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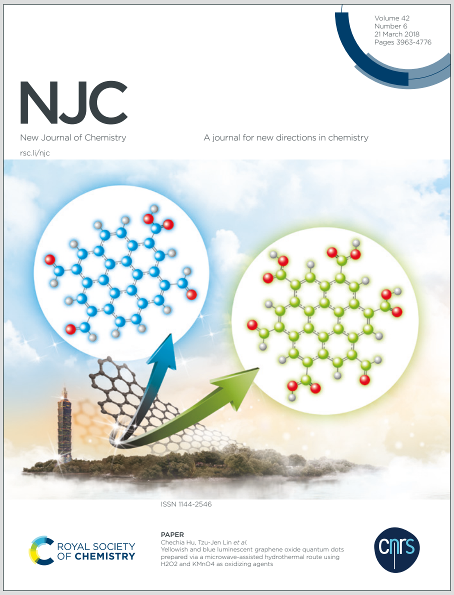

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ARTICLE

3d-4f metallacrown complexes with new sandwich core: synthesis, structures and single molecule magnet behavior

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Two heterometallic metallacrown complexes $[Er\{Cu_4(butyrat)_4\}_2]\cdot Cl_3\cdot MeOH\cdot 26H_2O$ (**1**) and $[Yb\{Cu_4(butyrat)_4\}_2]\cdot Cl_3\cdot MeOH\cdot 26H_2O$ (**2**) ($H_2butyrat$ = 3-aminobutyric hydroxamic acid) have been exhibited. X-ray crystallographic analysis reveals two complexes displayed nested-sandwich configurations with two 12-MC-4 metallacrown units capping a Ln^{III} in the centre. Magnetic studies revealed **1-2** have antiferromagnetic coupling interaction. Magnetic measurements show that complex **2** displays the frequency-dependence signals at a dc field of 1000 Oe, indicating field-induced single-molecule magnet behavior.

Introduction

Metallacrowns (MCs), inorganic analogues of organic crown ethers, are acknowledged with the metal and nitrogen atoms replacing the methylene carbon atoms of crown ethers to present [M-N-O] repeat units in metallacrown ring.[1-2] Pecoraro and Lah reported the first metallacrown examples in 1989, since then, many of these complexes have been constructed and characterized.[3-5] Researchers have successively developed various types of metalcrowns from 8-MC-4 to 60-MC-20 with the connections of the rings consisting of [M-N-O], [M-N-N], [M-N-C-O] and [M-N-C-N].[6-8] The Ln-based complexes may exist single-molecule magnets (SMMs) properties due to their large magnetic anisotropy arising from the large, uquenched orbital angular momentum.[9-14] Metallacrowns demonstrates a specific structural feature of a large amount of transition metal ions and rare earth ions located in a small volume, they would provides a large spin effect on the entire molecule to exhibit interesting and better magnetic phenomena.[15-23] The combination of high anisotropy of 3d ions and large spin-orbit of 4f ions in unique Metallacrown structure can provide a good way to obtain new molecular magnets. However, at present, 3d-4f MCs complexes with single molecular magnet properties mainly focus on Mn-Ln MCs complexes, and the structural feature only involved planar or warped MC structures.[24-30] To take advantage of the MC structural feature and develop intriguing configuration, it is still necessary to explore other structural types of MC and further discuss the relationship of structural properties.

Our group has great interest in the synthesis of metallacrowns and has reported a large number of metallacrowns in the previous study.[31-35] In order to continue our study, we chose 3-aminobutyric hydroxamic acid as ligand and synthesize two unprecedented complexes $[Er\{Cu_4(butyrat)_4\}_2]\cdot Cl_3\cdot MeOH\cdot 26H_2O$ (**1**) and $[Yb\{Cu_4(butyrat)_4\}_2]\cdot Cl_3\cdot MeOH\cdot 26H_2O$ (**2**), which have been characterized by X-ray single diffraction, Fourier transform infrared spectroscopy and X-Ray Powder Diffracter. Their magnetic properties were also explored in detail.

Experimental

Materials and synthesis

We first prepared 3-aminobutyric acid methyl ester hydrochloride by adding 3-aminobutyric acid in methanol and thionyl chloride solution under ice-water bath conditions, and then, the above reaction solution was refluxed in an oil bath and kept a constant temperature for 24 h. Then an aqueous solution of hydroxylamine hydrochloride and sodium hydroxide in a ratio of 1:3 was added into the above solution with the stirring at room temperature for 6 h. Last, the solution was acidified using 10 ml of hydrochloric acid and spin-evaporated to obtain the ligand. The synthesized method of this ligand has not been reported in the literature.

Syntheses

$[Er\{Cu_4(butyrat)_4\}_2]\cdot Cl_3^-\cdot MeOH\cdot 26H_2O$ (1)

$H_2butyha$ (0.118 g, 1 mmol) was dissolved in MeOH (15 mL) and $CuCl_2\cdot 2H_2O$ (0.086 g, 0.5 mmol) in acetonitrile (5 mL), followed by NEt_3 (0.01g, 1mmol) added to the previous solution. Then, $Er(NO_3)_3\cdot 5H_2O$ (0.045 g, 0.1 mmol) and NaCl (0.058 g, 1 mmol) were added to the above solution after stirring for 30 min. The color changed from dark green to navy blue immediately. Then the reaction solution was stired for

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about 3 h. The crystals were obtained through slow evaporation of the solvent. Black block crystals were obtained with yield 0.06 g, 39.0% based on Er salt. Elemental analysis calcd (%) for: $C_{33}H_{120}Cl_3Cu_8ErN_{16}O_{43}$: C, 17.90 %; H, 5.4 %; N, 10.13 %; found: C, 18.36 %; H, 5.29 %; N, 10.61 %. IR (KBr cm^{-1}): 3435 (s), 1580 (m), 1455 (vw), 1403 (w), 1341 (vw), 1270 (w), 1213 (vw), 1128 (w), 1037 (w), 1013 (w), 899 (vw), 851 (vw),746 (w), 620 (w), 443 (m).

$[Yb\{Cu_4(butyrat)_4\}_2]\cdot Cl_3^-\cdot MeOH\cdot 26H_2O$ (2)

Complex **2** is synthesized in the same way as complex **1** with $Yb(NO_3)_3\cdot 5H_2O$ (0.045 g, 0.1 mmol) and $CuBr_2$ (0.112 g, 0.5 mmol) instead of $Er(NO_3)_3\cdot 5H_2O$ and $CuCl_2\cdot 2H_2O$. Yield: 0.062 g, 38.0% based on Yb salt. Elemental analysis calcd (%) for: $C_{33}H_{120}Cl_3Cu_8N_{16}O_{43}Yb$: C, 17.86 %; H, 5.41 %; N, 10.10 %; found: C, 17.99 %; H, 5.36 %; N, 10.59 %. IR (KBr cm^{-1}): 3435 (s), 1578 (m), 1403 (w), 1341 (vw), 1270 (vw), 1128 (w), 1038 (w), 1013 (w), 899 (w), 852 (vw), 746 (w), 622 (w), 444 (w).

X-ray Crystallography

Single crystals of complexes **1**-**2** of the appropriate size were placed on an Agilent Xcalibur Eos Gemini CCD plate diffractometer at a certain temperature (complexes **1**-**2** were measured at 132 (4) K and 130 (11) K, respectively) by using Cu Kα radiation (λ = 1.54184 Å) measured by the graphite monochromatic method as the measurement light source, and the structural analysis of the complexes were completed by the software package Shelxl-2018/3. The direct method is used to solve the initial structure, the least-square method is used to refine the coordinates and anisotropic parameters of all non-hydrogen atoms using a full matrix program, and then the hydrogen atoms are hydrogenated using the Fourier method, followed by anisotropic purification. Crystallographic and structure refinement data are listed in Table S1. The selected bond distances and angles are summarized in Table S2–S3.

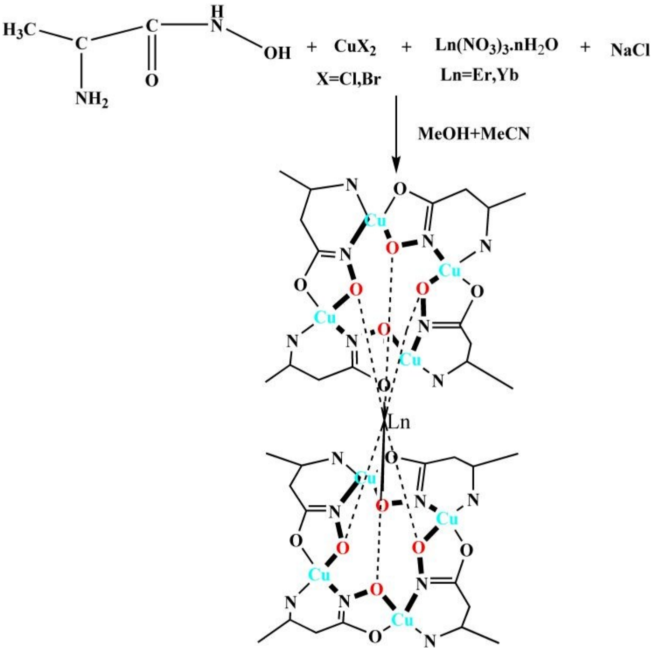
Physical Measurements

We performed elemental analysis of C, H and N on the Elementar Vario EL analyzer. The infrared spectrum was obtained on the Perkin-Elmer spectrum, and the samples were prepared as KBr particles. Powder X-ray diffraction (PXRD) was recorded on an XD-3 power diffractometer, which used a Cu-Kα X-ray source (λ = 1.54Å) to operate at 36 kV and 20 mA. Thermogravimetric analysis was performed on a PerkinElmer TGA-7 thermogravimetric analyzer at the heating rate of 10 °C min^{-1}, from 25 °C to 780 °C, under a flow of N_2 at 20.0 mL min^{-1}. Quantum Design MPMS-XL7SQUID magnetometer was used to collect the magnetic susceptibility data of the sample under a magnetic field of 1 kOe over a temperature range of 1.8-300 K. The measurement of the ac magnetic susceptibility was carried out by using an oscillation frequency in the range of 1−1000 HZ with 0 and 1000 Oe applied dc field.

Results and discussion

Crystal Structure

Complexes **1**-**2** were synthesized by the reaction of H_2butyrat ligand with Cu^{II} salts, Ln^{III} salts (Ln^{III} = Er^{III}, Yb^{III}) and Na^{I} salts in stoichiometric ratio 10:5:1:10 in MeOH and MeCN mixed solution, and isolated by slow evaporation of the solvents at room temperature (Scheme 1).



Scheme 1. Scheme of the way to obtain the $[12\text{-}MC_{CuII,}\ h_2buyrat\text{-}4]^{3+}$ unit.

Single-crystal X-ray diffraction analysis reveals that complex **1** belongs to monoclinic crystal system and *P*2(1) space group. The molecular structure contains a single-cap sandwich-like core with each face comprising a 12-MC-4 unit(Fig. 1). Two 12-MC-4 units (A and B) were linked together through a central Er^{III} ion, which bonds eight oxygen atoms from two 12-MC-4 ring. In this complex, the unbound anions (three chloride anions) are located around the structure of sandwich-like core. The whole molecule exhibit electric neutrality. For $[12\text{-}MC_{Cu}\text{-}4]$ unit, four Cu^{II} ions are assembled by four deprotonated polydentate ligands to form Cu−N−O connectivity ring. Each Cu^{II} ion exhibits four-coordinate, planar square geometry coordinating two N and two O atoms from the N_2O_2 pocket of the ligand. Two $[12\text{-}MC_{Cu}\text{-}4]$ as sandwich two sides all link to the center Er^{III} ion with the help of the eight oxygen atoms descended from oxime oxygens, which make Er^{III} ion locate into the eight-coordinate square anti-prism polyhedron. The plane distance between the upper and lower $[12\text{-}MC_{Cu}\text{-}4]$ planes is 3.552 Å. Cu-O-Er angles are 121.5(9)º for Cu1-O1-Er1, 122.0(9)º for Cu2-O3-Er1, 120.8(9)º for Cu3-O5-Er1, 122.9(9)º for Cu4-O7-Er1, 120.6(9)º for Cu5-O9-Er1, 121.30(9)º for Cu6-O11-Er1, 121.8(9)º for Cu7-O13-Er1 and 122.0(9)º for Cu8-O15-Er1, respectively. The average bond lengths of Cu-O and Cu-N on the equatorial plane are 1.94 Å and 1.976 Å, respectively, which are in the normal range of 1.916-1.95 Å and 1.894-2.022 Å. The chloride anion forms intermolecular hydrogen bonds with the four N-H groups of the spatially adjacent two complexes (N2-H2B···Cl2 = 2.620 Å, N8-H8B···Cl2

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= 2.468 Å, N14-H14B···Cl2 = 2.624 Å, N16-H16B···Cl2 = 2.633 Å). The complexes are packed through the weak interactions of four hydrogen bonds to form a one-dimensional chain (Fig. S3, ESI†). As show in Fig. S4, ESI†, the complex **1** further forms a two-dimensional network structure by weak interactions of extra four hydrogen bonds (N4-H4B···Cl1 = 2.512 Å, N6-H6B···Cl1 = 2.601 Å, N10-H10B···Cl1 = 2.526 Å and N12-H12B···Cl1 = 2.540 Å) on one-dimensional chain foundation.[36-41]

The structure of complex **2** is similar to the structure of complex **1** (Fig. S5, ESI†). In this complex, the unbound anions (three chloride anions) are located around the structure of sandwich-like core. The Yb-O bond lengths range from 2.256(15) to 2.328(14) Å. 1D coordination polymers can be obtained through four kind of hydrogen bonds interactions with the distances of 2.615 Å for N6-H6B···Cl1, 2.582 Å for N4-H4B···Cl1, 2.558 Å for N12-H12B···Cl1 and 2.584 Å for N10-H10B···Cl1) (Fig. S6, ESI†). Plane distance of **2** between the upper and lower [12-MC$_{Cu}$-4] planes is 3.526 Å. The coordination sphere of the Ln(III) ions are completed by eight equatorial oxygen atoms of ligand with the Yb-O bond lengths in the range of 2.256-2.328 Å.

Cu-N-O-Cu torsion angles lie within the range of 157.1-162.3º in **1** and 159.1-161.9º in **2**, respectively, indicating the nearly planarity for two 12-MC-4 planes. The ligands are concentrated above and below the xy plane and achieve an extended axial coordination environment for the central Ln^{III} ion, which have the distinct difference with that in the previous Cu-Ln complexes. Therefore, the comparison of our complexes with the previous reported Cu-Ln complexes shows the obvious difference. For the latter, they displayed the various structural configurations, such as batter-like,[3,7,42] linear,[43] cube[44], cycle,[45-47] dumbbell,[48] which distinguish the sandwich conformation in the resulting complex. The two 12-MC-4 units acting as faces of sandwich wrap one Ln ion in the center through the linking of eight hydroxamate O atoms from two 12-MC-4 units to accomplish the eight-coordination square pyramid coordination geometry for Ln ion.

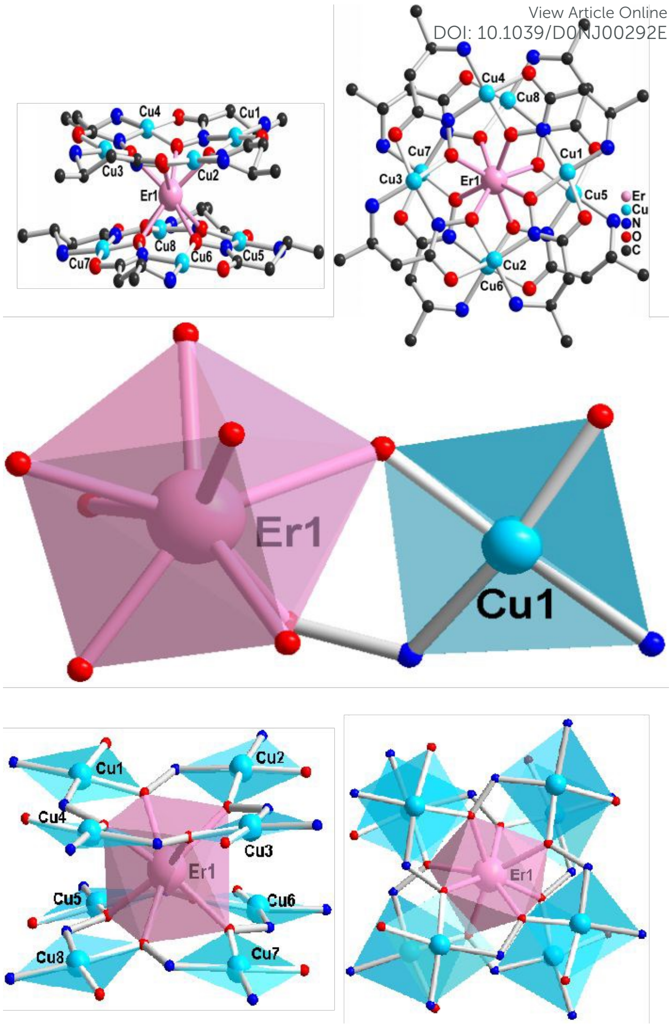

Figure 1. The structure of complex **1** with hydrogen atoms omitted for clarity (top). Local coordination spheres of Cu1^{II} ion and Er1^{III} ion (middle) and coordination geometries of core region (bottom).

Powder X-ray diffraction (PXRD)

The experimental RXRD patterns are in good agreement with the corresponding calculated patterns, confirming the high purity of the synthesized complexes (Fig. S1, ESI†).

Thermogravimetric analysis (TGA)

The thermogravimetric analysis (TGA) study revealed that complexes **1**-**2** have a two-step weight loss between room temperature and 780 °C (Fig. S2, ESI†). The first slowly weight loss occurs at 30-250 °C, and the weight losses are 20.1% for **1** and 17.03% for **2**, respectively, which are attributed to the loss of free solvent molecules (calculated 22.0% for **1** and 21.9% for **2**). As temperature increases, the frameworks of the two complexes start to decompose.

Static magnetic properties

The solid-state, variable-temperature dc magnetic susceptibility study of samples **1-2** were performed in the

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temperature range of 2–300 K under an applied magnetic field of 1000 Oe. The collect data were plotted as $\chi_M T$ *vs.* T (Fig. 2). Compounds **1**-**2** have room-temperature $\chi_M T$ values of 15.75 and 7.44 cm^3 mol^{-1} K. This is close to what is expected for eight Cu^{II} ions (S = 1/2, g=2) and one Er^{III} ion (S = 3/2, $^4I_{15/2}$) of 14.48 cm^3 mo^{-1} K for **1** and eight Cu^{II} ions (S=1/2, g=2) and one Yb^{III} ion (S = 1/2, $^2F_{7/2}$) of 5.57 cm^3 mo^{-1} K for **2**. For complex **1**, the $\chi_M T$ values of **1** firstly decrease slowly from 14.48 cm^3 mo^{-1} K at 300 K to 5.14 cm^3 mo^{-1} K at 5 K, and then drastically drop to 4.39 cm^3 mo^{-1} K at 1.8 K. The $\chi_M T$ product for **2** steadily decreases with decreasing temperature, reaching a minimum value of 1.41 cm^3 mo^{-1} K at 1.8 K. This type of behavior is consistent with the antiferromagnetic relationship between the metal centers.[49-51]

The magnetization data of complexes **1**-**2** were measured under magnetic field range 1-7 T and temperature range 1.8-8 K (Fig. S7, ESI†). For **1**, the magnetization sharply increased at low fields, and then slight increases to get saturation. Complex **1** showed a steady increase and was saturated at 7 T. The saturation values of the various field lines did not overlap significantly, indicating the presence of magnetic anisotropy and undetermined ground state in complex **1**. The magnetization of **2** kept to increase at the whole field without saturation. Complex **2** did not reach saturation at 7 T, its magnetization was 2.5473 μ_B. The variable field lines of complex **2** almost coincided, indicating that there are a large number of low excited states in complex **2**.[52-57]

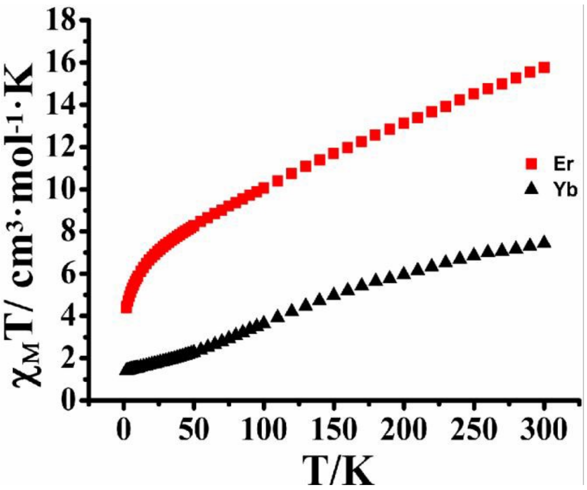

Figure. 2 χ_MT vs. T plots for complexes **1**-**2** over the temperature range 2-300 K under a magnetic field of 1000 Oe

Dynamic magnetic properties

In order to further investigate the dynamic magnetic behavior of three complexes, the temperature-dependent ac susceptibilities of **1**-**2** were determined in the range of 2-20 K under different dc fields. For complexes **1** and **2**, the in-phase (χ') and out-of-phase (χ'') magnetic susceptibilities do not exhibit temperature dependence under zero Oe dc field (Fig. S8, ESI† and Fig. S10, ESI†). But an external dc field was applied, **1**-**2** display frequency dependence. For **1**, owing to the limit of the instrument, the χ'' maximum signals were not probed above 1.8 K (Fig. S9, ESI†) under the condition of 1000 Oe field. The energy barrier (ΔE_{eff}) and relaxation time (τ_0) were only calculated through Debye equation: $\ln(\chi''/\chi') = \ln(\omega\tau_0) + E_{eff}/k_BT$. The perfect fitting plots and results are given in Fig. S11, ESI† and table. S4, ESI†. Complex **2** showed peak at 1000 Oe dc field (Figure 3). This means the emergence of SMM behaviour.[58-60] For most of the reported Cu-Ln compounds, Dy^{III} ion is the best candidate to design and construct SMMs owing to the strong spin-orbit coupling and extremely oblate electron density.[42-45] However, it is rarely seen for Cu-Yb compounds exhibiting single-molecule magnets. In this work, our Cu-Yb compound shows single-molecule magnet behavior. This may be due to our sandwich construction give the Yb^{III} ion an axially-coordinated ligand environment. Yb (III) has a more complicated energy splitting. When m_J =± 5/2, Yb (III) is mainly composed of oblate electron density with only small lobes extending toward the z-axis.[61] Considering that our sandwich-type compound has a central cavity along the z-axis direction, and the planar spacing of our Cu-Yb complex is 3.526 Å, which will be more conducive to axial extension. According to the fitting of Arrhenius equation $\tau = \tau_0 \exp(\Delta E_{eff} / k_BT)$ (where τ_0 is the pre-exponential factor, ΔE_{eff} is the effective energy barrier to the relaxation of the magnetization, and k_B is the Boltzmann constant), we can deduced ΔE_{eff} =6.84 K and τ_0 = 1.04×10^{-5} s for complex **2**, and we also compared the energy with that in the reported Cu-Ln SMMs(Table S6).[62-66]

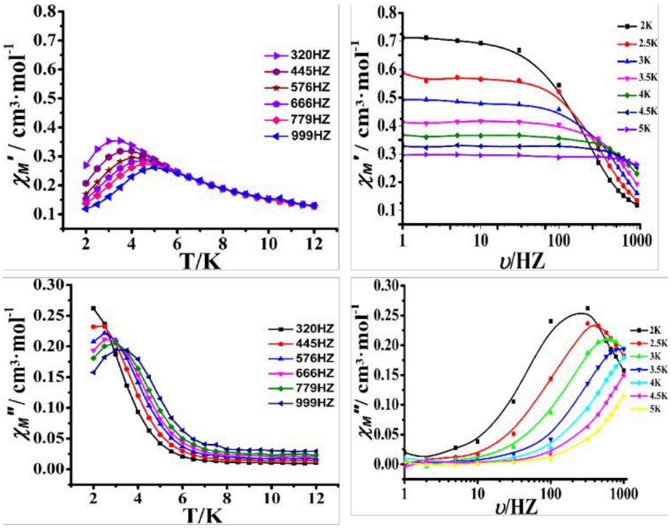

Figure 3. Temperature dependence (left) and frequency dependence (right) of the χ' (top) and χ'' (bottom) susceptibility measured at several temperatures and 1 kOe dc field for (**2**).

The Cole–Cole plots we have fitted of Yb^{III} (**2**) containing the χ' and χ'' data show a relatively symmetrical semi-circular shape, as shown in Fig. 4. At high temperatures, the Debye model gives α parameter of **2** below 0.3, which mainly indicates a single relaxation time in the present relaxation process (Table.

S5). The magnetization relaxation time (τ) and plotted as ln(τ) vs. 1/T of **2** were shown in Fig. 5.

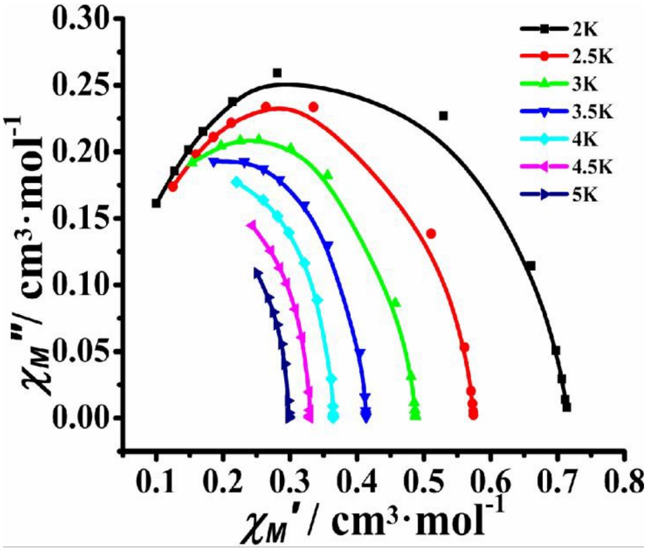

Figure 4. The Cole-Cole plots fitting of Yb^{III} (**2**) between 3.0 K and 6.0 K

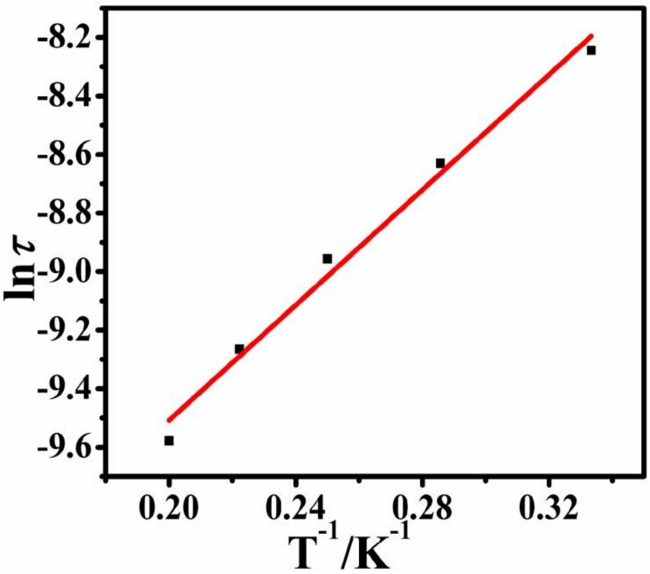

Figure 5. Magnetization relaxation time (τ), plotted as ln(τ) vs. 1/T for **2**. The solid lines being fits of the data using the experimental data.

Conclusions

In conclusion, we have successfully synthesized two complexes with sandwich construction. Magnetic susceptibility measurements reveal antiferromagnetic coupling interactions in complexes **1**-**2**. The alternating magnetic susceptibility measurements reveal that complex **2** show out-of-phase ac susceptibility signal, a typical of SMMs. The energy barrier for **2** assessed from ac susceptibility data is 6.84 K and the corresponding relaxation time is $\tau_0 = 1.04\times10^{-5}$ s.

Conflicts of interest

There are no conflicts to declare.

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