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ORIGINAL PAPER

# Synthesis, structural characterization, and magnetic properties of the metallamacrocycle $[Fe_6(C_{11}H_{11}N_2O_3)_6(C_4H_9NO)_6]$

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**Abstract** The 18-metallacrown-6 metallamacrocycle $[Fe_6(pmshz)_6(C_4H_9NO)_6]$ has been synthesized by the self-assembly reaction of iron ions with *N*-substituted salicylhydrazide ligands. Six Fe(III) ions and six deprotonated *N*-propanoyl-4-methylsalicylhydrazide ($H_3$ pmshz) ligands construct a planar 18-membered ring based on Fe–N–N–Fe linkage. Because of the coordination, the ligand enforces the stereochemistry of the Fe(III) ions as a propeller shape with alternating …ΔΛΔΛ… configurations. There is a strong antiferromagnetic exchange interaction between the paramagnetic iron centers.

**Keywords** Metallamacrocycle · Iron complexes · Synthesis · Magnetic properties

## Introduction

Metallamacrocycles have become important in recent years because of their diverse molecular architectures [1–3], their utilization as motifs for coordination networks [4–8], and their potential as host systems in various guest-recognition chemistries [9–15]. A variety of metallamacrocycles and cages have been found to form interesting host–guest systems with different metal ions of varying coordination and symmetry [16]. High nuclearity metal clusters and metallamacrocycles containing copper [5, 17], nickel [18, 19], and platinum [20–23] have increased interest in the engineering of large structures containing various metals. Metal ions such as Ga, Co, Fe, and Mn, which can easily form stable octahedral coordination, are found to yield hexanuclear metallamacrocycles with trianionic pentadentate ligands [24–26]. However manganese and iron have received special attention because of their ease of formation of metallamacrocycles and their interesting magnetic properties [27–30]. In this paper, we report a new potential pentadentate ligand *N*-propanoyl-4-methylsalicylhydrazide 18-metallacrown-6 compound, $[Fe_6(C_{11}H_{11}N_2O_3)_6(C_4H_9NO)_6]$ (**1**).

## Results and discussion

### *Infrared spectrum*

In the IR spectrum, the ligand contains bands at 1,668, 1,632, and 3,285 $cm^{-1}$ attributed to stretch vibrations of 2 C=O and N–H, respectively. Bands at 3,418 $cm^{-1}$ are assigned to O–H vibrations which may involve intramolecular hydrogen bonding. In the title compound, 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 disappearance of the band at 3,418 $cm^{-1}$ and the appearance of bands at 1,350 and 1,239 $cm^{-1}$ support the involvement of phenolic oxygen in coordination through deprotonation. The deprotonation and coordination are also confirmed by the band at 668 $cm^{-1}$, attributed to M–O linkages (phenolic and enolic oxygen), and the band at 559 $cm^{-1}$ assigned to M–N linkages [26, 31].

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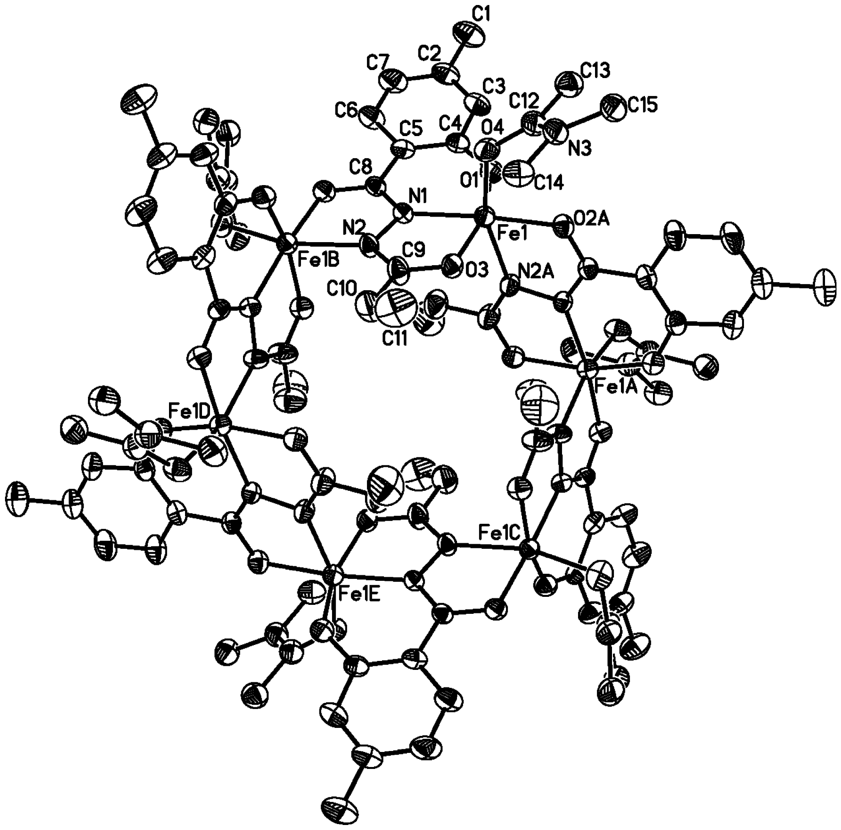


**Fig. 1** Molecular structure of compound **1** with atom labeling. All hydrogen atoms have been omitted for clarity

*Structure*

The title compound **1** crystallizes in the rhombohedral system with space group R-3. The molecular structure of compound **1** is shown in Fig. 1. Important bond distances and bond angles are presented in Table 1. The structure has a hexanuclear ring of iron atoms linked by six hydrazide N–N groups. The deprotonated ligand pmshz$^{3-}$ acts as a trianionic pentadentate bridging ligand and coordinates to Fe(III) cations via three oxygen atoms and two hydrazine nitrogen atoms (Scheme 1). One phenolate oxygen atom, O1, one carbonyl oxygen atom, O3, and one hydrazide nitrogen, N1, of the ligand are bound to one Fe(III) cation, and the other carbonyl oxygen atom, O2, and the other hydrazide nitrogen atom, N2, in the same ligand are chelated to an adjacent Fe(III) cation, and all the atoms in the ligand are almost coplanar. The ligand therefore enables the propeller configuration of all the Fe(III) cations in alternating Λ and Δ stereochemistry.

**Table 1** Selected bond distances (Å) and angles (°) of the title compound

| | | | | | |
|---|---|---|---|---|---|
| Fe1$^{\#1}$–O1 | 1.918(4) | Fe1$^{\#1}$–O2$^{\#2}$ | 2.021(3) | Fe1$^{\#1}$–O3 | 2.045(4) |
| Fe1$^{\#1}$–N1 | 2.045(4) | Fe1$^{\#1}$–O4 | 2.050(4) | Fe1$^{\#1}$–N2$^{\#2}$ | 2.107(4) |
| N1–N2 | 1.420(5) | | | | |

| | | | |
|---|---|---|---|
| O1–Fe1–O2$^{\#2}$ | 102.65(15) | O1–Fe1–O3 | 162.63(15) |
| O2$^{\#2}$–Fe1–O3 | 94.65(14) | O1–Fe1–N1 | 86.55(15) |
| O2$^{\#2}$–Fe1–N1 | 170.74(14) | O3–Fe1–N1 | 76.18(14) |
| O1–Fe1–O4 | 92.81(17) | O2$^{\#2}$–Fe1–O4 | 83.25(14) |
| O3–Fe1–O4 | 90.63(17) | N1–Fe1–O4 | 95.41(15) |
| O1–Fe1–N2$^{\#2}$ | 93.15(17) | O2$^{\#2}$–Fe1–N2$^{\#2}$ | 76.08(14) |
| O3–Fe1–N2$^{\#2}$ | 89.58(17) | N1–Fe1–N2$^{\#2}$ | 104.74(15) |
| O4–Fe1–N2$^{\#2}$ | 159.28(16) | | |

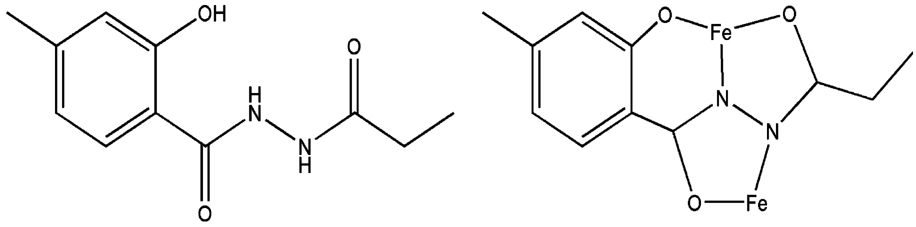
Symmetry codes: #1 $= x - y, x, -z + 1$, #2 $= y, -x + y, -z + 1$

All iron atoms are in a distorted octahedral FeN$_2$O$_4$ environment. The average neighboring Fe–Fe interatomic distance is 4.915 Å. The average Fe–Fe–Fe inter-atomic angle is 115.094°. The interatomic distance of N1–N2 in the 18-membered core ring is 1.420(5) Å. The approximate dimensions of the oval-shaped cavity in the molecule of the title compound are 4.66 Å in diameter at the entrance, approximately 9.642 Å at its largest diameter, and approximately 7.499 Å in depth.

*Magnetic study*

The magnetic behavior of the title compound was studied in the temperature range 2–300 K. The plot of $\chi_m T$ versus $T$ is shown in Fig. 2, the value of $\chi_m T$ of **1** decreased slightly with decreasing temperature from 21.76 $\mu_B$ at

**Scheme 1**



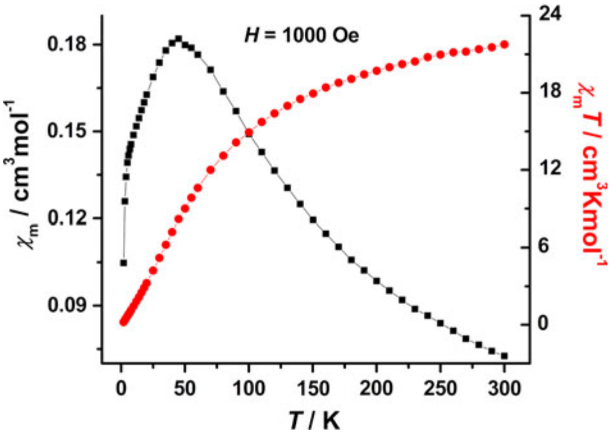


**Fig. 2** Plots of $\chi_mT$, $\chi_m$ versus temperature ($T$) from 2 to 300 K for complex **1**

300 K to 8.19 $\mu_B$ at 45 K. Below 45 K, it rapidly decreased to 0.21 $\mu_B$ at 2 K.

A simple model that only considers the intracluster exchange based on the nature of the exchange pathways was used in **1** of the Fe(III) hexamer (Fig. 1). The data above 2 K were simulated by use of Magpack [32] and an exchange Hamiltonian of the form $H = J_1S_1S_2$. The best fits obtained by use of this computing model are $J_1 = -2.1\ \mathrm{cm}^{-1}$, $D = 0\ \mathrm{cm}^{-1}$, and $g = 2.1$. The negative $J$ value suggests a pronounced intra-hexameric antiferromagnetic interaction between the Fe(III) ions through the bridging modes. As expected by consideration of the magneto-structural correlation of **1**, three kinds of magnetic pathways, all containing a hydroxyl group, can be considered. For the $\mu_3$-OH group in **1**, the interaction is predicted to be antiferromagnetic, with the long distances of Fe···Fe (4.915 Å). Concerning the zero-field splitting, a $D$ value of zero is logically possible [33] and consistent with the distorted octahedral coordination environment of Fe(III) ions in **1**. Obviously, the intra-hexamer magnetic interaction for **1** is almost completely compensated, and then contributions to the bulky magnetic behavior are insignificant [34], a feature common to most polynuclear iron complexes.

In summary, we designed an effective ligand H$_3$pmshz to prepare a metallamacrocyclic iron compound [Fe$_6$(pmshz)$_6$(C$_4$H$_9$NO)$_6$]. It crystallizes in the rhombohedral system with space group R-3. All metal atoms in the ring adopt a propeller configuration, and have alternating Λ and Δ configurations. The magnetic properties of the metallacrown molecules suggest a pronounced intra-hexameric antiferromagnetic interaction between the Fe(III) ions in the cyclic system.

## Experimental

### *Materials*

All reactions were carried out in air. Methanol (MeOH), ethanol (EtOH), *N*,*N*-dimethylformamide (DMF), *N*,*N*-dimethylacetamide (DMA), 4-methylsalicylic acid, acetic anhydride, benzene, sulfuric acid, hydrazine hydrate, sodium carbonate, and FeCl$_3$·6H$_2$O were purchased from China Sinopharm Chemical Reagent, and used as received with no further purification. All chemicals and solvents were reagent-grade.

### *Physical measurements*

$^1$H NMR spectra were recorded on a Bruker 400 MHz NMR spectrometer at room temperature. Chemical shifts were referenced to the residual solvent peak. Elemental analyses were recorded on a PE2400II elemental analyzer and basically agreed with calculated values. Infrared spectra were recorded from KBr pellets in the range 4,000–400 cm$^{-1}$ on a Shimazu FTIR-8900 spectrometer at room temperature. Variable-temperature magnetic susceptibility measurements were carried out on powdered samples in the 3–300 K temperature range, using a Quantum Design SQUID susceptometer in a 0.1 and 1.0 kg applied magnetic field.

### *2-Hydroxy-4-methylbenzoic acid 2-propanoylhydrazide* (H$_3$pmshz, C$_{11}$H$_{14}$N$_2$O$_3$)

The ligand was synthesized by reacting 2.60 g propionic anhydride (20.0 mmol) with 3.10 g 4-methylsalicylhyrazide (18.0 mmol) in 20 cm$^3$ DMF at 0 °C. The reaction mixture was stirred for 3 h and slowly warmed to room temperature. After leaving overnight in a refrigerator, the resulting white precipitate was isolated by filtration and rinsed with chloroform and diethyl ether. Yield: 90%; m.p.: 206–207 °C; IR: $\bar{\nu} = 1,668$ (C=O), 1,632 (C=O), 3,285

**Table 2** The crystallographic data for complex **1**

| | |
|---|---|
| Empirical formula | $C_{90}H_{120}Fe_6N_{18}O_{24}$ |
| FW (amu) | 2,173.12 |
| $T$ (K) | 295(2) |
| Crystal system, Space group | Hexagonal, R-3 |
| $a$ (Å) | 25.416(4) |
| $b$ (Å) | 25.416(4) |
| $c$ (Å) | 14.663(3) |
| $\alpha$ (°) | 90.00 |
| $\beta$ (°) | 90.00 |
| $\gamma$ (°) | 120.00 |
| V (Å$^3$) | 8,203(2) |
| $Z$, $D_{calcd}$ (g cm$^{-3}$) | 3, 1.287 |
| $F$(000) | 3,240 |
| $\mu$ (mm$^{-1}$) | 0.847 |
| Crystal size (mm$^3$) | 0.44 × 0.30 × 0.22 |
| No. of data/restraints/parameters | 25,534/4,121/3,109 |
| No. of reflections [$I > 2\sigma(I)$] | 4,119 |
| Goodness-of-fit on $F^2$ | 1.004 |
| Final $R$ indices [$I > 2\sigma(I)$] | $R_1 = 0.0703$[a] |
| $R$ indices (all data) | $wR_2 = 0.2296$[b] |

[a] $R_1(F) = \sum||F_o| - |F_c||/\sum|F_o|$

[b] $wR_2(F2) = \left[\sum w\left(F_o^2 - F_c^2\right)^2 / \sum w\left(F_o^2\right)^2\right]^{1/2}$, $w = 1/\left[\sigma^2\left(F_o^2\right) + (0.1200P)^2 + 18.3337P\right], P = \left(F_o^2 + 2F_c^2\right)/3$

(N–H), 3,418 (O–H) cm$^{-1}$; $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta = 12.04$ (s, 1H, Ph-OH), 10.16 (d, 2H, NH), 7.84–7.82 (d, 2H, Ph), 6.87–6.81 (s, 1H, Ph), 2.31 (s, 3H, Ph–CH$_3$), 2.27 (q, 2H, CH$_2$), 1.13 (t, 3H, –CH$_3$) ppm; $^{13}$C NMR (100.6 MHz, DMSO-$d_6$): $\delta = 171.77$ (Et–CO–NH–), 167.10 (Ar–CO–NH–), 159.33 (*o*–ArC–OH), 144.61 (*p*–ArC), 127.96 (*o*–ArC), 120.02 (*m*–ArC), 117.43 (–ArC), 111.55 (*m*–ArC), 26.38 (–CH$_2$–Me), 21.09 (Ar–CH$_3$), 9.62 (–CH$_3$) ppm.

*Hexa-μ-[2-(hydroxy-κO)-4-methylbenzoic acid-κO 2-propanoylhydrazidato(3-)-κN$^1$,κO:κN$^2$]hexa(N,N-dimethylacetamido)hexairon* (**1**, $Fe_6(C_{11}H_{11}N_2O_3)_6(C_4H_9NO)_6$) $H_3$pmshz (0.0222 g, 0.10 mmol) was dissolved in 10 cm$^3$ DMA, and 0.0270 g $FeCl_3 \cdot 6H_2O$ (0.10 mmol) was dissolved in 10 cm$^3$ DMF in another flask. The two solutions were mixed and stirred. Black block crystals suitable for X-ray diffraction were obtained after slow evaporation. Yield: 59%; IR: $\bar{\nu} = 1,350$ (C–O), 1,239 (C–O), 668 (Fe–O), 559 (Fe–N) cm$^{-1}$.

### *Crystallographic data collection and refinement of* ***1***

The crystals of **1** were mounted in glass capillaries with the mother liquid to prevent loss of the structural solvent molecules during X-ray diffraction data collection. Intensity data were collected at 295(2) K with graphite monochromatic MoK$\alpha$ radiation ($\lambda = 0.71073$ Å) on a Rigaku R-AXIS RAPID diffractometer. The structure was solved by direct methods and all non-hydrogen atoms were refined with anisotropic thermal data. All hydrogen atoms were located in calculated positions or in the positions from difference Fourier map. The positions and anisotropy from differences of non-hydrogen atoms were refined on $F^2$ by full-matrix least-squares techniques with the SHELXTL program package [35, 36]. The final refinement converged at $R_1 = 0.0703$, $wR_2 = 0.2296$. Details of the crystallographic data are given in Table 2. CCDC 747547 contains supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/date_request/cif.

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