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Synthesis, spectra and crystal structure of a novel 18-metallacrown-6 $[Mn_6(4\text{-ohashz})_6(CH_3OH)_6] \cdot 12CH_3OH$

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Abstract

A new macrocyclic manganese(III) 18-azametallacrown-6 compound with the formula of $[Mn_6(4\text{-ohashz})_6(CH_3OH)_6] \cdot 12$-$CH_3OH$ (4-ohashz = *N*-acetyl-(4-hydroxysalicylhydrazidate)) was synthesized and characterized. In this complex, the metal ion is forcing the stereochemistry of the ligands arranged into a propeller shape with alternating *Λ*/*Δ* configurations. The disc-shaped hexanuclear complex has a cavity in the center with a dimension of 8.69′ in diameter and 3.13′ in thickness and aligned approximately along the crystallographic *c*-axis, one-dimensional channels are formed.

Keywords: Metallacrown; Manganese complex; Crystal structure

Metallacrown and its analogies, as the first of a new class of molecule known as metallamacrocycles, have attracted considerable attention on supramolecular chemistry, self-assembly, host–guest chemistry and molecular recognition since the first report [1]. There are two types of metallacrown molecules. The first type has a cyclic structure with interlinked $[M–N–O]_n$ repeat unit as 9-metallacrown-3 [1,2], 12-metallacrown-4 [3,5–8], 15-metallacrown-5 [4,5], one or two metal ions could be coordinated in the center of the ring. Another type of metallacrown has a $[M–N–N]_n$ repeat unit, forming 18-metallacrown-6 [9–11], 24-metallacrown-8 [12] and 30-metallacrown-10 [13]. In this type of metallacrown, nitrogen atoms replace all oxygen atoms in the cyclic structure, while there is no central metal ion in the center of the ring structure. One, two or three dimensions of networks of metallacrown could be connected via facial interactions and anion bridging [14].

In the present communication, we report the synthesis, characterization and crystal structure of the manganese 18-metallacrown-6. The ligand *N*-acetyl-(4-hydroxysalicylhydrazide) [15] (**1**) ($H_3$4-ohashz, Scheme 1) was synthesized by reacting 4-hydroxy-salicylhydrazide (1.68, 10 mmol) with acetic anhydride (1.13 g, 12 mmol) in 30 ml of chloroform at 0 °C, then slowly warmed to room temperature and stirred for 2 h. The resulting white precipitate was filtered and rinsed with chloroform and diethyl ether.

$H_3$4-ohashz (0.105 g, 0.5 mmol) was dissolved in 20 ml methanol, manganese(II) acetate tetrahydrate (0.1235 g, 1.0 mmol) in 20 ml methanol was added and stirred. Dark brown rectangular crystals of $[Mn_6(4\text{-ohashz})_6(CH_3OH)_6] \cdot 12CH_3OH]$ (**2**) [16] were obtained after slow evaporation.

In the IR spectra of the complex the band of C=O is shifted to lower frequencies comparing with the ligand suggesting the coordination of carbonyl oxygen atom to the metal ion. The stretching vibration band δ (N–H) are significantly weakened in the spectra of the complex indicating the deprotonation of the group

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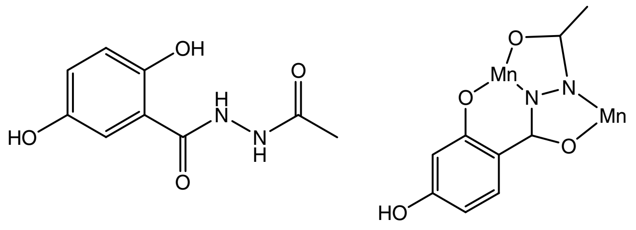

Scheme 1. Ligand $H_3$4-ohashz and basic binding sites in the complex.

and coordination of the hydrazide nitrogen atom to the metal ion. The bands of C–N at 1266 and 1331 cm^{-1} are shifted to 1519 cm^{-1} due to the deprotonation of NH group.

The structural representation of the title metallacrown molecule [17] is shown in Fig. 1, six Mn(III) ions and six *N*-acetyl-4-hydroxysalicyhydrazide(4-ohashz^{3-}) ligands construct a planar 18-membered ring which forms the manganese metallacrown core. The average neighboring Mn–Mn interatomic distances is 4.8558 Å. The average Mn–Mn–Mn interatomic angles is 112.963°. The approximate dimension of the oval-shaped cavity in the molecule of the title compound, measured between the opposite carbon atoms (C_{10}–C_{10}E, less 0.77 Å for the van der Waals radius of carbon), is 3.44 Å at the entrance, about 8.69 Å at its largest diameter (Mn_1–Mn_1E, less 0.60 Å for the van der Waals radius of manganese), and approximately 3.13 Å in depth. All manganese atoms in the title compound are in a distorted octahedral Mn(ONO)(NO)(O) environment. The typical Jahn–Teller elongation along the *z*-axis was observed because of the high-spin d^4 manganese(III) ion. The average axial bond distance (the average values of Mn_1–O_1 and Mn_1–N_1 bond distances: 2.260 Å) is about 0.345 Å longer than the average equatorial bond distance (the average value of Mn_1–O_2, Mn_1–O_3, Mn_1–O_4 and Mn_1–N_2 bond distances: 1.915 Å). The ligands are arranged into propeller shape with altering Λ/Δ stereochemistry as $\Delta\Lambda\Delta$ or $\Lambda\Delta\Lambda$ configurations [18].

There are intramolecular and intermolecular hydrogen bonds in the title compound. They are between the O–H of coordinated methanol molecules and the oxygen atoms of solvent methanol molecules, and between the O–H of solvent methanol molecules and phenol oxygen atoms.

The crystal packing structure of the complex shows that the disc-shaped hexanuclear clusters are aligned approximately along the crystallographic *c*-axis. The cavities of the clusters in the crystal structure are also aligned, and one-dimensional channels are formed, shown in Fig. 2. These channels could contain molecules with certain dimensions [11].

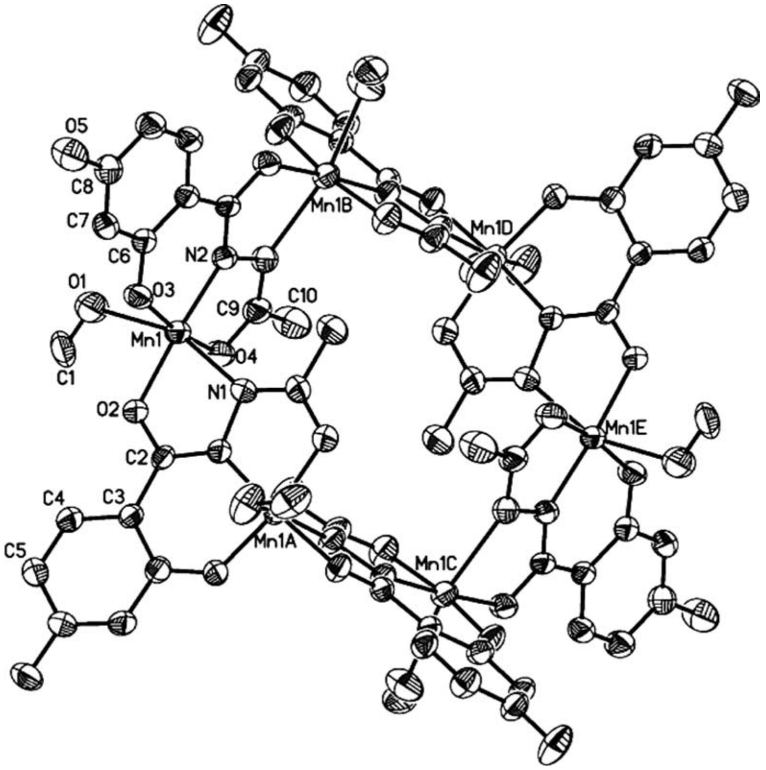

Fig. 1. Molecular structure of the title compound with atom labeling. H atoms are omitted for clarity.

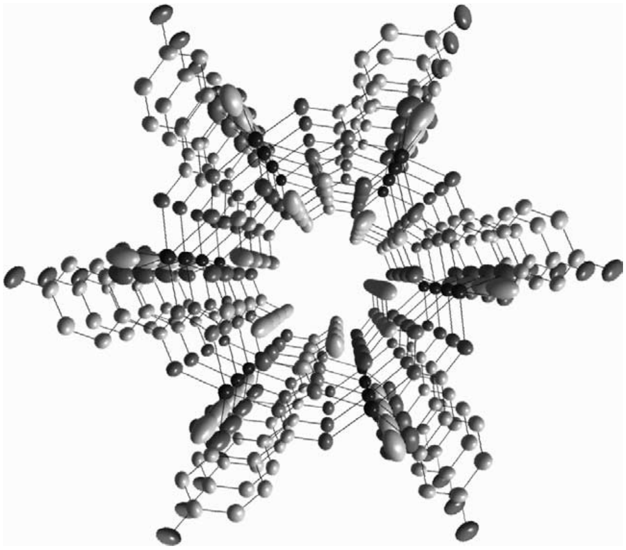

Fig. 2. Perspective view of $[Mn_6(4\text{-ohashz})_6(CH_3OH)_6] \cdot 12CH_3OH$ along the *c*-axis. H atoms are omitted for clarity.

Acknowledgement

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Appendix A. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC reference numbers 240166 for compound **2**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk).

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[15] $H_3$4-ohashz: Anal. Calcd. $C_9H_{10}N_2O_4$ requires: C, 51.42; H, 5.01; N, 13.32; Found: 50.98; H, 4.65; N, 13.13%. IR (cm^{-1}, KBr): $\nu = 3070, 1680, 1648, 1547, 1331, 1226$. ^1H NMR (DMSO-d_6, ppm) δ: 12.176; 10.242; 10.184–9.993 (s, 3H, Hs of amides and phenolic OH); 7.708–6.259 (br s, 3H at phenyl); 1.893(t, 3H at –CH_3).

[16] $Mn_6(4\text{-ohashz})_6(CH_3OH)_6] \cdot 12CH_3OH$: crystal of compound 2 is air-sensitive and loses its solvents of crystallization within 1 min IR (cm^{-1}, KBr): $\nu = 1640, 1612, 1070$.

[17] Crystal data for $[Mn_6(4\text{-hashz})_6(CH_3OH)_6] \cdot 12CH_3OH$: $C_{72}H_{108}Mn_6N_{12}O_{42}$, $M = 2143.34$, trigonal, space group $R\bar{3}$, $a = 30.217(2)$, $c = 9.322(1)$ Å, $\gamma = 120.00°$, $V = 7371.3(10)$ Å^3, $Z = 3$, $D_c = 1.449$ g/cm^3, $F(000) = 3330$, $\mu = 0.839$ mm^{-1}, 12238 observed reflections, 2869 independent reflections $R_{int} = 0.0918$. The final agreement factors are $R_1 = 0.0373$, $wR_2 = 0.0804$ with $I > 2\sigma(I)$.

[18] The Λ/Δ stereochemistry was defined using a skew line convention for the six-coordinated complexes based on the octahedron as described in Inorg. Chem. 1 (1970) 9.