

## 基于 2-[1-(2-羟基乙亚胺基)乙基]苯酚的六核铁(III) 配合物的合成、晶体结构、热稳定性及抗菌活性研究

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**摘要:** 利用三齿席夫碱配体 2-[1-(2-羟基乙亚胺基)乙基]苯酚( $H_2L$ )和二氰氨钠与氯化铁在甲醇中反应, 制备了一个新的具有中心对称性的六核铁(III)配合物 $[NaFe_6L_6(MeO)_6]Cl$ 。通过利用元素分析、红外光谱和 X-射线单晶衍射表征了该配合物的结构。配合物的晶体以三斜晶系  $P\bar{1}$  空间群结晶, 其晶体学参数  $a=1.162\ 5(2)\ nm$ ,  $b=1.396\ 4(2)\ nm$ ,  $c=1.504\ 2(2)\ nm$ ,  $\alpha=66.154(7)^\circ$ ,  $\beta=68.809(7)^\circ$ ,  $\gamma=73.296(7)^\circ$ ,  $V=2.053\ 6(5)\ nm^3$ ,  $Z=1$ ,  $R_1=0.059\ 3$ ,  $wR_2=0.156\ 4$ 。本文还研究了该配合物的热稳定性和抗菌活性。

**关键词:** 合成; 晶体结构; 铁(III)配合物; 席夫碱; 热稳定性; 抗菌活性

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## Synthesis, Crystal Structure, Thermal Stability, and Antimicrobial Activity of a Hexanuclear Iron(III) Complex Derived from 2-[1-(2-Hydroxyethylimino)ethyl]phenol

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**Abstract:** A new centrosymmetric hexanuclear iron(III) complex  $[NaFe_6L_6(MeO)_6]Cl$  has been synthesized from the tridentate Schiff base ligand 2-[1-(2-hydroxyethylimino)ethyl]phenol ( $H_2L$ ) and sodium dicyanamide with iron(III) chloride in methanol. The complex was characterized by elemental analyses, infrared spectroscopy, and X-ray single crystal determination. The crystal of the complex crystallizes as triclinic space group  $P\bar{1}$ , with  $a=1.162\ 5(2)\ nm$ ,  $b=1.396\ 4(2)\ nm$ ,  $c=1.504\ 2(2)\ nm$ ,  $\alpha=66.154(7)^\circ$ ,  $\beta=68.809(7)^\circ$ ,  $\gamma=73.296(7)^\circ$ ,  $V=2.053\ 6(5)\ nm^3$ ,  $Z=1$ ,  $R_1=0.059\ 3$ ,  $wR_2=0.156\ 4$ . Thermal stability and antimicrobial activity of the complex were studied. CCDC: 889111.

**Key words:** synthesis; crystal structure; iron complex; Schiff base; thermal stability; antimicrobial activity

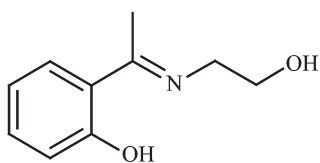
Transition metal complexes containing Schiff bases have been widely investigated due to their versatile structures<sup>[1-4]</sup> and biological applications<sup>[5-7]</sup>. Design, synthesis, and characterization of iron complexes with multi-dentate ligands are important in bioinorganic, material chemistry, and catalytic chemistry due to their importance as synthetic models for iron-containing enzymes<sup>[9]</sup>, and molecule-based magnetic materials<sup>[10-12]</sup>. Among the complexes, those

with high-nuclearity are of particular interest for their structures and magnetic properties<sup>[13-15]</sup>. 2-[1-(2-Hydroxyethylimino)ethyl]phenol ( $H_2L$ ; Scheme 1) is a tridentate Schiff base ligand. Up to now, only a tetranuclear copper(II) complex<sup>[16]</sup> and two polynuclear iron(III) complexes<sup>[12,17]</sup> have been reported with  $H_2L$ . The Fe atoms in the two iron complexes were bridged by acetate ligands. Recent research indicated that deprotonated methanol molecule is a potential

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Scheme 1 Schiff base ligand H<sub>2</sub>L

bridging ligand<sup>[18]</sup>. As a continuation of work on polynuclear iron(III) complexes with H<sub>2</sub>L, in this paper, a new methoxide-bridged hexanuclear iron(III) complex [NaFe<sub>6</sub>L<sub>6</sub>(MeO)<sub>6</sub>]Cl was prepared and structurally characterized.

## 1 Experimental

### 1.1 General methods and materials

2-Acetylphenol and 2-aminoethanol were purchased from Lancaster and used as received. All other chemicals with AR grade were obtained from Beijing Chemical Reagent Company. H<sub>2</sub>L was synthesized according to the literature method<sup>[19]</sup>. Elemental analyses for C, H and N were performed on a Perkin-Elmer 240C elemental analyzer. IR spectra were recorded on a Nicolet AVATAR 360 spectrometer as KBr pellets in the 4 000~400 cm<sup>-1</sup> region. Thermal stability analysis was performed on a Perkin-Elmer Pyris Diamond TG-DTA thermal analyses system.

### 1.2 Synthesis of the iron complex

A methanolic solution (10 mL) of FeCl<sub>3</sub> (1.0

mmol, 0.16 g) was added with stirring to a methanolic solution (10 mL) of H<sub>2</sub>L (1.0 mmol, 0.18 g) and sodium dicyanamide (1.0 mmol, 0.09 g). The mixture was stirred at room temperature for 30 min to give a deep red solution. After keeping the solution in air for a few days, red block-shaped crystals of the complex, suitable for X-ray crystal determination, were formed at the bottom of the vessel on slow evaporation of the solvent. The crystals were isolated, washed three times with methanol and dried in air. Yield: 45 %. Anal. Calcd. for C<sub>66</sub>H<sub>84</sub>ClFe<sub>6</sub>N<sub>6</sub>NaO<sub>18</sub> (%): C, 48.2; H, 5.2; N, 5.1. Found (%): C, 48.4; H, 5.1; N, 5.0 %. IR data (cm<sup>-1</sup>): 3 058 (w), 2 922 (w), 2 869 (w), 2 812 (w), 1 599 (vs), 1 541 (m), 1 440 (s), 1 323 (m), 1 233 (m), 1 162 (w), 1 135 (w), 1 067 (m), 923 (w), 876 (w), 849 (w), 755 (m), 583 (w), 466 (w), 420 (w).

### 1.3 Crystal structure determination

Diffraction intensities for the complex were collected at 298(2) K using a Bruker SMART Apex II CCD area detector with Mo K $\alpha$  radiation ( $\lambda$ =0.071 073 nm). Collected data were reduced using SAINT program<sup>[20]</sup>, and multi-scan absorption corrections were performed using SADABS program<sup>[21]</sup>. The structure of the complex was solved by direct method and refined against  $F^2$  by full-matrix least-squares method using SHELXTL package<sup>[22]</sup>. All of the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were

Table 1 Crystal data for the complex

Formula	C <sub>66</sub> H <sub>84</sub> ClFe <sub>6</sub> N <sub>6</sub> NaO <sub>18</sub>	Z	1
Mr	1642.9	$D_c / (\text{g} \cdot \text{cm}^{-3})$	1.328
$T / \text{K}$	298(2)	$\mu / \text{mm}^{-1}$	1.132
Radiation (Mo K $\alpha$ ), $\lambda / \text{nm}$	0.071 073	F(000)	850
Crystal shape / color	Block/red	Index range ( $h, k, l$ )	-14/13, -16/16, -15/18
Crystal size / mm	0.17×0.15×0.15	Measured reflections	10 951
Crystal system	Triclinic	Unique reflections ( $R_{\text{int}}$ )	7 445 (0.024 3)
Space group	$P\bar{1}$	Observed reflections ( $I > 2\sigma(I)$ )	4 590
$a / \text{nm}$	1.162 5(2)	Absorption correction	Multi-scan
$b / \text{nm}$	1.396 4(2)	Min. and max. transmission	0.831 / 0.848
$c / \text{nm}$	1.504 2(2)	Data / restraints / parameters	7 445 / 12 / 463
$\alpha / (^\circ)$	66.154(7)	Goodness-of-fit on $F^2$	1.029
$\beta / (^\circ)$	68.809(7)	$R_1, wR_2 (I > 2\sigma(I))^a$	0.059 3, 0.156 4
$\gamma / (^\circ)$	73.296(7)	$R_1, wR_2 (\text{all data})^a$	0.109 7, 0.195 2
$V / \text{nm}^3$	2.053 6(5)		

<sup>a</sup>  $R_1 = F_o - F_c / F_o$ ,  $wR_2 = [w(F_o^2 - F_c^2) / w(F_o^2)]^{1/2}$ .

**Table 2** Selected bond lengths (nm) and angles (°) for the complex

Fe1-O1	0.189 0(4)	Fe1-O2	0.203 9(4)	Fe1-O6A	0.203 7(4)
Fe1-O7	0.201 6(4)	Fe1-O9A	0.204 4(4)	Fe1-N1	0.214 4(5)
Fe2-O2	0.205 4(4)	Fe2-O3	0.188 3(4)	Fe2-O4	0.201 9(4)
Fe2-O7	0.202 7(4)	Fe2-O8	0.200 9(4)	Fe2-N2	0.215 7(5)
Fe3-O5	0.189 3(4)	Fe3-O8	0.202 2(4)	Fe3-O9	0.199 4(4)
Fe3-O6	0.205 1(3)	Fe3-O4	0.205 2(4)	Fe3-N3	0.212 5(5)
Na1-O4	0.229 8(3)	Na1-O6	0.232 1(4)	Na1-O2	0.235 0(4)
O1-Fe1-O7	93.6(2)	O1-Fe1-O6A	103.8(2)	O7-Fe1-O6A	90.8(2)
O1-Fe1-O2	159.9(2)	O7-Fe1-O2	75.7(1)	O6-Fe1-O2A	93.4(1)
O1-Fe1-O9A	99.6(2)	O7-Fe1-O9A	162.8(2)	O2-Fe1-O9A	94.6(2)
O1-Fe1-N1	86.6(2)	O7-Fe1-N1	102.4(2)	O6-Fe1-N1A	162.8(2)
O2-Fe1-N1	79.4(2)	O9-Fe1-N1A	89.6(2)	O3-Fe2-O8	97.2(2)
O3-Fe2-O4	161.1(2)	O8-Fe2-O4	76.6(2)	O3-Fe2-O7	95.4(2)
O8-Fe2-O7	162.1(2)	O4-Fe2-O7	95.1(2)	O3-Fe2-O2	105.4(2)
O8-Fe2-O2	89.2(2)	O4-Fe2-O2	92.5(1)	O7-Fe2-O2	75.2(1)
O3-Fe2-N2	85.9(2)	O8-Fe2-N2	98.5(2)	O4-Fe2-N2	77.6(2)
O7-Fe2-N2	95.1(2)	O2-Fe2-N2	165.6(2)	O5-Fe3-O9	98.1(2)
O5-Fe3-O8	95.2(2)	O9-Fe3-O8	162.4(2)	O5-Fe3-O6	162.2(2)
O9-Fe3-O6	76.1(2)	O8-Fe3-O6	94.3(2)	O5-Fe3-O4	104.6(2)
O9-Fe3-O4	90.0(2)	O8-Fe3-O4	75.6(2)	O6-Fe3-O4	92.3(2)
O5-Fe3-N3	86.4(2)	O9-Fe3-N3	97.6(2)	O8-Fe3-N3	94.6(2)
O6-Fe3-N3	77.8(2)	O4-Fe3-N3	165.7(2)	O4-Na1-O4A	180
O4-Na1-O6A	100.4(1)	O4-Na1-O6	79.6(1)	O6-Na1-O6A	180
O4-Na1-O2A	101.5(1)	O6-Na1-O2A	78.5(1)	O4-Na1-O2	78.8(1)
O6-Na1-O2	101.2(1)	O2-Na1-O2A	180		

Symmetry code for A:  $-x, 1-y, 1-z$ .

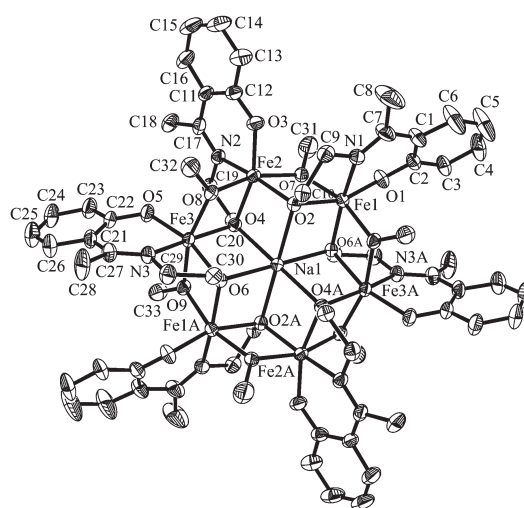
placed in geometrically ideal positions and constrained to ride on their parent atoms. Crystallographic data for the complex are summarized in Table 1. Selected bond lengths and angles are given in Table 2.

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## 2 Results and discussion

### 2.1 Structure description of the complex

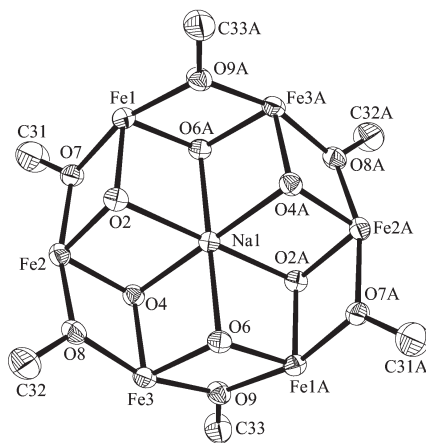
Fig.1 gives a perspective view of the complex together with the atomic labeling system. The asymmetric unit of the compound contains a centrosymmetric hexanuclear iron(III) complex cation with a Na atom located at the inversion center, and a disordered Cl anion. The central Na atom is coordinated by six deprotonated hydroxy O atoms from six different but symmetry related Schiff base ligands, forming an octahedral coordination. The Na-O bond



Displacement ellipsoids are drawn at the 30% probability level; H atoms and the disordered chloride anions are omitted for clarity; Atoms labeled with the suffix A or unlabeled are at the symmetry position  $-x, 1-y, 1-z$

**Fig.1** Molecular structure of the complex

lengths are comparable to those observed in complexes bearing  $\text{NaO}_6$  coordination<sup>[23-24]</sup>. The six Fe atoms are bridged by six methoxide ligands and six deprotonated hydroxy groups, forming a rim (Fig.2). The  $\text{Fe}\cdots\text{Fe}$  and  $\text{Fe}\cdots\text{Na}$  distances are in the ranges 0.318 4(1)~0.321 7(1) and 0.319 5(1)~0.320 7(1) nm, respectively. Each Fe atom on the rim is coordinated by two O atoms and one N atom from a Schiff base ligand, one hydroxy O atom from another Schiff base ligand, and two O atoms from two methoxide bridges. The bond lengths of  $\text{Fe-O(N)}$  are in the range of 0.188 3(4)~0.235 0(4) nm, which are similar to those observed in iron complexes with Schiff bases<sup>[13-15]</sup>. The oxidation states of all Fe centers are +3 based on the charge-balance consideration.



Atoms labeled with the suffix A are at the symmetry position  $-x, 1-y, 1-z$

Fig.2 Methoxide and hydroxy-bridged hexanuclear iron core with a sodium center

## 2.2 IR spectra

IR spectra of Schiff base  $\text{H}_2\text{L}$  and the complex provide information about the metal-ligand bonding. The strong absorption band at 1 613  $\text{cm}^{-1}$  for  $\text{H}_2\text{L}$  is assigned to the azomethine groups,  $\nu(\text{C}=\text{N})$ <sup>[25]</sup>. The band is shifted to lower wave number at 1 699  $\text{cm}^{-1}$  in the complex, what can be attributed to the coordination of the nitrogen atom of the azomethine group to the metal atom. The phenolic  $\nu(\text{Ar-O})$  in the free ligand exhibits strong band at 1 239  $\text{cm}^{-1}$ <sup>[26]</sup>. However, in the complex, the band appears at 1 233  $\text{cm}^{-1}$ , which may be assigned to the skeletal vibrations related to the phenolic oxygen of the Schiff base ligand<sup>[27]</sup>. Other

weak bands in the region 420~590  $\text{cm}^{-1}$  for the complex may be assigned to  $\nu(\text{Fe-O})$  and  $\nu(\text{Fe-N})$ <sup>[28]</sup>.

## 2.3 Thermal stability

Differential thermal (DT) and thermal gravimetric analyses (TGA) were conducted to examine the stability of the complex (Fig.3). The decomposition of the complex was started at about 115  $^{\circ}\text{C}$  and was completed at about 490  $^{\circ}\text{C}$ . The final residue is a mixture of  $\text{Fe}_2\text{O}_3$  and  $\text{Na}_2\text{CO}_3$ . The total weight loss of 69.3% is close to the calculated value (67.7%).

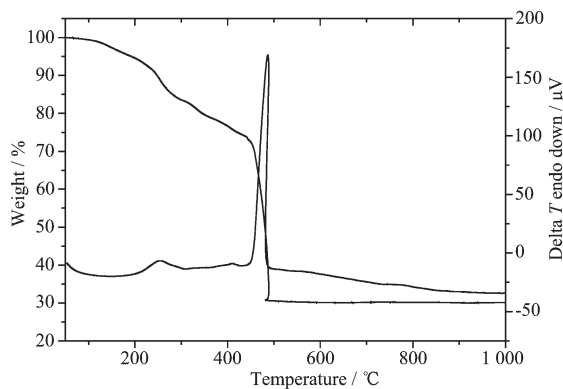


Fig.3 DT-TGA curve of the complex

## 2.4 Antimicrobial activity

Antimicrobial assay was carried out as that described in our previous work<sup>[29]</sup>. The free Schiff base ligand and the complex were screened for antibacterial activity against two Gram (+) bacterial strains (*Bacillus subtilis* and *Staphylococcus aureus*) and two Gram (-) bacterial strains (*Escherichia coli* and *Pseudomonas fluorescence*) by MTT method. The MIC (minimum inhibitory concentration) values of the compounds against four bacteria are listed in Table 3. Kanamycin and Penicillin G were used as standard drugs. The free Schiff base  $\text{H}_2\text{L}$  showed from weak to moderate activities against the four bacterial strains. In general, the complex showed stronger activities against the four bacteria strains than the free Schiff base. The complex showed the most effective activity against *B. subtilis* and *S. aureus*. The antifungal activities of the complex were also evaluated against two fungal strains (*Candida albicans* and *Aspergillus niger*) by MTT method (Table 3). Ketoconazole was used as a standard drug. It is notable that the complex showed weak activity against *A. niger*, which

Table 3 MIC values of H<sub>2</sub>L and the complex

Tested material	(mol·L <sup>-1</sup> )					
	<i>B. subtilis</i>	<i>S. aureus</i>	<i>E. coli</i>	<i>P. fluorescence</i>	<i>C. albicans</i>	<i>A. niger</i>
Complex	4.7	4.7	9.4	18.8	>150	37.5
H <sub>2</sub> L	18.8	37.5	37.5	75	>150	>150
Kanamycin	0.59	2.3	4.7	4.7	>150	>150
Penicillin G	2.3	4.7	>150	>150	>150	>150
Ketoconazole	>150	>150	>150	>150	4.7	18.8

has seldom observed in our previous work on Schiff base complexes.

### 3 Conclusions

In summary, a new centrosymmetric methoxide-bridged hexanuclear iron(III) complex with a sodium center derived from 2-[1-(2-hydroxyethylimino)ethyl]phenol was prepared and structurally characterized. The Schiff base ligand coordinates to the Fe atom through phenolate O, imine N and hydroxyl O atoms. Thermal stability and preliminary antimicrobial activity of the complex were presented. The complex may be used as interesting high-nuclearity magnetic material, which deserves further investigation.

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