Inorganic Chemistry Communications 14 (2011) 1136–1139

Contents lists available at ScienceDirect

Inorganic Chemistry Communications

journal homepage: www.elsevier.com/locate/inoche

A new dodecanuclear manganese single-molecule magnet from the arrangement of manganese triangles

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ARTICLE INFO

Article history:
Received 14 March 2011
Accepted 8 April 2011
Available online 16 April 2011

Keywords:
Azido bridge
Magnetoanisotropy
Single-molecule magnet
Superparamagnet
Nanoscale magnet

ABSTRACT

Bridging-azido ligands are used to create a new dodecanuclear manganese cluster $[Mn_{12}O_4(salox)_{12}(N_3)_4(MeOH)_6(H_2O)_2]\cdot 5MeOH\cdot 2H_2O$ ($\mathbf{1}\cdot 5MeOH\cdot 2H_2O$) from the arrangement of manganese triangles, $[Mn_3O]$. Single-crystal x-ray analysis shows that $\mathbf{1}\cdot 5MeOH\cdot 2H_2O$ contains a $[Mn^{III}_{12}(\mu_3\text{-}O)_4(\mu_2\text{-}N_3)_4]^{24+}$ core, constructed from four $[Mn^{III}{}_3O]^{7+}$ building units, which is a new structural type in the family of Mn_{12} complexes. Variable temperature magnetic susceptibility and magnetization measurements of the complex $\mathbf{1}\cdot 5MeOH\cdot 2H_2O$ were carried out. The magnetic data indicate that complex $\mathbf{1}\cdot 5MeOH\cdot 2H_2O$ exhibits antiferromagnetic with a non-zero ground state spin value of $S=4$. The frequency dependence of out-of-phase component in alternating current magnetic susceptibility and magnetic hysteresis loop measurements indicate that complex $\mathbf{1}\cdot 5MeOH\cdot 2H_2O$ is a new single-molecule magnet with a significant magnetoanisotropy of $U_{eff}=70$ K.

Polynuclear manganese clusters often exhibit large, and sometimes abnormally large, spin values in the ground state, and combined with a large magnetic anisotropy have led some of these species to be single-molecule magnets (SMMs). SMMs are attracting extensive attention because they represent nanoscale magnetic particles of a well-defined size [1,2]. They display sluggish magnetization relaxation phenomena such as magnetization hysteresis loops and frequency-dependent out-of-phase alternating current (AC) magnetic susceptibility [3,4]. The remarkable magnetic properties of an SMM arise from its high-spin ground state (S) split by a large negative axial zero-field splitting (ZFS, D) which results in an anisotropy energy barrier of $KV=|D|S_Z^2$ [5]. The development of rational syntheses of multinuclear metal complexes, especially containing high-spin manganese(III) ions, has been magnetically interesting due to the pronounced magnetic anisotropy provided by the Jahn–Teller (JT) distortion. Thus, many current routes to multinuclear SMMs culminate in manganese(III) containing complexes, to achieve the associated large single-ion anisotropy [6,7]. The use of salicylaldoxime ligands in manganese chemistry has proven to be extremely successful in the synthesis of new polynuclear complexes [8–12]. Some SMMs and single-chain-magnets (SCMs), using salicylaldoxime (H_2salox) and its derivatives, were reported [13–17]. Moreover, the azide bridging ligand often mediates ferromagnetic exchange between paramagnetic centers, and this property has been recently exploited in the preparation of some SMMs [18–20] and SCMs [21–24]. In the present study, a polynuclear manganese complex with azide and salicylaldoximate, which produces a new dodecanuclear manganese cluster, $[Mn_{12}O_4(salox)_{12}(N_3)_4(MeOH)_6(H_2O)_2]\cdot 5MeOH\cdot 2H_2O$ ($\mathbf{1}\cdot 5MeOH\cdot 2H_2O$), is investigated. Complex $\mathbf{1}\cdot 5MeOH\cdot 2H_2O$ reveals a novel structural arrangement of $[Mn^{III}{}_3O]^{7+}$ and displays an obvious frequency-dependent out-of-phase component in AC magnetic susceptibilities and magnetic hysteresis loop measurements, which are indicative of SMM behavior.

$Mn(ClO_4)_2\cdot 6H_2O$, NEt_3, NaN_3, and H_2salox in a 1:1:1:1 ratio leads to a dark green methanol solution. Ether was slowly diffused into the solution to yield dark green-brown needle crystals of $[Mn_{12}O_4(salox)_{12}(N_3)_4(MeOH)_6(H_2O)_2]\cdot 5MeOH\cdot 2H_2O$ ($\mathbf{1}\cdot 5MeOH\cdot 2H_2O$) in a 23% yield [25]. The infrared (IR) spectrum of complex **1** shows a simple ν_{as} absorption at 2057 cm^{-1} and a moderately intense band at 1597 cm^{-1} in the carbonyl stretching region, with enhanced intensity and complexity in the azido and C=N stretching regions. X-ray crystallographic results of the product readily explain the origin of the spectroscopic modifications. Complex $\mathbf{1}\cdot 5MeOH\cdot 2H_2O$ crystallizes in triclinic space groups $P\bar{1}$ with $a=12.4812(4)$ Å, $b=14.2985(4)$ Å, $c=19.0003(6)$ Å, $\alpha=85.4138(10)°$, $\beta=99.608(2)°$, $\gamma=66.4047(11)°$, $V=2968.21(16)$ Å^3, $Z=1$. $R(R_w)=0.0603$ (0.1297), and the molecule lye in the central position and the asymmetric unit contains the whole cluster, five MeOH and two water molecules [26]. The ORTEP representation of $\mathbf{1}\cdot 5MeOH\cdot 2H_2O$ is shown in Fig. 1. Complex $\mathbf{1}\cdot 5MeOH\cdot 2H_2O$ can be described as two $[Mn^{III}{}_6O_2(salox)_6(N_3)_2(MeOH)_3(H_2O)]$ subunits bridged by two oximato O atoms (O6,

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doi:10.1016/j.inoche.2011.04.007

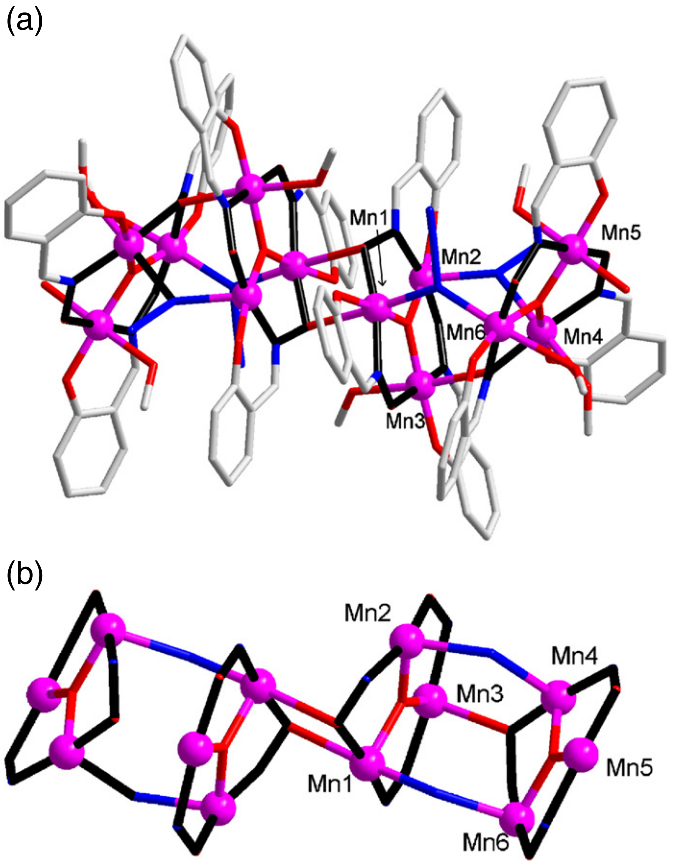

Fig. 1. (a) Crystal structure drawing of complex $\mathbf{1}\cdot5MeOH\cdot2H_2O$ and (b) arrangement of the four $[Mn_3O]$ triangles. Hydrogen atoms have been omitted for clarity.

O6'). Each Mn_6 subunit consists of six Mn ions arranged as two $[\mathrm{Mn^{III}}_3(\mu_3\text{-}O^{2-})]^{7+}$ triangles bridged by two end-on azides and one oximato with an ~41° canting angle between the two Mn_3 planes (Fig. 1S). All manganese atoms are assigned as trivalent based on (i) the clear presence of the JT axial elongation, as expected for a high-spin d^4 ion in near-octahedral geometry and (ii) bond valence sum (BVS) calculations (Table 2S) [27–29]. The Mn ions can be divided into two groups: four $\mathrm{Mn^{III}}$ ions (Mn1, Mn3, Mn4 and Mn5) with six-coordination and two $\mathrm{Mn^{III}}$ ions (Mn2 and Mn6) with square pyramidal five-coordination. Peripheral ligations around each Mn_6 subunit are provided by four $\eta^1{:}\eta^1{:}\eta^1{:}\mu_2$ salox^{2-} ions, two $\eta^1{:}\eta^1{:}\eta^2{:}\mu_3$ salox^{2-} ions, and two $\eta^2{:}\mu_2$ N_3^- ions. Three MeOH and one H_2O molecules terminally complete the sixth coordination position around Mn3, Mn4 and Mn5. In addition, there is one hydrogen bonding interaction which involves the oximato O atom and the O atom of a terminal MeOH from a neighboring Mn_{12} molecule to form a 1-D supramolecular chain [O11···O18' 2.790 Å] (Fig. 2S).

Solid-state, variable-temperature magnetic susceptibility measurements were performed on fresh microcrystalline samples of complex $\mathbf{1}\cdot5MeOH\cdot2H_2O$ suspended in eicosane to prevent torquing; the results are shown in Fig. 2. The direct current (DC) magnetic susceptibility data were collected in the 1.8–300 K range in a 1.0 kG magnetic field. The $\chi_M T$ value of complex $\mathbf{1}\cdot5MeOH\cdot2H_2O$ decreases steadily from 31.9 emu mol^{-1} K at 300 K with decreasing temperature, reaching 11.6 emu mol^{-1} K at 10 K, and then decreases sharply to 2.5 emu mol^{-1} K at 1.8 K. The $\chi_M T$ value at 300 K for complex $\mathbf{1}\cdot5MeOH\cdot2H_2O$ is lower than 36.0 emu mol^{-1} K, the value expected for a $\mathrm{Mn^{III}}_{12}$ complex with noninteracting metal centers with $g = 2.0$, which may be due to the antiferromagnetic interactions between Mn ions. The decrease of the $\chi_M T$ value with decreasing temperature also indicates antiferromagnetic coupling within complex

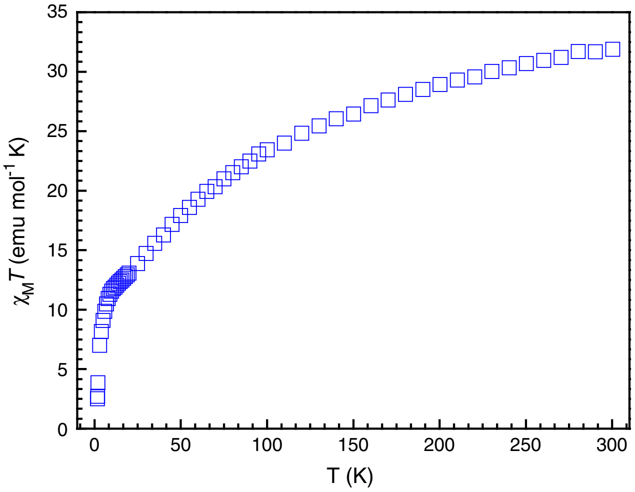

Fig. 2. Plots of $\chi_M T$ vs. T for $\mathbf{1}\cdot5MeOH\cdot2H_2O$ in an applied field of 1 kG from 2.0 to 300 K.

$\mathbf{1}\cdot5MeOH\cdot2H_2O$. The rapid decrease observed in the $\chi_M T$ value at 2.0–10 K range is most likely due to zero-field splitting effects and perhaps weak intermolecular interactions mediated by the hydrogen bonding in the crystal structure. A theoretical treatment of the susceptibility data using the Kambe approach is not feasible due to the topological complexity and low symmetry of $\mathbf{1}\cdot5MeOH\cdot2H_2O$ [30]. Instead, our efforts focused on the determination of the S value of $\mathbf{1}\cdot5MeOH\cdot2H_2O$ from variable-temperature and variable-field magnetization (M) measurements in the 2.0–4.0 K and 1–5 T ranges, respectively (Fig. 3). The fits of the data using the program ANISOFIT [31], assuming that only the ground state is populated, were poor and suggest complications from low-lying excited states even at these relatively low temperatures. The measurements of the AC magnetic susceptibility were performed on fresh microcrystalline samples of complex $\mathbf{1}\cdot5MeOH\cdot2H_2O$ in the temperature range 1.8–20 K in a zero DC field and a 3.5 G AC field oscillating at frequencies in the 10–10,000 Hz range. The results for a representative sample of complex $\mathbf{1}\cdot5MeOH\cdot2H_2O$ are shown in Fig. 4. If the magnetization vector can relax fast enough to keep up with the oscillating field, there is no imaginary (out-of-phase) susceptibility signal (χ_M''), and the real (in-phase) susceptibility (χ_M') is equal to the DC susceptibility. In contrast, if the barrier to magnetization relaxation is significant compared to the thermal energy (kT), there is a nonzero χ_M'' signal and the in-phase signal decreases. In addition, the χ_M'' signals will

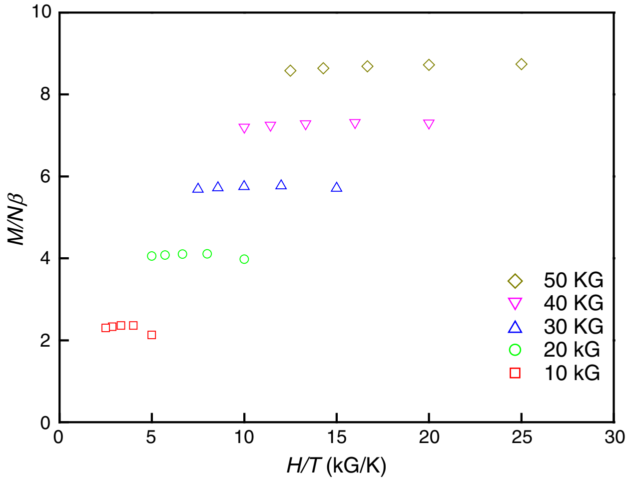

Fig. 3. Plot of reduced magnetization ($M/N\beta$) vs. H/T for complex $\mathbf{1}\cdot5MeOH\cdot2H_2O$ at the indicated field.