[\text{Yb}(\text{SiW}_{11}\text{O}_{39})_2] \cdot x \text{H}_2\text{O}$ [31], which should be attributed to the different site symmetry and coordination environment of Yb^{3+} .

The $\chi_M T$ value of **4** at 300 K is theoretically expected to be $8.89 \text{ cm}^3 \text{ K mol}^{-1}$ for two magnetic isolated Yb(III) and two Cr(III) ions, but the experimental value of 7.58 (figure 4c) is much lower. In case of **1** without other paramagnetic metal ion, $[\text{Y}_2(\text{H}_2\text{O})_{14} \text{Cr}(\text{OH})_6 \text{Mo}_6 \text{O}_{18}] [\text{Cr}(\text{OH})_6 \text{Mo}_6 \text{O}_{18}] \cdot 14 \text{H}_2\text{O}$, the magnetic behavior of Cr(III) is just that of isolated magnetic center; and **3** having only Yb(III) paramagnetic center, $[\text{Yb}_2(\text{H}_2\text{O})_{14} \text{Al}(\text{OH})_6 \text{Mo}_6 \text{O}_{18}] [\text{Al}(\text{OH})_6 \text{Mo}_6 \text{O}_{18}] \cdot 14 \text{H}_2\text{O}$, exhibits a weak

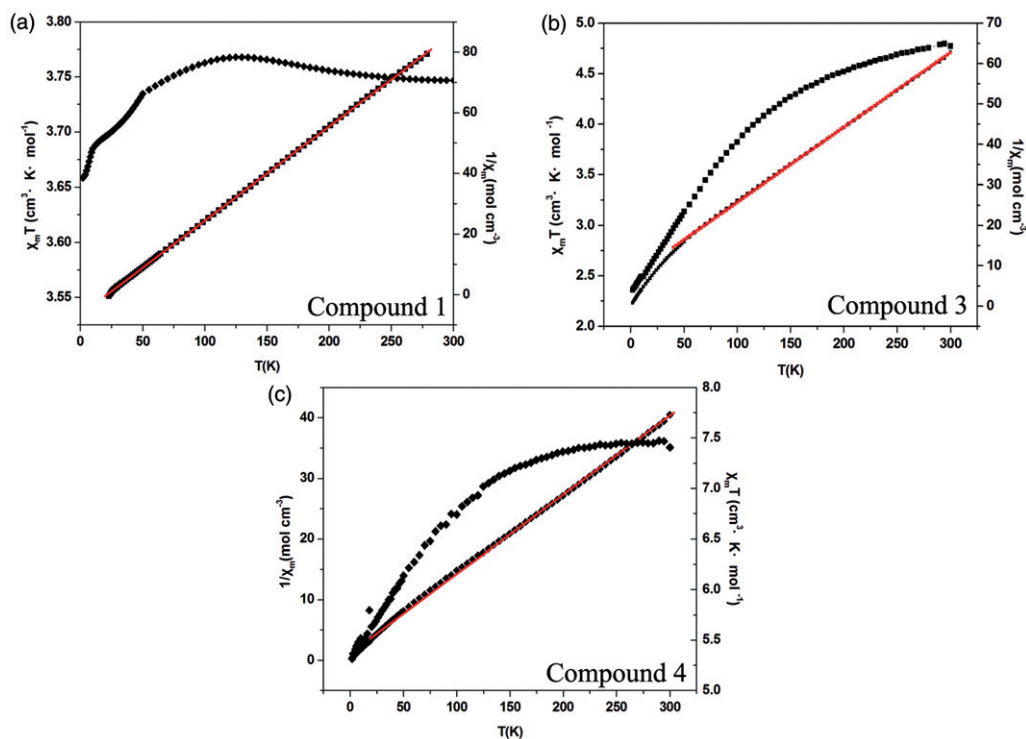


Figure 4. The χ_M^{-1} and $\chi_M T$ vs. T plots of **1**, **3**, and **4**.

antiferromagnetic exchange interaction. So the low $\chi_M T$ value of **4** in 300 K may be the result of the interaction between Yb(III) atoms *via* hydrogen bonds and between Yb(III) atom and Cr(III) atom *via* OWO linkage which is not considered as a good exchange pathway. The fitting to the χ_M^{-1} versus T plots gives a negative Weiss constant $\theta = -17.78$ K and Curie constant $C = 8.10$ cm³ K mol⁻¹.

4. Conclusion

Four compounds based on Anderson-type polyoxoanions have been synthesized. The $[\text{M}(\text{OH})_6\text{M}_6\text{O}_{18}]^{3-}$ (M = Cr and Al) and $[\text{RE}_2(\text{H}_2\text{O})_{14}\text{M}(\text{OH})_6\text{M}_6\text{O}_{18}]^{3+}$ (RE = Y and Yb) in the crystal are linked tightly *via* hydrogen bonding interactions forming four 3-D supramolecular compounds. Magnetic studies indicate that the hydrogen-bonds linking the ytterbium(III) units provide the exchange pathway.

Supplementary material

The crystal structure data have been deposited with numbers: 420541, 420658, 420659, 420805 for **1–4**, respectively, at ICSD database, FIZ Karlsruhe,

Hermann-von-Helmholtz-Platz 1, D-76344 Eggenstein-Leopoldshafen; E-mail: Crysdade@fiz-karlsruhe.de. Supplementary data associated with this article: figures S1–S4 and table S1.

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