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Synthesis, crystal structure and magnetic properties of an enneanuclear manganese cluster containing mixed chelating ligands

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A new mixed-valence [Mn_9] cluster of formulae [$Mn_9O(OH)_3Cl_4(N_3)_3(hmp)_6(dpkd)_3$]·$1.5CH_3CN\cdot 3H_2O$ (**1**·$1.5CH_3CN\cdot 3H_2O$, where hmp^- and $dpkd^{2-}$ are the anion of 2-hydroxymethylpyridine and the dianion of the *gem*-diol form of the dpk, respectively) has been synthesized and characterized by single-crystal X-ray diffraction, IR spectra, elemental analysis and magnetic measurements. Single-crystal structural analysis shows that complex **1** contains a [Mn_9] core with a new structural topology in the Mn clusters, in which the centered six Mn^{III} atoms compose a trigonal antiprism and the peripheral residual three Mn^{II} atoms can be seen as the skirt hem of this antiprism. DC magnetic susceptibility studies indicate that the overall antiferromagnetic interactions between Mn ions are present in the cluster. Fitting the data of magnetization and extrapolation of the $\chi_M'T$ suggest the spin ground states of $S = 3.5$, and no out-of-phase (χ_M'') signals are present in the alternating current (AC) susceptibility.

1. Introduction

Polynuclear Mn clusters continue to attract great attention mainly because some of them can behave as single molecule magnets (SMMs), which hold a high-spin ground state (S) and a large negative axial zero-field splitting (ZFS, D), resulting in a significant energy barrier for reversal magnetization with the upper limit given by $S^2|D|$ or $(S^2 - 1/4)|D|$ for integer and half-integer spin, respectively [1,2]. In addition, such complexes show not only classical magnetization hysteresis but also quantum tunneling of magnetization (QTM) and quantum phase interference [3]. Thus, SMMs have been proposed as potential candidates for magnetic information storage and quantum computation [4]. However, the blocking temperature (T_B) of the present SMMs is too low for application. To improve the T_B of SMM, some research groups have employed multifarious synthetic methods [5] to obtain high nuclear Mn clusters by using different multidentate chelating ligands, such as 2-hydroxymethylpyridine (Hhmp) [6], di-2-pyridylketone (dpk) [7], methyl 2-pyridyl ketone oxime (mpkoH) [8], 1,1,1-tris(hydroxymethyl) ethane (H_3thme) [9]. It is believed that novel polynuclear Mn clusters would be obtained by combining two or more of these versatile chelating ligands in the reaction whatever the starting materials is Mn clusters precursors or Mn salts. Recently, we have obtained two mixed-valence polynuclear manganese clusters of formula [$Mn_{13}O_8(O_2CCH_3)_{12}$-$(hmpH)_2(hmp)_2(H_2O)_2(dpkd)_2$]($ClO_4$)·$6H_2O$ ([Mn_{13}]), and [$Mn_{16}O_8$-$(O_2CPh)_{14}(mpko)_4(dpkd)_4$]·$6H_2O$ ([Mn_{16}]), by introducing Hhmp or mpkoH ligand with dpk and [Mn_3] or [Mn_4] cluster as the precursors [10]. Importantly, the [Mn_{16}] cluster shows the peak of out-of-phase magnetic susceptibility above 2 K, representing a rare example in the [Mn_n] ($n > 12$).

In this paper, we still use the ligands of Hhmp, NaN_3 and dpk but the starting material is $MnCl_2\cdot 4H_2O$ in basic solution, obtaining an enneanuclear Mn cluster, [$Mn_9O(OH)_3Cl_4(N_3)_3(hmp)_6(dpkd)_3$]·$1.5CH_3CN\cdot 3H_2O$ (**1**·$1.5CH_3CN\cdot 3H_2O$), which shows a new structural topology of cluster core. Magnetic studies indicate that this complex shows overall antiferromagnetic interactions between Mn atoms, with the ground-state spin $S = 3.5$. Herein, we report the synthesis, structure and magnetic properties of **1**.

2. Experimental

2.1. General and physical measurements

All manipulations were carried out under aerobic conditions. The chemicals and solvents used in the synthesis were of reagent grade and were used without further purification. *Caution! Azide salts is potentially explosive and should be used in small quantities and with utmost care at all times.*

IR spectra (4000–400 cm^{-1}) were recorded on a VECTOR 22 spectrometer with samples prepared as KBr pellets. Elemental analyses (C, H and N) were performed on a Perkin Elmer 240C elemental analyzer. Direct current (DC) magnetic susceptibility and magnetization measurements were carried out on a Quantum Design

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MPMS-XL7 superconducting quantum interference device (SQUID) magnetometer. Measurements were performed on a microcrystalline sample of **1**·$1.5CH_3CN·3H_2O$ in the range 1.8–300 K with magnetic field up to 1.5 T. The alternating current (AC) susceptibility down to 1.8 K was performed in a zero DC field and a 1.0 Oe field oscillating at frequencies in the 1–1488 Hz range. Diamagnetic corrections were made for the sample holder as the background and the compound estimated from Pascal's constants [11].

2.2. Preparation of $[Mn_9O(OH)_3Cl_4(N_3)_3(hmp)_6(dpkd)_3]·1.5CH_3CN·3H_2O$ (**1**·$1.5CH_3CN·3H_2O$)

$MnCl_2·4H_2O$ (0.4906 g, 2.48 mmol), NaN_3 (0.1612 g, 2.48 mmol), di-2-pyridylketone (0.2283 g, 1.24 mmol) and 2-hydroxymethylpyridine (0.0251 g, 2.48 mmol) were dissolved in 15 mL CH_3CN. The mixture was stirred for 30 min and then solid $NMe_4OH·5H_2O$ (0.4492 g, 2.48 mmol) was added under vigorous stirring. The resulting solution was stirred for 4 h, filtered, and the filtrate was left undisturbed at ambient temperature. After ten days later, dark red crystals of **1**·$1.5CH_3CN·3H_2O$ were formed in about 40% yield, and were collected by filtration, washed with cold MeCN (3 × 10 mL) and Et_2O (3 × 10 mL), and dried in air. Elemental analysis (%) Calc. for **1**·$1.5CH_3CN·3H_2O$ ($C_{72}H_{73.5}Cl_4Mn_9N_{22.5}O_{19}$): C, 39.41; H, 3.37; N, 14.36. Found: C, 39.29; H, 3.45; N, 14.27%. Selected IR (KBr): 3380 (s), 2066 (s), 1602 (s), 1567 (w), 1478 (s), 1435 (m), 1366 (m), 1337 (w), 1286 (m), 1230 (m), 1156 (w), 1104 (w), 1072 (w), 1043 (s), 960 (w), 814 (m), 693 (s), 662 (s), 622 (s), 545 (s), 458 (w) cm^{-1}.

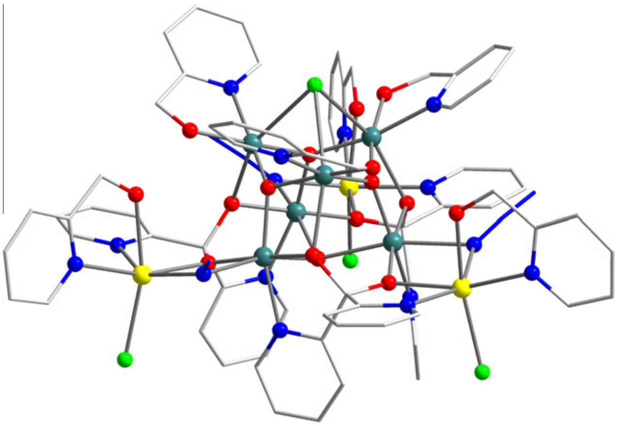

Fig. 1. Molecular structure of **1**. H atoms have been omitted for clarity. Mn^{II} yellow, Mn^{III} teal, Cl bright green, N blue, O red, C gray (Color online).

2.3. Single-crystal X-ray crystallography

Diffraction data for **1**·$1.5CH_3CN·3H_2O$ was collected on a Siemens (Bruker) SMART CCD diffractometer using monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at 291 K. The data reduction was made with the Bruker SAINT package [12]. Absorption correction was performed using the SADABS program [13]. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares using SHELXL-97 [14] with anisotropic displacement parameters for all non-hydrogen atoms. H atoms were introduced in calculations using the riding model with a uniform value of U_{iso}, which are tied 1.2 or 1.5 times to the parent atoms. The MeCN and H_2O solvent molecules are disordered and could not modeled properly. Thus program SQUEEZE, which is a part of the PLATON package of crystallographic software [15], was used to calculate the solvent disordered area and remove its contribution to the overall intensity data.

3. Results and discussion

3.1. Crystal structure of **1**

The molecular structure and the core of complex **1** are depicted in Figs. 1 and 2, respectively. Selected bond distances and bond angles are listed in Table 2. X-ray crystallographic studies reveal that **1** crystallizes in the hexagonal space group $P3c1$ with $Z = 2$ (Table 1). Complex **1** contains a $[Mn_9(\mu_3\text{-}O)(\mu_3\text{-}OH)_3(\mu_3\text{-}Cl)(Cl)_3(N_3)_3]^{12+}$ core that can be viewed as a trigonal antiprism consisting of Mn1, Mn2 and their symmetrically related ions, and the remaining three Mn atoms (Mn3, Mn3A and Mn3B) can be seen as the skirt hem of the antiprism. The six Mn atoms in the trigonal antiprism are linked by one vertex $\mu_3\text{-}Cl^-$ ion (Cl1), one vertex $\mu_3\text{-}O^{2-}$ ion (O4) and three $\mu_3\text{-}OH^-$ ions (O1, O1A and O1B). Other three Mn atoms (Mn3, Mn3A and Mn3B) are linked to the trigonal antiprism by three $dpkd^{2-}$ ions and three $\mu\text{-}N_3^-$ ions. The remaining coordination sites of Mn atoms of the cluster are completed by three terminal Cl^- (Cl2, Cl2A and Cl2B) and six hmp^- ions. All $dpkd^{2-}$ ions are $\eta^1:\eta^2:\eta^2:\eta^1:\mu_4$-coordinating, while all hmp^- ions adopt $\eta^1:\eta^1$-coordinating mode. All Mn atoms are near octahedrally coordinated with the Mn–O bond distances ranging from 1.886(5) to 2.263(9) Å and Mn–N bond distances ranging from 2.041(7) to 2.313(8) Å.

Close examination of the metric parameters and bond valence sum (BVS) calculations [16] for metal atoms of **1** reveal that Mn1, Mn2 are +3, and Mn3 is +2. Bond-valence sum (BVS) calculations [17] were also performed on the O atoms of the cluster to identify their protonation level, indicating that all hmpH and all dpk ligands are deprotonated and O4, O1 are O^{2-}, OH^-,

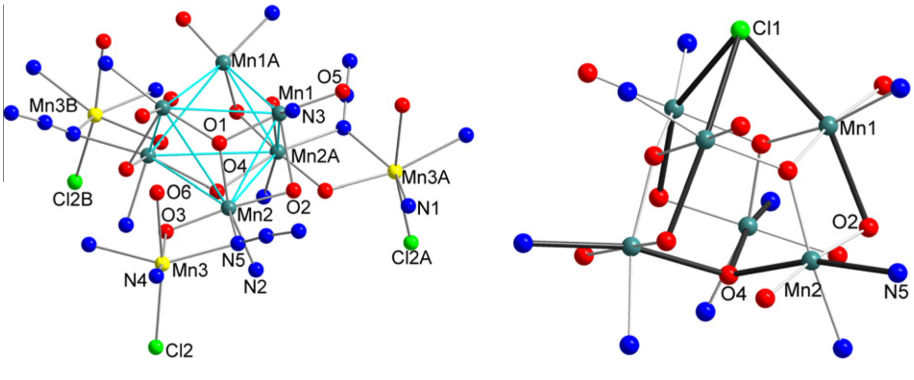

Fig. 2. Core structure of **1** (left figure) and the Jahn–Teller axes direction of Mn^{III} showing by bold black lines (right figure). Symmetry code: (A) $1 - y$, $-1 + x - y$, z; (B) $2 - x + y$, $1 - x$, z.