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Two high-nuclearity homo-/hetero-metallic magnetic materials based on a tripodal alcohol

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ABSTRACT

Two new polynuclear d-metal clusters based on pentaerythritol (H_4L), $[Mn_{12}]$ (**1**) and $[Mn_{10}Cd_2]$ (**2**) for short, were obtained from the reaction of H_4L, transition-metal salt and pivalic acid (Hpiv) in the mixed solvent under ambient conditions. Compound **1** crystallizes in the triclinic space group $P\bar{1}$, and consists of a dodecanuclear mixed-valent $[Mn^{III}_4Mn^{II}_8]$ cluster. When $Cd(NO_3)_2{\cdot}4H_2O$ was introduced into the reaction, compound **2** was resulted in, which displays the similar structural feature as compound **1**, fabricating a dodecanuclear heterometallic $[Mn^{III}_4Mn^{II}_6Cd^{II}_2]$ cluster, but crystallizes in the monoclinic space group $P2_1/c$. Interestingly, there are two μ_5-O bridges present in this structure, and it is rare. Magnetic susceptibilities of compounds **1** and **2** were measured, and antiferromagnetic interactions between metal centers were observed.

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1. Introduction

Since the initial discovery of dodecanuclear $[Mn_{12}]$ aggregate [1–3], the interest of designing and synthesizing high-nuclearity metal clusters has been fueled due to their intriguing structural diversity and rich potential applications such as magnetism, optics and catalysis [4–7]. In the past two decades, the cluster chemistry as a branch of coordination chemistry is well established and filled with many fantastic clusters such as transition (eg. Mn, Co, Fe, Ni) [8–11], lanthanide [12–15] and transition-lanthanide clusters [16–20]. However, the research of mixed d-metal clusters is still in its infancy.

A successful strategy to facilitate the high-nuclearity complex formation is the utilization of suitable ligand to control the hydrolysis of metal ions to obtain polynuclear complexes rather than intractable metal hydroxides and/or oxides. Several classes of ligands, such as carboxylates [21–24], polyketonates [25–27] and polyols [28–30], have been employed in this capacity, and show the superiority in this field.

In the current work, we choose pentaerythritol (H_4L) as a ligand on the basis of the following considerations: (i) it is a multidentate ligand with multiple coordination modes; (ii) as a member of polyols, it possesses the ability to built polynuclear clusters; (iii) the flexible tripodal geometry allows H_4L ligand to be used as potential expanders to incorporate more metal ions in the cluster [31–34]. On the other hand, the pivalate anions (piv^-) were selected as a supporting ligand to construct high-nuclearity metal clusters, which have been proved in many examples.

Herein, we report the syntheses and structures of two docecanuclear homo-/hetero-metallic clusters based on the tripodal alcohol ligand (H_4L) with the Hpiv as a supporting ligand. Compound **1** is a homometallic molecule, containing a mixed-valent $[Mn^{III}_4Mn^{II}_8]$ cluster with the molecular formula of $\{[Mn_{12}(O)_2(HL)_4(piv)_{10}(MeO)_2(MeOH)_2]{\cdot}3MeOH{\cdot}H_2O\}$, while compound **2** is a heterometallic 3d–4d molecule based on $[Mn^{III}_4Mn^{II}_6Cd^{II}_2]$ cluster with the molecular formula of $\{[Mn_{10}Cd_2(O)_2(HL)_4(piv)_{10}(MeO)_2(MeOH)_2]{\cdot}4MeOH\}$. The results of magnetic measurements display that there are antiferromagnetic interactions in both compounds **1** and **2**.

2. Experimental

2.1. Materials and physical measurement

All reagents and solvents were purchased commercially and used without further purification. Elemental analyses for C, H and N were carried out on a Perkin-Elmer analyzer at the Institute of Elemento-Organic Chemistry in Nankai University. The FT-IR spectra were recorded from KBr pellets in the range 400–4000 cm^{-1} on a Bio-Rad FTS 135 spectrometer. The magnetic properties were measured on a PPMS-9 ACMS magnetometer.

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2.2. Syntheses

2.2.1. Preparation of {[$Mn_{12}(O)_2(HL)_4(piv)_{10}(MeO)_2(MeOH)_2$]·3MeOH·$H_2O$} (**1**)

Triethylamine (0.5 mL) was added to a stirred solution of H_4L (0.136 g, 1 mmol), and $MnCl_2·4H_2O$ (0.099 g, 0.5 mmol) in 30 mL of MeOH and MeCN (1:1), and after stirring for 1 h at room temperature, Hpiv (0.102 g, 1 mmol) was added. The resulting mixture was heated to reflux for 30 min to give a dark-brown solution. The solution was cooled to room temperature, filtered and left to evaporate slowly. Well-shaped dark-brown crystals were obtained after two weeks, collected by filtration, washed with MeCN (3 mL) and MeOH (3 mL), and dried in air. Yield: 56 mg (54.3% based on Mn). *Anal.* Calc. for $Mn_{12}C_{77}H_{152}O_{46}$ (**1**): C 37.39, H 6.19. Found: C 37.79, H 6.06%. IR(KBr, cm^{-1}): 3364(b,s), 2956.7(m), 1544.9(s), 1485.1(vs), 1417.6(s), 1375.2(m), 1363.6(m), 1226.6(m), 1112.9 (m), 1022.2(m), 648.0(m), 584.4(s).

2.2.2. Preparation of {[$Mn_{10}Cd_2(O)_2(HL)_4(piv)_{10}(MeO)_2(MeOH)_2$]·4MeOH} (**2**)

Triethylamine (0.5 mL) was added to a stirred solution of H_4L (0.136 g, 1 mmol), and $MnCl_2·4H_2O$ (0.099 g, 0.5 mmol) in 30 mL of MeOH and MeCN (1:1), and after stirring for 1 h at room temperature, $Cd(NO_3)_2·4H_2O$ (0.077 g, 0.25 mmol) and Hpiv (0.102 g, 1 mmol) was added. The resulting mixture was heated to reflux for 30 min to give a dark-brown solution. The solution was cooled to room temperature, filtered and left to evaporate slowly. Well-shaped dark-brown crystals were obtained after two weeks, collected by filtration, washed with MeCN (3 mL) and MeOH (3 mL), and dried in air. Yield: 203 mg (62.5% based on Cd). *Anal.* Calc. for $Mn_{10}Cd_2C_{78}H_{154}O_{46}$ (**2**): C 36.00, H 5.96. Found: C 36.09, H 5.93%. IR(KBr, cm^{-1}): 3366(b,s), 2956.7(m), 1541.0(s), 1485.1 (vs), 1417.6(s), 1375.2(m), 1361.7(m), 1224.7(m), 1110.9(m), 1022.2(m), 650.0(m), 580.5(s).

2.3. Crystallographic studies

Suitable single crystals for **1** and **2** were selected for single-crystal X-ray diffraction analysis. Data were collected on an SuperNova, Single source at offset, Eos diffractometer with a Mo Kα radiation (λ = 0.71073 Å). All non-hydrogen atoms were solved using direct methods. All the calculations were solved by SHELXS-97 (direct methods) and refined by SHELXL-97 (full-matrix least-squares on F^2) program [35,36]. The hydrogen atoms were set in calculated positions and refined as riding atoms with common fixed isotropic thermal parameters. Detailed information about the crystal data and structure refinements are summarized in Table 1.

3. Results and discussion

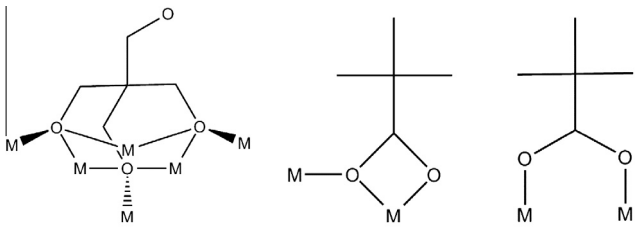
Compounds **1** and **2** were prepared by transition salts ($MnCl_2·4H_2O$, $Cd(NO_3)_2·4H_2O$), Hpiv, and H_4L ligands in a certain ratio. The coordination modes of HL^{3-} and piv^- ligands are shown in Scheme 1. The oxidation states of the metal centers and selected O atoms were determined by Bond–Valence Sum (BVS) calculations and the related data are summarized in Table 2.

3.1. Crystal structures of **1** and **2**

Single-crystal X-ray diffraction analyses display that compounds **1** and **2** have the analogous structures, as shown in Fig. 1, and the main difference is that compound **1** is a homometallic 3d cluster, while compound **2** is a heterometallic 3d–4d cluster. Thus, for the sake of brevity, we will limit our most discussion to compound **1**. Compound **1** crystallizes in the triclinic space group $P\bar{1}$, consisting of a discrete cluster, and the asymmetric unit contains half of the cluster, one and half lattice MeOH, and half of the lattice water molecule, which lies upon an inversion center. The metallic skeleton can be described as a mixed-valence (Table 2) dodecanuclear [$Mn^{III}_4Mn^{II}_8$] sandwich, in which the Mn^{III} ions are sandwiched by the Mn^{II} ions (Fig. 1a and c). The core of compound **1** consists of two [Mn_7] edge-sharing mono-capped octahedra, containing two rare μ_5-O^{2-} bridges, related by an inversion center. The peripheral of the metal core is occupied by the four tripodal HL^{3-}, ten piv^- anions, two MeO^- and two MeOH. The four tripodal ligands adopt one coordination type (Scheme 1A), which is triply deprotonated (HL^{3-}), bridging in an η^3:η^3:η^2:μ_5-fashion along the round of the Mn^{III} centers. The deprotonated piv^- ligands are of

Table 1
Data collection and processing parameters for **1** and **2**.

Compound	**1**	**2**
Formula	$Mn_{12}C_{77}H_{152}O_{46}$	$Mn_{10}Cd_2C_{78}H_{154}O_{46}$
Formula weight	2473.27	2602.23
T/K	143(10)	145(10)
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/c$
a (Å)	12.3978(3)	13.0653(4)
b (Å)	14.9707(5)	17.3618(5)
c (Å)	16.7371(6)	26.3010(9)
α (°)	65.063(3)	90.00
β (°)	72.859(3)	109.643(3)
γ (°)	76.120(3)	90.00
V (Å^3)	2667.67(15)	5618.9(3)
Z	1	2
ρ (mg/m^3)	1.540	1.538
μ (mm^{-1})	1.451	1.532
F(000)	1282	2672
θ range for data collection (°)	3.14–28.92	2.94–25.10
Reflections collected/unique	20085/9381	22274/9605
R_{int}	0.0287	0.0350
Data/restraints/parameters	9381/96/645	9605/130/668
GOF on F^2	1.055	1.053
R_1/wR_2 ($I > 2\sigma(I)$)	0.0515/0.1252	0.0614/0.1711
R_1/wR_2 (all data)	0.0629/0.1336	0.0815/0.1862
Largest different peak/hole (e Å^{-3})	1.042/−0.635	2.454/−0.844



Scheme 1. The coordination modes of HL^{3-} and piv^- ligands in **1** and **2**.

Table 2
Bond–Valence Sum (BVS) calculations for Mn and O atoms in **1** and **2**.

1			**2**		
Atom	BVS	Assignment	Atom	BVS	Assignment
O21	2.146	MeO^-	O19	2.188	MeO^-
O22	1.216	MeOH	O20	1.370	MeOH
O23	1.807	O^{2-}	O21	1.928	O^{2-}
Mn1	3.269	III	Mn1	3.297	III
Mn2	3.382	III	Mn2	3.390	III
Mn3	2.137	II	Mn3	2.078	II
Mn4	2.051	II	Mn4	1.911	II
Mn5	2.047	II	Mn5	2.084	II
Mn6	1.829	II			

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