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# Cube-like 12-MC-4 and Offset Stacked 10-MC-3 Metallacrowns: Synthesis, Structure, and Magnetic Properties

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**Abstract**. Two complexes  $[Mn^{III}_4(naphthsao)_4(naphthsaoH)_4]$  (1) and  $[Fe^{III}_6O_2(naphthsao)_4(O_2CPh)_6]$  (2) [naphthsao = 1-(1-hydroxy-naphthalen-2-yl)ethanone oxime] were obtained through the reactions of naphthsao ligand and MnCl<sub>2</sub>·4H<sub>2</sub>O or FeCl<sub>3</sub>·6H<sub>2</sub>O in the presence of triethylamine (Et<sub>3</sub>N). Their structures were determined by X-ray single crystal diffraction, elemental analysis, and IR spectra. Complex 1 dis-

Introduction

Single molecule magnets (SMMs) have caused great attention due to the potential applications in the high density information storage and quantum computing since the first SMM  $[Mn_{12}]$  was discovered in 1990s.<sup>[1–7]</sup> Since then, many SMMs have been designed and synthesized, for example, 3d-based SMMs, 3d/4f-based SMMs, and 4f-based SMMs according to metal species. 3d-based SMMs mainly derived from Mn and V complexes.<sup>[8–9]</sup> Because the ligand-field effect and structural configuration play an important on the magnetic properties of the complexes, it is still a great challenge for coordination chemists to synthesize new SMMs with the charming structures and properties.

The metallacrowns (MCs), a class of macrocyclic polynuclear complexes, can be considered as the inorganic analogues of organic crown ethers with methylene carbon atoms replaced by nitrogen atoms and metal ions in ring to exhibit M-N-O connectivity.<sup>[10–12]</sup> So far, based on the number of ring atoms including total atoms and metal ions, MCs demonstrate various structural types, such as 8-MC-4, 9-MC-3, 10-MC-5, 12-MC-3, 12-MC-4, 12-MC-6, 14-MC-7, 15-MC-5, 15-MC-6, 16-MC-4. 16-MC-8. 18-MC-6. 18-MC-9. 20-MC-10. 22-MC-11. 24-MC-6, 24-MC-12, 28-MC-14, 30-MC-10, 32-MC-8, 32-MC-16, 36-MC-12, 36-MC-18, 40-MC-10, 48-MC-24, and 60-MC-20.<sup>[13]</sup> Interestingly, these structural types have the relationship with the choice of ligands and metal ions. For example, the benzene ring-based salicyladoxime (sao) or hydroxamic acidligands are close to Mn ion,<sup>[14]</sup> whereas the pyridine-based sao-ligands or aminhydroxamic acid ligands have a tendency to Cu ions.<sup>[15]</sup> Therefore, it is important to choose the suitable ligand to construct the expected structures and estimate their properties.

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Liaocheng University 252000, Liaocheng, P. R. China plays 12-MC-4 metallacrown structural type with cube-like configuration and **2** shows an offset stacked 10-MC-3 structural type with the ring connectivity containing Fe–O–C–O–Fe–O–N–Fe–O–N. Magnetic susceptibility measurement reveals the ferromagnetic interactions and field-induced slow relaxation of the magnetization for **1**, whereas outof-phase signal is not observed for **2**.

MCs complexes usually possess different paramagnetic metallic ions and small volume, thus, these features make MCs present SMM behavior. Making the best of the small volume of MCs, the reactions of many paramagnetic metallic ions, such as Mn<sup>III</sup>, Co<sup>II</sup>, Fe<sup>II</sup>, Dy<sup>III</sup>, Tb<sup>III</sup>, and hydroximic acid or sao ligands resulted into Mn–MCs, heterometallic 3d-4f MCs with different structural types. Due to the difference in structures easily giving rise to the change of magnetic properties, although MC complexes with SMM behavior have been reported, it is still necessary to study the structure-magnetic properties relationship of new MCs and enrich the magnetic field.

So far, a large number of Mn MCs complexes have been documented and the structures mainly exhibited conventional structural types, such as the planar 9-MC-3, 12-MC-4, and nonplanar 15-MC-5,<sup>[16]</sup> whereas for Fe MCs complexes, few cases have been involved except the routine structural types.<sup>[17]</sup> To obtain new type MCs complexes and expand the metallic ions of MC ring, and to further discuss the effect of new structure on magnetic properties, we reported two new MCs complexes  $[Mn^{III}_4(naphthsao)_4(naphthsaoH)_4$  (1) and  $[Fe^{III}_6O_2(naphthsao)_4(O_2CPh)_6]$  (2). The former shows a cubelike 12-MC-4 structure, whereas the latter display an offset stacked 10-MC-3 structural type. Their magnetic properties also were explored in detail.

## **Results and Discussion**

1

The X-ray single-crystal structural analysis reveals that **1** crystallizes in the monoclinic space group  $C_2/c$  and contains two independent structural units (**1a** and **1b**) with the two units exhibiting similar molecular configuration (Figure 1). For **1a**, four Mn ions are hold together through eight ligands with four doubly-deprotonated at the oxime oxygen and phenolic hydroxyl groups, displaying  $\mu_3$ - $\eta^2$ : $\eta^1$ : $\eta^1$  (Scheme 1a) coordination fashion and four mono-deprotonated at phenolic hydroxyl group, showing  $\mu_2$ - $\eta^1$ : $\eta^1$  coordination fashion. With the bridging of oxime oxygen and nitrogen atoms, the molecule demonstrates a 12-MC-4 metallacrown structural type but the metall-

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acrown ring occurs to distort badly. It is worth noting that the oxime oxygen atoms from four doubly-deprotonated ligands further link the adjacent Mn ions to complete double bridging between two adjacent metal ions. Thus, **1a** also displays an analogous cube-like configuration with each face constituted by pentagon.



Figure 1. The molecular structure of complex 1 (a, b) and  $[\mathrm{Mn}_4(\mathrm{NO})_4]^{+8}$  core.



**Scheme 1.** The coordination motifs of naphthsao ligand in complex **1** (a, b) and **2** (c, d).

In 1a, all Mn<sup>III</sup> ions adopt six-coordinate distorted octahedral arrangements and N2O4 coordination sphere with six coordination atoms from two hydroxyl oxygen atoms, two oxime oxygen atoms and two oxime nitrogen atoms. The distances of Mn····Mn are in range 3.550(1)-3.977(1) Å with the shortest distance between Mn1 and Mn4, and the longest distance between Mn1 and Mn3, respectively. All Mn-O bond lengths are in range of 1.879(6) Å to 2.306(6) Å and Mn-N bond lengths are 1.98(7) to 2.279(8) Å in 1a. The +3 oxidation state of Mn ions is confirmed by the combination of bond length considerations (the presence of Jahn-Teller axes), charge balance considerations and BVS. calculations.<sup>[18]</sup> Because 1b possesses similar structure with 1a, the structural description of 1b is not discussed. In 1b, the shortest distance is Mn5-Mn7 and the longest distance is Mn7-Mn8. The ranges of Mn-O distances are 1.884(6) to 2.260(6) Å and of Mn-N distances 1.983(7) to 2.254(8) Å.

Because compound **1** shows two independent [Mn4](1a) molecules, there are a lot of C–H···O and C–H··· $\pi$  intermolecualr interactions. Interestingly, the [Mn4] unit has assembled with four neighboring [Mn4]' (**1b**) units by C–H··· $\pi$  interactions [C2–H2]··· $\pi$  (C133, C134, C135, C136, C137, C142) H···centroid 2.838 Å, C···centroid 3.682 Å, C–H···centroid 138°; [C48–H48]··· $\pi$  (C1, C2, C3, C4, C5, C10) H···centroid 2.874 Å, C···centroid 2.784 Å, C–H···centroid 174° and C–H···O hydrogen bonds [C78–H78···O32, H···O 2.472 Å, C···O 3.175 Å, C–H···O 133°] forming an undulated net running (Figure 2a). The [Mn4]' units have also assemble with four

[Mn4] through nine C–H··· $\pi$  interactions and a  $\pi$ ··· $\pi$  [(C37, C38, C39, C40, C41, C46) (C145, C146, C147, C148, C149, C154)],  $\pi$ ··· $\pi$  centroid 3.923 Å (Figure 2b).<sup>[19]</sup>



Figure 2. Intramolecular interaction of complex 1 with hydrogen bonding shown as dashed. Molecules of the same color are in the same hydrogen-bonded channel.

The X-ray single-crystal structural analysis reveals that 2 crystallize in the monoclinic space group  $C_2/c$  and the molecule consists of six Fe ions, four deprotonated ligands, six benzoate anions, two coordinated ethanol molecules, and two  $\mu_3$ -O<sup>2-</sup> anions (Figure 3). The structure is centrosymmetric and contains a hexanuclear  $[Fe_6(\mu_3-O)_2]^{14+}$  core with an off-set 10-MC-3 unit, in which two trinuclear subunits  $[Fe_3(\mu_3-O)_2]^{7+}$ were fused together through two naphthol O atoms (O4 and O4a) and two ketnoe oxime O atoms (O13 and O13a). A similar structure has been reported in the literature.<sup>[20]</sup> Four ligands adopt two coordinate motifs  $\mu_2$ - $\eta_1$ : $\eta_1$ : $\eta_1$ : $\eta_1$  and  $\mu_2$ - $\eta_2$ : $\eta_1$ : $\eta_2$  (Scheme 1c and d). Two ligands with  $\mu_2$ - $\eta_1$ : $\eta_1$ : $\eta_1$ : $\eta_1$  coordinate motif link Fe2 and Fe3 (Fe2a and Fe3a) and two ligand bond Fe1, Fe3a, Fe1a and Fe3 through  $\mu_4$ - $\eta_2$ : $\eta_1$ : $\eta_2$  coordinate motif. The average Fe-O bond lengths are 1.929(2) Å (Fe- $\mu_3$ -O<sub>hvdroxo</sub>), 2.023(2) Å (Fe-O<sub>benzoate</sub>), 2.038(2) Å (Fe-Okeynoe), and 2.104(3) Å (Fe-Oethanol), respectively. The similar coordination motifs have been also reported.<sup>[20]</sup> The Fe-N bond lengths are 2.089(3) and 2.127(3) Å. Each Fe ion completes its six-coordinate configuration. Fe1 has NO5 donor atoms with coordination atoms provided by two  $\mu_4$ - $\eta_2$ : $\eta_1$ : $\eta_2$ ligands, two benzoate anions, and one  $\mu_3$ -O<sup>2-</sup>. Fe2 is surrounded by one ligand, three benzoate anions, one ethanol molecule, and one  $\mu_3$ -O<sup>2</sup>. Fe3 is coordinated with one benzoate O atom, one  $\mu_3$ -O<sup>2</sup>, two naphthol O atoms, one ketone oxime O atoms from  $\mu_4$ - $\eta_2$ : $\eta_1$ : $\eta_2$  ligand and N from  $\mu_2$ - $\eta_1$ : $\eta_1$ : $\eta_1$  li-



Figure 3. The molecular structure of complex 2 (left) and  $[Fe_6(\mu_3-O)_2(\mu_2-O_2R)_6]^{8+}$  core (right).



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gand. The intramolecular Fe···Fe distances are in range of 3.2214(7)–3.4141(8) Å and the Fe–O–Fe bond angles are in range of 104.17(10)– $116.14(18)^{\circ}$ .

The complex **2** forms a two-dimensional network structure through C–H··· $\pi$  interactions [C59–H59]··· $\pi$  (C14, C20, C30, C41, C50, C39) with H···centroids 3.479 Å, C–H···centroid 16Å and  $\pi$ ··· $\pi$  interactions [(C48, C26, C55, C58, C56, C57) (C57, C56, C58, C55, C26, C48)],  $\pi$ ··· $\pi$  centroid 3.689 Å (Figure 4).



Figure 4. Intramolecular interaction of complex 2 with hydrogen bonding shown as dashed. Molecules of the same color are in the same hydrogen-bonded channel.

The variable-temperature magnetic susceptibilities of 1 and 2 were investigated in the temperature range 2–300 K under dc = 1000 Oe. For complex 1, the  $\chi_M T$  value is 10.8 cm<sup>3</sup>·K·mol<sup>-1</sup> at 300 K, which is significantly lower than the calculated spin-only value of 12 cm<sup>3</sup>·Kmol<sup>-1</sup> for four high-spin Mn<sup>III</sup> ions with g = 2.0 (Figure 5). In the range of 100–300 K, the value keeps steady, below 100 K, it increases rapidly to 17.5 cm<sup>3</sup>·K·mol<sup>-1</sup> at 5 K, indicating the presence of strong ferromagnetic interaction within the [Mn<sub>4</sub>] cluster. For complex **2**, the room temperature  $\chi_M T$  value of 24.5 cm<sup>3</sup>·K·mol<sup>-1</sup> is lower than that expected for six non-interacting Fe<sup>III</sup> ions (26.25 cm<sup>3</sup>·K·mol<sup>-1</sup>). Upon cooling, the value of  $\chi_M T$  decreases to 1.36 cm<sup>3</sup>·K·mol<sup>-1</sup> at 5 K. This behavior is



**Figure 5.** The plots of  $\chi_{\rm M}T$  vs. *T* for complexes 1 and 2.

consistent with antiferromagnetic exchange between the central metal atoms.

For probing the magnetic behavior of complex 1, the ac magnetization susceptibilities were investigated under a zero applied dc field at frequencies in the range of 100-779 Hz and the temperature range 4-20 K (Figure 6). The data are profiled as  $\chi_M'T$  (in-phase) vs. T and  $\chi_M''$  (out-of-phase) vs. T (Figure 6 left). As temperature decreasing, the in-phase signal increases, indicating the presence of a smaller S value than the ground state.<sup>[21]</sup> The  $\chi_M'T$  curves were extrapolated to 0 K from 5 K to get a value of 20 cm<sup>-3</sup>·mol<sup>-1</sup> K, which was in agreement with  $S = 6 \pm 1$  ground state. Both  $\chi_{\rm M}$  and  $\chi_{\rm M}$  " data show frequency dependence below 3 K, indicating SMM behavior. Owing to the limit of the instrument, the maximum signals of  $\chi_{\rm M}{}^{\prime\prime}$  were not probed below 1.8 K, thus, the energy barrier ( $U_{\text{eff}}$ ) and relaxation time ( $\tau_0$ ) cannot be calculated by the traditional Arrhenius equation.<sup>[22]</sup> Therefore, the energy  $U_{\rm eff}$  (0.3 K) and  $\tau_0$  (3.7 × 10<sup>-5</sup> s) were deduced through Debye mode (Figure 7 right).



**Figure 6.** The plots of in-of-phase  $(\chi_M T')$  and out-of-phase  $(\chi_M')$  signals in 0 Oe dc field for complex **1**.



**Figure 7.** Plots of  $\chi_{M}^{\prime\prime}$  vs. *T* at 1000 Oe dc field (left) and  $\ln(\chi^{\prime\prime}/\chi^{\prime})$  vs.  $T^{-1}/K^{-1}$  (right) for complex **1**.

#### Conclusions

Two complexes  $[Mn^{III}_4(naphthsao)_4(naphthsaoH)_4]$  (1) and  $[Fe^{III}_6O_2(naphthsao)_4(O_2CPh)_6]$  (2) were synthesized by the naphthsaoH<sub>2</sub>. Complexes 1 and 2 are both the distorted metallacrown by structure analysis. Magnetic susceptibilities show the ferromagnetic interactions and field dependent slow magnetization relaxation in complex 1 and antiferromagnetic interactions in complex 2.

## **Experimental Section**

Materials and Physical Methods: All materials were analytical grade and used as purchased from commercial sources. Elemental analyses Zeitschrift für anorganische und allgemeine Chemie

of C, H and N were carried out through an Elemental Vario EL analyzer. The IR spectra were recorded as KBr pallets on the Perkin– Elmer Spectrum. The magnetic susceptibilities were measured on crystalline samples at the temperature range 1.8–300 K under an applied field of 1 KOe with a Quantum Design SQUID magnetometer MPMS-XL17. AC susceptibility measurements were investigated in a zero applied dc field and 1000 Oe dc field for **1**.

**X-ray Crystallography:** X-ray diffraction single-crystal data measurement for **1** and **2** were performed with a Bruker Smart CCD areadetector diffractometer (Mo- $K_a$  radiation,  $\lambda_{Mo} = 0.71073$  Å) at room temperature. The program SAINT was used for integration of the diffraction profiles, and the semiempirical absorption corrections were applied using SADABS.<sup>[23]</sup> All structures were solved by direct methods using SHELXS-97 and refined by full least-matrix least-squares on all  $F^2$  data with SHELXS-97.<sup>[24]</sup>

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-1863505 (1) and CCDC-1863506 (2) (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http:// www.ccdc.cam.ac.uk).

**IR Spectroscopy:** By comparing the infrared spectra of the ligands and their complexes, we could draw the following conclusions: there was a  $-CH_3$  vibrational absorption peak in the range of 3100– 2900 cm<sup>-1</sup>, and a C=O stretching vibrational absorption peak in the range of 1615–1630 cm<sup>-1</sup>. The 624 cm<sup>-1</sup> was assigned to the vibration absorption of the *M*–O bond. The 431 cm<sup>-1</sup> was classified as the stretching vibration absorption of *M*–N bond.

**Synthesis of 1-(1-Hydroxy-naphthalen-2-yl)ethanone oxime**  $(H_2L)$ :<sup>[25]</sup> A solution of hydroxylamine hydrochloride (6.300 g, 0.09 mol) and sodium hydrogen carbonate (5.040 g, 0.06 mol) in water (20 mL) was stirred for 0.5 h. Afterwards, 1-(2-hydroxy-naphthalen-1-yl) ethanone (8.3 g, 0.045 mol) in 20 mL ethanol was added. The mixed solution was kept stirring for 5 h until the solution was clear. The resulting solution was evaporated through a rotary evaporator to remove excess ethanol, filtered, and finally dried. Yield: 6.74 g, 75%. C<sub>12</sub>H<sub>11</sub>O<sub>2</sub>N: calcd. C 71.63; H 5.51; N 6.96%; found: C 71.46; H 5.38; N 6.72%. **IR** (KBr):  $\tilde{v} = 3464$  (br), 3329 (br), 1625 (w), 1586 (w), 1513 (s), 1436 (s), 1351 (s), 1278 (s), 1231 (s), 1143 (w), 1034 (vw), 1009 (w), 956 (m), 923 (m), 878 (vw), 813 (s), 779 (w), 742 (s), 643 (w), 588 (w), 566 (w), 494 (w), 434 (w) cm<sup>-1</sup>.

**Synthesis of Complex 1:** MnCl<sub>2</sub>·4H<sub>2</sub>O (0.124 g, 0.63 mmol) and oxime ligand (H<sub>2</sub>L) (0.124 g, 0.63 mmol) were reacted in the mixed solution of 1:1 ethanol (10 mL)/acetonitrile (10 mL) in the presence of triethylamine (NEt<sub>3</sub>, 0.03 mL, 0.25 mmol). The solution was stirred for 5 h at room temperature and filtered. The filtrate was left undisturbed to allow slow evaporation of the solvent. Black single crystals suitable for X-ray diffraction were obtained after two weeks. Yield: 20.0 mg, 16% (based on Mn). C<sub>96</sub>H<sub>76</sub>Mn<sub>4</sub>N<sub>8</sub>O<sub>16</sub>: calcd. C 65.76; H 4.42; N 3.48%; found: C 65.46; H 4.35; N 3.18%. **IR** (KBr):  $\tilde{v} = 3422$  (br), 3160 (w), 3054 (w), 2920 (w), 1618 (m), 1561 (m), 1452 (m), 1365 (w), 1301 (w), 1238 (s), 1209 (w), 1158 (w), 1124 (w), 1031 (m), 1022 (m), 954 (s), 782 (s), 766 (m), 746 (m), 614 (w), 557 (w), 451 (m), 431 (w) cm<sup>-1</sup>.

Synthesis of Complex 2:  $FeCl_3$ · $6H_2O$  (0.124 g, 0.63 mmol), sodium benzoate (NaO<sub>2</sub>Ph) (0.090 g, 0.75 mmol) and oxime ligand (H<sub>2</sub>L) (0.124 g, 0.63 mmol) were reacted in the mixed solution of 1:1 ethanol

(10 mL) /acetonitrile (10 mL) in the presence of triethylamine (0.03 mL, 0.25 mmol). The solution was stirred for 5 h at room temperature and filtered. The filtrate was left undisturbed to allow slow evaporation of the solvent. Black single crystals suitable for X-ray diffraction were obtained after three weeks. Yield: 40 mg, 32% (based on Mn). Fe<sub>6</sub>N<sub>4</sub>O<sub>24</sub>C<sub>94</sub>H<sub>76</sub>: calcd. C 57.01; H 3.86; N 2.83%; found: C 56.87; H 3.69; N 2.66%. **IR** (KBr):  $\tilde{v} = 3448$  (s), 2925 (w), 1617 (w), 1594 (m), 1555 (m), 1522 (w), 1402 (s), 1342 (w), 1236 (w), 1236 (w), 1146 (w), 1025 (w), 941 (m), 822 (m), 744 (w), 721 (s), 672 (w), 615 (w), 474 (m) cm<sup>-1</sup>.

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Cube-like 12-MC-4 and Offset Stacked 10-MC-3 Metallacrowns: Synthesis, Structure, and Magnetic Properties

