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Esterification of the ligand: Synthesis, characterization and crystal structure of a iron(III) 18-metallacrown-6 complex with methyl 4-(5′-chlorosalicylhydrazinocarbonyl) butyrate

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ABSTRACT

The multidentate ligand, 4-(5′-chlorosalicylhydrazinocarbonyl) butyric acid, has been synthesized and reacted with $FeCl_3$ to produce the iron(III) 18-metallacrown-6 complex $[Fe^{III}_6(C_{13}H_{12}N_2O_5Cl)_6(CH_3OH)_6]\cdot 5CH_3OH$. In the complex the ligand 4-(5′-chlorosalicylhydrazinocarbonyl) butyric acid was esterified and transferred into methyl 4-(5′-chlorosalicylhydrazinocarbonyl) butyrate. In the crystal structure, the hexanuclear 18-membered rings of iron atoms are linked by six hydrazide N–N groups. The deprotonated and esterified ligand acts as a trianionic pentadentate ligand, one phenolate oxygen, one hydrazide nitrogen and one carbonyl oxygen in the ligand are bound to one Fe^{3+} cation, and the other carbonyl oxygen plus the other hydrazide nitrogen in the same ligand are chelated to an adjacent Fe^{3+} cation. In hydrochloric acid the metallacrown $[Fe^{III}_6(C_{13}H_{12}N_2O_5Cl)_6(CH_3OH)_6]\cdot 5CH_3OH$ can be treated with $SnCl_2$ to obtain purified ester methyl 4-(5′-chlorosalicylhydrazinocarbonyl) butyrate.

1. Introduction

Metallacrowns and its analogues have attracted considerable attention. In the structure, metallacrowns exhibit a cyclic hole generally analogous to crown ether with transition metal ions and nitrogen atoms replacing the methylene carbon atoms [1,2]. Metallacrowns [9-MC-3] [3], [12-MC-4] [4], [15-MC-5] [5,6], [12-MC-6] [7], [16-MC-8] [8], [18-MC-6] [9,10], [18-MC-8] [7], [24-MC-6] [11], [30-MC-10] [12], [36-MC-12] [13], [40-MC-10] [14], [60-MC-20] [15], stacking metallacrowns [16,17] as well as a variety of dimers and fused metallacrowns [18,19] have been reported.

Metallacrowns have been studied not only for their esthetic appeal but also for their potential functions. As a result of the presence of transition metal ions in the metallacrown ring, metallacrowns may be used as cation, anion, and molecular recognition agents; catalysts; building blocks for extended solids; magnetism; biologic agents and sensors [20–23]. Several copper-pyrazolate-based metallacrown systems show catalytic activity [24–27].

Taking the similarity between salicylhydrazides and carboxylic acids with salicyl-bis-hydrazide into account, we have expanded the types of precursor ligand with the intention of catalyzing esterification. We have previously shown that propenoic acids with salicyl-bis-hydrazide can be translated to esters in self-assembly process of the iron 18-MC-6 metallacrowns $[Fe^{III}_6(C_{12}H_9N_2O_5)_6(H_2O)_2(CH_3OH)_4]$ and $[Fe^{III}_6(C_{12}H_8N_2O_5Cl)_6(H_2O)_4(CH_3OH)_2]$ [28,29]. In this paper we report a new esterification of 4-(5′-chlorosalicylhydrazinocarbonyl) butyric acid (H_4cshcba) (**2**) via metallacrowns and the synthesis, characterization and crystal structure of iron(III) 18-MC-6 metallacrown $[Fe^{III}_6(C_{13}H_{12}N_2O_5Cl)_6(CH_3OH)_6]\cdot 5CH_3OH$ (**3**) (Scheme 1).

2. Experimental

2.1. Chemicals

Chemicals for the synthesis of compounds were used as purchased. Methanol, ethanol and chloroform were used without any further purification. 5-Chlorosalicylic acid, sulfuric acid, hydrochloric acid, hydrazine hydrate, glutaric anhydride, pyridine, $FeCl_3\cdot 6H_2O$ and $SnCl_2\cdot 2H_2O$ were purchased from China Sinopharm Group Chemical Reagent Co., Ltd. All chemicals and solvents were reagent grade. 5-Chlorosalicylhydrazide was prepared according to literature procedures [30].

2.2. Characterization

C, H and N elemental analysis were performed on a Perkin Elmer 2400 Series II CHNS/O Analyzer. Fe was determined by atomic absorption spectroscopy on a Shimadzu AA-6300 Spectrophotom-

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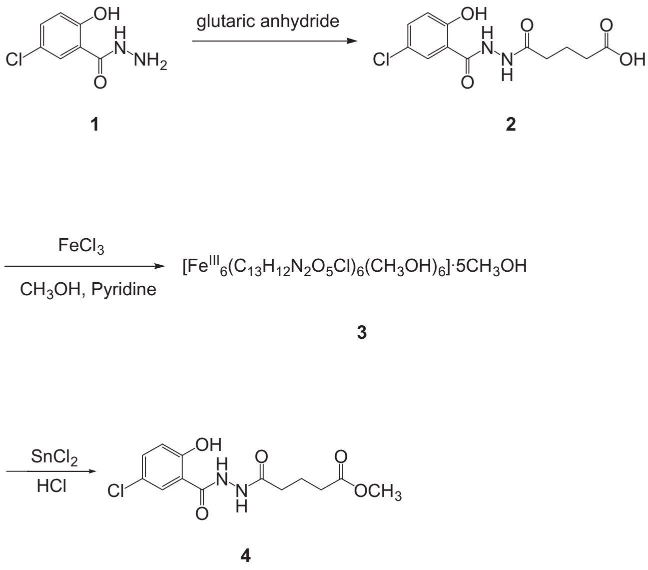

Scheme 1. Synthetic routes and chemical structures of the compounds.

eter. Melting points were obtained using a digital melting-point apparatus, TP Micro Printer S-X6. Infrared spectra were recorded on a Thermo Nicolet Corporation NEXUS 470 FT-IR Spectrometer in the 4000–400 cm^{-1} region, using KBr pellet. UV–Vis spectra were recorded on a Perkin Elmer Lambda 35 UV–Vis Spectrometer. ^{1}H NMR and ^{13}C NMR spectra measurements were performed on a Avance *III* 400 MHz NMR spectrometer at 25 °C, operating at 400 MHz in 5 mm tubes. Chemical shifts were referenced to residual solvent peak. Thermogravimetry (TG) carried out on Perkin–Elmer Diamond DSC TG-DTA 6300 thermal analyzer. Variable-temperature dc magnetic susceptibility data were collected on the polycrystalline samples over a 2–300 K temperature range at 1 KOe under zero field cooled conditions using a Quantum Design SQUID MPMS XL-7 magnetometer.

2.3. Synthesis of 4-(5′-chlorosalicylhydrazinocarbonyl) butyric acid (H_4cshcba) (**2**)

A solution of glutaric anhydride (2.80 g, 0.024 mol) in chloroform (50 mL) was slowly added to a solution of 5-chlorosalicylhydrazide (3.73 g, 0.02 mol) in chloroform (50 mL) at 0 °C. The reaction mixture was warmed to boiling point and stirred for 5 h. Then the mixture was filtered and rinsed with ethanol. Yield: 86%; m.p. 247–248 °C; Cal. for $C_{12}H_{13}N_2O_5Cl$: C 47.92, H 4.36, N 9.31; Found: C 47.88, H 4.38, N 9.36; ^{1}H NMR(DMSO-d_6), δ ppm: 11.94 (bs, 1H; –PhOH), 10.54 (s, 1H; –PhCONH–), 10.26 (s, 1H; PhCONH–NH), 7.90 (s, 1H; *o*-PhCH), 7.49–7.46 (d, 1H; *p*-PhCH), 7.01–6.99 (d, 1H; *m*-PhCH), 2.31–2.24 (m, 4H; $-CH_2-CH_2-CH_2-$), 1.80–1.76 (m, 2H; $-CH_2-CH_2COOH$); ^{13}C NMR (DMSO-d_6), δ ppm: 174.59 (–COOH), 170.89 ($-NHCO-CH_2-$), 165.46 (–PhCONH–), 157.75 (–PhCOH), 133.95 (*p*-PhC), 128.43 (*o*-PhC), 123.21 (*m*-PhC-Cl), 119.67 (–PhC–CO–), 117.04(*m*-PhC), 33.23 ($-NHCO-CH_2-$), 32.68 ($-CH_2-COOH$), 20.87 ($-CH_2-CH_2COOH$); IR (KBr pellet, cm^{-1}): νOCO–H, 3301 s, broad; νO–H, 3190 versus broad; νN–H, 2974 s, broad; νO–H, 2638 s, broad; νC=O, 1701 versus; νC=N–C=N, 1601 versus; ν(C–OH)$_{phenolic}$, 1218 s, 1115 s.

2.4. Synthesis of $[Fe^{III}_6(C_{13}H_{12}N_2O_5Cl)_6(CH_3OH)_6]\cdot 5CH_3OH$ (**3**)

A mixture of **2** (3.00 g, 10 mmol) in methanol (100 mL) and $FeCl_3\cdot 6H_2O$ (3.24 g, 12 mmol) in methanol (20 mL) was stirred for 20 min. Then pyridine (10 mmol) dissolved in methanol (10 mL) was added. The resulting dark brown solution was stirred for 2 h at 40 °C and refluxed for 4 h, and filtered. After 7 days, black crystals were deposited from the mother liquor. In the complex **3** the ligand **2** has been esterified and transferred into methyl 4-(5′-chlorosalicylhydrazinocarbonyl) butyrate (H_3mcshcb) (**4**). Yield: 41%; Cal. For $C_{89}H_{116}Cl_6Fe_6N_{12}O_{41}$: C 41.79, H 4.57, N 6.57, Fe 13.10; Found: C 41.62, H 4.39, N 6.62, Fe 13.22. IR (KBr pellet, cm^{-1}): νOH, 3187 versus broad; νC=O, 1729 s; νC=N–C=N, 1608 versus; ν(Fe–O)$_{phenolic}$, 449%.

2.5. Preparation of methyl 4-(5′-chlorosalicylhydrazinocarbonyl) butyrate (H_3mcshcb) (**4**)

To obtain **4**, the solution of **3** was directly concentrated under reduced pressure. Then a solution of $SnCl_2\cdot 2H_2O$ (6.77 g, 30 mmol) in 3 mol L^{-1} HCl (50 mL) was added to the residue of **3** at 0 °C. The resultant mixture was slowly warmed to 30 °C and stirred for 4 h, and filtered. The resulting white precipitate was rinsed with 2 mol L^{-1} HCl, and dried under vacuum to afford white solid compound **4**. Yield: 47%; m.p. 207–208 °C; Cal. for $C_{13}H_{15}ClN_2O_5$: C 49.60, H 4.80, N 8.90; Found: C 49.51, H 4.63, N 8.81; ^{1}H NMR (DMSO-d_6), δ ppm: 11.94 (s, 1H; –PhOH), 10.54 (s, 1H; –PhCONH–), 10.27 (s, 1H; $-NHCO-CH_2-$), 7.90 (s, 1H; *o*-PhCH), 7.48–7.46 (d, 1H; *p*-PhCH), 7.01–6.99 (d, 1H; *m*-PhCH), 3.60 (s, 3H; $-OCH_3$), 2.31–2.24 (m, 4H, $-CH_2-CH_2-CH_2-$), 1.79–1.82 (m, 2H; CH_2-CH_2COOH); ^{13}C NMR (DMSO-d_6), δ ppm: 174.57 ($-NHCO-CH_2$), 170.89 (–COO–), 165.49 (–PhCO–), 157.78 (–PhC–OH), 133.94 (*p*-PhC), 128.43 (*o*-PhC), 123.22 (*m*-PhC-Cl), 119.67 (–PhC–CO–), 117.03 (*m*-PhC), 49.05 ($-OCH_3$), 33.25 ($-NHCO-CH_2-$), 32.70 ($-CH_2-COOCH_3$), 20.89 ($-CH_2-CH_2COOH$); IR (KBr pellet, cm^{-1}): νO–H, 3191 s, broad; νN–H, 2946 s, broad; νC=O, 1729 s; νC=N–C=N, 1605 versus; ν(C–OH)$_{phenolic}$, 1216 s, 1182 s.

2.6. X-ray crystal structure determination

A black crystal of the complex **3** with approximate dimensions of 0.30 × 0.06 × 0.05 mm^3 was placed on a Bruker Smart APEX diffractometer. Intensity data were collected with a graphite monochromatic Mo Kα radiation (λ = 0.71073 Å) at 123(2) K. From a total of 37800 reflections corrected by SADABS [31,32] in the $1.93 \le \theta \le 25.50$ range, 20319 were independent with R_{int} = 0.0523, of which 13638 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 was refined by full-matrix least-squares procedures on F^2 with SHELXTL program package [32]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in calculated positions and were refined using a riding model. The final refinement converged at $R_1 = 0.0417$, $wR_2 = 0.1274$ ($w = 1/[\sigma^2(Fo^2)+(0.0260)^2 + 0.6771P]$, where $P = (Fo^2 + 2Fc^2)/3$) (for 20319 unique reflections), (Δ/σ)max = 0.006, $S = 1.161$, $(\Delta\rho)$max = 0.855 and $(\Delta\rho)$min = -0.612 e/Å^3. Crystal data and refinement details are presented in Table 1.

3. Results and discussion

3.1. Synthesis of iron(III) metallacrown **3**

The metallacrown **3** was synthesized via the reaction of $FeCl_3\cdot 6H_2O$ with the ligand 4-(5′-chlorosalicylhydrazinocarbonyl) butyric acid which has been prepared previously by a procedure through a direct reaction between 5-chlorosalicylhydrazide and glutaric anhydride, in the methanol + pyridine solution (Scheme 2). The complex **3** is black crystalline solid.

Table 1
Crystallographic data.

Empirical formula	$C_{89}H_{116}Cl_6Fe_6N_{12}O_{41}$
Formula weight	2557.74
Crystal system	triclinic
Space group	$P\bar{1}$
a (Å)	14.482(3)
b (Å)	14.772(3)
c (Å)	27.064(5)
α (°)	85.460(3)
β (°)	89.074(3)
γ (°)	73.162(3)
V (Å^3)	5524.2(19)
Z	2
D_{calc} (g/cm^3)	1.538
μ (mm^{-1})	1.002
$F(000)$	2640
Crystal size (mm)	0.30 × 0.06 × 0.05
θ range (°)	1.93–25.50
Index ranges	$-13 \le h \le 17$ $-17 \le k \le 17$ $-32 \le l \le 32$
Observed reflections	37800
Independent reflections (R_{int})	20319 (0.0523)
R_1[a]	0.0417
wR_2[b]	0.1274
Goodness-of-fit	1.161

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$.

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

In iron(III) metallacrown **3**, the ligand 4-(5′-chlorosalicylhydrazinocarbonyl) butyric acid has been esterified and transferred into H_3mcshcb (**4**, Chart 1). The synthesis system play an important role in the formation of new ligand. Through the analysis of the reaction system $[Fe^{III}_6(C_{13}H_{12}N_2O_5Cl)_6(CH_3OH)_6]\cdot 5CH_3OH$, we deduce that the esterification of carboxylic acid with salicylbis-hydrazide is a new internal esterification by metallacrown itself, which are defined as an internal self-catalytic reaction [33]. For the 18-MC-6 iron(III) metallacrown, $[Fe^{III}_6(C_{13}H_{12}N_2O_5Cl)_6(CH_3OH)_6]$, in the internal self-catalytic reaction, the reactant is $[Fe^{III}_6(C_{11}H_9N_2O_3Cl\text{–}COOH)_6(H_2O)_m(CH_3OH)_n]$ ($m = 1$–6, $n = 1$–6) which contains the mainly ligand 4-(5′-chlorosalicylhydrazinocarbonyl) butyric acid with a carboxylic acid group –COOH. The carboxylic acid group can be combined with iron, then reacted with a activity coordination of methanol to produce ester. Eventually the product $[Fe^{III}_6(C_{11}H_9N_2O_3Cl\text{–}COOCH_3)_6(CH_3OH)_6]$ was obtained by the internal self-catalytic reaction. In the catalytic reaction the iron can be identified as the catalytic center.

3.2. Isolation of H_3mcshcb

To obtain the ester methyl 4-(5′-chlorosalicylhydrazinocarbonyl) butyrate, we have treated the metallacrown **3** with $SnCl_2$ in hydrochloric acid (Eq. (1)). The reduction takes place and leads to separate into methyl 4-(5′-chlorosalicylhydrazinocarbonyl) butyrate and reduced Fe^{3+}. In the process of preparation, to obtain ester with good-yield, the resulting dark brown solution that had been formed by the reaction of ligand **2** with Fe^{3+} will be directly concentrated under reduced pressure to obtain the residue of **3**. This is a solid material that is formed by complete evaporation of the solvent which was used for the reaction between **2** and iron(III) chloride to make **3**, before any attempt is made to crystallise **3**.

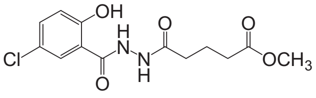
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Chart 1. H_3mcshcb (**4**).

$$[Fe^{III}_6(C_{13}H_{12}N_2O_5Cl)_6(CH_3OH)_6]\cdot 5CH_3OH + SnCl_2 + HCl \rightarrow C_{13}H_{15}ClN_2O_5 + FeCl_2 + SnCl_4 + CH_3OH \quad (1)$$

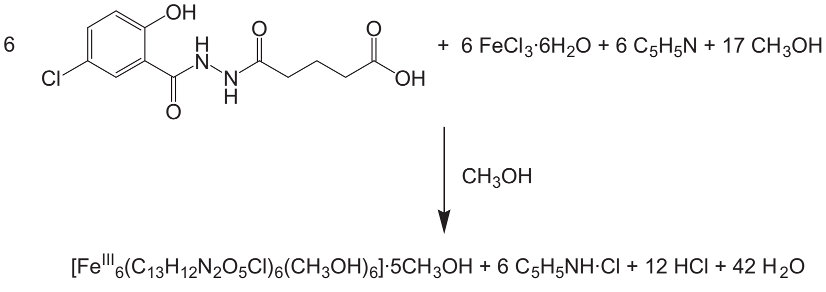
3.3. Characterization

In the IR spectra, the ligand **2** shows stretching bands attributed to C=O, C=N, C–OH (phenolic) and N–H at 1701, 1601, 1218 and 1115, and 2974 cm^{-1}, respectively [34]. Bands at 3301, 3190 and 2638 cm^{-1} are assigned to νO–H vibrations which may be involving intramolecular hydrogen bonding, while bands at 1218 and 1115 cm^{-1} are attributed to νO–H (phenolic) [35,36]. In addition, a strong band found at 1601 cm^{-1} is assigned to C=N–N=C group [34–36].

The IR spectra of the esterified ligand **4** are similar to **2**. The stretching bands attributed to C=O, C=N, C–OH (phenolic) and N–H at 1729, 1605, 1216 and 1182, and 2946 cm^{-1}, respectively. Band at 3191 cm^{-1} is assigned to νO–H vibration with intramolecular hydrogen bonding. The strong band at 1605 cm^{-1} is assigned to C=N–N=C group.

In the complex **3**, 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 Fe(III) ion. The broad band at 3187 cm^{-1} is reasonably assigned to OH stretching vibration which is attributable to coordinated methanol molecules. The C=N–N=C framework seen at l605 cm^{-1} in the ligand **4** shifted to 1608 cm^{-1} upon coordination to Fe(III) ion. The appearance of the band at 449 cm^{-1} supports the involvement of phenolic oxygen in coordination through deprotonation (Fe–O, phenolic). The biding sites in **3** are similar to previously reports [9], which is also consistent with the X-ray structural analysis.

The ^{1}H NMR of the ligand **2** presents a multiplet in the range δ 1.80–1.76 for the methylene protons with a group –CH_2COOH; a multiplet in the range δ 2.31–2.24 for the methylene protons with group –NHCO– and –COOH, respectively; a doublet in the range δ 7.01–6.99 for the phenyl proton 3-PhCH; a doublet in the range δ



Scheme 2. Synthetic route and chemical structures of the iron(III) metallacrown **3**.

7.49–7.46 for the phenyl proton 4-PhCH; a singlet at δ 7.90 for the phenyl proton 6-PhCH; two singlet at δ 10.54 and 10.26 for the hydrazine protons; a singlet at δ 11.94 for the phenolic hydroxyl group proton. In the ^{13}C NMR spectra of the ligand **2**, five peaks between 110 ppm and 140 ppm are possible, concluded to be the five isolated carbon of phenyl ring, in addition to one carbon is concluded in the range of 150–160 ppm. Three methylene carbons fall into the 20–40 ppm, the three carbonyl carbons are judged in the 165–175 ppm region. All these assignments are in good agreement with the spectra obtained.

For the esterified ligand **4**, the assignments of ^{1}H NMR and ^{13}C NMR are similar to **2**, except methyl group. The methyl protons of **4** present a singlet at δ 3.60 in the ^{1}H NMR spectra. Its methyl carbon present a peak at 49.05 ppm in the ^{13}C NMR.

Table 2
Selected bond lengths (Å) and angles (°) in **3**.

Bond lengths			
Fe1–N1	2.097(7)	Fe4–N8	2.061(7)
Fe1–O6	2.002(6)	Fe4–O25	2.078(7)
Fe2–N4	2.035(6)	Fe5–N10	2.047(7)
Fe2–O10	2.043(6)	Fe5–O28	2.027(7)
Fe3–N6	2.038(7)	Fe6–N12	2.038(8)
Fe3–O15	2.046(6)	Fe6–O33	2.043(6)
Bond angles			
O1–Fe1–O6	100.9(2)	O19–Fe4–N7	94.8(3)
O1–Fe1–N1	93.9(3)	O24–Fe4–O21	91.4(2)
O8–Fe2–N4	86.8(2)	O20–Fe5–O28	92.5(3)
O2–Fe2–O10	93.7(2)	N10–Fe5–O31	92.6(3)
O9–Fe3–O15	94.6(2)	O32–Fe6–N12	86.2(3)
O15–Fe3–N5	87.9(2)	O32–Fe6–O36	91.0(2)

3.4. Crystal structure of 3

The iron(III) metallacrown **3** crystallizes in the triclinic system and space group $P\bar{1}$. The molecular structure of **3** is shown in Fig. 1. Important bond distances and angles are presented in Table 2. In ring 1 and 2, the two hexanuclear 18-membered rings of iron atoms are linked by six hydrazide N–N groups, respectively. The deprotonated and esterified ligand H$_3$mcshcb acts as a trianionic pentadentate ligand, one phenolate oxygen, one hydrazide nitrogen and one carbonyl oxygen in the ligand are bound to one Fe^{3+} cation, and the other carbonyl oxygen plus the other hydrazide nitrogen in the same ligand are chelated to an adjacent Fe^{3+} cation. The alternation of the connection that forced the cyclic ring system of **3** to form as following trains: ring 1, –N1–Fe1–N2–N3–Fe2–N4–N5–Fe3–N6–N1A–Fe1A–N2A–N3A–Fe2A–N4A–N5A–Fe3A–N6A–; and ring 2, ndash;N7–Fe4–N8–N9–Fe5–N10–N11–Fe6–N12–N7A–Fe4A–N8A–N9A–Fe5A–N10A–N11A–Fe6A–N12A–. All the iron atoms of the rings adopt distorted octahedron coordination geometry of the FeN$_2$O$_4$ type. The chirality of the metal centers in complex **3** are between the Λ and Δ forms. As can clearly be seen from the structure of **3**, all ligands have been esterified and transferred into H$_3$mcshcb. The average iron–oxygen/nitrogen distance is Fe1 2.034, Fe2 2.030, Fe3 2.037, Fe4 2.028, Fe5 2.033, and Fe6 2.034 Å, respectively. Owing to the d^5 high-spin electronic configuration of the iron(III) ion, there is no Jahn–Teller distortion in the FeN$_2$O$_4$ octahedron. The approximate dimensions of the oval-shaped cavity are about 10.12 Å for ring 1, and 10.07 Å for ring 2, at largest diameter at the center of the hole. The neighboring Fe···Fe interatomic distances in the 18-membered rings are 4.882–4.920 Å. There are not any solvent molecules in the 'host' hole of metallcrown **3**. At the same time, there are many kinds of intermolecular hydrogen bonds in **3**. These O–H···O hydrogen bond distances range between 2.610(8) and 2.874(8) Å. The hydrogen bonds in the crystal structure not only can form interesting architectures, but also fix dexterously the solvent molecules and carbomethoxy-group avoiding badly disorder.

3.5. Thermogravimetry

The TG curve of **3** exhibits four steps of weight losses with the increasing temperature. From 30 to 134 °C, the weight loss was 9.5%, it is assigned to loss of the outside solvents and the sublimation of the residue; from 134 to 420 °C, 44.4% of weight was lost, which contributed to the loss of coordinated methanol molecules, and the sublimation of the residue. From 420 to 608 °C, the TG curve descended equably, and the weight loss is 29.0%. The weight loss in this area should be deposition of the ligand mcshcb^{3-}. From 608 to 800 °C, there was no change in the spare weight.

3.6. Magnetic property

The magnetic property of powder **3**, obtained between 2 and 300 K using a Quantum Design SQUID MPMS XL-7 magnetometer, is shown in Fig. 2. For the iron(III) metallacrown **3**, the molar effective magnetic moment (μ_{eff}) shows the presence of an antiferromagnetic coupling between the Fe(III) spin 5/2 centers. The effective magnetic moment steadily decreased as the temperature

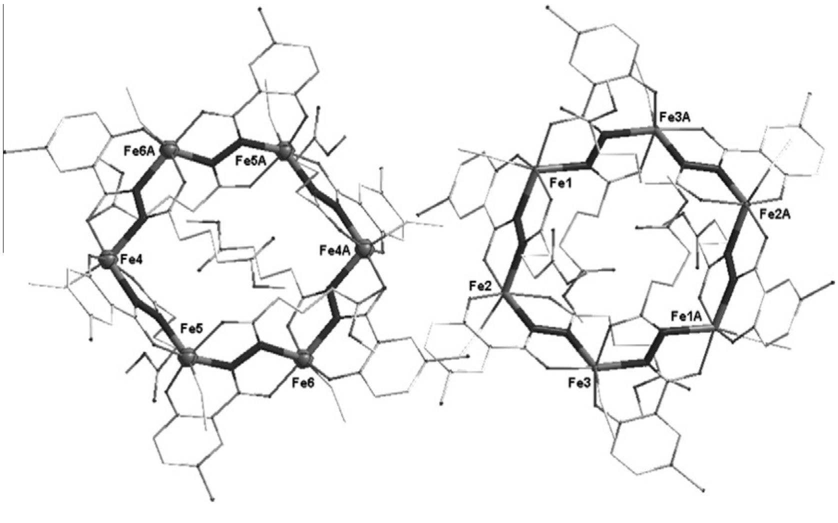


Fig. 1. Perspective view of **3** (solvent molecules and all hydrogen atoms have been omitted for clarity).

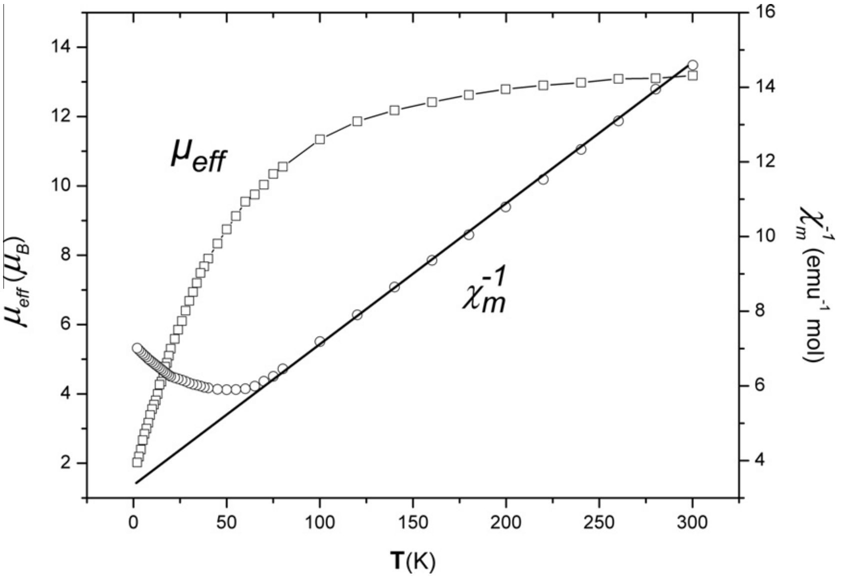


Fig. 2. Plots of χ_m^{-1} (○), μ_{eff} (□) vs. T and fitting line of μ_{eff} (–) for the iron(III) metallacrown **3**.

was lowered from 300 K (μ_{eff} = 13.22 μ_B) to 65 K (μ_{eff} = 9.75 μ_B) and then abruptly to reach 2.01 μ_B at 2.0 K (Fig. 2). The value of μ_{eff} at 300 K is smaller than the expected value (14.49 μ_B) for six noninteracting Fe^{III} ($S = 5/2$). This is a characteristic of antiferromagnetic coupling, which is confirmed by a fitting to the Curie–Weiss law with $\theta = -20.5$ K using the data within $T > 65$ K. With the lowering temperature, the interaction among the iron cluster becomes obvious. While the temperature cools to 2 K the moment μ_{eff} is 2.01 μ_B.

Below about 65 K, the magnetic measurements deviate significantly from the Curie–Weiss law suggesting that a magnetic model considering the various internal magnetic pathways within the Fe6 cluster should be analyzed to describe the low temperature data. The magnetic behavior of **3** might be due to a combination of the following causes, when taking the inverse center symmetry into account: (i) exchange interaction between the neighboring iron ions bridged by the hydrazide N–N groups; (ii) exchange interaction between the near-neighboring iron ions; (iii) exchange interaction between the para-neighboring iron ions; (iv) zero field splitting (ZFS) of the ground state of Fe^{III}. The equation describing the temperature dependence of the magnetic susceptibility must contain the following parameters: g, J_1 (exchange interaction between the neighboring iron ions); J_2 (exchange interaction between the near-neighboring iron ions); J_3 (exchange interaction between the para-neighboring iron ions); D (ZFS parameter for the iron(III) ions). The modeling of the magnetic based data upon such an equation is not reliable because overparametrization.

4. Conclusion

In conclusion, we have developed a novel macrocyclic hexanuclear iron(III) 18-metallacrown-6 complex, $[Fe^{III}_6(C_{13}H_{12}N_2O_5Cl)_6(CH_3OH)_6]\cdot 5CH_3OH$ (**3**), using heptadentate ligand 4-(5′-chlorosalicylhydrazinocarbonyl) butyric acid (H_4cshcba) (**2**) and characterized by X-ray diffraction. In the self-assembly process H_4cshcba was esterified and transferred into 4-(5′-chlorosalicylhydrazinocarbonyl) butyrate (H_3mcshcb) (**4**). In the crystal structure of **3**, there are two 18-membered metallacrown rings consisting of six Fe(III) and six trianionic ligands. In ring 1 and 2, the iron atoms are linked by six hydrazide N–N groups, respectively. The deprotonated and esterified ligand H_3mcshcb acts as a trianionic pentadentate ligand, one phenolate oxygen, one hydrazide nitrogen and one carbonyl oxygen in the ligand are bound to one Fe^{3+} cation, and the other carbonyl oxygen plus the other hydrazide nitrogen in the same ligand are chelated to an adjacent Fe^{3+} cation.

The metallacrown **3** can be further treated with $SnCl_2$ to obtain purified ester 4-(5′-chlorosalicylhydrazinocarbonyl) butyrate. The reduction takes place in hydrochloric acid and results in methyl 4-(5′-chlorosalicylhydrazinocarbonyl) butyrate and Fe^{2+}. H_3mcshcb is a special class of ester with bis-hydrazide. To our knowledge, this class of ester can not be synthesized via a modular acid-catalyzed approach.

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Appendix A. Supplementary material

CCDC 774695 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. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2011.10.021.

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