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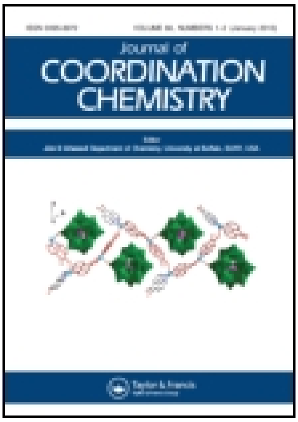

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An iron(III) 18-metallacrown-6 complex: synthesis, crystal structure, and bioactivity

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An iron(III) 18-metallacrown-6 complex: synthesis, crystal structure, and bioactivity

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A macrocyclic hexanuclear iron(III) 18-metallacrown-6 complex, $[Fe_6(C_9H_6BrN_2O_3)_6(CH_3OH)_4(H_2O)_2] \cdot 7CH_3OH \cdot 4H_2O$, has been prepared using a trianionic pentadentate ligand N-acetyl-5-bromosalicylhydrazidate, abshz^{3-}, and characterized by X-ray diffraction. The crystal structure contains a neutral 18-membered metallacrown ring consisting of six Fe(III) and six abshz^{3-} ligands. The 18-membered metallacrown ring is formed by combination of six structural moieties, [Fe(III)–N–N]. Due to meridional coordination of ligand to Fe^{3+}, the ligand enforces the stereochemistry of the Fe^{3+} ions as a propeller configuration with alternating Δ/Λ forms. Methanol and water are linked with Fe1, Fe1A, Fe,3 and Fe3A. The ratios of methanol to water are 0.76 : 0.24 for Fe1 and Fe1A, and 0.30 : 0.70 for Fe3 and Fe3A, which results in four component crystals of metallacrown rings with ratio of 0.168 : 0.072 : 0.532 : 0.228. Antibacterial screening data showed that the iron metallacrown has moderate antimicrobial activity against *Bacillus subtilis*.

Keywords: Metallacrown; Iron complex; Crystal structure; Antimicrobial activity

1. Introduction

There has been growing interest in synthesis and characterization of metallacrowns, due to their strong visible absorption spectra, redox activities, magnetism, molecular recognition, and bioactivities. Generally metallacrowns exhibit a cyclic hole analogous to crown ethers with transition metal ions and a nitrogen replacing the methylene carbons. At present, metallacrowns with Mn(III), Fe(III), Ni(II), Cu(II), Zn(II), Ga(III), and V(V)O metal ions, [9-MC-3] [1], [12-MC-4] [2], [15-MC-5] [3], [12-MC-6] [4], [16-MC-8] [5], [18-MC-6] [6, 7], [18-MC-8] [4], [30-MC-10] [8], [36-MC-12] [9], [40-MC-10] [10], and [60-MC-20] [11] have been reported. In metallacrowns, the cyclic structure of [M–N–O] or [M–N–N] was termed the chelate ring. The constructing ligand, hydroxamic acid, and salicylhydrazide will be termed the main ligand. Other ligands, usually solvent and/or other small molecule and anion, are termed

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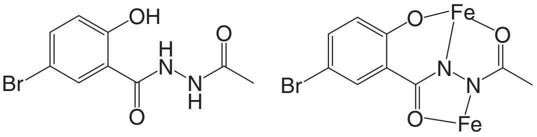
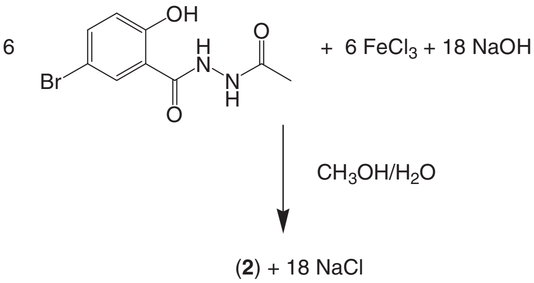


Scheme 1. Ligand H_3abshz and basic bonding sites in **2**.



Scheme 2. Synthesis of **2**.

secondary ligand. In the complex of metallacrown containing [M–N–N] repeat units, each metal was coordinated with two main ligands and one secondary ligand, forming a distorted octahedral geometry [3–8]. The studies showed that the secondary ligand can be changed *via* adjustment of solvent, while the chelate ring kept the structure without change [12, 13].

In our previous studies to examine the mode of binding and possible antagonistic or synergistic effects, antibacterial screening data showed that 18-$MC_{Mn(III)N(anshz)}$-6 and 18-$MC_{Mn(III)N(abshz)}$-6 metallacrowns are more active than simple manganese salts or carboxylate complexes [6, 14]. Taking into account that most metallacrowns are from hydroxamic acids, our interests focus on the type of salicylhydrazides. Our interest in the chemistry of metallacrowns with solvents was stimulated by the question of how change in solvent of metallacrown ring will influence reactivity and bioactivity.

In continuation of our work on preparation of metallacrown complexes with 5-bromosalicylhydrazide, we now report an iron(III) 18-metallacrown-6 compound with pentadentate main ligand N-acetyl-5-bromosalicylhydrazide (**1**) (H_3abshz, scheme 1), $[Fe_6(C_9H_6BrN_2O_3)_6(CH_3OH)_4(H_2O)_2]\cdot 7CH_3OH\cdot 4H_2O$ (**2**) (scheme 2). Complex **2** has three coordination sites with two secondary ligands. In an attempt to examine the mode of binding and possible antagonistic or synergistic effects, antibacterial studies of the metallacrown complex against four different bacteria have been measured by Minimum Inhibitory Concentrations (MIC).

2. Experimental

2.1. *Materials*

Chemicals for the syntheses of the compounds were used as purchased. Methanol, ethanol, and N,N-dimethylformamide (DMF) were used without purification.

5-Bromosalicylic acid, sulfuric acid, hydrazine hydrate, acetic anhydride, chloroform, diethyl ether, sodium hydrate, and $FeCl_3 \cdot 6H_2O$ were purchased from China Sinopharm Group Chemical Reagent Co., Ltd., Shanghai, China. 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. *Characterization*

Infrared spectra were measured on a Thermo Nicolet Corporation NEXUS FT-IR spectrometer as KBr pellets from 4000 to 400 cm^{-1}. UV-Vis spectra were recorded on a Shimadzu-UV-2501 PC recording spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian Inova 600 MHz NMR spectrometer at 25°C. Chemical shifts are referenced to residual solvent peak. C, H, and N elemental analysis were performed on a Perkin Elmer 2400 CHN elemental analytical instrument, Fe was determined by atomic absorption spectroscopy on a Perkin Elmer 1100B spectrophotometer. Positive and negative electrospray ionization mass spectra (ESI-MS) were performed on an API-2000 LC/MS/MS system for **2** in methanol.

2.3. *Synthesis of N-acetyl-5-bromosalicylhydrazide (H_3abshz) (1)*

H_3abshz was synthesized by reacting acetic anhydride (6.8 g, 66.8 mmol) with 5-bromosalicylhydrazide (12.4 g, 50.0 mmol) in 120 ml of chloroform at 0°C. The reaction mixture was slowly warmed to room temperature and stirred for 8 h. After staying overnight in a refrigerator, the resulting white precipitate was filtered and rinsed with chloroform and diethyl ether. Yield: 11.5 g, 84%. Found: C, 39.45; H, 3.51; N, 10.43%. Calcd for $C_9H_9N_2O_3Br$: C, 39.59; H, 3.33; N, 10.26%. IR (KBr pellet, cm^{-1}): υO–H, 3302 vs; υN–H, 3181 vs, broad; υC=O, 1659 s; υC=N, 1641 s; υC=N–C=N, 1597 vs; υN–C=O, 1566 vs; δN–H, 1479 vs; υ(C–OH)$_{\text{al}}$, 1285 vs; υ(C–OH)$_{\text{phenolic}}$, 1235 s, 1126 s; υC–Br, 1018 s. ^{1}H NMR (DMSO-d$_6$), δ ppm: 10.55 (s, 1H, Ar–CO–NH–); 10.31 (s, 1H, Me–CO–NH–); 8.04 (s, 1H, o-ArH); 7.58 (d, 1H, p-ArH); 6.96 (d, 1H, m-ArH); 1.96 (s, 3H, –CH_3). ^{13}C NMR (DMSO-d$_6$), δ ppm: 168.38 (Me–CO–); 165.23 (Ar–CO–); 158.13 (o-ArC–OH); 136.88 (p-ArC); 131.62 (o-ArC); 120.25 (ArC–); 117.92 (m-ArC); 110.86 (m-ArC–Br); 21.25 (–CH_3). UV-Vis (CH_3OH, nm), $\lambda_{max}(\epsilon)$: 314, 247.

2.4. *Synthesis of 18-MC$_{Fe(III)N(abshz)}$-6 ($[Fe_6(C_9H_6BrN_2O_3)_6(CH_3OH)_4(H_2O)_2] \cdot 7CH_3OH \cdot 4H_2O$) (2)*

H_3abshz (0.27 g, 1.0 mmol) was dissolved in 80 ml of methanol, and 0.27 g (1.0 mmol) of $FeCl_3 \cdot 6H_2O$ was dissolved in 20 mL of water in another flask. The two solutions were mixed and stirred for 1 h, then the solution was adjusted to pH = 4~5 with 1% sodium hydroxide. The color of the mixture changed to dark brown, was stirred for 2 h continuously and then filtered. After slow evaporation of the mother liquor for two weeks, dark brown block crystals were obtained from the filtrate. Yield: 0.17 g, 42%. Found: C, 32.76; H, 3.66; N, 7.27; Fe, 13.94%. Calcd for $C_{65}H_{92}Br_6Fe_6N_{12}O_{35}$: C, 32.31; H, 3.84; N, 6.96; Fe, 13.87%. ESI-MS (*m*/*z*): 997, $[Fe_6(H_2O)_2(\text{abshz})_6 + 2H]^{2+}$; 995, $[Fe_6(CH_3OH)(\text{abshz})_6 + 2H]^{2+}$; 979, $[Fe_6(\text{abshz})_6 + 2H]^{2+}$. IR (KBr pellet, cm^{-1}):

υH–OH, 3422 s, broad; υC=O, 1648 vs; υC=N–C=N, 1592 vs; υN–C=O, 1553 vs; υFe–O(phenolic), 447 s. UV-Vis (CH_3OH, nm), λ_{max}: 517, 316, 232.

2.5. *X-ray analysis*

Crystals of **2** suitable for X-ray were obtained as described above. A crystal of **2** with dimensions 0.40 × 0.40 × 0.35 mm was mounted in a glass capillary with the mother liquor to prevent loss of the structural solvents during X-ray diffraction data collection. Intensity data were collected with graphite monochromatic Mo-Kα radiation ($\lambda = 0.71073$ Å) at 292(2) K on a Bruker Smart APEX diffractometer. From a total of 23,479 reflections corrected by psi-scan absorption correction of XPREP [15, 16] in the $1.50 \le \theta \le 25.25$ range, 8700 were independent, of which 6395 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 hydrogens were located in calculated positions and/or in 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 [15, 16]. The final refinement converged at $R_1 = 0.0406$, $wR_2 = 0.1019$ ($w = 1/[\sigma^2(Fo^2) + (0.0502P)^2 + 0.0000P]$, where $P = (Fo^2 + 2Fc^2)/3$), $(\Delta/\sigma)\max = 0.003$, $S = 0.925$, $(\Delta\rho)\max = 0.759$ and $(\Delta\rho)\min = -0.631$ e Å^{-3}.

2.6. *Biological activity*

The antimicrobial activity of the compounds was assessed by their ability to inhibit growth of *Staph. aureus*, *E. coli*, *Bac. subtilis* and *Prot. vulgaris* in Mueller–Hinton broth medium. The MIC in µg mL^{-1} against the four bacteria was measured. Bacteria concentration was 10^5–10^6 cfu mL^{-1}. Serial concentrations of the compounds in methanol were tested. The solvent showed no antimicrobial action.

3. Results and discussion

3.1. *Synthesis of the complex*

Iron metallacrown **2** was synthesized *via* $FeCl_3 \cdot 6H_2O$ with deprotonated N-acetyl-5-bromosalicylhydrazide in mixed methanol and water solution (figure 1, scheme 2), followed by addition of 1% sodium hydroxide. During the reaction, the color of the mixture changed to dark brown. The final complex is brown crystalline solids, soluble in methanol.

3.2. *Spectral characterization*

In IR spectra, **1** shows stretching bands attributed to C=O, C=N, C–OH (phenolic) and NH at 1659, 1641, 1126, and 1178, and 3181 cm^{-1}, respectively [17]. Bands at 3302, 2932, and 2683 cm^{-1} are assigned to υ(O–H) vibrations which may involve intramolecular hydrogen bonds, while bands at 1126 and 1178 cm^{-1} are attributed to υ(O–H)

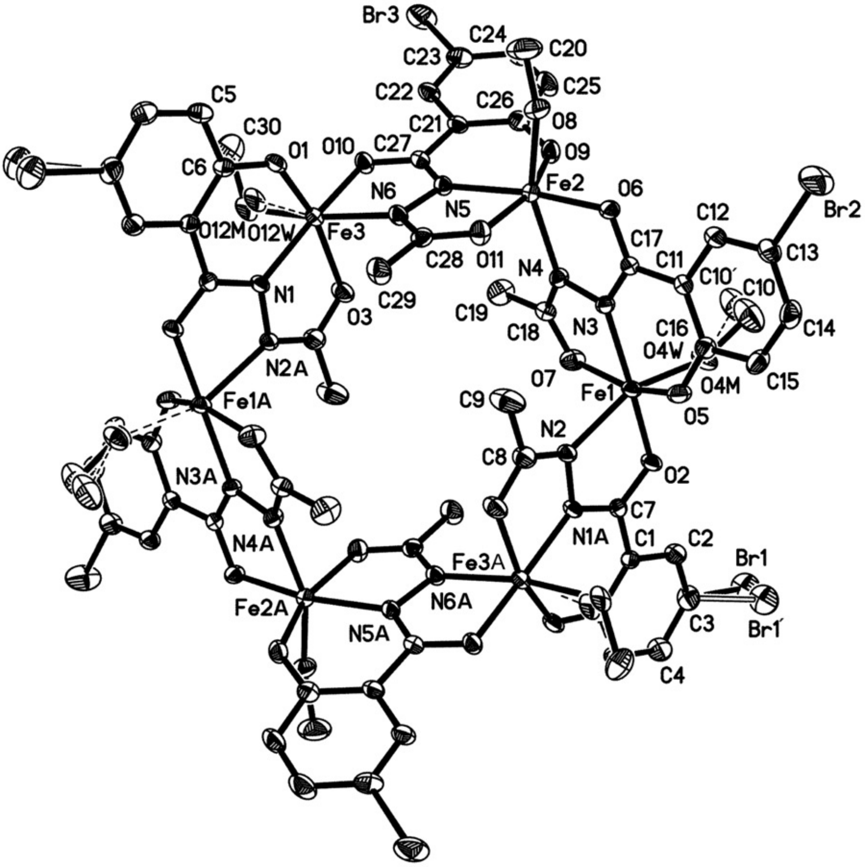


Figure 1. Perspective view of **2**, solvent molecules and all hydrogens have been omitted for clarity.

(phenolic) [18, 19]. A strong band at 1597 cm^{-1} is assigned to C=N–N=C [17–19]. In **2**, the absence of the N–H and C=O stretches is consistent with deprotonation of the CONH groups and coordination to Fe(III). The broad band at 3422 cm^{-1} is reasonably assigned to OH stretch, and the band is attributable to coordinated H_2O [20]. The C=N–N=C framework at 1597 cm^{-1} in the ligand shifts to 1592 cm^{-1} upon coordination to Fe. The disappearance of the bands at 3302, 2932, and 2683 cm^{-1} and the appearance of the bands at 1308 and 1248 cm^{-1} support the involvement of phenolic oxygen in coordination through deprotonation. This is confirmed by the band at 447 cm^{-1} assigned to Fe–O (phenolic).

The UV-Vis spectra of ligand and complex were recorded using 10^{-4} mol L^{-1} solution in methanol. The spectra of the ligand have an intense absorption near 247 nm, which can be attributed to intraligand charge transfer transition $\pi \rightarrow \pi^*$. Bands at 314 nm are also attributed to charge transfer transition $\pi \rightarrow \pi^*$ of the aromatic ring structure, confirmed by the band at the same site for **2**. The spectra of **2** display absorptions at 232, 316, and 517 nm. The bands at 232 nm can be attributed to internal ligand $\pi \rightarrow \pi^*$ or $n \rightarrow \pi^*$ transition of the benzene rings, the substituted group of acetylhydrazide and π conjugation. The absorption maxima at 316 nm can be assigned to charge transfer transition $\pi \rightarrow \pi^*$ of aromatic ring and the absorption maxima at 517 nm is assigned to d–d transition of the iron ions. Other peaks of the spectra are not easily found, perhaps covered by the absorptions near 232 nm and 316 nm.

^{1}H NMR of the ligand is a singlet at δ 1.96 for the methyl protons, a doublet at δ 6.96 for the aromatic *m*-ArH, a doublet at δ 7.58 for the aromatic *p*-ArH, a singlet at δ 8.04 for the aromatic proton *o*-ArH, two singlets at δ 10.31 and 10.55 for the hydrazine protons. In the ^{13}C NMR spectra of the ligand, three peaks at 118 ppm, 132 ppm, and 137 ppm are possible concluded to be the three isolated carbons of the aromatic ring; the other three carbons are at 110 ppm for the carbon linked with bromine atom, 120 ppm for the carbon linked with C=O group, and 158 ppm for the carbon linked with OH group. The CH_3 carbon falls into the 20–30 ppm range, the two carbonyl carbons are judged in the 165–175 ppm region. All these assignments are in agreement with the spectra obtained.

3.3. *Description of structure 2*

Complex **2** crystallizes in the triclinic system and space group $P\bar{1}$. A diagram of the crystal structure of **2** is presented in figure 1. The crystallographic data are summarized in table 1, and selected bond distances and angles are given in table 2.

In the structure there is a hexanuclear chelate ring of irons linked by six hydrazide N–N groups. The deprotonated main ligand abshz^{3-} is trianionic pentadentate, one phenolate oxygen, one carbonyl oxygen and one hydrazide nitrogen are bound to one Fe^{3+}, and the other carbonyl oxygen plus the other hydrazide nitrogen in the same

Table 1. Crystallographic data.

Empirical formula	$C_{65.5}H_{94}Br_6Fe_6N_{12}O_{35.5}$
Formula weight	2432.03
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions (Å, °)	
a	12.176(5)
b	14.899(6)
c	14.984(6)
α	69.675(6)
β	77.955(6)
γ	73.273(6)
Volume (Å^3), *Z*	2423.1(16), 1
Calculated density (Mg m^{-3})	1.676
μ (mm^{-1})	3.432
F(000)	1228
Crystal size (mm^3)	0.40 × 0.40 × 0.35
θ range for data collection (°)	1.50–25.25
Index ranges	$-14 \le h \le 14$; $-17 \le k \le 17$; $-17 \le l \le 17$
Observed reflections	23,479
Independent reflections	8700
R_1	0.0406
wR_2	0.1019
Goodness-of-fit	0.957

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

Fe1–O5	1.939(2)	Fe3–O1	1.927(2)
Fe1–O2	2.001(2)	Fe3–O10	1.994(2)
Fe1–O7	2.046(2)	Fe3–O3	2.042(2)
Fe1–N3	2.046(2)	Fe3–N1	2.044(2)
Fe1–O4W	2.253(15)	Fe3–O12W	2.011(4)
Fe1–O4M	2.032(4)	Fe3–O12M	2.320(9)
Fe1–N2	2.102(3)	Fe3–N6	2.096(2)
Fe2–O9	1.936(2)	N3–N4	1.408(3)
Fe2–O6	1.998(2)	N5–N6	1.412(3)
Fe2–N5	2.046(2)	C16–O5	1.336(3)
Fe2–O8	2.090(2)	C26–O9	1.326(4)
Fe2–O11	2.037(2)	C17–O6	1.290(3)
Fe2–N4	2.118(2)	C28–O11	1.280(3)
O5–Fe1–O2	106.14(9)	O10–Fe3–O3	94.86(9)
O7–Fe1–N2	89.55(10)	N6–Fe3–O1	92.33(9)
O2–Fe1–O7	93.46(8)	O3–Fe3–N1	75.51(9)
O5–Fe1–N3	85.60(9)	O10–Fe3–N6	76.17(9)
O5–Fe1–O4M	90.94(12)	O3–Fe3–O12M	86.3(3)
O5–Fe1–O4W	98.9(4)	O3–Fe3–O12W	92.47(14)
O9–Fe2–O6	108.48(9)	N1–Fe3–N6	110.52(10)
O6–Fe2–O11	90.10(9)	N4–N3–Fe1	116.28(16)
N5–Fe2–O11	75.77(9)	N3–N4–Fe2	111.94(16)
O8–Fe2–O11	90.83(10)	N6–N5–Fe2	115.56(16)
O6–Fe2–N4	75.74(8)	N5–N6–Fe3	112.74(16)

ligand chelate to an adjacent Fe^{3+}. The specific connectivity of atoms forming the chelate ring is –Fe1–N3–N4–Fe2–N5–N6–Fe3–N1–N2A–Fe1A–N3A–N4A–Fe2A–N5A–6A–Fe3A–N1A–N2–. Therefore, the ligand forces all Fe^{3+} cations into a propeller configuration with alternating Δ/Λ stereochemistry as $\Delta\Lambda\Delta$ forms (figure 1). Three secondary methanol and/or waters coordinate metal centers with Δ configuration on one face of the metallacrown, and the remaining three secondary methanol and/or waters coordinate to the other metal centers with Λ configuration on the other face of the metallacrown. The two faces of the disc-shaped hexanuclear ring have opposite chiralities. This organization results in the 18-membered hexanuclear chelate ring system with an [–Fe–N–N–] repeat unit. The approximate dimensions of the oval-shaped cavity are estimated by SHELXTL, with about 8.23 Å diameter at the entrance and about 10.30 Å at its largest diameter at the centre of the cavity. All atoms in the ligand are almost co-planar and all irons in **2** are octahedral FeN_2O_4. The average adjacent Fe $\cdots$ Fe separations are of 4.904 Å for Fe1 $\cdots$ Fe2, 4.881 Å for Fe2 $\cdots$ Fe3, and 4.899 Å for Fe3 $\cdots$ Fe1A, respectively. The bond lengths and angles around Fe(III) showed some distortions of the octahedron. The Jahn–Teller effect was not observed because of the high-spin d^5 Fe(III). These distortions were related to the character of $abshz^{3-}$ and its bridging model. With Fe1, for example, the bond length between Fe1 and O7 from coordinated $abshz^{3-}$, 2.046 Å, is shorter than the bond length between Fe1 and O4W from coordinated water, 2.253 Å. Also, due to steric hindrance of the matrix coordinated $abshz^{3-}$ with phenyl, the bond angle between Fe1–O5 and Fe1–O2 is 106.14°. There are no solvent molecules in the "host" cavity of the complex, but there are many methanol and water molecules around the cavity of the metallacrown in the complex. Based on the crystal data, the molecular formula $[Fe_6(C_9H_6BrN_2O_3)_6(CH_3OH)_{4.12}(H_2O)_{1.88}]\cdot 7.38CH_3OH\cdot 4.12H_2O$ had been surmised.

Table 3. MIC of **1** and **2** in $\mu g\,mL^{-1}$.

Compounds	*E. coli* (Gram$^-$)	*Bac. subtilis* (Gram$^+$)	*Prot. vulgaris* (Gram$^-$)	*Staph. aureus* (Gram$^+$)
$FeCl_3 \cdot 6H_2O$	800	600	800	800
1	900	400	400	400
2	200	25	800	100
Amoxicillin	130	2	500	20
Norfloxacin	0.1	2	$\leq$0.02	2

Compared to the molecular formula confirmed, $[Fe_6(C_9H_6BrN_2O_3)_6 \times (CH_3OH)_4(H_2O)_2] \cdot 7CH_3OH \cdot 4H_2O$, the methanols are different. In the packing diagram, crystal packing shows that rings of metallacrowns are stacked along the *a* axis. At the same time, there are many kinds of intermolecular hydrogen bonds in **2**, most O–H···O type, with hydrogen bond distances from 2.334(16) Å to 2.969(14) Å.

In the crystal structure of **2**, there are marked differences in the secondary ligands of Fe1 and Fe1A, and Fe3 and Fe3A. There are two types of secondary ligand, methanol and water, which link with Fe1, Fe1A, Fe3, and Fe3A, respectively. The ratios of methanol to water are 0.76 : 0.24 for Fe1 and Fe1A, and 0.30 : 0.70 for Fe3 and Fe3A, which results in four component crystals of metallacrown ring $[Fe_6(C_9H_6BrN_2O_3)_6(CH_3OH)_4(H_2O)_2]$ with ratio of 0.168 : 0.072 : 0.532 : 0.228.

3.4. *ESI-MS*

Electrospray ionization mass spectroscopy, a soft ionization technique, has proved useful in providing fragmentation pathways of formally neutral salt complexes [21–23]. In **2**, the methanol solution gave some peaks at *m/z* 997, 995, and 979, corresponding to metallacrown chelate ring ions, $[Fe_6(H_2O)_2(abshz)_6 + 2H]^{2+}$, $[Fe_6(CH_3OH)(abshz)_6 + 2H]^{2+}$ and $[Fe_6(abshz)_6 + 2H]^{2+}$, respectively. All of the peaks keep the chelate ring, but the secondary ligand changes greatly.

3.5. *Antimicrobial activity*

Minimum inhibitory concentrations of **1** and **2** against *Staph. aureus*, *E. coli*, *Bac. subtilis*, and *Prot. vulgaris* are listed in table 3. Data for amoxicillin and norfloxacin are included for comparison for bacteria. Compound **1** has poor antimicrobial activities against all of the tested microorganisms, but **2** has good behavior except with *Prot. vulgaris*. Metallacrown **2** shows better activity against Gram$^+$ bacteria *Staph. aureus* and *Bac. Subtilis* than Gram$^-$ bacteria *E. coli* and *Prot. vulgaris* in antimicrobial assay. While **1** has relatively weak antimicrobial effect against all of the tested microorganisms, **2** shows its best antibacterial activity against *Bac. subtilis*.

4. Conclusion

In this work, **2** was synthesized *via* $FeCl_3 \cdot 6H_2O$ with the deprotonated N-acetyl-5-bromosalicylhydrazide. Due to meridional coordination of the ligand to Fe^{3+}, the ligand enforces the Fe^{3+} stereochemistry as a propeller configuration with alternating Δ/Λ forms. The other important structural feature in **2** is that there is not only a vacant cavity in the center of the 18-metallacrown-6 core ring, but also opposite chiralities on the two faces of the metallacrown ring system. This novel iron 18-metallacrown-6 compound has moderate antimicrobial activity against *Bac. subtilis*.

In the crystal structure of **2**, there are methanol and water ligands linking with Fe1, Fe1A, Fe3 and Fe3A, respectively. The methanol and water may be active points of metallacrown compound, which is important for macroporous compounds. Some catalytic activity and enzyme analogues of metallacrown compounds can be expected.

Supplementary material

CCDC 622308 contains the supplementary crystallographic data for **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 CB2 1EZ, UK; Fax: +44 1223 336 033; or Email: deposit@ccdc.cam.ac.uk).

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