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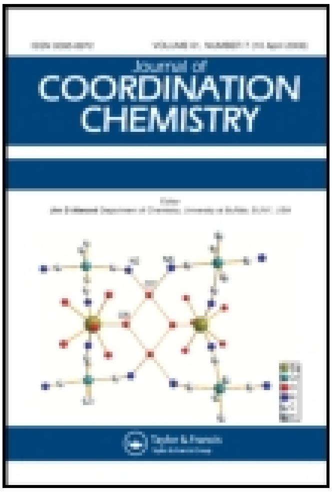

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Esterification and isolation of the carboxylic acid with salicyl-bis-hydrazide via coordination of iron(III) 18-metallacrown-6 complex

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Esterification and isolation of the carboxylic acid with salicyl-bis-hydrazide *via* coordination of iron(III) 18-metallacrown-6 complex

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The trianionic heptadentate ligand, (*Z*)-3-(5′-bromosalicylhydrazinocarbonyl) propenoic acid ((*Z*)-H_4bshcpa), has been synthesized in good yield and reacted with $FeCl_3 \cdot 6H_2O$ to produce $[Fe^{III}_6(C_{12}H_8N_2O_5Br)_6(H_2O)_2(CH_3OH)_4] \cdot 8H_2O \cdot 8CH_3OH$. The complex has been characterized by single-crystal X-ray diffraction. In the self-assembly process the ligand was esterified and transferred into (*Z*)-methyl 3-(5′-bromosalicylhydrazinocarbonyl) propenoate ((*Z*)-H_3mbshcp). In the crystal structure, the neutral Fe(III) complex contains an 18-membered metallacrown ring consisting of six Fe(III) and six trianionic ligands. The 18-membered metallacrown ring is formed by six structural moieties of the type [Fe(III)–N–N]. Due to the meridional coordination of the ligands to Fe^{3+}, the ligands enforce stereochemistry of the Fe^{3+} ions as a propeller configuration with alternating Λ/Δ forms. The metallacrown can be treated with $SnCl_2$ to obtain purified ester. In addition, we have also obtained reduced esterified ligand, methyl 3-(5′-bromosalicylhydrazinocarbonyl) propanoate (H_3mbshcp), with Zn powder as reductant.

Keywords: Metallacrown; Iron complex; Crystal structure; Esterification

1. Introduction

Metallacrowns and analogues have attracted considerable attention [1, 2]. Metallacrowns, with Mn(III), Fe(III), Ni(II), Cu(II), Zn(II), Ga(III), and V(V)O, [9-MC-3] [3, 4], [12-MC-4] [5–7], [15-MC-5] [8–10], [12-MC-6] [11], [16-MC-8] [12], [18-MC-6] [13–16], [18-MC-8] [11], [30-MC-10] [17], [36-MC-12] [18], [40-MC-10] [19], [60-MC-20] [20], stacking metallacrowns [21, 22] as well as a variety of dimers and fused metallacrowns [23, 24] have been reported to date.

These complexes concentrate a large number of metal ions per unit volume, leading to interesting behaviors, such as strong visible absorption spectra, magnetism and bioactivity. Metallacrowns have already been related to sensors [25], molecular recognition [26], and chiral building blocks [27, 28].

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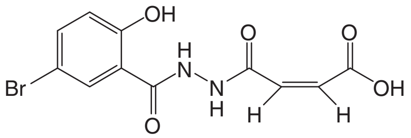


Scheme 1. Ligand (*Z*)-H_4bshcpa.

Metallacrowns are typically prepared using salicylhydroxamic acids (H_3shi) and salicylhydrazides (H_3shz). Taking the similarity between H_3shz and carboxylic acids with salicyl-bis-hydrazide into account, we have expanded the types of precursor ligand with the intention of modifying chemical properties [29–31]. In this article, we report a new potentially heptadentate ligand (*Z*)-3-(5′-bromosalicylhydrazinocarbonyl) propenoic acid (**1**) ((*Z*)-H_4bshcpa, scheme 1) and an iron(III) 18-metallacrown-6 complex $[Fe^{III}_6(C_{12}H_8N_2O_5Br)_6(H_2O)_2(CH_3OH)_4]\cdot 8H_2O\cdot 8CH_3OH$ (**2**). In the self-assembly process (*Z*)-3-(5′-bromosalicylhydrazinocarbonyl) propenoic acid is esterified and transferred into (*Z*)-methyl 3-(5′-bromosalicylhydrazinocarbonyl) propenoate ((*Z*)-H_3mbshcp) (**3**). The deprotonated (*Z*)-methyl 3-(5′-bromosalicylhydrazinocarbonyl) propenoate ((*Z*)-mbshcp^{3-}) bridges neighboring ions through its hydrazide N–N group. In addition, the metallacrown can be treated with $SnCl_2$ and/or Zn powder to obtain purified ester (*Z*)-H_3mbshcp and methyl 3-(5′-bromosalicylhydrazinocarbonyl) propanoate (H_3mbshcp) (**4**), respectively.

2. Experimental

2.1. *Materials*

Chemicals for the synthesis of the compounds were used as purchased. Methanol, ethanol, chloroform, and ethyl acetate were used without purification. 5-Bromosalicylic acid, sulfuric acid, hydrazine hydrate, maleic anhydride, pyridine, $FeCl_3\cdot 6H_2O$, hydrochloric acid, Zn powder, and $SnCl_2\cdot 2H_2O$ were purchased from China Sinopharm Group Chemical Reagent Co., Ltd. All chemicals and solvents were of reagent grade. 5-Bromosalicylhydrazide was prepared according to literature procedures [32].

2.2. *Characterization*

^{1}H and ^{13}C NMR spectra were recorded on a Varian Inova 400 MHz NMR spectrometer at 25°C. Chemical shifts are referenced to residual solvent. Infrared (IR) spectra were measured on a Thermo Nicolet Corporation NEXUS 470 FT-IR Spectrometer as KBr pellets from 4000 to 400 cm^{-1}. UV-Vis spectra were recorded on a Perkin-Elmer Lambda 35 UV/Vis Spectrometer. Thermogravimetry (TG) carried out on Perkin-Elmer Diamond DSC TG-DTA 6300 thermal analyzer. C, H, N, and S elemental analyses were performed on a Perkin-Elmer 2400 Series II CHNS/O Analyzer. Fe was determined by atomic absorption spectroscopy on a Shimadzu AA-6300 Spectrophotometer. Melting points were obtained using a digital melting-point apparatus, TP Micro Printer S-X6. Variable-temperature DC magnetic susceptibility data were collected on polycrystalline samples from 2 to 300 K at 1 KOe under zero field cooled conditions using a Quantum Design SQUID MPMS XL-7 magnetometer. Cyclic voltammetry (CV) was performed on an Eco Chemie Autolab Eletrochemical analyzer. The experiments were carried out in a three-electrode cell with platinum electrode and glassy-carbon electrode as the working electrodes, a Ag/AgCl electrode saturated with KCl as the reference electrode. The supporting electrolyte is tetrabutylammonium perchlorate (tbap) recrystallized twice from ethanol and dried under vacuum. Pure nitrogen was insufflated in the solution of the compounds to remove oxygen. All electrochemical measurements were carried out at room temperature.

2.3. *Synthesis of (Z)-3-(5′-bromosalicylhydrazinocarbonyl) propenoic acid ((Z)-H_4bshcpa) (1)*

A solution of maleic anhydride (5.88 g, 60 mmol) in chloroform (150 mL) was slowly added to a solution of 5-bromosalicylhydrazide (11.55 g, 50 mmol) in chloroform (300 mL) at 0°C. The reaction mixture was warmed to boiling point and stirred for 5 h. After the resulting mixture was concentrated under reduced pressure, the residue was filtered and rinsed with ethanol. Yield: 89%; determination of the melting point of (*Z*)-H_4bshcpa shows that sublimation and oxidation occurred at 201°C; Calcd for $C_{11}H_9N_2O_5Br$ (%): C, 40.14; H, 2.76; N, 8.51. Found (%): C, 39.90; H, 2.66; N, 8.42. ^1H NMR (DMSO-d_6), δ ppm: 11.93 (bs, 1H; –PhOH), 10.83 (bs, 2H; –NH–NH–), 8.03 (s, 1H; *o*-PhCH), 7.61 (d, 1H; *p*-PhCH), 6.97 (d, 1H; *m*-PhCH), 6.38–6.47 (m, 2H; –CH=CH–); ^{13}C NMR (DMSO-d_6), δ ppm: 167.67 (–COOH), 164.08 (–CO–PA), 162.47 (Ph–CO–), 161.18 (PhC–OH), 136.95 ($_{\text{–NHCO}}$–CH=), 133.57 (*p*-PhC), 131.99 (*o*-PhC), 127.29 (=CH–$_{\text{COOH}}$), 120.21 (PhC–$_{\text{CO–}}$), 118.22 (*m*–PhC), 111.00 (PhC–Br); IR (KBr pellet, cm^{-1}): ν(O–H), 3174 s, broad; ν(N–H), 3060 s, broad; ν(C=O), 1722 s; ν(C=C), 1658 s; ν(C=N–C=N), 1604 s.

2.4. *Synthesis of $[Fe^{III}_6(C_{12}H_8N_2O_5Br)_6(H_2O)_2(CH_3OH)_4]\cdot 8H_2O\cdot 8CH_3OH$ (2)*

A mixture of $FeCl_3\cdot 6H_2O$ (3.24 g, 12 mmol) in methanol (20 mL) and (*Z*)-H_4bshcpa (3.29 g, 10 mmol) in methanol (150 mL) was stirred for 20 min. Pyridine (10 mmol) dissolved in methanol (10 mL) was then added. The resulting dark-brown solution was stirred for 2 h at 40°C, refluxed for 4 h, and filtered. After 7 days, black triclinic crystals deposited from the mother liquor. In the complex, **1** has been esterified and transferred into (*Z*)-methyl 3-(5′-bromosalicylhydrazinocarbonyl) propenoate ((*Z*)-H_3mbshcp) (**3**). Yield: 52%; Calcd for $C_{84}H_{116}N_{12}O_{52}Br_6Fe_6$ (%): C, 34.31; H, 3.98; N, 5.72; Fe, 11.40. Found (%): C, 34.08; H, 3.79; N, 5.48; Fe, 11.25. IR (KBr pellet, cm^{-1}): ν(HO–H), 3439 vs, broad; ν(OH), 3136 s, broad; ν(C=O), 1726 s; ν(C=C), 1649 s; ν(C=N–C=N), 1591 s.

2.5. *Preparation of (Z)-methyl 3-(5′-bromosalicylhydrazinocarbonyl) propenoate ((Z)-H_3mbshcp) (3)*

To obtain **3**, compound **2** is treated with $SnCl_2\cdot 2H_2O$. In the preparation, the resulting dark-brown solution formed by the reaction of ligand with $FeCl_3\cdot 6H_2O$ will be directly concentrated under reduced pressure to obtain the residue **2**.

A solution of $SnCl_2 \cdot 2H_2O$ (6.77 g, 30 mmol) in 6 mol L^{-1} HCl (50 mL) was added to the residue of **2** at 0°C. The resultant mixture was slowly warmed to 40°C, stirred for 4 h, and filtered. The resulting white precipitate was rinsed with 6 mol L^{-1} HCl and dried under vacuum to afford white solid. Yield: 88%; m.p. 172–174°C, determination of the melting point of (*Z*)-H_3mbshcp shows sublimation occurred at 168°C; Calcd for $C_{12}H_{11}N_2O_5Br$ (%): C, 42.00; H, 3.53; N, 8.17. Found (%): C, 41.89; H, 3.47; N, 8.08. ^{1}H NMR (DMSO-d_6), δ ppm: 12.00 (s, 1H; −PhOH), 10.98 (s, 1H; −PhCONH−), 10.77 (s, 1H; −NHCO−$_{CH2=}$), 8.04 (s, 1H; *o*-PhCH), 7.62 (d, 1H; *p*-PhCH), 7.09 (d, 1H; $_{-NHCO}$−CH=), 6.54 (d, 1H; *m*-PhCH), 6.44 (d, 1H; =CHCOO−), 3.68 (s, 3H; $-OCH_3$); ^{13}C NMR (DMSO-d_6), δ ppm: 166.95 (−COO−), 163.59 (−NHCO−$_{CH=}$), 161.28 (PhCO−), 157.20 (PhC−OH), 136.27 (*p*-PhC), 131.99 ($_{-NHCO}$−CH=), 131.35 (=CH−$_{COO-}$), 127.23 (*o*-PhC), 119.61 (PhC−$_{CO-}$), 117.59 (*m*-PhC), 110.32 (*m*-PhC−Br), 51.69 ($-OCH_3$); IR (KBr pellet, cm^{-1}): ν(O–H), 3230 s, broad; ν(N–H), 3174 s, broad; ν(C=O), 1729 s; ν(C=C), 1640 s; ν(C=N–C=N), 1596 vs.

2.6. *Preparation of methyl 3-(5′-bromosalicylhydrazinocarbonyl) propanoate (H_3mbshcp) (4)*

H_3mbshcp was synthesized similar to the synthesis procedure of **3**. Zinc powder (19.61 g, 300 mmol) was added to a solution of the residue of **2** in water (50 mL) at 0°C, and concentrated hydrochloric acid was added dropwise to the above solution with stirring. The resultant mixture was slowly warmed to 30°C and kept for 4 h. Compound **4** was extracted with ethyl acetate and the ethyl acetate extract was washed several times with 1 mol L^{-1} HCl, and evaporated under reduced pressure. The residue was dried under vacuum to afford white solid. Yield: 90%; m.p. 159–161°C. Calcd for $C_{12}H_{13}N_2O_5Br$ (%): C, 41.75; H, 3.80; N, 8.12. Found (%): C, 41.63; H, 3.64; N, 8.00. ^{1}H NMR (DMSO-d_6), δ ppm: 11.96 (s, 1H; −PhOH), 10.59 (s, 1H; −PhCONH−), 10.40 (s, 1H; −NHCO−$_{CH2-}$), 8.03 (s, 1H; *o*-PhCH), 7.58 (d, 1H; *p*-PhCH), 6.94 (d, 1H; *m*-PhCH), 3.61 (s, 3H; $-OCH_3$), 2.48−2.57 (m, 4H; $-CH_2CH_2-$); ^{13}C NMR (DMSO-d_6), δ ppm: 178.02 (−NHCO−$_{CH2-}$), 174.89 (−COO−), 170.09 (PhCO−), 163.08 (PhC−OH), 141.73 (*p*-PhC), 136.42 (*o*-PhC), 125.05 (PhC−$_{CO-}$), 122.61 (*m*-PhC), 115.59 (*m*-PhC − Br), 56.84 ($-OCH_3$), 33.83 ($_{-NHCO}$−CH_2−), 33.27 (−CH_2−$_{COO-}$); IR (KBr pellet, cm^{-1}): ν(O–H), 3290 s, broad; ν(N–H), 3222 s, broad; ν(C=O), 1728 s; ν(C=N–C=N), 1601 vs.

2.7. *X-ray crystal structure determination*

A crystal of **2** with dimensions 0.40 mm × 0.10 mm × 0.06 mm was mounted in a glass capillary with the mother liquor to prevent the loss of solvents during X-ray diffraction data collection. Intensity data were collected with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at 289(2) K on a Bruker Smart APEX diffractometer. From a total of 30,898 reflections corrected by SADABS [33, 34] in the $1.47 \leq \theta \leq 26.00$ range, 11,562 were independent with $R_{int} = 0.0548$, of which 10,719 observed reflections with $I > 2\sigma(I)$ were used in the structural analysis. The structure was solved using direct methods and standard difference map techniques and refined by full-matrix least-squares on F^2 with SHELXTL [34, 35]. All non-hydrogen atoms were refined anisotropically. Hydrogens were included in calculated positions and refined using a

Table 1. Crystallographic data.

Empirical formula	$C_{76}H_{68}Br_6Fe_6N_{12}O_{36}$
Formula weight	2539.93
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions (Å, °)	
a	13.551(2)
b	15.571(2)
c	16.423(3)
α	96.936(2)
β	107.235(3)
γ	112.733(3)
Volume (Å^3), Z	2941.7(8), 1
Calculated density (mg cm^{-3})	1.434
Absorption coefficient (mm^{-1})	2.830
F(000)	1262
Crystal size (mm^3)	0.40 × 0.10 × 0.06
θ range for data collection (°)	1.47–26.00
Limiting indices	$-16 \le h \le 15$; $-19 \le k \le 19$; $0 \le l \le 20$
Observed reflections	30,898
Independent reflections	11,562 [$R_{\text{int}} = 0.0548$]
R indices (all data)	$R_1{}^{a} = 0.0534$; $wR_2{}^{b} = 0.1584$
Goodness-of-fit on F^2	1.121

[a] $R_1 = \sum \| F_o | - | F_c \| / \sum | F_o |$.
[b] $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$.

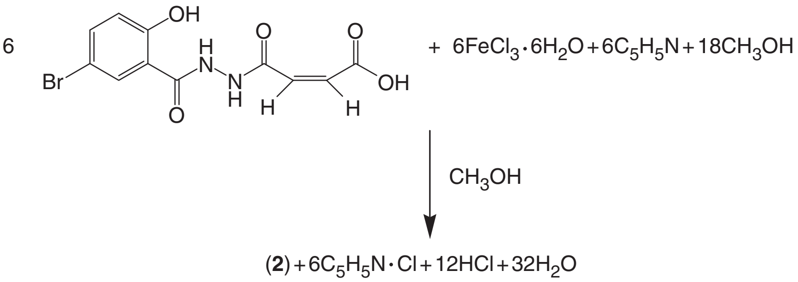
riding model. Problematic solvent disorder in **2** could not be modeled properly; thus, the contribution of the solvent to the diffraction pattern was subtracted from the observed data by the SQUEEZE method implemented in PLATON [36, 37]. The final refinement converged at $R_1 = 0.0534$, $wR_2 = 0.1584$ ($w = 1/[\sigma^2(F_o^2) + (0.0767P)^2 + 2.5839P]$, where $P = (F_o^2 + 2F_c^2)/3$) (for 11,562 unique reflections), $(\Delta/\sigma)\text{max} = 0.013$, $S = 1.121$, $(\Delta\rho)\text{max} = 0.608$ and $(\Delta\rho)\text{min} = -0.655$ e Å^{-3}. Crystal data and refinement details are presented in table 1.

3. Results and discussion

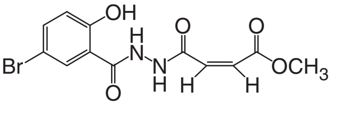
3.1. *Synthesis and characterization*

Iron metallacrown **2** was synthesized *via* the reaction of $FeCl_3 \cdot 6H_2O$ with (Z)-3-(5′-bromosalicylhydrazinocarbonyl) propenoic acid that has been prepared previously through direct reaction between 5-bromosalicylhydrazide [32] and maleic anhydride, in methanol + pyridine solution (scheme 2). Complex **2** was a dark-brown crystalline solid.

In **2**, compound **1** has been esterified and transferred into (Z)-H$_3$mbshcp (**3**, figure 1). The synthesis system plays an important role in the formation of the new ligand. Through the analysis of $[Fe^{III}_6(C_{12}H_8N_2O_5Br)_6(H_2O)_2(CH_3OH)_4] \cdot 8H_2O \cdot 8CH_3OH$, we deduce that the esterification of carboxylic acid with salicyl-bis-hydrazide is a new internal esterification by the metallacrown itself, defined as an internal self-catalytic reaction [38]. For the 18-MC-6 metallacrown $[Fe^{III}_6(C_{12}H_8N_2O_5Br)_6(H_2O)_2(CH_3OH)_4]$, the reactant is $[Fe^{III}_6(C_{10}H_5N_2O_3Br\text{–}COOH)_6(H_2O)_m(CH_3OH)_n]$ ($m = 1$–6, $n = 1$–6), which contains (Z)-H$_4$bshcpa with a carboxylic acid group. The carboxylic acid group



Scheme 2. Synthesis of iron metallacrown **2**.



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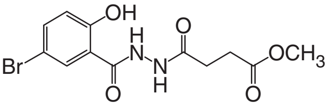

4

Figure 1. (*Z*)-H_3mbshcp (**3**) and H_3mbshcp (**4**).

can be combined with iron, then reacted with a coordinated methanol to produce ester (Z)-H_3mbshcp. Eventually $[Fe^{III}_6(C_{10}H_5N_2O_3Br–COOCH_3)_6(H_2O)_2(CH_3OH)_4]$ can be obtained by the internal self-catalytic reaction. In the catalytic reaction, iron can be identified as the catalytic center.

Metallacrown with esterified ligand was obtained by tuning the pH of reactant solution to control hydrolysis of metal ion and deprotonation of the esterified ligand, confirmed by the spectral characterization. In the IR spectra of **2**, the absence of the N–H stretching vibration is consistent with the deprotonation of the –NH–NH– group and coordination to Fe(III), which may indicate that (*Z*)-H_3mbshcp adopts the complete deprotonated (*Z*)-mbshcp^{3-} form. The C=N–N=C framework at 1604 cm^{-1} in the ligand shifted to 1591 cm^{-1} upon coordination to Fe. So the basic binding sites in **2** are similar to the previous reports [13], which is also consistent with the X-ray structural analysis.

CV suggests that **2** is electrochemically inactive in methanol in the range +1.5 to −1.5 V, consistent with the conclusion in the literature [10]. The absence of redox activity of the metallacrown indicates redox stability. The ligand stabilizes three iron ions in methanol.

3.2. *Isolation of (Z)-H_3mbshcp and H_3mbshcp*

To obtain (*Z*)-H_3mbshcp in high yield, the metallacrown is concentrated under reduced pressure. The residue is treated with $SnCl_2$ in hydrochloric acid and results in purified (*Z*)-H_3mbshcp.

The esterified ligand **3** is an ester with bis-hydrazide, which cannot be synthesized *via* a modular acid-catalyzed approach. The reaction between **1** and $FeCl_3$ is a self-assembly process, which yields an highly organized molecular architecture that allows efficient electron transfer and subsequent esterification. The yield was calculated on the basis of the starting ligand, giving metallacrown with ester in 98% yield.

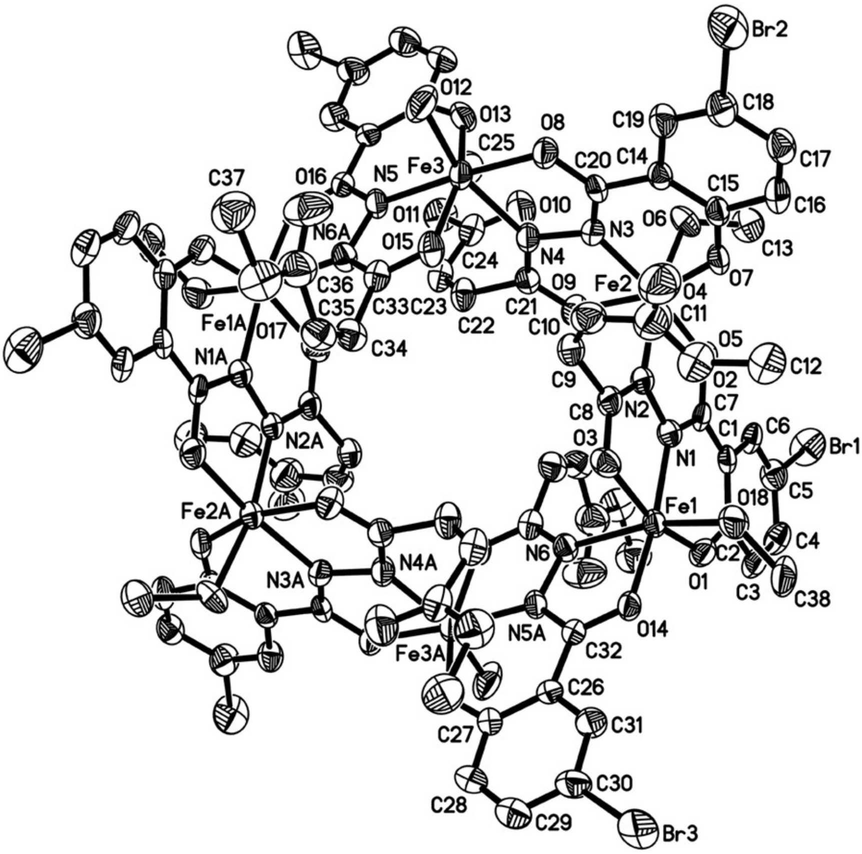

Figure 2. Perspective view of **2**, solvent molecules and all hydrogens have been omitted for clarity.

To obtain purified ester, the Fe^{III} metallacrown was reduced according to equation (1).

$$(\mathbf{2}) + SnCl_2 + HCl \rightarrow C_{12}H_{11}N_2O_5Br + FeCl_2 + SnCl_4 \qquad (1)$$

The Fe^{III} metallacrown can also be treated with Zn powder in a solution of hydrochloric acid according to equation (2), but ester **4** is significantly different to **3** in which the double bond C=C in was reduced to single bond C–C (figure 1).

$$(\mathbf{2}) + Zn + HCl \rightarrow C_{12}H_{13}N_2O_5Br + FeCl_2 + ZnCl_2 \qquad (2)$$

3.3. *Crystal structure of 2*

Complex **2** crystallizes in the triclinic system, space group *P*-1. A diagram of the crystal structure of **2** is presented in figure 2. The bond lengths and angles in **2** show normal values; important bond distances and angles are presented in table 2. The average iron–oxygen/nitrogen distance is Fe1 2.028 Å, Fe2 2.020 Å, and Fe3 2.024 Å.

The structure exhibits a hexanuclear ring of irons linked by six hydrazide N–N groups. The deprotonated (*Z*)-mbshcp^{3-} is a trianionic pentadentate ligand, one

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

Fe1–O1	1.887(3)	C2–O1	1.309(5)
Fe1–O14	1.992(2)	C7–N1	1.337(4)
Fe1–N1	2.050(3)	C7–O2	1.327(4)
Fe1–O3	2.056(3)	N1–N2	1.424(4)
Fe1–O18	2.063(3)	C8–O3	1.293(4)
Fe1–N6	2.120(3)	C8–N2	1.307(5)
Fe2–O7	1.895(3)	C11–O4	1.149(7)
Fe2–O2	1.995(2)	C11–O5	1.298(7)
Fe2–N3	2.021(3)	C15–O7	1.334(5)
Fe2–O9	2.050(3)	C20–N3	1.294(5)
Fe2–O6	2.066(3)	C20–O8	1.308(4)
Fe2–N2	2.093(3)	N3–N4	1.443(4)
Fe3–O13	1.898(3)	C21–N4	1.317(5)
Fe3–O8	1.994(3)	C21–O9	1.254(4)
Fe3–N5	2.001(3)	C24–O10	1.214(6)
Fe3–O15	2.051(3)	C24–O11	1.319(6)
Fe3–N4	2.099(3)	C32–O14	1.300(4)
Fe3–O12	2.103(3)	C36–O16	1.238(7)
O1–Fe1–O14	103.57(11)	O8–Fe3–N4	75.58(11)
O1–Fe1–N1	86.25(12)	N5–Fe3–N4	104.75(12)
O14–Fe1–N1	170.17(11)	O15–Fe3–N4	89.33(12)
O1–Fe1–O3	162.70(11)	O13–Fe3–O12	93.65(15)
O14–Fe1–O3	93.73(11)	O8–Fe3–O12	82.65(12)
N1–Fe1–O3	76.46(11)	N5–Fe3–O12	96.30(13)
O1–Fe1–O18	94.76(15)	O15–Fe3–O12	89.17(13)
O14–Fe1–O18	84.26(12)	N4–Fe3–O12	157.84(13)
N1–Fe1–O18	95.67(13)	C33–O15–Fe3	114.9(2)
O3–Fe1–O18	86.69(13)	O1–C2–C1	125.0(3)
O1–Fe1–N6	94.16(13)	O2–C7–N1	117.2(3)
O14–Fe1–N6	76.87(10)	N1–C7–C1	122.6(3)
N1–Fe1–N6	102.11(12)	C7–N1–N2	114.1(3)
O3–Fe1–N6	89.89(12)	C8–N2–N1	109.7(3)
O18–Fe1–N6	160.57(13)	O3–C8–N2	124.7(3)
O7–Fe2–O2	104.29(11)	N2–C8–C9	116.3(3)
O7–Fe2–N3	85.99(11)	C10–C9–C8	127.2(4)
O2–Fe2–N3	169.65(12)	C9–C10–C11	131.2(5)
O7–Fe2–O9	162.11(11)	O4–C11–O5	129.7(6)
O2–Fe2–O9	93.59(11)	O4–C11–C10	119.5(5)
N3–Fe2–O9	76.12(11)	C11–O5–C12	113.3(5)
O7–Fe2–O6	83.39(15)	O7–C15–C14	122.9(3)
O2–Fe2–O6	92.23(12)	N3–C20–O8	122.0(3)
N3–Fe2–O6	87.73(12)	N3–C20–C14	119.9(3)
O9–Fe2–O6	95.34(13)	C21–N4–N3	108.7(3)
O7–Fe2–N2	95.16(13)	O9–C21–N4	124.3(3)
O2–Fe2–N2	76.41(11)	N4–C21–C22	115.7(3)
N3–Fe2–N2	104.21(12)	C23–C22–C21	129.9(4)
O9–Fe2–N2	89.69(12)	C22–C23–C24	120.8(4)
O6–Fe2–N2	167.87(10)	O10–C24–O11	123.2(5)
O13–Fe3–O8	101.14(12)	O10–C24–C23	125.0(5)
O13–Fe3–N5	86.11(12)	C24–O11–C25	117.2(4)
O8–Fe3–N5	172.72(13)	O14–C32–C26	119.4(3)
O13–Fe3–O15	161.92(11)	O15–C33–C34	119.2(3)
O8–Fe3–O15	96.93(12)	O16–C36–O17	120.4(5)
N5–Fe3–O15	75.83(11)	O16–C36–C35	128.0(5)
O13–Fe3–N4	94.60(15)	C36–O17–C37	117.2(4)

phenolate oxygen, one carbonyl oxygen, and one hydrazide nitrogen bound to one Fe^{3+}; the other carbonyl oxygen plus the other hydrazide nitrogen in the same ligand are chelated to an adjacent Fe^{3+}. The specific connectivity of atoms forming the ring is –Fe1–N1–N2–Fe2–N3–N4–Fe3–N5–N6A–Fe1A–N1A–N2A–Fe2A–N3A–N4A–Fe3A–N5A–N6–. Therefore, the ligand is forcing all Fe^{3+} cations into a propeller configuration with alternating Λ/Δ stereochemistry as $\Lambda\Delta\Lambda$ forms (figure 2). Two methanol and one water coordinated at the metal centers with Λ configuration are found on one face of the metallacrown, and the remaining two methanols and one water coordinated to the Δ metal centers are found on the other face of the metallacrown. The six methyl acrylate groups were also on both sides of the ring with alternating forms. The two faces of the disc-shaped hexanuclear ring have opposite chiralities, resulting in the 18-membered hexanuclear core ring system with an [Fe–N–N] repeat unit. There are no solvent molecules in the "host" cavity of **2**. It is also observed that all irons in **2** are in an octahedral FeN_2O_4 environment, in which there is no Jahn–Teller distortion. The average neighboring $Fe\cdots Fe$ separation is 4.905 Å. A packing diagram in a unit cell is shown in figure S1. As can clearly be seen from figure S1, the molecules translating one unit cell along the *a* direction are stacked.

3.4. *Thermogravimetry*

The TG curve of **2** exhibits four weight losses with increasing temperature. From 41°C to 210°C, **2** loses 13.8% weight, assigned to loss of the outside solvents; from 210°C to 384°C, weight loss of 25.1% is ascribed to the loss of coordinated water and methanol and sublimation of the residue. To this temperature, all of the solvent molecules and coordinated small molecules are lost. From 384°C to 592°C, the weight loss is 38.9% from composition of (*Z*)-mbshcp^{3-}. From 592°C to 800°C, as the residue transformed into Fe_2O_3, the TG curve shows almost no change in weight.

3.5. *Magnetic properties*

The magnetic properties of polycrystalline samples of **2** are shown in figure 3 between 2 K and 300 K. The molar effective magnetic moment (μ_{eff}) shows the presence of an antiferromagnetic coupling between the Fe(III) spin 5/2 centers. For **2**, the effective magnetic moment steadily decreased as the temperature was lowered from 300 K ($\mu_{eff} = 13.18\mu_B$) to 65 K ($\mu_{eff} = 9.75\mu_B$) and then abruptly to reach $2.01\mu_B$ at 2.0 K. The value of μ_{eff} at 300 K is smaller than the expected value ($14.49\mu_B$) for six noninteracting Fe^{III} ($S = 5/2$). This is characteristic of antiferromagnetic coupling, which is confirmed by fitting to the Curie–Weiss law with $\theta = -22.4$ K using data from 65 K to 300 K. With lowering temperature, interactions among the iron cluster become obvious. At 2 K the moment μ_{eff} is $2.01\mu_B$.

4. Conclusion

We have synthesized a macrocyclic hexanuclear iron(III) 18-metallacrown-6 complex, $[Fe^{III}_6(C_{12}H_8N_2O_5Br)_6(H_2O)_2(CH_3OH)_4]\cdot 8H_2O\cdot 8CH_3OH$, using a heptadentate

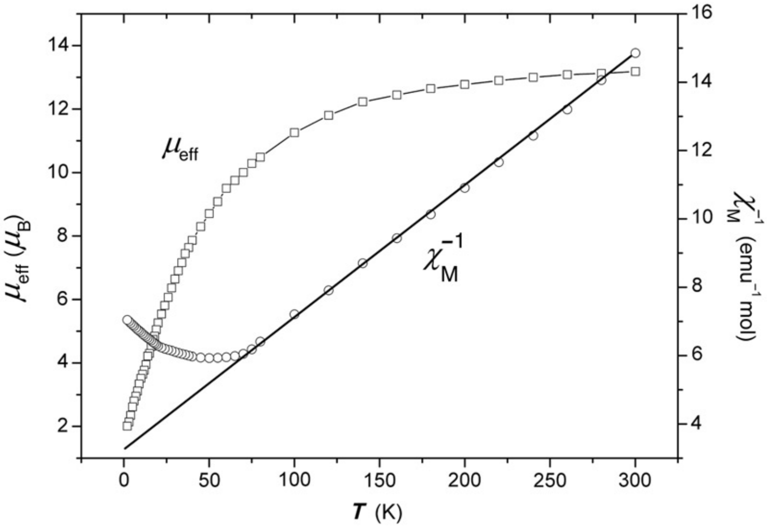

Figure 3. Plots of χ_M^{-1} (○), μ_{eff} (□) *vs.* *T* and fitting line of μ_{eff} (—) for **2**.

ligand, (*Z*)-3-(5′-bromosalicylhydrazinocarbonyl) propenoic acid. Single-crystal X-ray structure analysis of **2** showed that the neutral Fe(III) complex contains an 18-membered metallacrown ring consisting of six [Fe(III)–N–N] units. Due to the meridional coordination of the ligand to Fe^{3+}, the ligand enforces the stereochemistry of Fe^{3+} as a propeller configuration with alternating Λ/Δ forms. The other important structural features in **2** are that there is a vacant cavity in the center of 18-metallacrown-6 core ring and opposite chiralities on the two faces of the metallacrown ring system. In the self-assembly all ligands were esterified. The metallacrown can be treated with $SnCl_2$ to obtain purified ester. In addition, we have also obtained methyl 3-(5′-bromosalicylhydrazinocarbonyl) propanoate, with Zn powder.

Supplementary material

CCDC 679990 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 CB21EZ, UK; Fax: +44 1223 336 033; or Email: deposit@ccdc.cam.ac.uk).

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