Controllable synthesis, crystal structure and magnetic properties of Monoer-Dimer Cocrystallized MnIII Salen-type composite material

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ABSTRACT

By the reaction of manganese-Schiff-base complexes with penta-anionic Anderson heteropolyanion, a new supramolecular architecture $[Mn_2(Salen)_2(H_2O)_2][Mn(Salen)(H_2O)_2]_2Na[IMo_6O_{24}] \cdot 8H_2O$ (**1**) (salen = N,N′-ethylene-bis(salicylideneiminate)) has been isolated. Compound **1** was characterized by the single-crystal X-ray diffraction, elemental, IR and thermal gravimetric analyses. Structural analysis reveals that the unit cell simultaneously contains Mn^{III}-Salen dimer and monomer cation fragments, for which the Anderson-type polyanions serve as counter anions. In the packing arrangement, all the Mn^{III} dimers are well separated by polyoxometalate units and form tertiary structure together with Mn^{III} monomers. Interestingly, different from the previous work, in the exact same reaction conditions, we are able to template Mn^{III}-Salen complexes into different configurations by varying the charge state of polyanions. Besides, the magnetic properties of **1** were also examined by using both dc and ac magnetic field of the superconducting quantum interference devices. Most importantly, our fitting of the experimental data to a Heisenberg-type spin model shows that there exists a ferromagnetic exchange interaction ~5 K between the spins ($S = 2$) on Mn^{III} in the dimer, while antiferromagnetic ones exist among monomers and dimer (~2 K). This meta-magnetic state could induce a slight spin frustration at low temperature, which would in turn affect the magnetic behavior. In addition, our ac field measurement of the susceptibilities suggests a typical signature for a single-molecule magnet.

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1. Introduction

Single-molecule magnets (SMM), well-fined nanosized superparamagnetic magnets, have attracted much attention since they were found more than two decades ago [1], not only because of their potential for applications in quantum computing and high-density information storage, but also their flexibility to chemically and structurally manipulate molecular structures, thus making SMM more controllable [2]. In this field, trivalent manganese ions (Mn^{III}) are especially suitable for carrying electron spins owing to their intrinsic large ground state spin quantum number and

uniaxial anisotropy [3—5]. Moreover, from the perspective of ligand, the ideal molecular structure should not only be able to stabilize the coordination environment of the metal center, but also have controllable subunits in order to manipulate the reactivity and magnetic behaviors to adapt different synthesis conditions and application environments, respectively. The tetradentate Schiff-base ligands (Salen) and their analogues have been extensively studied and widely used as an important ingredient to elaborate various types of magnetic materials [6—8]. Therefore, in the past few years, Salens have become one of the most booming areas for the construction of molecule-based magnetic materials, especially SMM and SCM [9,10]. So far, a large number of binuclear SMM and SCM based on Mn^{III}-Salen have been isolated. Meanwhile, people have carried out the in-depth study on the structural and magnetic behavior of these compounds, making a series of important scientific progresses and promoting the development of the molecule-based magnetic materials [11—14].

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It is worthwhile deepening our study in the synthesis of Salen-type Mn complexes based on the extensive research performed by the other researchers in this field, thus still making the research highly rewarding, such as controllable SMM structures and new effective spin models. Since the Mn-Salen family is an important subunits, a systematic exploration of the relationship between structural and magnetic behaviors can facilitate the rational design and synthesis of molecule-based magnets with new effective spin models [15,16]. As reported by many researchers, the counter anions of different compositions and structures have a crucial effect on the molecular configuration, spatial arrangement and even magnetic behavior of Mn-Salen complexes [17]. However, since the traditional anions such as NO_3^-, ClO_4^-, Ac^- and other charge pinning are difficult to be further regulated, there is currently little work that has discussed the correlations between the different charge numbers of iso-structural counter anions and the molecular configuration as well as magnetic properties of Mn-salen complexes.

Previously we used three negative charges in the B-series Anderson-type polyanion $[XMo_6(OH)_6O_{18}]^{3-}$ (X = Al and Cr) to react with classic Mn-Salen complex and successfully isolated Mn-dimer based supramolecular aggregations [18]. Because the molecular configurations of the A and B-series polyanions are exactly the same but their charge states are quite different, they are ideal molecular models to start with. To examine the dependence of structural and magnetic properties on the Coulomb forces, we have selected higher negative charges $[IMo_6O_{24}]^{5-}$ as a precursor to compare with the previous work. Herein, a new monomer-dimer Mn^{III} Schiff-base unit was crystallized in a hybrid compound $[Mn_2(Salen)_2(H_2O)_2][Mn(Salen)(H_2O)_2]_2Na[IMo_6O_{24}]\cdot8H_2O$ (**1**) and its magnetic properties were studied in details. We have found that (i) our newly synthesized compound is formed by Mn monomer and dimers, (ii) an interesting magnetic interaction structure, i.e., slight spin frustration within the molecular complex, and (iii) most importantly the typical behavior of SMM in this compound.

In the following discussion, we will first introduce our methods in section 2, discuss our results in section 3, and draw some general conclusions in section 4.

2. Experimental

2.1. Synthesis

$Na_5[IMo_6O_{24}]\cdot3H_2O$ (1.26 g, 1.0 mmol) was dissolved in 20 ml distilled water. Then, 20 ml methanol solution containing freshly prepared $[Mn(salen)(H_2O)]_2(ClO_4)_2\cdot H_2O$ (0.88 g, 1 mmol) was quickly added to above solution. The dark-brown reaction mixture was sealed and stirred in a conical flask at 35 °C for 2 days. After filtration, the filtrate was slowly evaporated at room temperature. After filtration, the filtrate was sealed with parafilm containing tiny pores for facilitating slow evaporation at room temperature. Dark-brown stick-like crystals of compound **1** were isolated after one week. After filtration, the remaining 31% were washed with methanol and dried in the air. The chemical formula for the compound **1** is $C_{34}H_{56}Mn_2N_7IMo_6O_{45}$. We found the percentages of the elements, compared with the theoretical values, are as follows: 19.11 (19.49) % for C, 5.16 (4.68) % for N, 5.26 (5.98) % for I, 5.76 (6.05) % for Mn, 29.12 (27.36) % for Mo. TG analyses have indicated that there are approximately 6 lattice water molecules in the unit cell of the compound (See SI-Fig. S3).

2.2. Characterization

All related chemicals were purchased and used without further purification. The starting materials $[Mn(salen)(H_2O)]_2(ClO_4)_2\cdot H_2O$ and $Na_5[IMo_6O_{24}]\cdot3H_2O$ were synthesized according to the previous work in the literature [19–21] and characterized by infrared (IR) spectroscopy. Elemental analyses for iodide, molybdenum and manganese atoms were analyzed on a PLASMA-SPEC (I) ICP atomic emission spectrometer. The crystallographic data were collected at a temperature of 296(2) K on a Rigaku R-axis Rapid IP diffractometer using graphite monochromatic $MoK\alpha$ radiation ($\lambda = 0.71073$ Å). Suitable crystals were mounted in a thin-glass tube and transferred to the goniostat. Multi-scan absorption correction was applied. Iodide, molybdenum and manganese atoms were located by Direct Methods, and successive Fourier syntheses revealed the remaining atoms. Refinements were achieved by the full-matrix method on F^2 using the Shelxtl-97 crystallographic software package [22–24]. In the final refinement, all the non-hydrogen atoms were anisotropically refined. H atoms bonded with the C and N atoms of the Salen ligand were fixed on the calculated atomic positions. The H atoms on the water molecules could not be located from the difference Fourier maps and were directly included in the final molecular formula. The elemental analysis and the charge balance have confirmed their presence. The highest residual peak and the deepest dip are 1.750 and -0.704 e $Å^{-3}$, respectively. The detailed crystal data and structure refinement are given in Table 1. Selected bond lengths and angles are listed in SI (Table S1). Crystallographic data (excluding structure factors) for the structure have been deposited with the Cambridge Crystallographic Data Center (CCDC), with the depository number CCDC-1057001. IR spectra were recorded in the range of 400–4000 cm^{-1} on an Alpha Centaurt Fourier-Transformed IR (FTIR) Spectrophotometer using KBr pellets. Thermal gravimetric (TG) analyses were performed on a Perkin-Elmer TGA-7 instrument in the flowing N_2 with a heating rate of 10 °C·min^{-1}. The ultra-violet–visible (UV–Vis) absorption spectrum was obtained using a 752 PC UV–Vis spectrophotometer. The magnetic susceptibility measurements were carried out with the use of a Superconducting Quantum Interference Device (SQUID), produced by Quantum Design, magnetometer MPMS-XL. The magnetic measurements

Table 1
Crystal data and structure refinements for **1**.

Compound	1
Empirical formula	$C_{64}H_{68}IMn_4Mo_6N_8NaO_{44}$
Formula weight	2649.1(9)
Temperature (K)	293(2) K
Wavelength, (Å)	0.71073 Å
Crystal system	triclinic
Space group	$P\bar{1}$
a(Å)	14.204(3)
b(Å)	14.876(3)
c (Å)	14.877(3)
α(°)	92.33(3)
β(°)	111.67(3)
γ(°)	112.03(3)
Volume (Å^3)	2649.1(9)
Z	1
Calculated density (g cm^{-3})	1.629
Absorption coefficient (mm^{-1})	1.521
F(000), e	2628
θ range for data collection	3.01–25.00°
Limiting indices	$-16 \le h \le 16$, $-17 \le k \le 17$, $-17 \le l \le 17$
Reflections collected/unique/R_{int}	20696/9268/[R(int) = 0.0310]
Completeness to theta = 25.00, %	99.20%
Refinement method	Semi-empirical from equivalents
Data/restraints/parameters	9268/5/613
Goodness-of-fit on F^2	1.064
Final R indices [I > 2σ(I)]	R1 = 0.0509, wR2 = 0.1230
R indices (all data)	R1 = 0.0649, wR2 = 0.1274
Largest diff. peak and hole	1.750 and -1.51 e.Å^{-3}

$R_1 = \sum||F_0|-|F_c||/\sum|F_0|$,
$wR_2 = \sum[w(F_0^2-F_c^2)^2]/\sum[w(F_0^2)^2]^{1/2}$.