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两个锰的 18- 氮杂金属冠醚 -6 配合物的合成、晶体结构和磁性质研究

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以负三价、五啮的 *N*- 乙酰水杨酰肼 ($ashz^{3-}$) 作为配体, 合成了二个大环六核氮杂金属冠醚 $[Mn^{III}_6(ashz)_6(MeOH)_6]\cdot 6MeOH$ (**1**) 和 $[Mn^{III}_6(ashz)_6(DMF)_6]\cdot 3DMF$ (**2**)。晶体学数据是: 配合物 **1**, 三方晶系, 空间群 $R\bar{3}$, $a = b = 24.806(2)$, $c = 11.260(1)$ Å, $Z = 3$, $\mu = 1.007 mm^{-1}$, $R = 0.0572$, $wR = 0.1142$; 配合物 **2**, 三方晶系, 空间群 $R\bar{3}$, $a = b = 26.629(3)$, $c = 23.298(4)$ Å, $Z = 6$, $\mu = 0.856 mm^{-1}$, $R = 0.0671$, $wR = 0.1661$。这两个配合物属 18- 氮杂金属冠醚 -6 结构类型, 冠醚分子具有晶体学 C_{3i} 对称性。配体 $ashz^{3-}$ 通过它的肼基的 N-N 桥连金属原子, 从而形成有中央空穴的六核锰的大环配合物。变温磁化率 (4 ~ 275K) 研究表明, 配合物 **1** 中金属离子间存在着反铁磁性耦合。

关键词: 金属冠醚 锰 水杨酰肼 晶体结构 磁性质

分类号: O614.7+11 O626 O646.8 O723

Syntheses, Crystal Structures and Magnetic Property of the Two Mn (III) 18-azaMetallacrown-6 Complexes

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Two macrocyclic hexanuclear azaMetallacrowns, $[Mn^{III}_6(ashz)_6(MeOH)_6]\cdot 6MeOH$ (**1**) and $[Mn^{III}_6(ashz)_6(DMF)_6]\cdot 3DMF$ (**2**), were prepared using a trianionic pentadentate ligand N-acylsalicylhydrazide ($ashz^{3-}$). The crystal data are trigonal $R\bar{3}$, $a = b = 24.806(2)$, $c = 11.260(1)$ Å, $Z = 3$, $\mu = 1.007 mm^{-1}$, $R = 0.0572$, $wR = 0.1142$ for complex **1** and trigonal $R\bar{3}$, $a = b = 26.629(3)$, $c = 23.298(4)$ Å, $Z = 6$, $\mu = 0.856 mm^{-1}$, $R = 0.0671$, $wR = 0.1661$ for complex **2**. They are of 18-azametallacrown-6 structure type. The metallacrown molecules in two title complexes have a crystallographic C_{3i} symmetry. The triple-deprotonated ligand $ashz^{3-}$ in the title complexes bridges the metal ions by a hydrazide N-N group, forming a hexanuclear manganese metallmacrocycle with a cavity in the center. The magnetic susceptibility (4 ~ 275K) study indicates that there is an antiferromagnetic exchange interaction in the title compound **1**. CCDC: 192835(complex **1**); 192836(complex **2**).

Keywords: metallacrown manganese salicylhydrazide crystal structure magnetic property

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0 Introduction

Metallacrowns have emerged as a new type of inorganic host molecules and considered to be molecular recognition agents[1~5]. They exhibit selective recognition of cations and anions and can display intramolecular magnetic exchange interactions and also can be used as building blocks for chiral layered solids. The tetradentate ligands, salicylhydroxamic acid (H_3shi), were used as the template ligand in the synthesis of the metallacrowns with $[-M-N-O-]_n$ repeat structural unit. In this kind of metallacrown, H_3shi serves as a bridging ligand between the two neighboring metal centers, and forms a five-membered chelate ring by a hydroximate group and a six-membered chelate ring by an iminophenolate group. The chelation gave the metallmacrocycles additional stabilization. Design and synthesis of a new type of metallacrown, azaMetallacrown, have garnered increasing attention over the past four years[6~10]. Herein we report the syntheses, crystal structures and magnetic properties of two 18-azaMetallacrown-6 complexes with a pentadentate *N*-acylsalicylhydrazide $C_9H_7N_2O_3$ ($ashz^{3-}$), $[Mn(C_9H_7N_2O_3)(CH_3OH)]_6 \cdot 6CH_3OH$ (**1**) and $[Mn(C_9H_7N_2O_3)(C_3H_7NO)]_6 \cdot 3C_3H_7NO$ (**2**). The ligands bridge the metal ions using a hydrazide N-N group and form three chelate rings in each metal center.

1 Experimental

1.1 Synthesis

1.1.1 Synthesis of Ligand

3.41g(33.4mmol) amount of acetic anhydride and 4.24g (27.9mmol) of salicylhydrazide were added to 60mL of chloroform at 0℃. The reaction mixture was slowly warmed to room temperature and stirred for 4h. After staying for overnight at refrigerator, the resulting white precipitate was filtered and rinsed with chloroform and diethyl ether (5.1g. 95.0% yield). m. p.: 179 ~ 181℃.

1.1.2 Synthesis of metallamacrocycles

$[Mn_6(ashz)_6(MeOH)_6] \cdot 6MeOH$ (**1**): 0.194g (1.0mmol) amount of H_3ashz was dissolved in 20mL of methanol, and 0.261g (1.0mmol) of manganese perchlorate hexahydrate was dissolved in 20mL of methanol in another flask. The two solutions were mixed and stirred for 10min., then filtered. The combined solution was allowed to stand for 3d, whereupon dark brown rectangular crystals were obtained (0.122 g, 52.6% yield). Anal. Calcd. for $C_{66}H_{90}Mn_6N_{12}O_{30}$ (%): C, 42.59; H, 4.88; N, 9.03; O, 25.79. Found: C, 42.38; H, 4.72; N, 9.41; O, 25.60. IR(KBr disc, cm^{-1}): 1602(s), 1563(s), 1508(vs), 1406(s), 1244(m), 697(m), 597(m), 551(m), 408(m).

$[Mn_6(ashz)_6(DMF)_6] \cdot 3DMF$ (**2**): 0.040g (0.2 mmol) amount of H_3ashz was dissolved in 10mL of DMF, and 0.049g (0.2mmol) of manganese acetate tetrahydrate was dissolved in 10 ml of DMF in another flask. The two solutions were mixed and stirred for five minutes, then filtered. The combined solution was allowed to stand for 3d, whereupon dark brown rectangular crystals were obtained. Anal. Calcd. for $C_{81}H_{105}Mn_6N_{21}O_{27}$(%): C, 45.58; H, 4.96; N, 13.78; O, 20.24, Found: C, 45.39; H, 4.88; N, 14.09; O, 20.02.

1.2 X-ray Crystallography

A crystal with dimensions of 0.64 × 0.64 × 0.46mm for complex **1** and a crystal with dimensions of 0.56 × 0.56 × 0.42mm for complex **2** were mounted in a glass capillary with the mother liquor, respectively. The diffraction data were recorded on a Siemens Smart 1000 CCD areadetector diffractometer with graphite-monochromated Mo$K\alpha$ radiation ($\lambda = 0.71073$Å), the scan mode being ω. Intensity data of the two title complexes were corrected for Lp factors and ψ absorption. The structures were solved by direct methods using SHELXL-97. All non-hydrogen atoms were refined with anisotropic thermal parameters. Except some hydrogen atoms of lattice solvent molecules, most of the hydrogen atoms in complexes **1** and **2** were located in calculated positions or in the positions from difference Fourier map. The crystallographic data of the two compounds are given in Table 1. CCDC numbers for the two compounds are 192835 and 192836, respectively.

Table 1　Crystallographic Data

formula	$C_{66}H_{90}Mn_6N_{12}O_{30}$ (**1**)	$C_{81}H_{105}Mn_6N_{21}O_{27}$ (**2**)
formula weight	1861.14	2134.50
crystal system	trigonal	trigonal
space group	$R\bar{3}$	$R\bar{3}$
a/Å	24.806(2)	26.629(3)
b/Å	24.806(2)	26.629(3)
c/Å	11.260(1)	23.298(4)
α/(°)	90	90
β/(°)	90	90
γ/(°)	120	120
V/Å^3	6000.5(8)	14308(3)
Z	3	6
D_{calc}/(Mg · m^{-3})	1.545	1.486
μ/mm^{-1}	1.007	0.856
F(000)	2880	6624
θ_{max}, θ_{min}/(°)	25.07, 1.64	25.03, 1.96
No. of unique reflections	2366	5586
No. of observed reflections	1359	3676
No. of parameters	175	412
R_1, wR_2	0.0572, 0.1142	0.0671, 0.1661
GOF	1.000	1.083
largest diff. peak*(hole)/(e · Å^{-3})	0.39(−0.65)	0.66(−0.66)

*Largest peak(hole) in difference Fourier map.

2　Results and Discussion

2.1　Structure Description

The molecular structures of the two title complexes are shown in Fig. 1 and 2, respectively. The selected bond lengths and bond angles in complexes 1 and 2 are listed in Tables 2 and 3, respectively.

There are three hexanuclear molecules with crystallographic C_{3i} symmetry in complex **1**, including one crystallographic independent hexanuclear molecule with symmetry center at (1/3, 2/3, 1/6). However, there are six hexanuclear molecules with crystallographic C_{3i} symmetry in complex **2**, in which there are two crystallographic independent hexanuclear molecules, i.e. the molecule **a** containing Mn(1) with symmetry center at (1/3, 2/3, 1/6) and the molecule **b** containing Mn(2) with symmetry center at (0, 0, 0).

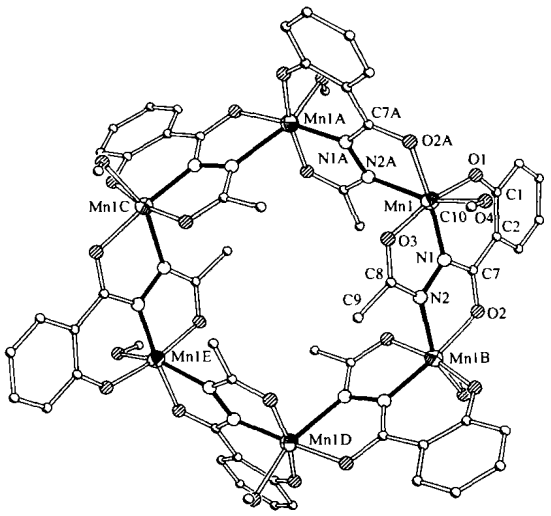

Fig. 1　Molecular structure of complex **1**

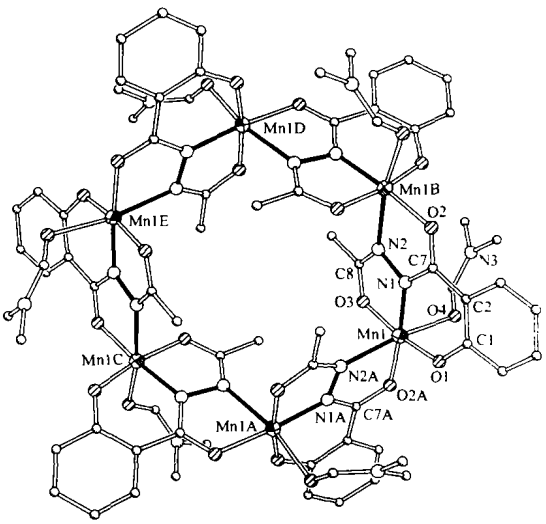

Fig. 2　Molecular structure of complex **2**

Table 2 Selected Bond Lengths(Å) and Angles(°) for Complex 1

Mn(1)-O(1)	1.843(3)	Mn(1)-O(3)	1.922(3)	Mn(1)-N(1)	1.953(4)
Mn(1)-O(2A)	2.004(3)	Mn(1)-N(2A)	2.250(4)	Mn(1)-O(4)	2.277(3)
O(1)-C(1)	1.347(6)	O(2)-C(7)	1.295(5)	O(3)-C(8)	1.302(6)
O(4)-C(10)	1.434(7)	N(1)-C(7)	1.319(6)	N(1)-N(2)	1.413(5)
N(2)-C(8)	1.305(6)	C(2)-C(7)	1.463(7)	C(8)-C(9)	1.506(7)
O(5)-C(11)	1.397(11)	Mn(1)···Mn(1A)	4.9011(9)	Mn(1)···Mn(1C)	8.284(1)
Mn(1)···Mn(1E)	9.626(2)	O(4)···O(2F)	2.919(5)		
O(1)-Mn(1)-O(3)	169.2(2)	O(1)-Mn(1)-N(1)	90.2(2)	O(3)-Mn(1)-N(1)	79.9(2)
O(1)-Mn(1)-O(2A)	96.2(1)	O(3)-Mn(1)-O(2A)	93.7(1)	N(1)-Mn(1)-O(2A)	173.6(2)
O(1)-Mn(1)-N(2A)	97.4(2)	O(3)-Mn(1)-N(2A)	89.5(2)	N(1)-Mn(1)-N(2A)	105.3(2)
O(2A)-Mn(1)-N(2A)	73.9(1)	O(1)-Mn(1)-O(4)	88.6(2)	O(3)-Mn(1)-O(4)	88.4(1)
N(1)-Mn(1)-O(4)	97.8(2)	O(2A)-Mn(1)-O(4)	82.5(1)	N(2A)-Mn(1)-O(4)	156.1(2)

Symmetry codes: A: $x-y+2/3$, $x+1/3$, $-z+1/3$; C: $1-y$, $x-y+1$, z; E: $2/3-x$, $1/3-y+1$, $-z+1/3$; F: $-x+y-1/3$, $-x+1/3$, $z+1/3$.

Table 3 Selected Bond Lengths(Å) and Angles(°) for Complex 2

Mn(1)-O(1)	1.859(3)	Mn(1)-O(3)	1.932(3)	Mn(1)-N(1)	1.939(4)
Mn(1)-O(2A)	1.972(3)	Mn(1)-N(2A)	2.229(4)	Mn(1)-O(4)	2.272(4)
N(1)-N(2)	1.418(5)	Mn(2)-O(5)	1.851(4)	Mn(2)-O(7)	1.929(4)
Mn(2)-N(4)	1.938(4)	Mn(2)-O(6F)	1.979(3)	Mn(2)-O(8)	2.248(4)
Mn(2)-N(5F)	2.296(4)	N(4)-N(5)	1.420(6)		
O(1)-Mn(1)-O(3)	170.51(14)	O(1)-Mn(1)-N(1)	90.48(15)	O(3)-Mn(1)-N(1)	80.04(15)
O(1)-Mn(1)-O(2A)	96.23(14)	O(3)-Mn(1)-O(2A)	93.26(14)	N(1)-Mn(1)-O(2A)	173.26(16)
O(1)-Mn(1)-N(2A)	93.45(15)	O(3)-Mn(1)-N(2A)	89.18(15)	N(1)-Mn(1)-N(2A)	103.76(15)
O(2A)-Mn(1)-N(2A)	75.27(13)	O(1)-Mn(1)-O(4)	91.57(16)	O(3)-Mn(1)-O(4)	88.11(15)
N(1)-Mn(1)-O(4)	89.90(16)	O(2A)-Mn(1)-O(4)	90.55(14)	N(2A)-Mn(1)-O(4)	165.39(15)

Symmetry codes: A: $x-y+2/3$, $x+1/3$, $-z+1/3$; F: $x-y$, x, $-z$.

Up to now, hexanuclear metallacrowns with Co (Ⅲ)[9], Fe (Ⅲ)[10] and Mn (Ⅲ)[6, 7] ions have been prepared. These hexanuclear metallacrown molecules have a psudo C_{3i} symmetry and a crystallographic center symmetry, but not crystallographic C_{3i} symmetry. As illustrated in Fig. 3, the metallacrown molecules in $[Mn_6(ashz)_6(MeOH)_6]\cdot 6MeOH$(**1**) and $[Mn_6(ashz)_6(DMF)_6]\cdot 3DMF$(**2**) have a crystallographic C_{3i} symmetry, as compared with the crystallographic center symmetry in $[Mn_6(ashz)_6(DMF)_6]\cdot 2DMF$[7].

The Mn (Ⅲ) ions in the two title complexes have an octahedral coordination with Mn(ONO)(NO)(O) type. The manganese atom in the two title azaMetallacrowns is coordinated by a phenolate oxygen [O(1)], a diazine nitrogen [N(1)], and an acyl oxygen [O(3)] of a trianionic pentadentate ligand, an acyl oxygen [O(2A)] and a diazine nitrogen [N(2A)] of an adjacent trianionic ligand and an oxygen [O(4)] of a coordinated methanol molecule or DMF molecule. The equatorial plane is formed by O(1), N(1), [O(3)] and [O(2A)]. The atom O(4) lies trans to N(2A) of

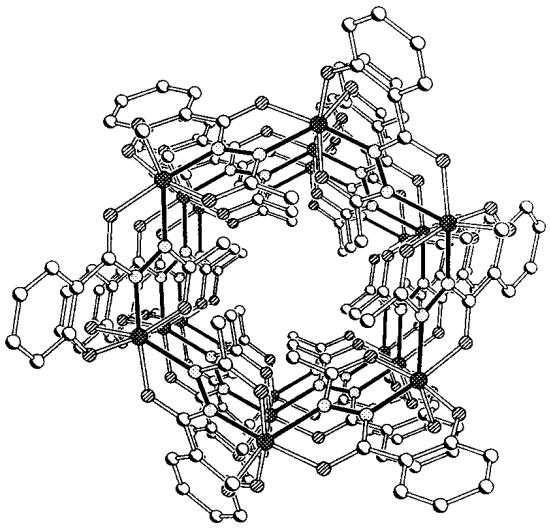

Fig. 3 Packing diagram of complex **1** along the *c* axis

the adjacent trianionic ligand, O(4) is from coordinated methanol molecule in complex **1** or DMF molecule in complex **2**.

The two title hexanuclear azaMetallacrowns exhibit a 18-membered ring of six manganese atoms linked by six hydrazide N-N groups. The deprotonated ligand $ashz^{3-}$ acts as a trianionic pentadentate ligand. All ring metal ions in the two azaMetallacrowns adopt the propeller configurations. The typical Jahn-Teller elongation along the *z*-axis for the manganese (Ⅲ) ions of the two title compounds is observed. In complex **1**, the axial bond distances of Mn-N and Mn-O are more than 0.273Å longer than the corresponding basal bond distances. In molecule **a** of complex **2**, the axial manganese-oxygen and manganese-nitrogen distances are 0.290Å and 0.351Å longer than the corresponding basal Mn-O/N distances, respectively; in molecule **b** of complex **2**, the axial Mn-O and Mn-N distances are 0.358Å and 0.328Å longer than the corresponding basal Mn-O/N distances, respectively.

In complex **1**, the approximate dimensions of the oval-shaped cavity are about 3.56 Å (less 1.57Å for the van der waals radii of the carbon atoms) in diameter at the entrance, about 5.29Å (less 1.37Å for the van der waals radii of the manganese atom) at its largest diameter at the center of the cavity. Torsion angles for N(2A)-Mn(1)-N(1)-N(2) and Mn(1)-N(1)-N(2)-Mn(1A) are $-89.2(4)°$ and $173.1(2)°$, respectively. The M···M···M interatomic angle in the 18-membered core ring of the title compound **1** is 115.4°, which is close to interior angle in *n*-hexagon of 120°. There exits hydrogen bond between O atom(phenolic) and OH group (coordinated methanol), O(4)-H(O4)···O(2*n*), (symmetry code: *n*, $-x+y-1/3$, $-x+1/3$, $z+1/3$) in complex **1**, distance of O(4)···O(2n) being 2.919Å.

The average dimensions of the oval-shaped cavity in complex **2** is about 3.45Å (less 1.57Å for the van der Waals radii of the carbon atoms) in diameter at the entrance, about 5.21Å(less 1.37Å for the van der Waals radii of the manganese atoms) at its largest diameter at the center of cavity, about 10.00Å in thickness. Torsion angles for N(2A)-Mn(1)-N(1)-N(2), Mn(1)-N(1)-N(2)-Mn(1B) and N(5F)-Mn(2)-N(4)-N(5), Mn(2)-N(4)-N(5)-Mn(2G) are $-83.2(4)°$, $176.3(2)°$ and $-90.2(4)°$, $169.8(2)°$ respectively. The M···M···M interatomic angle of the 18-member core rings in both molecules of complex **2** are 116.58(1)° and 112.08(2)°, which are close to interior angle in *n*-hexagon of 120°.

2.2 Magnetic Properties

As shown in Fig. 4, the calculated value of the molar effective magnetic moment (μ_{eff}) of the title compound **1** is consistent with the value observed. The μ_{eff} value at 273K is 9.03μ_B, which is smaller than the sum value expected for a six spin-only paramagnetic systems with $S=2$ ($\mu_{eff}=12.00\mu_B$). With temperature decreasing, the μ_{eff} values firstly decrease slightly, reaching 8.01μ_B at 40K, and then decrease rapidly after 40K, reaching 3.38μ_B at 4.2K. This indicated the presence of an antiferromagnetic coupling between the Mn (Ⅲ) spin centers and this is further suggested by a negative Weiss constant $\theta=-17.8$K, derived from the Curie-Weiss law fit in the temperature ranging from 4.2 to 273K. Structurally, the magnetic super-exchanges would likely propagate between the neighboring centers (J_1), between the near-neighboring centers (J_2) and between the opposite centers (J_3). When the six Mn (Ⅲ) centers are simplified to be arranged in the symmetry of D_{6h}, a least-squares fit for the data within

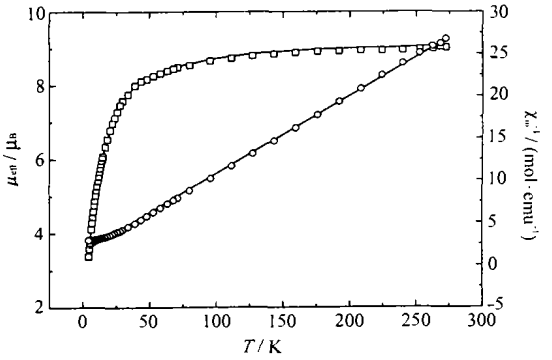

Fig. 4 Effective magnetic moment (μ_{eff}) and the inverse susceptibility χ_m^{-1} data as a function of temperature for the title compound **1**, where open dots for observed results, and solid lines attached to χ_m^{-1} and μ_{eff} for fitting curves based on the Curie-Weiss law and on an super-exchange fit, respectively

$T > 7.9$K obtains the parameters $J_1/k = -2.31(3)$ K, $J_2/k = -1.12(4)$ K, $J_3/k = -0.51(8)$ K and the agreement factor $F = \sum[(\chi_{obs} - \chi_{cal})^2/\chi_{obs}] = 4.83 \times 10^{-3}$. The negative values of J demonstrate an antiferromagnetic coupling between the paramagnetic centers. The antiferromagnetic nature of the interaction can be understood in terms of overlap through the bridging group between the single occupied metal d orbitals.

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