An 18-Membered Hexanuclear Manganese $(MnN_2)_6$ Metalladiazamacrocycle

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The macrocyclic hexanuclear manganese(III) 18-metallacrown-6, $[Mn_6(pmshz)_6(DMF)_4(C_2H_5OH)_2]\cdot 4DMF$ (**1**), where $pmshz^{3-}$ is *N*-propionyl-*N′*-5-methylsalicylhydrazide, has been synthesized by self-assembly and structurally characterized. The ring is formed by the succession of six structural moieties of the type [Mn(III)-N-N] with hydrazide N-N groups bridging the ring Mn ions. The ligand enforces the metal ions to form the stereochemistry of a configuration with alternate $\ldots\Delta\Lambda\Delta\Lambda\ldots$-type enantiomeric chiral units. The peripheral core ring is ∼18.6 Å in diameter and ∼12.4 Å in thickness. The title metallacrown exhibits photoluminescent properties in the solid state and a weak antiferromagnetic exchange interaction.

Key words: 18-Metallacrown-6, Self-assembly, Hexanuclear Complex, Photoluminescence, Antiferromagnetic Exchange

Introduction

Metallamacrocycles are an interesting class of compounds because of their diverse molecular architectures [1], their utilization as motifs for coordination networks [2] and their potential as host systems in guest inclusion chemistry [3]. Diaza-bridged metalladiazamacrocycles have received considerable interest because of their beautiful architecture [1, 2, 4], unique magnetic properties [1, 2] and bioactivity [1, 2]. These compounds can be readily assembled using the trianionic pentadentate ligand *N*-acylsalicylhydrazide with metal ions such as manganese, iron, cobalt, or gallium [1, 2]. Manganese and iron cations have received special attention due to their ease of formation of metallamacrocycles and interesting magnetic properties [1]. Controlling the ring size and nuclearity of metallamacrocycles and their properties has recently become of interest. The results have shown that the nature of the *N*-acyl substituent can influence the size and nuclearity of the macrocyclic complex [1]. As part of our efforts to understand these effects on the molecular structure of the metalladiazamacrocycles, and to develop a better understanding of their self-assembly and spectroscopic behavior, we report here the structure, luminescence and magnetic properties of a manganese 18-metallacrown-6 complex $[Mn_6(pmshz)_6(DMF)_4(C_2H_5OH)_2]\cdot 4DMF$ (**1**).

Table 1. Crystal structure data for **1**.

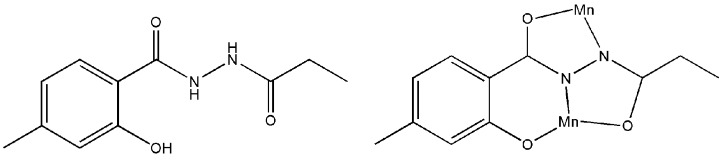
Formula	$C_{94}H_{132}Mn_6N_{20}O_{28}$
M_r	2319.8
Crystal size, mm^3	0.42 × 0.327 × 0.213
Crystal system	triclinic
Space group	$P\bar{1}$
a, Å	11.026(2)
b, Å	16.974(3)
c, Å	17.052(3)
α, deg	64.49(3)
β, deg	86.78(3)
γ, deg	71.29(3)
V, Å^3	2715.4(9)
Z	1
D_{calcd}, g cm^{-3}	1.416
$\mu(MoK_\alpha)$, cm^{-1}	0.758
$F(000)$, e	1206
hkl range	±11, ±18, ±18
Refl. measured/unique/R_{int}	25371/6914/0.0332
Param. refined	668
$R1(F)/wR2(F^2)$[a] (all refls.)	0.0612/0.1627
GoF (F^2)[b]	1.079
$\Delta\rho_{fin}$ (max/min), e Å^{-3}	1.28/−0.94

[a] $R1 = \|F_o| - |F_c\|/\Sigma|F_o|$, $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, $w = [\sigma^2(F_o^2) + (0.0556P)^2 + 16.3478P]^{-1}$, where $P = (\mathrm{Max}(F_o^2, 0) + 2F_c^2)/3$; [b] $\mathrm{GoF} = [\Sigma w(F_o^2 - F_c^2)^2/(n_{obs} - n_{param})]^{1/2}$.

Experimental Section

Measurements of physical properties

All commercially available chemicals were of A. R. grade, and all solvents used were purified by standard methods. Car-



Scheme 1. Ligand H_3pmshz and the coordination mode of its trianion in **1**.

Table 2. Selected bond lengths (Å) and angles (deg) of **1**.

Mn1–O1	1.864(4)	Mn1–O2	1.923(4)
Mn1–N1	1.944(4)	Mn1–O4	1.972(4)
Mn1–O3	2.249(4)	Mn1–N2	2.269(4)
Mn2–O7	1.858(4)	Mn2–O5	1.925(4)
Mn2–N3	1.945(4)	Mn2–O8	1.961(4)
Mn2–O6	2.233(4)	Mn2–N4	2.251(5)
Mn3–O11	1.861(4)	Mn3–O9	1.925(4)
Mn3–N5	1.941(5)	Mn3–O10	1.984(4)
Mn3–O12	2.219(4)	Mn3–N6	2.267(5)
O1–Mn1–O2	168.68(16)	O1–Mn1–N1	90.38(17)
O2–Mn1–N1	80.33(17)	O1–Mn1–O4	96.53(16)
O2–Mn1–O4	93.36(15)	N1–Mn1–O4	171.20(17)
O1–Mn1–O3	86.82(16)	O2–Mn1–O3	88.43(16)
N1–Mn1–O3	100.09(16)	O4–Mn1–O3	85.77(15)
O1–Mn1–N2	91.94(17)	O2–Mn1–N2	95.99(17)
N1–Mn1–N2	99.69(17)	O4–Mn1–N2	74.72(15)
O3–Mn1–N2	160.19(15)	O7–Mn2–O5	171.03(16)
O7–Mn2–N3	91.13(17)	O5–Mn2–N3	79.98(16)
O7–Mn2–O8	95.35(16)	O5–Mn2–O8	93.59(15)
N3–Mn2–O8	172.94(16)	O7–Mn2–O6	91.21(15)
O5–Mn2–O6	88.57(15)	N3–Mn2–O6	95.97(17)
O8–Mn2–O6	86.71(15)	O7–Mn2–N4	94.09(17)
O5–Mn2–N4	88.92(16)	N3–Mn2–N4	101.75(17)
O8–Mn2–N4	75.05(16)	O6–Mn2–N4	161.39(15)
O11–Mn3–O9	169.75(16)	O11–Mn3–N5	90.43(17)
O9–Mn3–N5	79.95(17)	O11–Mn3–O10	101.04(16)
O9–Mn3–O10	88.69(15)	N5–Mn3–O10	168.41(16)
O11–Mn3–O12	89.30(16)	O9–Mn3–O12	88.52(16)
N5–Mn3–O12	97.69(17)	O10–Mn3–O12	84.23(15)
O11–Mn3–N6	93.13(16)	O9–Mn3–N6	92.59(16)
N5–Mn3–N6	103.82(18)	O10–Mn3–N6	74.16(15)
O12–Mn3–N6	158.32(16)		

bon, nitrogen and hydrogen analyses were performed 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. ^{1}H NMR spectra were measured on an FT-600A spectrometer in [D_6]DMSO solution, with TMS as internal standard. Fluorescence measurements were made on a Hitachi F-4500 spectrophotometer. The excitation and emission slit widths were 1 nm. 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.

Crystal structure determination

The intensity data of **1** were collected at 296 K on a Rigaku R-AXIS RAPID diffractometer with graphite-monochromatized MoK_α radiation (λ = 0.71073 Å). A summary of crystallographic data and details of the structure refinement are listed in Table 1. 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. The hydrogen atoms were assigned a common isotropic displacement factor and included in the final refinement cycles by using geometrical restraints. All calculations were performed with the program package SHELXTL [6]. Selected bond lengths and angles are listed in Table 2 [7].

Preparation of the ligand

The ligand N-propionyl-N'-5-methylsalicylhydrazine (H_3pmshz) (Scheme 1) was synthesized by reacting 2-hydroxy-4-methylbenzohydrazine (1.66 g, 10 mmol) with propionic anhydride (1.56 g, 12 mmol) in 25 mL of chloroform at 0 °C. The reaction mixture was slowly warmed to r. t. and stirred for 5 h. The resulting white precipitate was filtered and rinsed with chloroform and diethyl ether. It was then dried *in vacuo* over P_2O_5. Yield: 1.72 g, 77.4 %. Melting point: 215 – 216 °C. – Elemental analysis data for $C_{11}H_{14}N_2O_3$: calcd. C 59.45, H 6.35, N 12.60; found C 59.61, H 6.29, N 12.72. – ^{1}H NMR (600 MHz, [D_6]DMSO, ppm): δ = 11.94 (s (br), 1H), 10.45 (s (br), 1H) (both amide NH's), 10.05 (s, 1H, phenolic OH), 7.77 (s, 1H, o-Ar-H), 7.59 (d, 1H, p-Ar-H), 6.75 (d, 1H, m-Ar-H), 2.30 (s, 3H, Ar-CH_3), 2.20 (q, 2H, -CH_2-), 1.06 (t, 3H, -CH_3). – IR (KBr pellet, cm^{-1}): ν = 3334 (s), 3309 (s), 3078(br), 2975 (m), 2877 (w), 1664 (s), 1637 (s), 1618 (s), 1542 (s), 1512 (m), 1479 (s), 1419 (m), 1371 (m), 1311 (s), 1276 (w), 1249 (s), 1209 (m), 1178 (m), 1153 (w), 1120 (m), 1057 (m), 955 (m), 878 (s), 825 (m), 767 (m), 594 (s), 549 (m).

Preparation of [$Mn_6(pmshz)_6(DMF)_4(C_2H_5OH)_2$]·4DMF (1)

H_3pmshz (0.22 g, 1.0 mmol) was dissolved in 20 mL DMF and ethanol (3 : 1), and 0.20 g (1.0 mmol) of $MnCl_2$· $4H_2O$ (0.20 g, 1.0 mmol) in DMF was added at r. t. The mixture was stirred for 10 min, then the dark brown solution was filtered. Mn(II) is oxidized to Mn(III) by atmospheric oxygen. After standing for 18 days, crystals of **1** were obtained from the filtrate as dark brown blocks. Yield: 52 %. M. p. > 300 °C (dec.). – Elemental analysis for $C_{94}H_{132}Mn_6N_{20}O_{28}$:

calcd. C 48.49, H 5.58, N 11.70; found C 48.61, H 5.49, N 11.78 %. – IR (KBr pellet, cm^{-1}): ν = 3445 (br), 3066 (w), 2939 (w), 1655 (s), 1608 (s), 1575 (s), 1558 (s), 1498 (s), 1458 (w), 1423 (s), 1389 (s), 1354 (m), 1325 (m), 1244 (m), 1176 (w), 1120 (w), 1014 (w), 962 (w), 887 (w), 862 (w), 814 (w), 763 (w), 748 (w), 698 (w), 676 (w), 669 (m), 626 (w), 592 (w), 543 (w), 432 (w).

Results and Discussion

IR spectra

The IR spectrum of **1** shows the band of C=O shifted to lower frequencies as compared with the ligand suggesting the coordination of the carbonyl oxygen atom to the Mn^{3+} ion. The stretching vibration bands ν(N-H) are significantly weakened in the spectra of **1** indicating the deprotonation of the hydrazine group and coordination of the hydrazide nitrogen atoms to Mn^{3+} ions. The bands ν(C-N) at 1276 and 1311 cm^{-1} are shifted to 1558 cm^{-1} due to the deprotonation of the NH group.

Structure description

Compound **1** crystallizes in the triclinic space group $P\bar{1}$ with $Z = 1$. The molecular structure is shown in Fig. 1. The ligand H_3pmshz that exists in solution in its enol form has three replaceable protons and hence can coordinate as a trianion *via* three oxygen atoms and two hydrazinic nitrogen atoms. Six Mn(III) ions and six deprotonated pmshz^{3-} ligands construct a planar 18-membered ring based on the Mn-N-N-Mn linkages of the title azametallacrown. Each manganese ion is in a distorted octahedral environment. While the O2, N2 and O3 atoms of a given ligand bind to one manganese atom, O4 and N1 bind to the adjacent manganese atom in a back-to-back fashion leading to a cyclic structure consisting of 6 manganese metal ions with successive metal centers in an alternating...ΔΛΔΛ...-type chiral configuration (Fig. 1). The remaining coordination site of each manganese atom is satisfied by the oxygen atom of a DMF or EtOH solvate molecule. The distances for Mn–N-(diazine), Mn–O(phenolate), and Mn–O(carbonyl) are in the ranges 1.941 – 2.269, 1.858 – 1.864, and 1.961 – 1.984 Å, respectively. The Mn(III)–O (CH_3CH_2OH) distance is 2.249 Å, the Mn(III)–O(DMF) distances are 2.219 and 2.233 Å. The solvent molecules in the complex are directed away from the ring. The terminal alkyl groups of the tails of 3 ligands (red) are above the cyclic structure, while the rest of them (green) are below. In the $[Mn\text{-}N\text{-}N]_6$ ring the Mn···Mn interatomic distances of neighboring atoms are 4.896(2) Å, while the Mn···Mn···Mn angles are 114.65°. The average axial manganese-oxygen/nitrogen distance of 2.248 Å in **1** is approximately 0.328 Å longer than the average basal Mn–O/N distance of 1.920 Å. This typical Jahn-

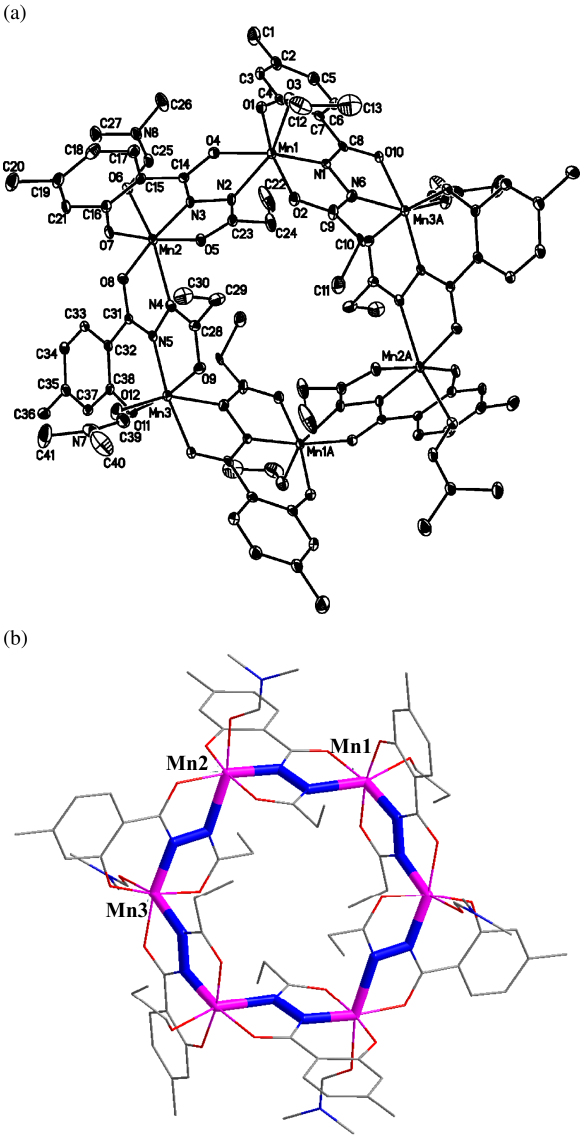


Fig. 1. (a) Molecular structure of **1** with crystallographic atom labeling adopted. H atoms and free solvent molecules are omitted for clarity. (b) The ring is formed by the succession of six structural moieties of the type [Mn(III)-N-N] with hydrazide N-N groups bridging the ring Mn cations (color online).

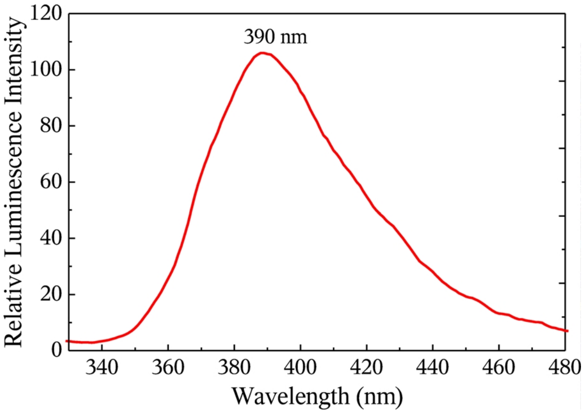


Fig. 2. Emission spectrum of **1** in the solid state at room temperature (EX slit = 1.0 nm).

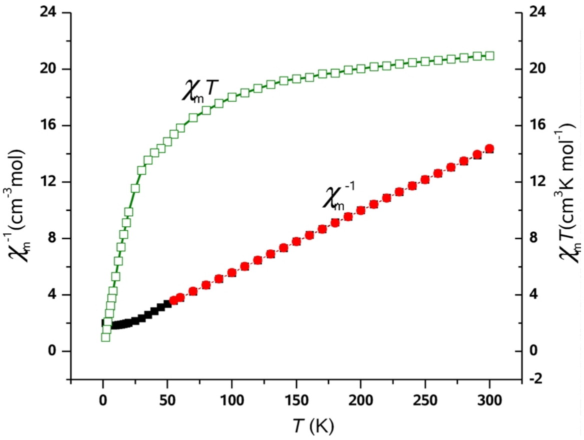


Fig. 3. Plot of $\chi_m T$ and χ^{-1} *vs.* T of polycrystalline **1**.

Teller elongation along the z axis of the manganese(III) ion was also observed in other manganese(III) compounds [5]. The manganese ions in the ring of **1** adopt a propeller configuration, despite the Jahn-Teller distortion of high-spin d^4 manganese(III) ions. The core of the disc-shaped hexanuclear metallamacrocycle is ~2.1 nm in diameter and ~1.0 nm in thickness. There are no solvent molecules in the 'host' cavity of the metallacrown. The presence of aliphatic groups at the core of the molecular disc and its outer areas provides a non-polar nature to this neutral molecule.

Photoluminescent properties

The photoluminescent properties of **1** were investigated. A solid sample of **1** displayed a strong photoluminescence emission band at 390 nm (λ_{ex} = 244 nm) at room temperature (Fig. 2), which can be proposed to originate from the coordination of H_3anhz to the Mn atoms (ligand-to-metal charge transfer, LMCT).

Magnetic properties

The variable-temperature magnetic susceptibility data of **1** were recorded between 300 and 2 K. Plots of $\chi_m T$ and the inverse magnetic susceptibility χ^{-1} *versus* T are shown in Fig. 3. They point to a typical, weakly coupled antiferromagnetic behavior. The values of $\chi_m T$ decrease slightly with decreasing temperature from 20.953 cm^3 K mol^{-1} at 300 K to 14.861 cm^3 K mol^{-1} at 50 K. Below 50 K, $\chi_m T$ decreases rapidly and reaches 1.000 cm^3 K mol^{-1} at 2 K. This behavior is similar to that reported for other manganese metalladiazamacrocycles [2].

Conclusion

In conclusion, a novel 18-metallacrown-6 molecule, $[Mn_6(pmshz)_6(DMF)_4(C_2H_5OH)_2]\cdot 4DMF$ (**1**), has been synthesized and structurally characterized. Photoluminescent and magnetic properties of $[Mn_6(pmshz)_6(DMF)_4(C_2H_5OH)_2]\cdot 4DMF$ in the solid state were studied. Further attempts to optimize the factors that govern nuclearity and size of metalladiazamacrocycles and their photoluminescent behavior are being pursued in our group, and the results will be communicated later.

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[7] CCDC 720509 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.