



Original article

Structure and magnetic property of bimetallic hexanuclear cluster based on 5-chlorosalicylaldehyde oxime



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ABSTRACT

The bimetallic hexanuclear cluster $[\text{Mn}_4\text{Ni}_2\text{O}_2(\text{Cl-Sao})_6(\text{CH}_3\text{OH})_8]\cdot 10\text{CH}_3\text{OH}$ (**1**) was synthesized. Single-crystal X-ray analysis reveals that **1** consists of two $[\text{Mn}_2\text{Ni}(\mu_3\text{-O})(\text{Cl-Sao})_3]$ subunits linked together *via* two pairs of long Ni–O bonds involving two oximate oxygen atoms and two phenolate oxygen atoms. Each Mn and Ni center achieves six-coordination with axial methanol molecules. The spin centers of the Mn^{III} and Ni^{II} ions exchange magnetic coupling through O^{2-} , $\text{O}^-_{\text{phenolate}}$ and –N–O–bridges. The magnetic properties of the cluster have been investigated.

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1. Introduction

Molecule-based magnetic materials, such as single-molecular magnets (SMMs), photomagnets, magneto-optical materials, magnetic conductors, ferroelectromagnets, chiral magnets, and multifunctional materials have attracted increasing interest over the last few years [1]. The design and synthesis of SMMs is of particular interest, for their magnetic bistability potentially allows devices for ultimate high-density memory storage and quantum computing [2,3]. Manganese based SMMs have been studied the most, with focus on the paramagnetic nature of the manganese ion in various oxidation states, which provides interesting magnetic properties [4–6]. Detailed studies of the solid state and frozen solution magnetic properties of a family of oxime-based hexanuclear Mn(III) SMMs (Mn6 SMMs) led to the first established solid state magnetostructural correlations for any SMM, demonstrating that their solid state magnetic properties are crucially dependent on very small changes in geometry; in particular, the Mn–N–O–Mn torsion angles of the metal oxime core [7,8].

We are interested in introducing other transition metal ions into the Mn6 system and studying how structure change affecting the magnetic properties. In this paper, we report the synthesis, structural characterization, and magnetic properties study of a bimetallic hexanuclear cluster based on 5-chlorosalicylaldehyde oxime (Cl-H₂Sao), $[\text{Mn}_4\text{Ni}_2\text{O}_2(\text{Cl-Sao})_6(\text{CH}_3\text{OH})_8]\cdot 10\text{CH}_3\text{OH}$.

2. Experimental

All chemicals and solvents were commercial products and used without further purification. Elemental analyses of C, H, and N were performed by a Carlo Erba 1106 elemental analyzer. Metal analyses of Mn and Ni were performed by ICP-AES. IR spectra were recorded as KBr pellets on a Nicolet 750 FTIR spectrophotometer. Magnetic data were recorded using a Quantum Design SQUID magnetometer. To avoid orientation in the magnetic field, the samples were pressed in a home-made Teflon sample holder equipped with a piston. The data were corrected for diamagnetism of the constituent atoms using Pascal's constants. The X-ray diffraction measurements for **1** were collected on a Bruker Apex SMART CCD system equipped with Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) at room temperature. Cell constants and an orientation matrix for data collection were obtained by least-squares refinement of the diffraction data from 7497 unique reflections. The structure was solved by direct methods and refined by a full matrix least squares technique based on F^2 using the SHELX program [9]. The crystallographic data for the four compounds are summarized in Table 1, and selected bond lengths and torsion angles are list in Table 2.

To pale pink solutions of $\text{Mn}(\text{ClO}_4)_2\cdot 6\text{H}_2\text{O}$ (1 mmol) in MeOH (20 mL) were added equivalent amounts of the Cl-H₂Sao (1 mmol, 10 mL), and five times of Et₃N (0.7 mL). After 30 min of stirring, the $\text{Ni}(\text{ClO}_4)_2\cdot 6\text{H}_2\text{O}$ (0.5 mmol) in MeOH (20 mL) was added. The solutions were left stirring for 30 min, filtered, and then left to slowly evaporate. Dark green single crystals suitable for X-ray diffraction study were obtained after 2 days. Elemental anal. calcd. (found) for **1** (formula $\text{C}_{30}\text{H}_{45}\text{Cl}_3\text{Mn}_2\text{N}_3\text{NiO}_{16}$): C 36.82 (36.75),

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Table 1
Crystal data and structure refinement of **1**.

Compound	1
Empirical formula	C ₃₀ H ₄₅ Cl ₃ Mn ₂ N ₃ NiO ₁₆
Formula weight	978.63
Temperature (K)	293(2)
Wave length (Å)	0.71073
Crystal system	Monoclinic
space group	P2(1)/n
A (Å)	16.7834(7)
b (Å)	14.6048(5)
c (Å)	18.1792(7)
α (°)	90
β (°)	107.193(4)
γ (°)	90
Volume (Å ³)	4256.9(3)
Z	4
Calculated density (Mg m ⁻³)	1.527
Absorption coefficient (mm ⁻¹)	1.278
F (000)	2012
Crystal size (mm)	0.25 × 0.22 × 0.21
θ range for data collection (°)	2.54–25.00
Limiting indices	-19 ≤ h ≤ 19, -17 ≤ k ≤ 17, -21 ≤ l ≤ 19
Reflections collected/unique	28,130/7497
R(int)	0.0669
Completeness to θ=25	0.999
Max. and min. transmission	0.7752 and 0.7407
Refinement method	Full-matrix least-squares on F ²
Data/restraints/parameters	7497/4/522
Goodness-of-fit on F ²	1.018
Final R indices [I > 2σ(I)]	R1 = 0.0419, wR2 = 0.0888
R indices (all data)	R1 = 0.0682, wR2 = 0.0988
Largest diff. peak and hole (e Å ⁻³)	0.790 and -0.358

H 4.64 (4.44), N 4.29 (4.34) %. ICP result calcd. (found): Mn, 11.0 (11.2); Ni 6.2 (6.0) %. IR (KBr pellet) = 416.1 (m), 466.6 (m), 533.1 (w), 626.8 (s), 648.1 (s), 679.5 (vs), 749.5 (s), 789.4 (w), 827.8 (w), 856.8 (w), 918.5 (vs), 1026.1 (vs), 1098.6 (m), 1124.4 (m), 1153.9 (m), 1170.8 (m), 1202.5 (s), 1277.0 (vs), 1327.8 (w), 1392.5 (vs), 1440.0 (s), 1471.4 (m), 1527.9 (s), 1597.5 (vs), 3392.3 (s) cm⁻¹.

3. Results and discussion

Single crystal X-ray diffraction analysis reveals that the complex **1** (Fig. 1), like most Mn6-Sao systems, consists of two off-set [Mn₂NiO]⁶⁺ triangles lined together via two oximate oxygen atoms from two η¹:η²:η¹:μ₃ Cl-Sao²⁻ ligands and two phenolate oxygen atoms derived from two η²:η¹:η¹:μ₃ Cl-Sao²⁻ ligands. The remaining two oximate(-2) ligands each bridge one Ni^{II} ion in an

Table 2
Selected bond lengths (Å) and torsion angles (°) for **1**.

Mn(1)–O(1)	1.832(2)	Mn(2)–O(1)	1.836(2)
Mn(1)–O(2)	1.886(2)	Mn(2)–O(4)	1.906(2)
Mn(1)–O(7)	1.934(2)	Mn(2)–O(3)	1.914(2)
Mn(1)–N(1)	2.034(3)	Mn(2)–N(2)	2.012(3)
Mn(1)–O(11)	2.274(3)	Mn(2)–O(6)#1	2.235(2)
Mn(1)–O(10)	2.276(3)	Mn(2)–O(8)	2.403(3)
Ni(1)–O(5)	2.028(2)	Ni(1)–O(1)	1.971(2)
Ni(1)–O(9)	2.111(2)	Ni(1)–N(3)	1.998(3)
Ni(1)–O(5)#1	2.167(2)	Ni(1)–O(6)	2.011(2)
Mn(1)–Mn(2)	3.2343(7)		
Mn(1)–N(1)–O(3)–Mn(2)	9.9(3)	Mn(2)–N(2)–O(5)–Ni(1)	36.6(2)
Ni(1)–N(3)–O(7)–Mn(1)	11.2(3)	Mn(2)–N(2)–O(5)–Ni(1)#1	66.09(19)

Symmetry transformations used to generate equivalent atoms: #1 -x+2, -y, -z.

η¹:η¹:η¹:μ fashion, thus forming a [Mn^{III}₄Ni₂(μ₃-O)₂(μ₃-ONR)₂(μ-ONR)₄(μ-OR')₂]⁴⁺ core. The remaining axial coordination sites on the Mn and Ni ions are filled by methanol molecules. All Mn^{III} and Ni^{II} ions display a six-coordinate distorted octahedral geometry, and the Jahn–Teller axes of all three ions are nearly parallel to each other and are roughly perpendicular to the [Mn₂NiO]⁶⁺ plane. The oxidation states for the two manganese(III) ions and nickel(II) ions were established by charge–valence considerations, bond length distances, and bond valence sum (BVS) [11] calculations with the obtained values of 3.24, 3.22 and 2.16 for Mn1, Mn2 and Ni1, respectively. The nearest distance between Mn ions different from Mn₄Ni₂ cores is 9.659 Å, Mn–Ni distance is 9.087 Å, and Ni–Ni distance is above 10 Å, which indicates that the inter-cluster magnetic interaction can be neglected. Adjacent molecules are linked by intermolecular H bonds to form a 1D infinite chain structure (Fig. 2), and there is no obvious π–π stacking interaction between phenolate.

Solid-state DC (direct current) magnetic susceptibility (χ_M) data were collected in a 0.1 T field in the 1.8–300 K range (Fig. 3). The χ_MT value for **1** decreases steadily from 11.59 emu K mol⁻¹ at 300 K to 5.47 emu K mol⁻¹ at 35 K, and then decreases sharply to 1.14 at 1.8 K. The χ_MT value at 300 K for **1** is lower than 14 emu K mol⁻¹, the value expected for a Mn₄Ni₂ complex with non-interacting metal centers between Mn and Ni ions. The decrease of the χ_MT value with decreasing temperature also indicates antiferromagnetic coupling within complex **1**. The rapid decrease observed in the χ_MT value at 35–1.8 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. The non-superposition of the M–H data (Fig. 4) on a

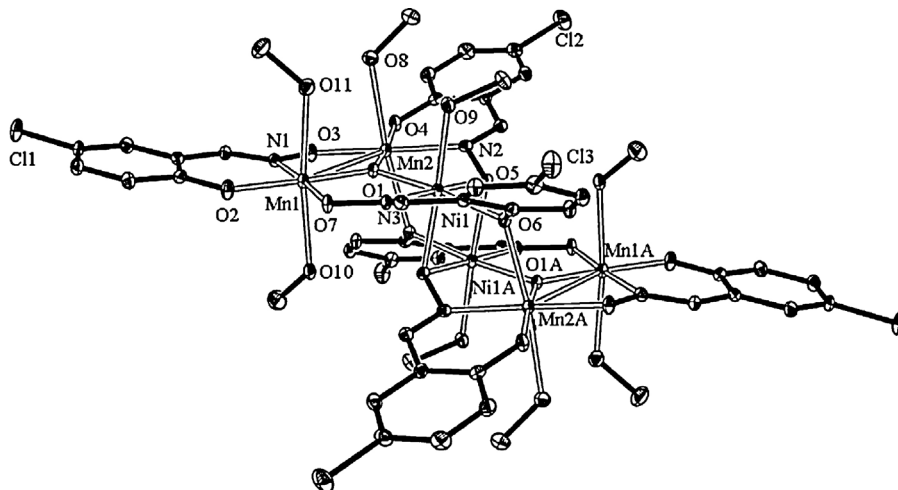


Fig. 1. Perspective view of the complex **1** (30% thermal probability ellipsoids, for clarity hydrogen atoms and uncoordinated methanol molecules are omitted).

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