

Synthesis, Characterization, and Crystal Structure of a Metallamacrocycle

Dingjun Zhang,^{*,[a]} Yuxian Chen,^[a] Qiang Zhao,^[a] and Youzhi Wu^[a]

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Abstract. The novel macrocyclic decanuclear manganese(III) 30-metallacrown-10 compound $[\text{Mn}_{10}(\text{RS-3-chmshz})_{10}(\text{DMF})_{10}] \cdot 9\text{DMF}$ (**1**) was synthesized by self-assembly and characterized ($\text{H}_3\text{RS-3-chmshz} = N-((R,S)\text{-3-cyclohexenyl})\text{-5-methylsalicylhydrazide}$). Compound **1** is a 30-membered decanuclear metallamacrocycle and crystallizes in triclinic space group $P2_1/c$, in an alternating $\dots\Delta\Delta\Delta\Delta\dots$ -type chiral con-

figuration. The decanuclear systems measure ~ 2.6 nm in diameter and ~ 1.1 nm in thickness. The racemic $N-((R,S)\text{-3-cyclohexenyl})$ group directing into the cavity of the metallamacrocycle shows the alternate R,S chiral configuration. Magnetic measurements on the title 30-metallacrown-10 compound show weak antiferromagnetic exchange interaction.

Introduction

The field of metallamacrocycles has undergone explosive growth over the past decades due to their potential technological applications in many areas such as molecular recognition, separation processes, and catalysis.^[1] Much research work has been devoted to control their size, nuclearity, and physicochemical properties.^[2] Diaza-bridged metallamacrocycles, termed metalladiazamacrocycles, have received considerable interest because of their potential to be used as secondary building blocks for the construction of two- or three-dimensional network structures.^[3] To prepare architectures with the desired structures and properties, it is important to understand the delicate factors that influence the formation of these systems. The nuclearity and the shape of the metallamacrocycles could be modulated by controlling the steric interactions caused by N -acyl tails of the ligands.^[4] Recently, a novel diaza-bridged metallamacrocycle was prepared by combination of a distorted octahedral Mn^{III} or Fe^{III} ion and the asymmetrical bridging ligand N -acyl salicylhydrazide, where the size and nuclearity of the metalladiazamacrocycle could be modulated by controlling the steric repulsions between the ligands in the macrocyclic ring system.^[5] We report here the synthesis and characterization of a novel 30-Metallacrown-10 compound, $[\text{Mn}_{10}(\text{RS-3-chmshz})_{10}(\text{DMF})_{10}] \cdot 9\text{DMF}$ (**1**) (Figure 1) ($\text{H}_3\text{RS-3-chmshz} = N-((R,S)\text{-3-cyclohexenyl})\text{-5-methylsalicylhydrazide}$) (Scheme 1).

Results and Discussion

The IR spectrum of **1** shows that, in comparison with the ligand, the $\text{C}=\text{O}$ band is shifted to lower frequencies, which

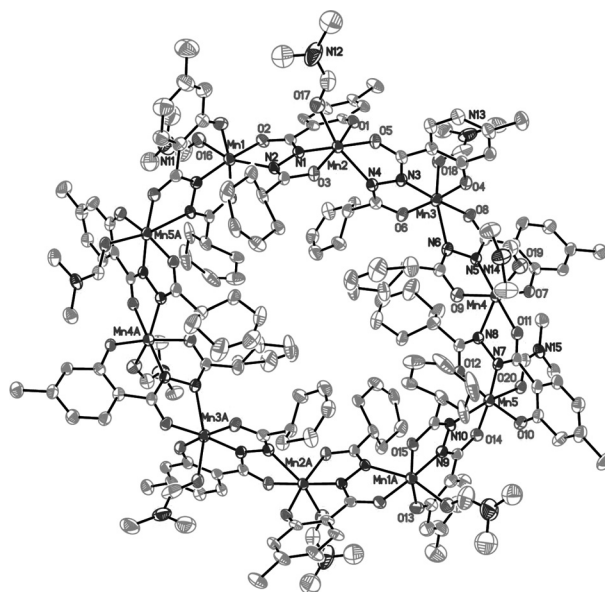
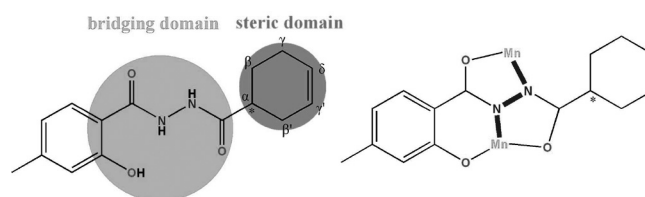


Figure 1. Molecular structure of the title compound with manganese, nitrogen, and oxygen atom labeling. Hydrogen atoms and free solvent molecules are omitted for clarity.



Scheme 1. The ligand $\text{H}_3\text{RS-3-chmshz}$ and basic binding sites in the complex.

suggests the coordination of a carbonyl oxygen atom to a Mn^{3+} ion. The stretching vibration band $\delta(\text{N-H})$ is significantly weakened in the spectrum of **1**, which indicates deprotonation

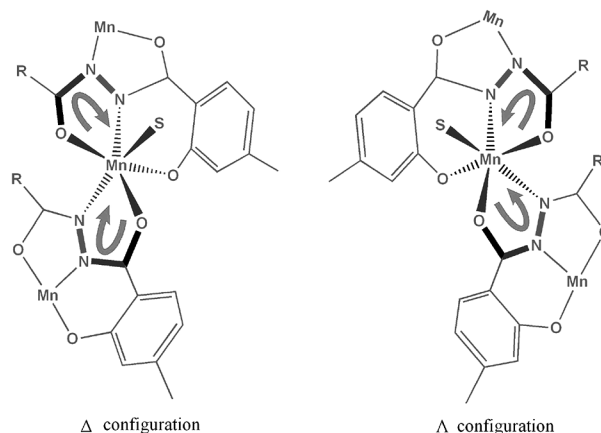
* Prof. Dr. D. Zhang
Fax: +86-9312976378
E-Mail: zhangdjpublic@yahoo.cn

[a] State Key Laboratory of Gansu Advanced Non-ferrous Metal Materials
Lanzhou University of Technology
Lanzhou 730050, P. R. China

of the group and coordination of the hydrazide nitrogen atom to the Mn^{3+} ion. The C–N bands at 1307 and 1241 cm^{-1} are shifted to 1555 cm^{-1} due to deprotonation of the NH group.

Compound **1** was obtained by reaction of manganese acetate tetrahydrate with $\text{H}_3\text{RS-3-chmshz}$ in a metal to ligand molar ratio of 1:1 in DMF.^[6] Crystallographic analysis revealed that compound **1** is a 30-membered decanuclear metallamacrocyclic of the formula $[\text{Mn}_{10}\text{L}_{10}(\text{DMF})_{10}] \cdot 9\text{DMF}$, which crystallizes in triclinic space group $P2_1/c$ in an alternating $\dots\Delta\Delta\Delta\Delta\dots$ -type chiral configuration similar to other decanuclear manganese or iron metalladiazamacrocycles (Scheme 2). The deprotonated pentadentate ligand, chmshz^{3-} acts as a trianionic ditopic bridging ligand and hence coordinates through three oxygen atoms and two hydrazinic nitrogen atoms. A phenolate oxygen atom (O1) a hydrazide nitrogen atom (N1) and a carbonyl oxygen atom (O3) of the chosen ligand are each bound to a manganese atom in tridentate chelating mode, the other carbonyl oxygen atom (O2) and the other hydrazide nitrogen atom (N2) are bound to the adjacent manganese atom in bidentate chelating mode (Figure 2). The metal atoms are connected through a hydrazide N–N linkage as shortest path in this type of binding mode. Each Mn^{3+} ion in **1** is in a distorted octahedral MnN_2O_4 environment with a very distinct Jahn–Teller extension. The Jahn–Teller distortion results in elongation of the axial manganese–oxygen/nitrogen (Mn1–O2, O15, O16/N2, N9) bond lengths by ~ 0.3 Å relative to the other Mn–O/N bond lengths. The resulting decanuclear system measures ~ 2.6 nm in diameter and ~ 1.1 nm in thickness. The bond lengths for Mn–N(diazine), Mn–O(phenolate), and Mn–O(carbonyl) are in the ranges 1.928(2)–2.272(1) Å, 1.842(2)–1.870(1) Å, and 1.959(2)–1.999(2) Å, respectively. The successive manganese atoms of the $\dots\Delta\Delta\Delta\Delta\dots$ chiral sequence lead to a small difference in Mn···Mn interatomic distances and Mn···Mn···Mn interatomic angles. The neighboring Mn···Mn interatomic distances in **1** alternate between 4.85 and 4.89 Å, whereas the Mn···Mn···Mn angles are between 122.3° and 141.9°. The average value of 133.4° for the Mn···Mn···Mn angles is close to that expected (144°) for a planar cyclodecane structure. The terminal *R,S*-3-cyclohexenyl groups of the tails of five ligands are directed upside the cyclic structure, whereas the rest of them are directed down the cycle. Lah et al. reported 36-membered dodecanuclear manganese metalladiazamacrocycles, obtained by using the ligand *N*-cyclohexanoylsalicylhydrazide.^[7] The introduction of a sterically demanding α -branched *N-R,S*-3-cyclohexenyl group did not expand the ring size of the metallamacrocycles, from an decanuclear to a dodecanuclear system as we expected. The largest diameter of the inner cavity measured between Mn1 and the symmetry-related Mn1A at the opposite position is ~ 15.7 Å, the size of the accessible hydrophobic core is ~ 6.7 Å at the entrance.

A magnetic study carried out on **1** is shown in in Figure 3. The magnetic susceptibilities of **1** were measured on crystalline samples in the temperature range of 2 K to 300 K under 1000 Oe to confirm the charge value of the manganese atoms. The plot of $\chi_{\text{M}}T$ and the inverse magnetic susceptibility (χ^{-1}) of vs. T shows a typical weakly coupled antiferromagnetic behavior. The $\chi_{\text{M}}T$ product of 3.40 $\text{cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$ at 300 K is close



Scheme 2. A schematic diagram showing the Δ and Λ configurations of the metal atoms of the propeller like bidentate/tridentate binding modes, observed in **1**.

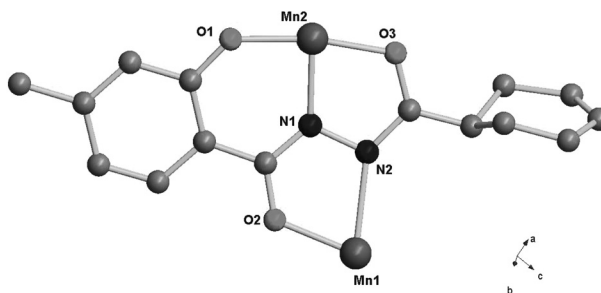


Figure 2. O1, N1, and O3 atoms bound to one manganese atom, whereas O2 and N2 atoms are bound to the adjacent manganese atom in a back-to-back fashion.

to the typical value for magnetically dilute. The value of $\chi_{\text{M}}T$ increases gradually to approximately 2.48 $\text{cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$ at 50 K, then decreases sharply to a value of approximately 0.25 $\text{cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$ at 2 K.

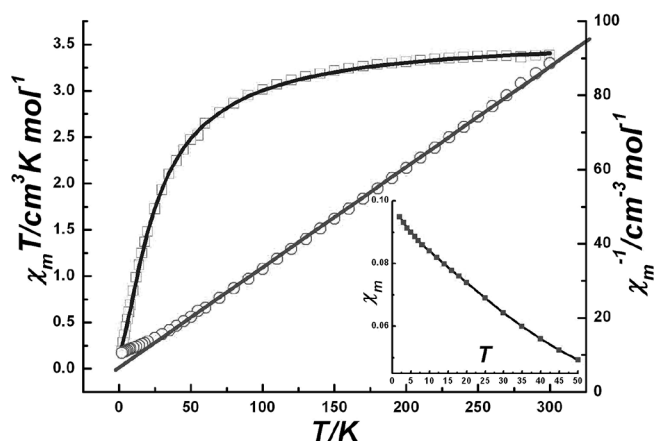


Figure 3. Plots of $\chi_{\text{M}}T$ and χ^{-1} vs. T of a polycrystalline sample of **1**. The solid line corresponds to the best fit.

Conclusions

We were able to accomplish the synthesis of the novel 30-Metallacrown-10 compound $[\text{Mn}_{10}(\text{RS-3-}$

chmshz)₁₀(DMF)₁₀·9DMF. The minimal modification in the bridging domain of the potential pentadentate ligand, whereas all remaining parts of the ligand were kept the same, led to different chelation modes around the macrocyclic ring metal atoms. This work may provide useful information for investigations on metallamacrocycles.

Experimental Section

All reagents not specifically listed below were obtained from commercial sources and were used as received. Carbon, nitrogen and hydrogen analyses were determined using a Vario EL elemental analyzer. IR spectra were recorded with a Nicolet Avatar 360 FT-IR instrument using KBr discs in the 400–4000 cm^{−1} region. ¹H NMR spectra were measured with a FT-400A spectrometer in [D₆]DMSO solution, with TMS as internal standard. 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 Oe. The diamagnetic correction for each complex was calculated using Pascal's constants. The intensity data were collected at 296 K with a Bruker Smart APEX II diffractometer with graphite-monochromatized Mo-*K*_α radiation (λ = 0.71073 Å). 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 program package SHELXTL. Non-hydrogen atoms with geometrical rigidity were refined anisotropically, but non-hydrogen atoms with geometrical flexibility were refined isotropically; hydrogen atoms attached to the nondisordered part were assigned isotropic displacement coefficients *U*(H) = 1.2 *U*(C) or 1.5 *U*(C_{methyl}), and their coordinates were allowed to ride on their respective atoms.

The ligand *N*-((*R,S*)-3-cyclohexenyl)-5-methylsalicylhydrazide (H₃RS-3-chmshz) was synthesized by reaction of 2-hydroxy-4-methylbenzohydrazide (1.66 g, 10 mmol) with (*R,S*)-3-cyclohexenecarboxylic anhydride (2.81 g, 12 mmol) in chloroform (25 mL) at 5 °C, afterwards the mixture was slowly warmed to room temperature and stirred for 3 h. The resulting colorless precipitate was filtered and rinsed with chloroform and diethyl ether to give the colorless solid product *N*-((*R,S*)-3-cyclohexenyl)-5-methylsalicylhydrazide. It was then dried in vacuo over P₂O₅. Yield: 1.67 g, 60.9 %. C₁₅H₁₈N₂O₃ Calc: C 65.68, H 6.61, N 10.21 %; Found: C 65.75, H 6.51, N 10.37 %. ¹H NMR (400 MHz, [D₆]DMSO): δ = 11.97 (s, 1 H, –Ph–OH); 10.48 (s, 1 H, –NH–); 10.10 (s, 1 H, –NH–); 7.78–7.76 (d, 1 H, –Ph); 6.77–6.74 (t, 2 H, –Ph); 5.69 (s, 2 H, –CH=CH–); 3.35 (s, 1 H, –CO–CH–); 2.53–2.46 (p, 3 H, –Ph–CH₃); 2.29–1.84 (p, 6 H, –CH₂–CH₂–CH₂–). IR (KBr pellet): $\tilde{\nu}$ = 3332 cm^{−1} (s), 3296 (s), 3064 (br), 1653 (s), 1636 (s), 1622 (s), 1616 (s), 1607 (m), 1602 (m), 1575 (s), 1569 (s), 1558 (s), 1539 (s), 1520 (s), 1506 (s), 1495 (s), 1488 (s), 1472 (s), 1464 (m), 1457 (s), 1436 (s), 1418 (s), 1394 (m), 1386 (m), 1374 (m), 1362 (m), 1339 (s), 1307 (s), 1241 (s), 1200 (m), 1180 (m), 1117 (m), 1029 (m), 950 (m), 891 (m), 864 (m), 825 (m), 779 (w), 736 (m), 720 (m), 668 (s), 648 (m), 592 (m), 516 (m) cm^{−1}.

The dark brown block crystals of **1** were grown and recrystallized from DMF with slow evaporation at room temperature over a period of 30 days (H₃RS-3-chmshz:Mn(OAC)₂·4H₂O = 1:1). Yield: 47 %. C₂₀₇H₂₈₁Mn₁₀N₃₉O₄₉ Calc: C 55.48, H 6.32, N 8.44 %; Found: C 55.34, H 6.41, N 8.57 %. IR (KBr pellet): $\tilde{\nu}$ = 3440 cm^{−1} (br), 3070 (w), 1657 (s), 1610 (s), 1572 (s), 1563 (s), 1555 (s), 1495 (s), 1429 (s), 1390 (s), 1364 (m), 1344 (m), 1324 (m), 1291 (w), 1277 (w), 1245 (s), 1209 (m), 1177 (s), 1161 (m), 1138 (w), 1119 (s), 1104 (s), 1066

(m), 1014 (s), 959 (s), 918 (s), 900 (s), 875 (s), 835 (s), 821 (s), 789 (s), 764 (s), 748 (s), 699 (m), 677 (s), 628 (s), 592 (s), 566 (m), 545 (m), 503 (m), 472 (s), 442 (s) cm^{−1}.

The IR spectrum of **1** shows that the C=O band is shifted to lower frequencies compared to the ligand, which suggests the coordination of a carbonyl oxygen atom to a Mn³⁺ ion. The stretching vibration band δ (N–H) disappears in the spectrum of **1**, which indicates deprotonation of the group and coordination of the hydrazide nitrogen atom to the Mn³⁺ ion. The bands of C–N at 1307 and 1241 cm^{−1} are shifted to 1555 cm^{−1} due to the deprotonation of the NH group.

CCDC-750878 contains the supplementary crystallographic data for (**1**). These data 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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References

- [1] a) Z. H. Ni, H. Z. Kou, L. F. Zhang, C. H. Ge, A. L. Cui, R. J. Wang, Y. D. Li, O. Sato, *Angew. Chem.* **2005**, *117*, 7920–7923; *Angew. Chem. Int. Ed.* **2005**, *44*, 7742–7745; b) N. Shan, S. J. Vickers, H. Adams, M. D. Ward, J. A. Thomas, *Angew. Chem.* **2004**, *116*, 4028–4031; *Angew. Chem. Int. Ed.* **2004**, *43*, 3938–3941; c) M. A. Galindo, S. Galli, J. A. R. Navarro, M. A. Romero, *Dalton Trans.* **2004**, *17*, 2780–2785; d) T. L. Stott, M. O. Wolf, A. Lam, *Dalton Trans.* **2005**, *4*, 652–653.
- [2] Z. H. Ni, L. F. Zhang, V. Tangoulis, W. Wernsdorfer, A. L. Cui, O. Sato, H. Z. Kou, *Inorg. Chem.* **2007**, *46*, 6029–6037.
- [3] a) M. Moon, I. Kim, M. S. Lah, *Inorg. Chem.* **2000**, *39*, 2710–2711; b) D. Moon, M. S. Lah, *Inorg. Chem.* **2005**, *44*, 1934–1940; c) D. Moon, J. Song, B. J. Kim, B. J. Suh, M. S. Lah, *Inorg. Chem.* **2004**, *43*, 8230–8232.
- [4] a) S. X. Liu, S. B. Lin, Z. C. Lin, C. Lin, J. Q. Huang, *Angew. Chem.* **2001**, *113*, 1118–1121; *Angew. Chem. Int. Ed.* **2001**, *40*, 1084–1087; b) R. P. John, D. Moon, M. S. Lah, *Supramol. Chem.* **2007**, *19*, 295–308; c) J. M. Dou, M. L. Liu, D. C. Li, D. Q. Wang, *Eur. J. Inorg. Chem.* **2006**, 4866–4871; d) D. Moon, K. Lee, R. P. John, G. H. Kim, S. J. Suh, M. S. Lah, *Inorg. Chem.* **2006**, *45*, 7991–7993; e) R. P. John, K. Lee, B. J. Kim, B. J. Suh, H. Rhee, M. S. Lah, *Inorg. Chem.* **2005**, *44*, 7109–7121; f) S. Lin, S. X. Liu, Z. Chen, B. Z. Liu, S. Gao, *Inorg. Chem.* **2004**, *43*, 2222–2224; g) R. P. John, K. Lee, M. S. Lah, *Chem. Commun.* **2004**, 2660–2661; h) W. Liu, K. Lee, M. Park, R. P. John, D. Moon, Y. Zou, X. F. Liu, H. C. Ri, G. H. Kim, M. S. Lah, *Inorg. Chem.* **2008**, *47*, 8807–8812.
- [5] a) M. Park, R. P. John, D. Moon, K. Lee, G. H. Kimb, M. S. Lah, *Dalton Trans.* **2007**, *14*, 5412–5418; b) K. Lee, R. P. John, M. Park, D. Moon, H. C. Ri, G. H. Kim, M. S. Lah, *Dalton Trans.* **2008**, *7*, 131–136.
- [6] Crystal data for [Mn₁₀(RS-3-chmshz)₁₀(DMF)₁₀·9DMF (**1**): C₂₀₇H₂₈₁Mn₁₀N₃₉O₄₉, *M* = 4649.12 g·mol^{−1}, monoclinic, space group *P*2₁/c, *a* = 13.019(3), *b* = 28.230(6), *c* = 34.679(7) Å, β = 99.76(3)°, *V* = 12561(4) Å³, *T* = 296(2) K, *Z* = 2, μ = 0.559 mm^{−1}, GOF = 1.109, 22010 reflections measured (0.994 ≤ θ ≤ 25.00°), final *R*1 = 0.1093 [*I* > 2 σ (*I*)], *wR*2 = 0.3020, CCDC-750878.
- [7] R. P. John, J. Park, D. Moon, K. Lee, M. S. Lah, *Chem. Commun.* **2006**, 3699–3700.

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