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A Hetero Trinuclear Manganese(III)-Iron(II) Complex Derived from *N*,*N*′-Bis(5-Chlorosalicylidene)-1,2-Diaminoethane: Synthesis, Crystal Structure, and Antimicrobial Activity[1]

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Abstract—A new hetero trinuclear manganese(III)-iron(II) complex, $[Mn(ClSalen)(H_2O)]_2[Fe(CN)_5(NO)] \cdot CH_3OH \cdot H_2O$, where ClSalen is the dianionic form of *N*,*N*′-bis(5-chlorosalicylidene)-1,2-diaminoethane, has been prepared and characterized by elemental analyses, IR, and single crystal X-ray crystallographic determination (CIF file CCDC no. 1024666). The crystal of the complex is orthorhombic: space group $Pca2_1$, $a = 27.784(2)$, $b = 10.8876(6)$, $c = 15.1755(8)$ Å, $V = 4590.5(4)$ Å^3, $Z = 2$, $R_1 = 0.0596$, $wR_2 = 0.1406$. The bis-Schiff base ligand coordinates to the Mn atom through two phenolate O and two imine N atoms. Each Mn atom in the complex is in octahedral coordination, with the equatorial donor atoms come from the Schiff base ligand, and with the axial donor atoms come from a water O atom and a cyanide N atom. The effects of the complex on the antimicrobial activity against *Staphylococcus aureus*, *Escherichia coli*, and *Candida albicans* were studied.

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INTRODUCTION

Schiff bases are a kind of important ligands in coordination chemistry [1–3]. In recent years, metal complexes of Schiff bases have attracted dramatically attention due to their versatile biological activity, such as antifungal, antibacterial and antitumor [4–6]. It has been shown that the Schiff base complexes derived from salicylaldehyde and its derivatives with primary amines, bearing the N_2O, N_2S, NO_2 or NSO donor sets, have interesting biological activity [7–10]. In addition, the molecular design of extended structures starting from molecular precursors is of great interest. A preferred way to construct such materials is to use ionic building blocks in which one unit contains a potential bridging ligand and another contains a potential coordination site [11]. In the present paper, the preparation, characterization and antimicrobial activity of a new hetero trinuclear manganese(III)-iron(II) complex, $[Mn(ClSalen)(H_2O)]_2[Fe(CN)_5(NO)] \cdot CH_3OH \cdot H_2O$, where ClSalen is the dianionic form of *N*,*N*′-bis(5-chlorosalicylidene)-1,2-diaminoethane (H_2ClSalen), is reported.

EXPERIMENTAL

Material and methods. 5-Chlorosalicylaldehyde and ethane-1,2-diamine were purchased from Fluka. Other reagents and solvents were analytical grade and used without further purification. Elemental (C, H, and N) analyses were made on a PerkinElmer Model 240B automatic analyser. Infrared (IR) spectra were recorded on an IR-408 Shimadzu 568 spectrophotometer. X-ray diffraction was carried out on a Bruker SMART 1000 CCD area diffractometer.

Synthesis of the complex. 5-Chlorosalicylaldehyde (0.312 g, 2 mmol) and ethane-1,2-diamine (0.060 g, 1 mmol) were reacted in methanol (30 mL) at ambient temperature for 1 h. To the mixture was added $Mn(ClO_4)_2 \cdot 6H_2O$ (0.362 g, 1 mmol) with stirring for 30 min. Then, the methanol solution of the above brown solution was carefully layered on the top of an aqueous solution (5 mL) of $Na_2[Fe(CN)_5(NO)] \cdot 2H_2O$ (0.298 g, 1 mmol) in a test tube. Deep brown single crystals of the complex, suitable for single crystal X-ray diffraction, were formed after a few days. The yield was 413 mg.

Selected IR data (ν, cm^{-1}): 2027 s, ν(N_3), 1632 s, ν(C=N).

For $C_{75}H_{63}N_{20}O_{16}Cl_8Mn_4Fe_2$			
anal. calcd., %:	C, 42.58;	H, 3.00;	N, 13.24.
Found, %:	C, 42.31;	H, 3.12;	N, 13.39.

X-ray structure determination. Data were collected from a selected crystal mounted on a thin glass fiber. The data for the complex were processed with SAINT [12] and corrected for absorption using SADABS [13]. Multi-scan absorption corrections were applied with ψ-scans [14]. The structure was solved by direct meth-

[1] The article is published in the original.

Table 1. Crystallographic data and experimental details for the complex

Parameter	Value
Habit; color	Block; deep brown
Formula weight	2115.5
Temperature, K	298(2)
Crystal size, mm	$0.23 \times 0.21 \times 0.17$
Radiation (λ, Å)	MoK_α (0.71073)
Crystal system	Orthorhombic
Space group	$Pca2_1$
Unit cell dimensions:	
a, Å	27.783(2)
b, Å	10.8876(6)
c, Å	15.1755(8)
V, Å^3	4590.5(4)
Z	2
ρ_{calcd}, g cm^{-3}	1.530
F(000)	2138
Absorption coefficient, mm^{-1}	1.146
θ Range for data collection, deg	2.38–25.06
Index ranges, h, k, l	$-30 \le h \le 33$; $-12 \le k \le 12$; $-18 \le l \le 18$
Reflections collected	40274
Independent reflections (R_{int})	8108 (0.0847)
Reflections with $I > 2\sigma(I)$	5531
Number of parameters	581
Restraints	4
Goodness-of-fit on F^2	1.074
Final R indices ($I > 2\sigma(I)$)	$R_1 = 0.0596$, $wR_2 = 0.1406$
R indices (all data)	$R_1 = 0.1105$, $wR_2 = 0.1649$
Largest difference peak and hole, e Å^{-3}	0.874, –0.348

od using the program SHELXS-97 and refined by full-matrix least-squares techniques on F^2 using anisotropic displacement parameters [15]. The water and methanol hydrogen atoms were located from a difference Fourier map and refined isotropically, with O–H and H···H distances restrained to 0.85(1) and 1.37(2) Å, respectively. The remaining hydrogen atoms were placed at the calculated positions. Idealized H atoms were refined with isotropic displacement parameters set to 1.2 (1.5 for methyl groups) times the equivalent isotropic U values of the parent carbon atoms. The crystallographic data for the complexes are listed Table 1. Selected bond distances and angles are listed in Table 2.

Supplementary material has been deposited with the Cambridge Crystallographic Data Centre (no. 1024666; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

The Schiff base H_2ClSalen was readily prepared by the condensation of 1 : 2 molar ratio of ethane-1,2-diamine with 5-chlorosalicylaldehyde in methanol at ambient temperature. The Schiff base was not isolated and used directly to the synthesis of the complex with $Na_2[Fe(CN)_5(NO)] \cdot 2H_2O$. Crystals of the complex are very stable at room temperature. The results of the elemental analyses are in accord with the composition suggested for the complex.

In order to compare the IR spectrum of the complex with the free Schiff base, small quantity of H_2ClSalen was prepared. The IR spectrum of the Schiff base contains medium C–O absorption band at 1243 cm^{-1}. The band disappeared on complexation and new C–O absorption band appeared at 1093 cm^{-1} in the spectrum of the complex, indicating that the

Table 2. Selected bond distances (Å) and angles (deg) for the complex

Bond	*d*, Å	Bond	*d*, Å
Fe(1)–N(7)	1.630(8)	Fe(1)–C(36)	1.929(8)
Fe(1)–C(35)	1.930(7)	Fe(1)–C(37)	1.939(8)
Fe(1)–C(33)	1.941(9)	Fe(1)–C(38)	1.951(11)
Mn(1)–O(1)	1.867(5)	Mn(1)–O(2)	1.885(5)
Mn(1)–N(2)	1.974(6)	Mn(1)–N(1)	1.989(7)
Mn(1)–O(5)	2.238(5)	Mn(1)–N(5)	2.326(8)
Mn(2)–O(4)	1.886(5)	Mn(2)–O(3)	1.887(5)
Mn(2)–N(3)	1.973(6)	Mn(2)–N(4)	1.974(6)
Mn(2)–O(6)	2.246(5)	Mn(2)–N(6)	2.327(7)
Angle	ω, deg	Angle	ω, deg
N(7)Fe(1)C(36)	95.9(3)	N(7)Fe(1)C(35)	95.6(3)
C(36)Fe(1)C(35)	90.5(3)	N(7)Fe(1)C(37)	93.6(3)
C(36)Fe(1)C(37)	89.9(3)	C(35)Fe(1)C(37)	170.7(3)
N(7)Fe(1)C(33)	92.5(4)	C(36)Fe(1)C(33)	171.5(4)
C(35)Fe(1)C(33)	88.8(3)	C(37)Fe(1)C(33)	89.4(3)
N(7)Fe(1)C(38)	178.8(4)	C(36)Fe(1)C(38)	83.3(3)
C(35)Fe(1)C(38)	85.4(3)	C(37)Fe(1)C(38)	85.5(4)
C(33)Fe(1)C(38)	88.3(4)	O(1)Mn(1)O(2)	92.5(2)
O(1)Mn(1)N(2)	174.7(3)	O(2)Mn(1)N(2)	92.6(2)
O(1)Mn(1)N(1)	92.8(3)	O(2)Mn(1)N(1)	174.7(3)
N(2)Mn(1)N(1)	82.1(3)	O(1)Mn(1)O(5)	89.3(2)
O(2)Mn(1)O(5)	93.7(2)	N(2)Mn(1)O(5)	89.2(2)
N(1)Mn(1)O(5)	85.7(2)	O(1)Mn(1)N(5)	93.6(3)
O(2)Mn(1)N(5)	95.2(3)	N(2)Mn(1)N(5)	87.2(3)
N(1)Mn(1)N(5)	85.2(3)	O(5)Mn(1)N(5)	170.6(2)
O(4)Mn(2)O(3)	93.7(2)	O(4)Mn(2)N(3)	174.5(3)
O(3)Mn(2)N(3)	91.9(2)	O(4)Mn(2)N(4)	92.3(3)
O(3)Mn(2)N(4)	174.0(2)	N(3)Mn(2)N(4)	82.1(3)
O(4)Mn(2)O(6)	89.2(2)	O(3)Mn(2)O(6)	92.9(2)
N(3)Mn(2)O(6)	90.5(2)	N(4)Mn(2)O(6)	86.9(2)
O(4)Mn(2)N(6)	92.9(2)	O(3)Mn(2)N(6)	92.7(2)
N(3)Mn(2)N(6)	86.9(2)	N(4)Mn(2)N(6)	87.3(3)
O(6)Mn(2)N(6)	173.9(2)		

Schiff base coordinates to the metal atom through deportonated form. The infrared spectrum of the complex displays intense absorption band at 1618 cm^{-1}, which can be assigned to the C=N stretching frequencies of the Schiff base ligand, whereas for the free Schiff base the corresponding absorption band is observed at higher wave number, 1636 cm^{-1}. The shift of the band on complexation indicates coordination of the imine nitrogen to the metal center [16]. In the spectrum of the complex, strong bands observed at 2153 and 2127 cm^{-1} are assigned to the absorptions of the non-bridging and bridging cyanide groups [17]. The strong band observed at 1911 cm^{-1} is assigned to the absorption of the NO group.

The molecular structure of the complex is shown in Fig. 1. The complex is a cyanido-bridged heteronuclear manganese(III)-iron(II) species, with Mn···Fe separations of 5.15–5.18 Å. In addition, there are one water molecule and one methanol molecule in the lattice of the crystal. In the complex, the Mn atom is coordinated by two phenolate O and two imine N atoms of the Schiff base ligand, defining the equatorial plane, and by one water O atom and one cyanide N atom, occupying the two axial positions, generating an octahe-

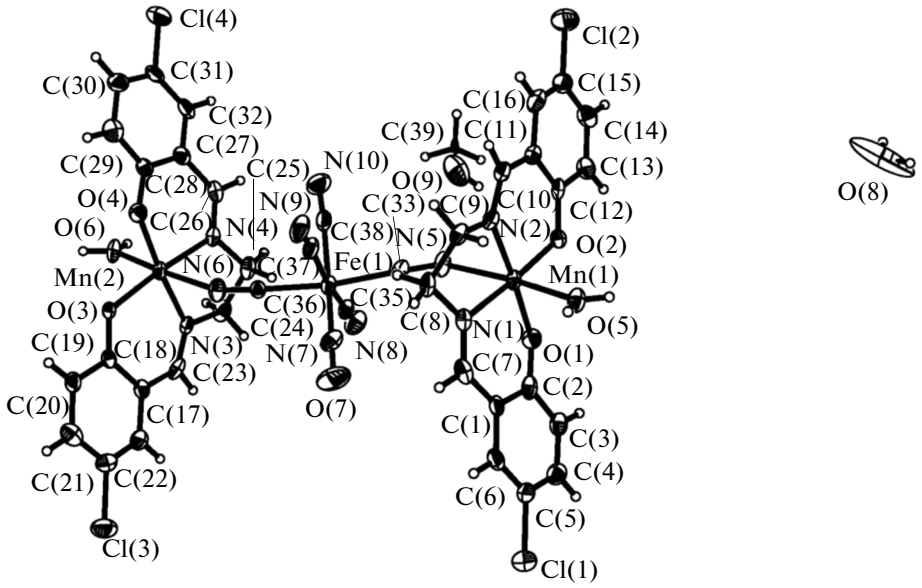

Fig. 1. Perspective view of the complex with 30% probability thermal ellipsoids.

dral geometry. The two axial bonds are much longer than the basal bonds, which is caused by the Jahn–Teller effects. The bond distances subtended at the Mn atoms are comparable to those observed in similar manganese(III) complexes with Schiff bases [18–20]. The dihedral angles between the benzene rings C(1)–C(6) and C(11)–C(16), and C(17)–C(22) and C(27)–C(32) of the Schiff base ligands are 7.8(3)° and 5.4(3)°, respectively. The Fe atom in the complex is coordinated by five C atoms from cyanide ligands and one N atom of NO group, generating an octahedral geometry. The bond distances subtended at the Fe atom are comparable to those observed in similar complexes with Fe–C and Fe–N bonds [21].

In the crystal structure of the complex, the [Mn(ClSalen)(H_2O)] moieties are linked by a [Fe$(CN)_5$(NO)] core. The hetero trinuclear complex molecules are linked through intermolecular O–H···O hydrogen bonds (Table 3), generating 1D chains along the axis-*c* direction (Fig. 2). The chains are further linked through intermolecular O–H···N hydrogen bonds, to form a three dimensional network. In addition, there are π···π interactions among the chains in the *b* axis direction (Table 4).

Qualitative determination of antimicrobial activity was done using the disk diffusion method [22, 23]. The results are summarized in Table 5. A comparative study of minimum inhibitory concentration (MIC) values of the free Schiff base and the complex indicated that the complex has more effective activity than the free Schiff base. Generally, this is caused by the greater lipophilic nature of the complexes than the

Table 3. Geometric parameters of hydrogen bonds for the complex*

D–H···A	Distance, Å			Angle D–H···A, deg
	D–H	H···A	D···A	
O(8)–H(8*A*)···O(7)^{i}	0.85	2.53	3.085(18)	124
O(6)–H(6*C*)···O(1)^{ii}	0.85	2.62	3.393(7)	151
O(6)–H(6*C*)···O(2)^{ii}	0.85	2.09	2.788(7)	139
O(5)–H(5*B*)···O(4)^{iii}	0.85	2.61	3.417(8)	159
O(5)–H(5*B*)···O(3)^{iii}	0.85	2.16	2.793(7)	131

* Symmetry codes: ^{i} $-x, -1+y, 1+z$; ^{ii} $x, y, -1+z$; ^{iii} $x, y, 1+z$.

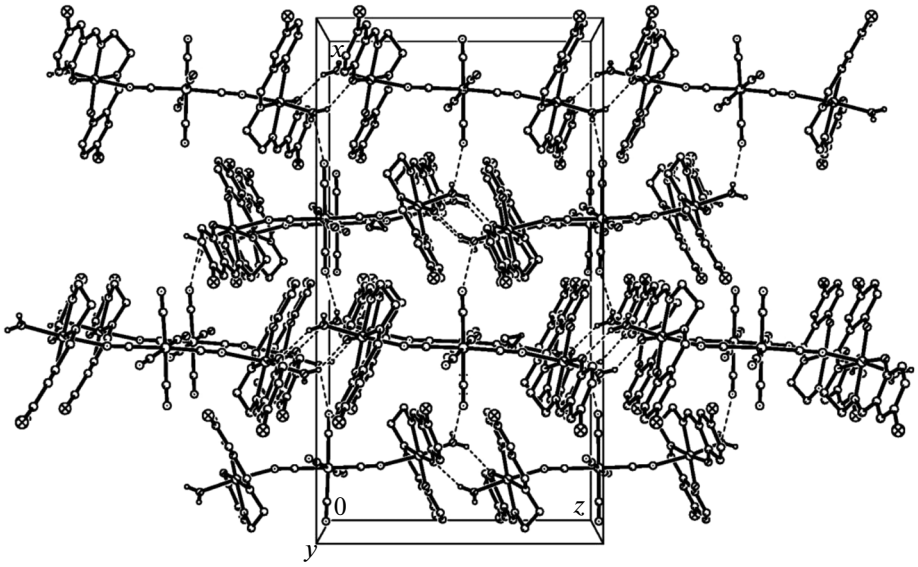

Fig. 2. Molecular packing structure of the complex. Hydrogen bonds are drawn as dashed lines.

ligands. Such increased activity of the metal chelates can be explained on the basis of chelating theory [24]. On chelating, the polarity of the metal atoms will be reduced to a greater extent due to the overlap of the ligand orbital and partial sharing of positive charge of the metal atoms with donor atoms. Further, it increases the delocalization of *p*-electrons over the whole chelate ring and enhances the lipophilicity of the complexes. This increased lipophilicity enhances the penetration of the complexes into lipid membrane and blocks the metal binding sites on enzymes of microorganisms.

From Table 5, it can be seen that the complex has greater antibacterial and antifungi activities against *Escherichia coli* and *Candida albicans* when compared to the reference drug Tetracycline. Yet, for *Staphylococcus aureus*, the activity of the complex is much weak.

In summary, a new hetero trinuclear manganese(III)-iron(II) complex derived from the bis-Schiff base ligand *N*,*N*'-bis(5-chlorosalicylidene)-1,2-diaminoethane has been prepared and characterized. The crystal structure of the complex was confirmed by X-ray single crystal structure determination. The Mn and Fe atoms in the complex are in octahedral coordination. The biological test showed that the complex has effective activities against *Escherichia coli* and *Candida albicans*.

Table 4. π···π Interactions (Å) of the complex*

$Cg(1)\cdots Cg(2)^{iii}$	4.750(3)	$Cg(4)\cdots Cg(10)^{iv}$	4.971(3)
$Cg(3)\cdots Cg(4)^{iii}$	3.759(3)	$Cg(8)\cdots Cg(10)^{iii}$	3.808(3)
$Cg(2)\cdots Cg(5)^{v}$	4.764(3)		

* *Cg*(1), *Cg*(2), Cg(3), *Cg*(4) and *Cg*(5) are the centroids of the Mn(1)–O(2)–C(12)–C(11)–C(10)–N(2), C(27)–C(28)–C(29)–C(30)–C(31)–C(32), C(1)–C(2)–C(3)–C(4)–C(5)–C(6), C(17)–C(18)–C(19)–C(20)–C(21)–C(22), and C(11)–C(12)–C(13)–C(14)–C(15)–C(16) rings, respectively. Symmetry codes: ^{iv} $1/2 - x, y, 1/2 + z$; ^{v} $1/2 - x, y, -1/2 + z$.

Table 5. MIC values (μg/mL) for the antimicrobial activities of the tested compounds

Compound	*Staphylococcus aureus*	*Escherichia coli*	*Candida albicans*
H_2ClSalen	32	256	>1024
The complex	4	2	64
Tetracycline	0.30	2.15	>1024

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