

NOVEL 24-MEMBERED OCTANUCLEAR MANGANESE(III) METALLACROWN

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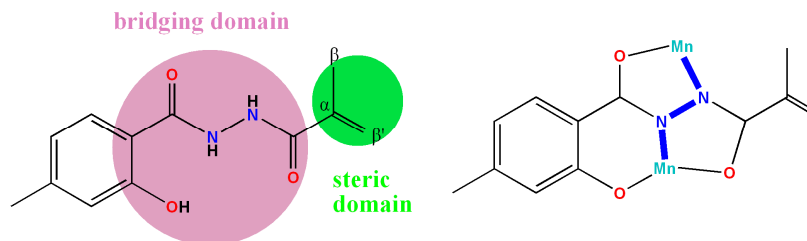
ABSTRACT. A novel octanuclear manganese metalladiazamacrocycle (**1**) was synthesized employing a new pentadentate ligand *N*-methacryl-5-methylsalicylhydrazide (H₃mamshz) by supramolecular self assembly. The backbone of this metal-organic assembly is a repeating unit of Mn–N–N–Mn linkage that extends to complete a 24-membered cyclic structure involving 8 manganese(III) centers. Successive manganese centers are in an octanuclear cyclic structure. The temperature-dependent magnetic properties show a typical weakly coupled antiferromagnetic behaviour.

KEY WORDS: Manganese, Octanuclear, Metalladiazamacrocycle, Pentadentate ligand, Antiferromagnetic behavior

INTRODUCTION

Metallamacrocycles have become important in recent years because of their interesting molecular architecture [1], multinuclear structures [2] and magnetic properties [3]. They have also been used as building blocks for the construction of two- or three-dimensional network structures [4]. A variety of metallamacrocycles and cages were found to form interesting host-guest systems with different metal ions of varying coordination and symmetry [5]. Metal ions such as Ga, Co, Fe and Mn that can easily form stable octahedral coordination, are found to yield hexanuclear metallamacrocycles with trianionic pentadentate ligands [6]. However manganese and iron have received special attention because of their ease of formation of metallamacrocycles and interesting magnetic properties [7]. Controlling the size and nuclearity of metallamacrocycles and their properties has quite recently become of interest. Although there have been reports of metallamacrocycles and metallacrowns of high nuclearity containing iron and manganese, formation of stable cyclic high nuclearity structures has been an uphill task.

We report here a novel 24-membered octanuclear manganese metalladiazamacrocycle, [Mn₈(mamshz)₈(DMA)₈][Mn₈(mamshz)₈(DMA)₆(H₂O)₂]·2DMA·4H₂O (**1**), a cyclic structure derived from employing a trianionic pentadentate ligand *N*-methacryl-5-methylsalicylhydrazide (H₃mamshz) (Scheme 1).



Scheme 1. Ligand and basic binding sites of compound **1**.

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EXPERIMENTAL*Materials and physical measurements*

All chemicals used were of analytical grade and were used in this experiment without further purification.

Carbon, nitrogen and hydrogen analyses were determined using a Vario EL elemental analyzer. IR spectra were recorded on a Nicolet Avatar 360 FT-IR instrument using KBr discs in the 400–4000 cm^{-1} region. ^1H NMR spectra were measured on a FT-400A spectrometer in $\text{dms}\text{-}d_6$ solution, with TMS as internal standard. The intensity data were collected at 296 K on a Bruker Smart APEX II diffractometer with graphite-monochromatized Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). The structure was solved by direct methods and refined by full matrix least-squares techniques on F^2 with all non-hydrogen atoms treated anisotropically. All calculations were performed with the SHELXTL program package. Non-hydrogen atoms with geometrical rigidity were refined anisotropically, but non-hydrogen atoms with geometrical flexibility were refined isotropically; hydrogen atoms attached to the non-disordered part were assigned isotropic displacement coefficients $U(\text{H}) = 1.2U(\text{C})$ or $1.5U(\text{C}_{\text{methyl}})$, and their coordinates were allowed to ride on their respective atoms. Temperature-dependent magnetic susceptibility measurements were carried out on powdered samples between 2 and 300 K using a Quantum Design MPMS-7XL SQUID magnetometer. Field-cooled magnetization data were collected at $H = 1000 \text{ Oe}$. The diamagnetic correction for complex was calculated using Pascal's constants.

Preparation of H_3mamshz

To a 35 mL of chloroform solution at 0 °C, containing 3.09 mL (22 mmol) of triethylamine and 1.72 g (20 mmol) of methacrylic acid was added 2.49 mL (20 mmol) of trimethylacetyl chloride with stirring. The solution was then brought slowly to room temperature. After stirring for 30 min 2.32 g (20 mmol) of 2-hydroxy-4-methylbenzohydrazide was added to it and stirring was continued for another 40 min. It is then layered with 20 mL of hexane; a white suspension appears which was then left aside for complete precipitation. The product (H_3mamshz) obtained was filtered, washed successively with a 1:1 mixture of chloroform and hexane, and then with ether. The compound was recrystallised from ethanol to yield 2.80 g (60 %). Elemental data for $\text{C}_{12}\text{H}_{14}\text{N}_2\text{O}_3$ calc: C 61.53, H 6.02, N 11.96%; found: C 61.64, H 6.18, N 11.82%. ^1H NMR (400 MHz, $\text{dms}\text{-}d_6$, ppm): δ 12.00 (1H, s, ArOH); 10.47 (1H, s, ArCONH); 10.12 (1H, s, MeCONH); 7.80–7.78 (1H, d, $J = 8 \text{ Hz}$, *o*-ArH); 6.78–6.75 (1H, t, $J = 8.8 \text{ Hz}$, *m*-ArH); 5.82 (1H, s, $-\text{CO}-\text{C}-\text{CH}_2-$); 5.51 (1H, s, $-\text{CO}-\text{C}-\text{CH}_2-$); 2.29 (3H, s, ArCH_3); 1.92 (3H, s, COCH_3). IR (KBr pellet, cm^{-1}): 3324(s), 3103(w), 3066(w), 3016(w), 2980(w), 2931(w), 2879(w), 2738(m), 2717(w), 2681(w), 2623(w), 2603(w), 2526(w), 2495(w), 1662(s), 1647(m), 1614(s), 1545(s), 1514(s), 1481(s), 1423(m), 1375(m), 1315(s), 1286(s), 1250(s), 1209(s), 1174(s), 1145(s), 1119(s), 1038(m), 1014(s), 957(s), 924(s), 881(s), 835(s), 827(s), 816(m), 769(s), 737(m), 704(m), 673(w), 596(s), 559(s), 509(w), 455(w), 436(m), 411(w).

Preparation of compound 1. The dark brown block crystals of $[\text{Mn}_8(\text{mamshz})_8(\text{DMA})_8][\text{Mn}_8(\text{mamshz})_8(\text{DMA})_6(\text{H}_2\text{O})_2]\cdot 2\text{DMA}\cdot 4\text{H}_2\text{O}$ (**1**) were obtained by slow diffusion of manganese(II) acetate into a DMA (N,N-dimethylacetamide) solution of H_3mamshz at room temperature over a period of 4 weeks ($\text{H}_3\text{mamshz} : \text{Mn}(\text{OAc})_2\cdot 4\text{H}_2\text{O} = 1:1$). Yield: 71%. Melting point: $>300 \text{ }^\circ\text{C}$ (dec.). Elemental data for $\text{C}_{256}\text{H}_{332}\text{Mn}_{16}\text{N}_{48}\text{O}_{70}$ calc: C 50.57, H 5.50, N 11.06%; found: C 50.43, H 5.64, N 11.21%. IR (KBr pellet, cm^{-1}): 3433(br), 2922(m), 1608(s), 1562(s), 1498(s), 1427(s), 1394(s), 1350(s), 1327(s), 1246(s), 1215(m), 1176(s), 1161(w), 1119(m), 1061(w), 1018(m), 960(s), 928(s), 877(m), 816(m), 779(w), 764(s), 748(s), 698(m), 679(s), 648(s), 626(s), 594(m), 563(m), 513(m), 476(m), 442(s).

RESULTS AND DISCUSSION

IR spectra

The IR spectra of H₃mamshz and compound **1** are listed in Table 1. The data of compound **1** show the stretching vibration of the C=O band shifted to lower frequencies and the O-H (phenolic) shifted to higher frequencies compared with the ligand, suggesting the coordination of carbonyl oxygen atom and the O (phenolic) atom to Mn³⁺ ion. The stretching vibration band (N-H) disappeared in the spectra of compound **1** indicating the deprotonation of the group and coordination of the hydrazide nitrogen atom to the Mn³⁺ ion. The bands of C-N at 1286 and 1315 cm⁻¹ are shifted to 1562 cm⁻¹ due to the deprotonation of NH group.

Table 1. IR spectra of H₃mamshz and compound **1**.

Compound	v(C=O)	v(O-H) (phenolic)	v(N-H)	δ(C-H) (aromatic)
H ₃ mamshz	1660	3320	3040	769
1	1610	3440	-	681

Table 2. Crystal data and structure refinement of compound **1**.

Identification code	Compound 1
CCDC	796822
Empirical formula	C ₂₅ H ₃₃ N ₄ O ₇ Mn ₁₆
Formula weight	6077.4
Temperature (K)	296(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	<i>P</i> ₁
<i>a</i> (Å)	20.725(5)
<i>b</i> (Å)	26.712(6)
<i>c</i> (Å)	29.357(7)
<i>α</i> /deg	77.353(4)
<i>β</i> /deg	73.717(3)
<i>γ</i> /deg	74.031(3)
Volume (Å ³)	14820(6)
<i>Z</i>	2
Calculated density (Mg m ⁻³)	1.360
Absorption coefficient (mm ⁻¹)	0.738
<i>F</i> (000)	3174
Crystal size (mm ³)	0.310 × 0.267 × 0.225
Range for data collection	0.994° to 25°
Independent reflections	19645
Refinement method	Full-matrix least-squares on <i>F</i> ²
Limiting indices	-19 ≤ <i>h</i> ≤ 22, -28 ≤ <i>k</i> ≤ 28, -31 ≤ <i>l</i> ≤ 31
Goodness-of-fit on <i>F</i> ²	1.030
Final R indices [<i>I</i> > 2 sigma(<i>I</i>)]	R ¹ = 0.0962, R ² = 0.2655
Largest diff. peak and hole (eÅ ⁻³)	1.539 and -0.998

X-ray diffraction data of compound **1**

The molecular structure of the title azametallacrown is shown in Figure 1. Single-crystal X-ray analysis showed that compound **1** crystallizes in triclinic space group *P*-1. There are two octanuclear metallamacrocyclic: [Mn₈(mamshz)₈(DMA)₈] (ring A) and

$[\text{Mn}_8(\text{mamshz})_8(\text{DMA})_6(\text{H}_2\text{O})_2]$ (ring B), two DMA and four H_2O molecules in an asymmetric unit (Table 1). Eight Mn(III) ions and eight deprotonated *N*-methacryl-5-methylsalicylhydrazidate (mamshz^{3-}) ligands assemble to form a planar 24-membered ring based on Mn-N-N-Mn linkage in the title azametallacrown. The ligand binds to the metal in a back-to-back fashion, resulting in an octanuclear cyclic structure. The adoption of a sequence of chiralities by a certain kind of macrocycle is triggered by the tendency of the system to choose the lowest energy macrocycle (Figure 1, Table 2).

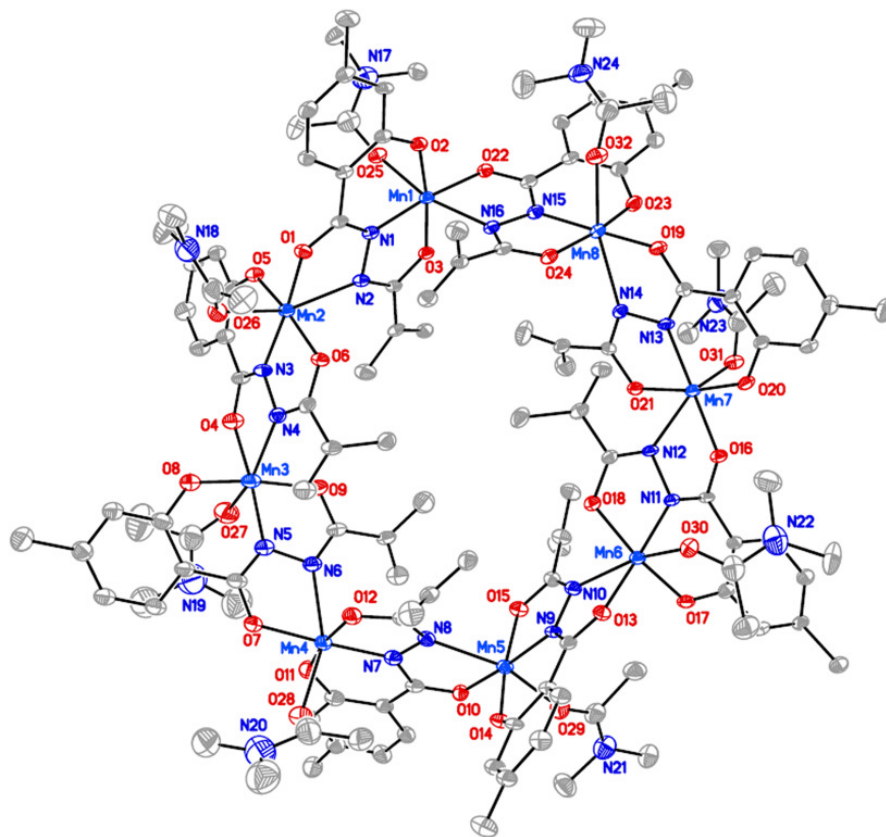


Figure 1. Molecular structure of the ring A of the title compound **1** with Mn, N, O atoms labeling. H atoms and free solvent molecules are omitted for clarity.

All manganese ions in **1** are in a distorted octahedral MnN_2O_4 environment with a very distinct Jahn–Teller extension. The resulting octanuclear systems measure ~ 21.5 Å in diameter and ~ 10 Å in thickness. The neighboring Mn...Mn interatomic distances are 4.904(2)–4.983(2) Å and 4.871(2)–4.984(2) Å in ring A and ring B, respectively.

The Mn...Mn...Mn interatomic angles in the 24-membered core rings are in the range 121.07(3)–134.38(2)° and 121.32(3)–130.27(4)° in the ring A and ring B, respectively. These values are quite close to the value of the interior angle in an *n*-octagon (135°). The bond distances for Mn–N (diazine), Mn–O (phenolate), and Mn–O (carbonyl) are in the ranges 1.92–

2.36, 1.85–1.89, and 1.94–1.99 Å, respectively. The Mn(III)–O(DMA) bond distances are from 2.21 to 2.30 Å. The Mn(III)–O (H₂O) bond distances are from 2.24 to 2.25 Å. The terminal groups of the tails of 4 ligands are directed to the top of the cyclic structure, while the rest are directed down the cycle. The disc like molecule offers a cavity with an entrance diameter ~ 3.6 Å and ~ 12.9 Å at the interior which may serve as potential molecular recognition site. There are no molecules in the ‘host’ cavity of the metallacrown.

The local environment of each metal centre of high-spin d^4 Mn(III) ion has the same Jahn-Teller elongated octahedral geometry as in other manganese metallamacrocycles [6]. The Jahn-Teller distortion results in elongation of the axial manganese-oxygen/nitrogen bond lengths by ~ 0.3 Å relative to the other Mn–O/N bond lengths. The cyclic structure of the compound leaves a nano disc-shaped molecule (Table 3, Table 4).

Table 3. Selected bond lengths (Å) of compound **1**.

Bond	Length	Bond	Length	Bond	Length	Bond	Length
Mn1–O2	1.858(6)	Mn3–O8	1.874(9)	Mn5–O14	1.861(8)	Mn7–O20	1.852(7)
Mn1–O3	1.899(6)	Mn3–O9	1.945(8)	Mn5–O15	1.918(7)	Mn7–O21	1.934(7)
Mn1–N1	1.939(8)	Mn3–N5	1.960(9)	Mn5–O10	1.943(7)	Mn7–N13	1.961(8)
Mn1–O22	1.951(6)	Mn3–O4	1.995(8)	Mn5–N9	1.947(8)	Mn7–O16	1.979(6)
Mn1–N16	2.271(8)	Mn3–O27	2.212(11)	Mn5–O29	2.207(9)	Mn7–O31	2.286(8)
Mn1–O25	2.302(7)	Mn3–N4	2.261(9)	Mn5–N8	2.297(9)	Mn7–N12	2.319(8)
Mn2–O5	1.854(7)	Mn4–O11	1.873(8)	Mn6–O17	1.865(7)	Mn8–O23	1.862(7)
Mn2–N3	1.925(8)	Mn4–O12	1.941(8)	Mn6–O18	1.931(7)	Mn8–O24	1.927(7)
Mn2–O6	1.929(7)	Mn4–N7	1.949(9)	Mn6–N11	1.940(8)	Mn8–N5	1.945(8)
Mn2–O1	1.952(7)	Mn4–O7	1.980(8)	Mn6–O13	1.955(7)	Mn8–O19	1.950(7)
Mn2–O26	2.276(8)	Mn4–O28	2.237(9)	Mn6–O30	2.303(7)	Mn8–O32	2.288(8)
Mn2–N2	2.358(8)	Mn4–N6	2.265(9)	Mn6–N10	2.349(9)	Mn8–N14	2.345(8)

Table 4. Selected bond angles of Compound **1**.

Angles	(°)	Angles	(°)	Angles	(°)
O2–Mn1–O3	172.1(3)	N1–Mn1–O22	172.7(3)	O2–Mn1–O25	86.7(3)
O2–Mn1–N1	92.3(3)	O2–Mn1–N16	89.7(3)	O3–Mn1–O25	92.2(3)
O3–Mn1–N1	79.9(3)	O3–Mn1–N16	93.2(3)	N1–Mn1–O25	91.2(3)
O2–Mn1–O22	94.5(3)	N1–Mn1–N16	102.1(3)	O22–Mn1–O25	91.9(3)
O3–Mn1–O22	93.4(3)	O22–Mn1–N16	75.2(3)	N16–Mn1–O25	166.3(3)

Magnetic measurements

The temperature dependence of the magnetic susceptibility of compound **1** has been determined at a 1000 Oe field in 2–300 K temperature range. The diamagnetic correction was evaluated using Pascal’s constants. As shown in Figure 2, the observed $\chi_M T$ value for Compound **1** at 300 K is 58.67 cm³ K mol⁻¹ and upon cooling from 300 to 35 K, $\chi_M T$ decreases slowly to approximately 30.24 cm³ K mol⁻¹ and then drops very rapidly to reach 2.41 cm³ K mol⁻¹ at 2 K. Figure 2 shows a typical weakly coupled antiferromagnetic behaviour. Thus, by fitting the magnetic susceptibility data at high temperatures, $T > 35$ K, to the Curie Weiss expression $\chi^{-1}(T) = C/(T+\theta)$, we obtained the Weiss constant, $\theta = -32.61$ K for **1**.

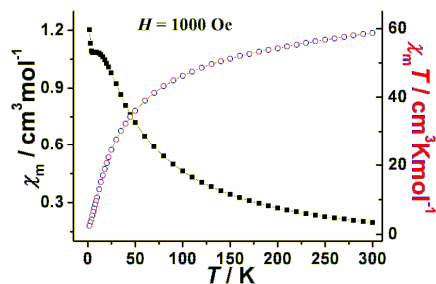


Figure 2. Plot of $\chi_m T$ and χ^{-1} vs. T of polycrystalline sample of **1**.

CONCLUSION

In this study, we were able to prepare a novel metallamacrocyclic $[\text{Mn}_8(\text{mamshz})_8(\text{DMA})_8][\text{Mn}_8(\text{mamshz})_8(\text{DMA})_6(\text{H}_2\text{O})_2] \cdot 2\text{DMA} \cdot 4\text{H}_2\text{O}$. The systematic and detailed investigation of the factors that govern the sequence of the stereochemistry of the metal center, the nuclearity and size of the macrocycle, and the final architecture of this type of macrocyclic assembly are currently underway.

The supplementary crystallographic data for (**1**) have been deposited under the number CCDC 796822 and can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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