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Two Mn_6 single-molecule magnets with sulfur-contained capping ligand

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ABSTRACT

The reactions of $Mn(ClO_4)_2{\cdot}6H_2O$, 1-(2-hydroxyphenyl)ethanone oxime (abbr. as MeSao), NEt_3 and thiophene-2-carboxylic acid/thiophene-3-carboxylic acid (2-TCA/3-TCA) lead to $[Mn_6O_2(MeSao)_6(2\text{-TCA})_2(EtOH)_4(H_2O)_2](EtOH)_2$ (**1**) and $[Mn_6O_2(MeSao)_6(3\text{-TCA})_2(EtOH)_4(H_2O)_2](EtOH)_2$ (**2**), respectively. Their structures can be described as a core of the $[Mn^{III}{}_6O_2(Mesao)_6(O_2C\text{-thiophene})_2(EtOH)_4]$ consisting two off-set, stacked $[Mn^{III}{}_3(\mu^3\text{-}O^{2-})]^{7+}$ triangular subunits linked by two central oximato O-atoms and two O-atoms from phenoxide group. Magnetic investigation revealed that **1** and **2** all have a spin ground state $S = 4$, and both complexes show single-molecule magnet behaviors with similar energy barriers $U_{eff} \sim 45$ K.

1. Introduction

With the demand and development of basic elements for nanoscale memory storage and quantum computation, single-molecule magnets (SMMs) appear as promising candidates [1]. SMMs based on transition-metal (TM) ions are normally featured by two factors: a large ground-state spin S and Ising anisotropy with negative zero-field splitting D, which leads to the energy barrier U between the two fundamental states S and $-S$ in double-well model equal to S^2D or $(S^2 - 1/4)D$ for integer or half-integer spin ground-states, respectively [2].

The first and well studied SMMs were the Mn_{12} family, typically with $S = 10$ spin ground-state, and the effective energy barrier of magnetization relaxation (U_{eff}) as large as 74.4 K [3]. This held the record for the SMMs barrier until an $S = 12$ member of the cluster family with general formula $[Mn^{III}{}_6O_2(R\text{-sao})_6(O_2CR)_2(ROH)_m(H_2O)_n]$ (hereafter abbreviated as Mn_6), which possesses the new U_{eff} record-value of 86 K, was discovered by G. Christou and E. K. Brechin et al. [4]. Recently another Mn_6 SMM using the salicylamidoximes claims achieved an equal record-high barrier value of 86 K [5]. The detail investigation with lots of Mn_6 family members showed that the structural distortion in the Mn_6 molecule was crucial to its SMM behavior [4a]. The increased steric bulk and nonplanarity of the R-sao ligands cause a shortening of the distance between the phenolato oxygen-square pyramidal and Mn and a severe twisting of the Mn–N–O–Mn moieties within each Mn_3 subunit. The exchange interactions within each Mn_3 triangle depend strongly and solely on this individual Mn–O–N–Mn torsion angles α: the bigger the torsion angle, the larger (FM) the pairwise (Mn_2) ferromagnetic interaction; the smaller the Mn–N–O–Mn torsion angle, the larger pairwise antiferromagnetic (AFM) interaction. There is a "magic area" (30.4°–31.3°) for the torsion angles α, above and below which the pairwise exchange interaction would be ferromagnetic or antiferromagnetic [4a].

Besides the effort to look for compounds with larger barrier U_{eff} and higher blocking temperature T_B, there lies another important issue that is fundamental for the practical exploitation of SMMs – the grafting of these nanoscale molecular magnets on the surfaces of substrate to obtain nano-devices which can be testified and processed. There have been many relative studies based on Mn_{12} systems [6]. However, recently XMCD and XAS investigation showed the adsorbates of Mn_{12} complexes on gold undergo structural deformations, with concomitant disappearance of SMM behavior [7]. The request of new robust SMM-surface binding candidates draws researcher's interest to the Mn_6 system which can be functionalized with groups (typically sulfur-contained carboxylic acid) that could provide strong binding with the substrate such as Au surface. E. K. Brechin and co-workers studied the grafting of two Mn_6 SMMs on the Au(111) surface, which demonstrated that the stoichiometry of the molecular cores is preserved after grafting and a sub-monolayer distribution of isolated clusters on the gold surface [8]. R. Sessoli and co-workers covalently grafted Fe_4 SMMs on the gold surface using sulfur-contained ligands and demonstrated the reaction with the substrate affords a monolayer of electronically intact clusters doubly linked to the surface via Au–S bonds, by a combination of STM, XAS/XMCD and XPS studies [9].

Herein, we report two new Mn_6 clusters with slightly different sulfur-contained capping ligands show SMM behavior, which are possible surface-binding candidates.

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2. Experimental

2.1. Materials and measurements

Mesao was synthesized and purified by previous reported procedure [10]. The other reagents and solvents for the synthesis and analysis were commercially available and used as received without further purification. Elemental analysis of carbon, nitrogen, hydrogen and sulfur was performed using an Elementary Vario EL analyzer. Magnetic susceptibility measurements were carried out on polycrystalline samples tightly packed and sealed in a capsule in the 2–300 K temperature range using a Quantum Design MPMSXL5 SQUID susceptometer. Diamagnetic corrections were applied to the observed paramagnetic susceptibilities using Pascal's constants [11].

2.2. Synthesis

2.2.1. Synthesis of $[Mn_6O_2(MeSao)_6(2\text{-}TCA)_2(EtOH)_4(H_2O)_2](EtOH)_2$ (**1**)

To a 20 mL ethanol solution of Mesao (0.5 mmol, 0.075 g), 2-TCA (0.5 mmol, 0.064 g), $Mn(ClO_4)_2{\cdot}6H_2O$ (0.5 mmol, 0.18 g) and 0.14 mL NEt_3 was added. The mixture was stirred for 1 hour and filtered. X-ray diffraction quality black cubic crystals of **1** were obtained in 1 week by slow evaporation. Yield based on Mn: 60%. Elemental *Anal.* Calc. for $Mn_6C_{68}H_{82}N_6O_{25}S_2$: C, 45.96; H, 4.65; N, 4.65. Found: C, 46.89; H, 4.73; N, 4.72%.

2.2.2. Synthesis of $[Mn_6O_2(MeSao)_6(3\text{-}TCA)_2(EtOH)_4(H_2O)_2](EtOH)_2$ (**2**)

The synthesis procedure was similar to **1** with the change of 2-TCA to 3-TCA. Yield based on Mn: 70%. *Anal.* Calc. for $Mn_6C_{68}H_{82}N_6O_{25}S_2$: C, 45.96; H, 4.65; N, 4.73. Found: C, 46.13; H, 4.82; N, 4.66%.

Caution! Perchlorate salts are potentially explosive. Only a small amount of material should be used and handled with care.

2.3. X-ray crystallography

The crystallographic data for the single crystals of compounds **1** and **2** were collected at 293 K on a Nonius KappaCCD diffractometer with a 2.0 kW sealed anode source using graphite monochromated Mo Kα radiation of $\lambda = 0.71073$ Å [12]. Empirical absorption corrections were applied using the Sortav program [13]. The structures of **1** and **2** were well solved by direct method and refined by full-matrix least-squares on F^2 using SHELX program [14]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were constrained to ideal geometry and were included in the refinement in the riding model approximation. Details of the data collection parameters and crystallographic information for complexes **1** and **2** are summarized in Table 1.

Table 1
Crystallographic data for compounds **1** and **2**.

	1	**2**
Empirical formula	$Mn_6C_{68}H_{82}N_6O_{25}S_2$	$Mn_6C_{68}H_{82}N_6O_{25}S_2$
Formula weight	1777.17	1777.17
Crystal dimension (mm)	0.30 × 0.35 × 0.35	0.41 × 0.38 × 0.21
Crystal system	Triclinic	Triclinic
Space group	*P*-1	*P*-1
a (Å)	11.3653(2)	11.3079(3)
b (Å)	14.0936(3)	14.1780(4)
c (Å)	14.2313(3)	14.3342(5)
α (°)	66.9132(2)	66.8913(12)
β (°)	77.0004(3)	71.6283(10)
γ (°)	72.5110(2)	76.3226(11)
V (Å^3)	1985.1(7)	1989.2(7)
Z	1	1
ρ_{cal} (g/m^3)	1.505	1.522
μ (mm^{-1})	1.058	1.056
F(0 0 0)	852	940
Theta range for data collection	3.46–25.03	3.47–27.44
Index ranges	$-13 \leqslant h \leqslant 13$, $-16 \leqslant k \leqslant 16$, $-16 \leqslant l \leqslant 16$	$-14 \leqslant h \leqslant 14$, $-18 \leqslant k \leqslant 18$, $-18 \leqslant l \leqslant 18$
Reflections collected	4763	4979
Independent reflections (R_{int})	0.0524	0.0707
R_1 (all)	0.0397	0.0471
wR_2	0.1187	0.1114
Goodness-of-fit on	0.860	0.945

$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $wR = |\Sigma w(|F_o|^2 - |F_c|^2)|/\Sigma|w(F_o)^2|^{1/2}$.

3. Results and discussion

3.1. Description of the geometry structures

The structures of **1** and **2** can be described (Fig. 1) as a core of the $[Mn^{III}{}_6O_2(Mesao)_6(O_2C\text{-thiophene})_2(EtOH)_4]$ consisting two off-set, stacked $[Mn^{III}{}_3(\mu^3\text{-}O^{2-})]^{7+}$ triangular subunits linked by two central oximato O-atoms and two O-atoms from phenoxide group. Three octahedrally coordinated Mn^{III} ions in each subunit form a triangle by sharing a μ_3-oxo center, with the interatomic distances and torsion angle listed in Table 2. Each Mn···Mn edge of the triangle is bridged by an oxime (N···O) group from one Mesao ligand, such that in both complexes the coordination spheres of the Mn ions are completed by two terminal thiophene carboxylates (one on each triangle), a phenoxide O-atom, and a terminal alcohol solvate molecule and/or H_2O molecule. All Mn ions are in the +3 oxidation state, as confirmed by combination of bond-length considerations, BVS calculations, and charge-balance. All Mn^{III} ions display a six-coordinate distorted octahedral geometry, and the Jahn–Teller axes of all three Mn^{III} ions are nearly parallel to each other and are roughly perpendicular to the $[Mn^{III}{}_3O]$ plane. The nearest distance of Mn ions in different Mn_6 core is about 8.559 Å (for **1**) and 8.484 Å (for **2**), respectively, which indicates that the inter-cluster magnetic interaction can be neglected. The structures of **1** and **2** are very similar to each other as there is only one difference in the molecules (the sulfur position in the thiophene group). There are several differences with the interatomic distances and Mn–N–O–Mn torsion angles. There are two torsion angle α above the "magic area" (30.4°–31.3°) [4] and one below it, yet the average torsion angle α_v in **2** (30.35°) is a little larger than that in complexes **1** (29.89°). The phenolato oxygen to square pyramidal Mn distance (Mn3···O1) in **2** is similar with that in **1**, but the Mn1′···O1 distance in **2** is longer than that in **1** correspondingly. This suggests that in **2** the twisting of the Mn–N–O–Mn moieties within each Mn_3 subunit is little more severe than that in complex **1**.

3.2. Magnetic properties

DC measurements of the magnetic susceptibility, performed on complexes **1** and **2** in the 2–300 K range with an applied field of 1 kOe, are plotted as $\chi_M T$ versus *T* in Fig. 2. The $\chi_M T$ values at 300 K are 17.53 and 17.40 cm^3 K mol^{-1} for **1** and **2**, respectively, which are close to the spin-only ($g = 2.0$) value of 18.00 cm^3 K mol^{-1} expected for six high-spin Mn^{III} ions at room temperature. For both complexes, the $\chi_M T$ data above 20 K decreases monotonically with temperature, indicating the dominant antiferromagnetic character of the interactions between metal centers. The $\chi_M T$ value at 2 K is about 6.5 cm^3 K mol^{-1} for **1** and **2**, which is consistent with an $S = 4$ spin ground-state, with the effect of magnetic anisotropy taken into account.