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Synthesis, crystal structure and bioactivity of a novel 18-metallacrown-6 $[Mn_6(H_2O)_6\ (anshz)_6]\cdot 10DMF$

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Abstract

A novel macrocyclic hexanuclear manganese(III) 18-metallacrown-6 compound, $[Mn_6(H_2O)_6\ (anshz)_6]\cdot 10DMF$, has been prepared using a trianionic pentadentate ligand *N*-acetyl-5-nitrosalicylhydrazide ($anshz^{3-}$) and characterized by X-ray diffraction (DMF = *N*,*N*-dimethylformamide). The crystal structure contains a neutral 18-membered metallacrown ring consisting of six Mn(III) and six $anshz^{3-}$ ligands. The 18-membered metallacrown ring is formed by the succession of six structural moieties of the type [Mn(III)—N—N]. Due to the meridional coordination of the ligand to the Mn^{3+} ion, the ligand enforces the stereochemistry of the Mn^{3+} ions as a propeller configuration with alternating Δ/Λ forms. The disc-shaped hexanuclear ring shows at its largest diameter about 7.14 Å at entrance, about 9.76 Å at the center of the cavity, respectively. Antibacterial screening data showed that the manganese metallacrown has strong antimicrobial activity against *Bacillus subtilis*.

Keywords: Metallacrown; Manganese complexes; Crystal structures; Bioactivity

1. Introduction

Metallacrowns and its analogies have attracted considerable attention since the first report of metallacrown ether [1]. In the structure, metallacrowns (MC) [2–4] exhibit a cyclic hole generally analogous to crown ethers [5] with transition metal ions and a nitrogen atom replacing the methylene carbons. The presence of transition metal ions in the metallacrown ring leads to a class of molecules with features distinct from the simple organic crowns, such as strong visible absorption spectra, redox activity, magnetism, molecular recognition and bioactivity.

Metallacrowns have two types of molecules. Among them, one type has a cyclic structure with interlinked [M—N—O] repeat unit, the other has a [M—N—N] repeat unit. In second 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 [6]. To this day, metallacrowns, with Mn(III), Fe(III), Ni(II), Cu(II), Zn(II), Ga(III) and V(V)O metal ions, [9-MC-3] [7], [12-MC-4] [8–12], [15-MC-5] [13–16], [12-MC-6] [17], [16-MC-8] [18], [18-MC-6] [19], [18-MC-8] [17], [30-MC-10] [20], stacking metallacrowns [21–23] as well as a variety of dimers and fused metallacrowns [9,13,24,25] have been reported. Metallacrowns are typically prepared using hydroxamic acids and/or ketonoximic acids as constructing ligands (Scheme 1(a)), while suitable organic molecules such as salicylhydrazides [19,20,26], picoline-tetrazolylamides [27], diethyl ketipinate [23], 3-hydroxy-2-pyridone [28] or 3-thione-1,2-dithione-4,5-dithiolato [29] have also been used.

In the previous studies with an attempt to examine the mode of binding and possible antagonistic or synergetic effects, antibacterial screening data showed that 15-$MC_{Mn(III)N(shi)}$-5 and 12-$MC_{Mn(III)N(shi)}$-4 metallacrowns are more active than the simple manganese herbicide or

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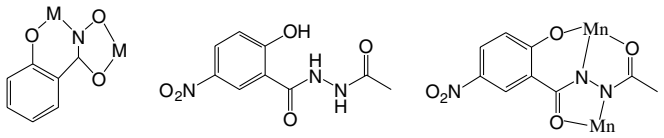


(a) (b) (c)

Scheme 1. Basic biding sites of shi^{3-} (a), ligand H_3anshz (b), and basic biding sites in compound **2** (c).

carboxylate complexes [16]. Taking into account that all the metallacrowns relative to the studies are the type of hydroxamic acids our interest was focused on the type of salicylhydrazides [19].

In the present paper, we report a new potential pentadentate ligand *N*-acetyl-5-nitrosalicylhydrazidate (**1**) (H_3anshz, Scheme 1(b)) and a novel manganese(III) 18-metallacrown-6 compound, $[Mn_6(H_2O)_6(anshz)_6]\cdot 10DMF$ (**2**) (Scheme 1(c), DMF = *N*,*N*-dimethylformamide). The triply deprotonated *N*-acetyl-5-nitrosalicylhydrazide ($anshz^{3-}$) of the title compound **2** may bridge the neighboring ions through its hydrazide N—N group shown in Scheme 1(c). In addition, the meridional coordination of the $anshz^{3-}$ to the Mn^{3+} cation forces the neighboring Mn^{3+} cations into a propeller configuration. The existence of intermolecular hydrogen bonds makes the title compound **2** more stable. Minimum inhibitory concentrations (MIC) against four different bacteria species of the metallacrown complex were also measured.

2. Experimental

2.1. Materials

Chemicals for the synthesis of the compounds were used as purchased. Methanol, ethanol and *N*,*N*-dimethylformamide (DMF) were used without any further purification. 5-Nitrosalicylic acid, sulfuric acid, hydrazine hydrate, acetic anhydride, diethyl ether, and $Mn(AcO)_2\cdot 4H_2O$ were purchased from China Sinopharm Group Chemical Reagent Co., Ltd. All chemicals and solvents were reagent grade. The *Staphylococcus aureus*, *Escherichia coli*, *Bacillus subtilis* and *Proteus vulgaris* were purchased from China Center for Type Culture Collection.

2.2. Synthesis of the ligand H_3anshz (1)

5-Nitrosalicylhydrazide was synthesized according to the literature procedure [30]. Acetic anhydride (6.8 g, 66.8 mmol) and 5-nitrosalicylhydrazide (11.0 g, 56.0 mmol) were added to 120 mL of chloroform at 0 °C. The reaction mixture was slowly warmed to room temperature and stirred for 8 h. After staying for overnight at refrigerator, the resulting light-yellow precipitate was filtered and rinsed with chloroform and diethyl ether. Yield: 12.2 g, 91.1%. The determination of melting point of **1** shows the sublimation and oxidation occurred at 310 °C. Calc. for $C_9H_9N_3O_5$: C, 45.19; H, 3.80; N, 17.57. Found: C, 45.50; H, 3.71; N, 17.65%. IR (KBr pellet, cm^{-1}): *v*O—H, 3298 vs; *v*N—H, 3103 vs, broad; *v*C=O, 1684 s; *v*C=N, 1624 vs; *v*C=N—C=N, 1604 vs; *v*NO_2, 1574 vs; *v*N—C=O, 1525 vs; *δ*N—H, 1488 vs; *v*$(C—OH)_{al}$, 1293 vs; *v*$(C—OH)_{phenolic}$, 1235 s, 1126 s; *δ*Ar, 748 s. ^{1}H NMR (DMSO), *δ*ppm: 10.70 (s, 1H, Ar—CO—NH—); 10.42 (s, 1H, Me—CO—NH—); 8.78 (s, 1H, *o*-ArH); 8.30 (d, 1H, *p*-ArH); 7.18 (d, 1H, *m*-ArH); 1.99 (s, 3H, —CH_3). ^{13}C NMR (DMSO), *δ* ppm: 170.40 (Me—CO—); 166.26 (*o*-ArC—OH); 165.97 (Ar—CO—); 142.08 (*m*-ArC—NO_2); 131.38 (*p*-ArC); 128.32 (*o*-ArC); 120.76 (ArC—); 119.11 (*m*-ArC); 23.19 (—CH_3).

2.3. $[Mn_6(H_2O)_6(anshz)_6]\cdot 10DMF$ (2)

H_3anshz (0.24 g, 1.0 mmol) was dissolved in 40 mL of 3:1 ethanol + DMF, and 0.25 g (1.0 mmol) of $Mn(AcO)_2\cdot 4H_2O$ was dissolved in 10 mL of ethanol in another flask. The two solutions were mixed and stirred for 2 h and the color of the mixture changed to dark brown, then filtered. After slow evaporation of the mother liquid in two weeks, dark brown block crystals were obtained from the filtrate. Yield: 62%. Calc. for $C_{84}H_{118}Mn_6N_{28}O_{46}$: C, 39.01; H, 4.61; N, 15.17; Mn, 12.75. Found: C, 39.16; H, 4.86; N, 15.38; Mn, 12.99%. IR (KBr pellet, cm^{-1}): *v*H—OH, 3377 s, broad; *v*C=O, 1656 vs; *v*C=N—C=N, 1607 vs; *v*NO_2, 1574 vs; *v*N—C=O, 1520 vs.

2.4. Physical measurements

Infrared spectra were measured on a Thermo Nicolet Corporation NEXUS FT-IR spectrometer as KBr pellets in the 4000–400 cm^{-1} region. UV–Vis spectra were recorded on a Shimadzu-UV-2501 PC recording spectrophotometer. C, H and N elemental analysis were performed on a Perkin–Elmer 2400 CHN elemental analytical instrument, Mn was determined by atomic absorption spectroscopy on a Perkin–Elmer 1100B spectrophotometer.

2.5. Biological activity

The antimicrobial activity of the complexes was assessed by their ability to inhibit the growth of *S. aureus*, *E. coli*, *B. subtilis* and *P. vulgaris* in Mueller–Hinton broth medium. The minimum inhibitory concentration in μg/mL against the four bacteria species was measured. Bacteria concentration was 500–800 cfu/mL and concentrations of 1600, 800, 400, 200, 100, 50, 25 μg/mL of the complex in 4:1 ethanol + DMF were tested. The solvent showed no antimicrobial action.

2.6. X-ray crystal structure determination

A crystal of the title compound **2** with dimensions of $0.40\times 0.30\times 0.20$ mm was mounted in a glass capillary with the mother liquor to prevent the loss of the structural

solvents during X-ray diffraction data collection. Intensity data were collected with a graphite monochromatic Mo Kα radiation ($\lambda = 0.71073$ Å) at 293(2) K on a Bruker Smart APEX diffractometer. From a total of 22054 reflections corrected by SADABS [31,32] in the $1.33° \leqslant \theta \leqslant 24.71°$ range, 9587 were independent with $R_{int} = 0.0571$, of which 7143 observed reflections with $I > 2\sigma(I)$ were used in the structural analysis. The structure was solved by direct methods. All non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were located in calculated positions and/or in the positions from difference Fourier map. The positions and anisotropic thermal parameters of all non-hydrogen atoms were refined on F^2 by full-matrix least-squares techniques with SHELXTL program package [32,33]. The final refinement converged at $R_1 = 0.0797$, $wR_2 = 0.1662$ $(w = 1/[\sigma^2(F_o^2)+(0.0633P)^2 + 0.0000P]$, where $P = (F_o^2 + 2F_c^2)/3)$ (for 9587 unique reflections), $(\Delta/\sigma)_{max} = 0.000$, $S = 1.150$, $(\Delta\rho)_{max} = 0.524$ and $(\Delta\rho)_{min} = -0.394$ e/Å^3. The crystallographic data are given in Table 1.

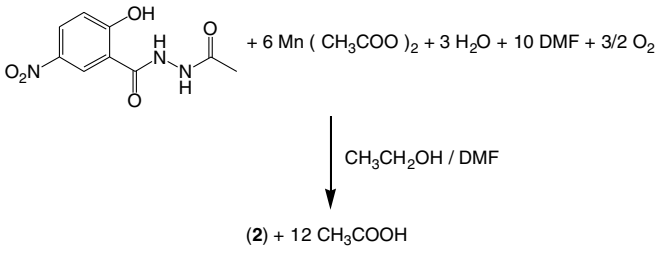
Table 1
Crystallographic data

Empirical formula	$C_{84}H_{118}Mn_6N_{28}O_{46}$
Formula weight	2585.71
Crystal system	Monoclinic
Space group	$P21/n$
a (Å)	20.598(4)
b (Å)	13.493(3)
C (Å)	20.706(4)
β (°)	95.28(3)
V (Å^3)	5730(2)
Z	2
D_{calc} (mg m^{-3})	1.499
μ (mm^{-1})	0.740
$F(000)$	2672.0
Crystal size (mm)	$0.40 \times 0.30 \times 0.20$
θ range (°)	1.33–24.71
Index ranges	$-23 \leqslant h \leqslant 24$; $-10 \leqslant k \leqslant 15$; $-24 \leqslant l \leqslant 24$
Observed reflections	22054
Independent reflections [R_{int}]	9587 [0.0571]
R_1	0.0797
wR_2	0.1662
Goodness-of-fit	1.150

3. Results and discussion

3.1. Synthesis of the complex

Manganese metallacrown **2** were synthesized via the aerial redox reaction of $Mn(AcO)_2 \cdot 4H_2O$ with the deprotonated 5-nitrosalicylhydrazide in 4:1 ethanol + DMF solution (Fig. 1; Scheme 2). The compound are dark brown crystalline solids.



Scheme 2.

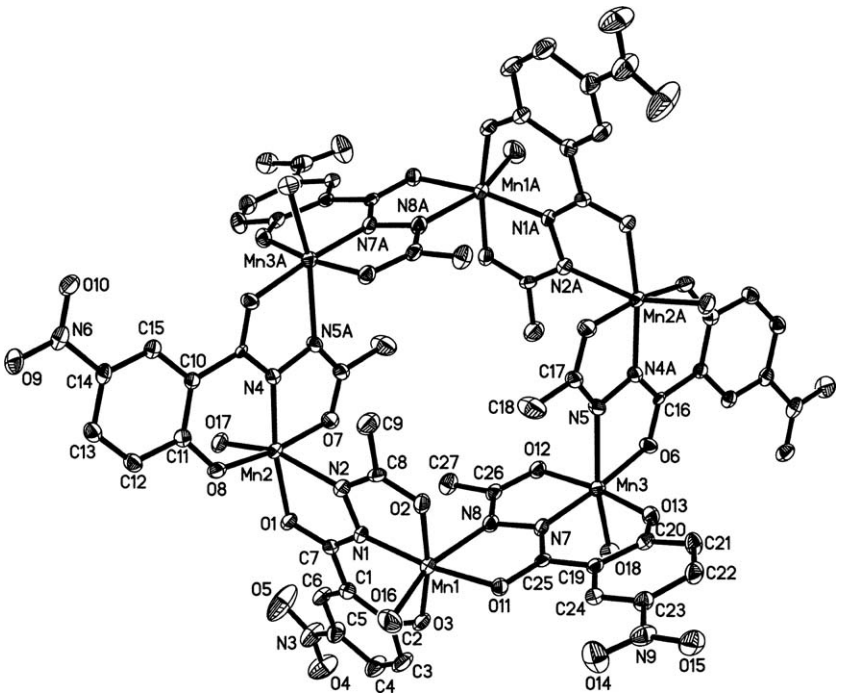


Fig. 1. Perspective view of compound **2**, solvent molecules and all hydrogen atoms have been omitted for clarity.

3.2. Spectral characterization

In the IR spectra, the ligand **1** shows stretching bands attributed to C=O, C=N, C—OH (phenolic) and NH at 1684, 1624, 1126 and 1235, and 3103 cm^{-1}, respectively [34]. Bands at 3298, 3199 and 2710 cm^{-1} are assigned to ν(O—H) vibrations which may be involving intramolecular hydrogen bonding, while band at 1126 and 1235 cm^{-1} is attributed to ν(O—H) (phenolic) [35,36]. In addition, a strong band found at 1604 cm^{-1} is assigned to C=N—N=C group [34–36]. In the title compound **2**, the absence of the N—H and C=O stretching vibration bands is consistent with the deprotonation of the CONH groups and coordination to the Mn(III) ion. The broad band at 3377 cm^{-1} is reasonably assigned to OH stretching vibrations, and the band is attributable to coordinated H_2O molecules [37]. The C=N—N=C framework seen at l604 cm^{-1} in the ligand shifted to 1607 cm^{-1} upon coordination to Mn atom. The disappearance of the bands at 3298, 3199 and 2710 cm^{-1} and the appearance of the bands at 1317 and 1275 cm^{-1} support the involvement of phenolic oxygen in coordination through deprotonation. This is confirmed by the band at about 450 cm^{-1} assigned to Mn–O (phenolic).

3.3. Description of structure 2

The title compound **2** crystallizes in the monoclinic system and space group $P21/n$. A diagram of the crystal structure of complex **2** is presented in Fig. 1. Important bond distances and bond angles are presented in Table 2.

The structure exhibits a hexanuclear ring of manganese atoms linked by six hydrazide N—N groups. The deprotonated ligand anshz^{3-} acts as a trianionic pentadentate ligand, one phenolate oxygen, one carbonyl oxygen and one hydrazide nitrogen in the ligand are bound to one Mn^{3+} cation, and the other carbonyl oxygen plus the other hydrazide nitrogen in the same ligand are chelated to an adjacent Mn^{3+} cation. The specific connectivity of atoms forming the ring is —Mn1—N1—N2—Mn2—N4—N5A—Mn3A—N7A—N8A—Mn1A—N1A—N2A—Mn2A—N4A—N5—Mn3—N7—N8—. Therefore, the ligand is forcing all Mn^{3+} cations into a propeller configuration with alternating Δ/Λ stereochemistry as $\Delta\Lambda\Lambda$ forms (Fig. 1). Three water groups coordinated at the metal centers with Λ configuration are found on one face of the metallacrown, and the remaining three water groups coordinated to the other metal centers with Δ configuration are found on the other face of the metallacrown. The two faces of the disc-shaped hexanuclear ring have opposite chiralities to each other. This organization results in the 18-membered hexanuclear core ring system with an [—Mn—N—N—] repeat unit. The approximate dimensions of the oval-shaped cavity are estimated by SHELXTL, with about 7.14 Å in diameter at entrance and about 9.76 Å at its largest diameter at the center of the cavity. It is also observed that the all atoms in the ligand are almost in co-plane and the all manganese atoms in title compound **2** are in an octahedral MnN_2O_4 environment (Fig. 2). The average neighboring Mn···Mn separation is of 4.885 Å. There are not any solvent molecules in the 'host' cavity of metallcrown in the title compound. In addition there are many kinds of intermolecular hydrogen bonds in the title compound **2**. All hydrogen bonds are between the O—H group from coordinated water and the oxygen atom of carbonyl from solvent DMF. The O—H···O hydrogen bond distances range from 2.643(7) to 2.752(6) Å.

Table 2
Selected bond lengths (Å) and bond angles (°) in compound **2**

Bond lengths			
Mn1—O3	1.871(4)	Mn3—O13	1.866(4)
Mn1—O2	1.911(4)	Mn3—O12	1.915(3)
Mn1—N1	1.929(4)	Mn3—N7	1.935(4)
Mn1—O11	1.963(3)	Mn3—O6	1.968(3)
Mn1—O16	2.193(5)	Mn3—O18	2.228(4)
Mn1—N8	2.267(4)	Mn3—N5	2.264(4)
Mn2—O8	1.889(3)	N1—N2	1.414(6)
Mn2—O7	1.912(4)	N7—N8	1.415(5)
Mn2—N4	1.944(4)	C7—O1	1.273(6)
Mn2—O1	1.967(3)	C8—O2	1.291(6)
Mn2—O17	2.181(4)	C2—O3	1.309(6)
Mn2—N2	2.296(4)		
Bond angles			
O3—Mn1—O2	170.08(15)	N7—Mn3—O18	94.36(16)
O3—Mn1—N1	90.47(17)	O6—Mn3—O18	88.78(15)
O2—Mn1—N1	79.78(17)	O13—Mn3—N5	92.03(16)
O3—Mn1—O11	99.14(15)	O12—Mn3—N5	91.85(15)
O2—Mn1—O11	90.67(15)	N7—Mn3—N5	101.77(16)
N1—Mn1—O11	170.24(17)	O6—Mn3—N5	74.82(14)
O3—Mn1—O16	89.6(2)	O18—Mn3—N5	163.07(15)
O2—Mn1—O16	89.6(2)	O12—Mn3—O18	85.83(16)
N1—Mn1—O16	96.01(19)	C7—N1—Mn1	132.0(4)
O11—Mn1—O16	85.88(17)	N2—N1—Mn1	114.9(3)
O3—Mn1—N8	92.15(17)	C8—N2—N1	109.1(4)
O2—Mn1—N8	91.91(15)	C8—N2—Mn2	140.5(4)
N1—Mn1—N8	103.40(16)	N1—N2—Mn2	107.8(3)
O11—Mn1—N8	74.66(14)	O4—N3—O5	121.1(6)
O16—Mn1—N8	160.49(18)	O4—N3—C5	120.5(5)
O8—Mn2—O7	170.29(15)	O5—N3—C5	118.4(6)
O8—Mn2—N4	90.21(16)	C17—N5—Mn3	141.9(3)
O7—Mn2—N4	80.07(16)	O10—N6—O9	122.9(5)
O8—Mn2—O1	97.89(15)	O10—N6—C14	118.4(4)
O7—Mn2—O1	91.79(15)	O9—N6—C14	118.7(5)
N4—Mn2—O1	170.85(16)	C25—N7—N8	114.1(4)
O8—Mn2—O17	90.27(16)	C25—N7—Mn3	131.5(4)
O7—Mn2—O17	91.29(16)	N8—N7—Mn3	114.3(3)
N4—Mn2—O17	98.90(17)	C26—N8—N7	110.2(4)
O1—Mn2—O17	85.36(16)	C26—N8—Mn1	141.2(4)
O8—Mn2—N2	94.16(15)	N7—N8—Mn1	107.7(3)
O7—Mn2—N2	87.70(15)	O14—N9—O15	121.8(5)
N4—Mn2—N2	101.09(17)	O14—N9—C23	119.3(5)
O1—Mn2—N2	74.21(15)	O15—N9—C23	118.9(5)
O17—Mn2—N2	159.50(17)	C7—O1—Mn2	119.3(3)
O13—Mn3—O12	170.73(15)	C8—O2—Mn1	113.7(3)
O13—Mn3—N7	90.83(16)	C2—O3—Mn1	129.7(3)
O12—Mn3—N7	80.14(16)	C16—O6—Mn3	120.0(3)
O13—Mn3—O6	92.42(15)	C11—O8—Mn2	129.3(3)
O12—Mn3—O6	96.71(15)	C25—O11—Mn1	119.6(3)
N7—Mn3—O6	175.36(15)	C26—O12—Mn3	113.5(3)
O13—Mn3—O18	92.85(16)	C20—O13—Mn3	128.5(3)

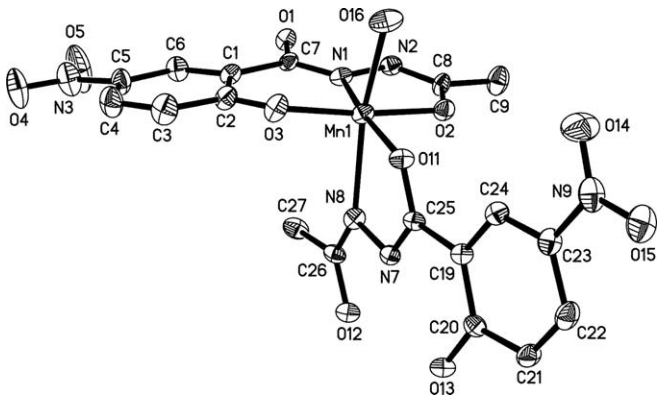


Fig. 2. The coordination environments of Mn(III) ion.

3.4. Antimicrobial activity

Minimum inhibitory concentrations of the complex **1** and **2** against *S. aureus*, *E. coli*, *B. subtilis* and *P. vulgaris* are listed in Table 3. As can clearly be seen from Table 3, both compounds are not strong antimicrobial activities against most of tested microorganisms. Moreover, in this study, the results do not indicate specificity against Gram-positive or Gram-negative bacteria in spite of it is generally expected that a much greater number would be active against Gram-positive than Gram-negative bacteria [38]. While compound **1** has formed relatively weak antimicrobial effect against all tested microorganisms except for *B. subtilis*, compound **2** has showed the most potent antibacterial activity against *B. subtilis*. Similar anti-microbial behavior (MIC = 50–100 μg/mL) has been previously reported for other metallacrowns [16,39]. However, comparison of the MIC values did not suggest that an increase in the metallacrown ring size case results in increased antimicrobial activity [39].

4. Conclusion

The title compound **2** is the first example of 18-metallacrown-6 compounds containing Mn^{3+} as ring ions with the ligand of **1**. Due to the meridional coordination of the ligand to the Mn^{3+} ion, the ligand enforces the stereochemistry of the Mn^{3+} ions as a propeller configuration with alternating Δ/Λ forms. The other important structural feature in $[Mn_6(H_2O)_6\ (anshz)_6]\cdot 10DMF$ is that there is not only a vacant cavity in the center of 18-metallacrown-6 core ring, but also the opposite chiralities on the two faces of the metallacrown ring system. This novel manganese 18-metallacrown-6 compound has showed strong antimicrobial activity against *B. subtilis*.

Table 3
Minimum inhibitory concentration (MIC) of compounds **1** and **2** in μg/mL

Microorganisms	Compounds	
	1	**2**
E. coli (Gram$^-$)	900	300
B. subtilis (Gram$^+$)	300	100
P. vulgaris (Gram$^-$)	600	300
S. aureus (Gram$^+$)	800	300

Acknowledgment

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Appendix A. Supplementary material

CCDC 282915 contain the supplementary crystallographic data for compound **2**. The data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK (fax: +44 1223 336 033; or deposit@ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.02.036.

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