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Manganese(III) Complexes Derived from *bis*-Schiff Bases: Synthesis, Structures, and Antimicrobial Activity[1]

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Abstract—Manganese(III) complexes derived from the *bis*-Schiff bases N,N'-*bis*(5-fluorosalicylidene)-1,2-diaminoethane (H_2L^a) and 3,4-*bis*(2-hydroxybenzylideneamino)pyridine (H_2L^b), respectively, have been prepared and characterized by elemental analyses, IR, and single crystal X-ray crystallographic determination (CIF files CCDC nos. 997243 (**I**), 995896 (**II**)). The crystal of $[MnL^a(\mu_{1,3}\text{-}N_3)]_n$ (**I**) is orthorhombic: space group $Pca2_1$, $a = 10.723(1)$, $b = 13.430(1)$, $c = 11.112(1)$ Å, $V = 1600.2(2)$ Å^3, $Z = 4$, $R_1 = 0.0264$, $wR_2 = 0.0649$. The crystal of $[MnL^b(N_3)(CH_3OH)]$ (II) is monoclinic: space group $C2/c$, $a = 22.792(1)$, $b = 14.4442(7)$, $c = 12.8637(6)$ Å, $\beta = 119.262(1)°$, $V = 3694.5(3)$ Å^3, $Z = 8$, $R_1 = 0.0367$, $wR_2 = 0.0776$. The *bis*-Schiff base ligands coordinate to the metal atoms through phenolate O and imine N atoms. Each metal atom in the complexes is in octahedral coordination. The effects of the complexes 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]. Recent research indicates that the halide-substituent groups in aromatic rings of Schiff bases can severely increase the antimicrobial activity [11]. In the present paper, the preparation, characterization and antimicrobial activity of two manganese(III) complexes, $[MnL^a(\mu_{1,3}\text{-}N_3)]_n$ (**I**) and $[MnL^b(N_3)(CH_3OH)]$ (**II**), with *bis*-Schiff bases N,N'-*bis*(5-fluorosalicylidene)-1,2-diaminoethane (**H_2L^a**) and 3,4-*bis*(2-hydroxybenzylideneamino)pyridine (**H_2L^b**), respectively, are reported.

EXPERIMENTAL

Material and methods. 5-Fluorosalicylaldehyde, salicylaldehyde and pyridine-3,4-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 240 B 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 I. 5-Fluorosalicylaldehyde (0.280 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. Then, sodium azide (0.065 g, 1 mmol) and manganese perchlorate hexahydrate (0.362 g, 1 mmol) dissolved in distilled water (5 mL) were added dropwise to the solution. The mixture was stirred until the color turned to deep brown in about 30 min. The filtered solution was allowed to slow evaporate at room temperature in an uncapped vial. Several days later, block crystals of the complex were obtained. The yield was 173 mg.

For $C_{16}H_{12}N_5O_2F_2Mn$			
anal. calcd., %:	C, 48.14;	H, 3.03;	N, 17.54.
Found, %:	C, 47.97;	H, 3.12;	N, 17.70.

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

Synthesis of II. Salicylaldehyde (0.245 g, 2 mmol) and pyridine–3,4–diamine (0.109 g, 1 mmol) were reacted in methanol (30 mL) at ambient temperature for 1 h. Then, sodium azide (0.065 g, 1 mmol) and manganese perchlorate hexahydrate (0.362 g, 1 mmol) dissolved in distilled water (5 mL) were added dropwise to the solution. The mixture was stirred until the color turned to deep brown in about 30 min. The fil-

[1] The article is published in the original.

Table 1. Crystallographic data and and structure refinement summary for **I** and **II**

Parameter	Value	
	I	**II**
Habit; color	Block; deep brown	Block; deep brown
Formula weight	399.2	444.3
Temperature, K	298(2)	298(2)
Crystal size, mm	0.30 × 0.27 × 0.27	0.33 × 0.30 × 0.27
Radiation (λ, A)	MoK_α (0.71073)	MoK_α (0.71073)
Crystal system	Orthorhombic	Monoclinic
Space group	$Pca2_1$	$C2/c$
Unit cell dimensions:		
a, Å	10.723(1)	22.792(1)
b, Å	13.430(1)	14.4442(7)
c, Å	11.112(1)	12.8637(6)
β, deg	90	119.262(1)
V, Å^3	1600.2(2)	3694.5(3)
Z	4	8
ρ_{calcd}, g cm^{-3}	1.657	1.598
F (000)	808	1824
Absorption coefficient, mm^{-1}	0.869	0.753
θ Range for data collection, deg	1.52–28.28	2.82–25.07
Index ranges	$-14 \le h \le 14$, $-17 \le k \le 17$, $-14 \le l \le 14$	$-27 \le h \le 24$, $-17 \le k \le 17$, $-15 \le l \le 15$
Reflections collected	18148	16740
Independent reflections (R_{int})	3969 (0.0318)	3265 (0.0446)
Reflections with $I > 2\sigma(I)$	3672	2471
Parameters	235	275
Restraints	1	1
Goodness-of-fit on F^2	1.050	1.032
Final R indices ($I > 2\sigma(I)$)	$R_1 = 0.0264$, $wR_2 = 0.0649$	$R_1 = 0.0367$, $wR_2 = 0.0776$
R indices (all data)	$R_1 = 0.0302$, $wR_2 = 0.0682$	$R_1 = 0.0608$, $wR_2 = 0.0867$
Largest difference peak and hole, e Å^{-3}	0.207 and –0.369	0.282 and –0.264

tered solution was allowed to slow evaporate at room temperature in an uncapped vial. Several days later, block crystals of the complex were obtained. The yield was 205 mg.

For $C_{20}H_{17}N_6O_3Mn$

anal. calcd., %:	C, 54.06;	H, 3.86;	N, 18.91.
Found, %:	C, 54.18;	H, 4.01;	N, 18.73.

Selected IR data (ν, cm^{-1}): 2071 s ν(N_3), 1626 s ν(C=N).

X-ray diffraction. Data were collected from selected crystals mounted on glass fibers. The data for the two complexes were processed with SAINT [12] and corrected for absorption using SADABS [13]. Multi-scan absorption corrections were applied with ψ-scans [14]. The structures were solved by direct methods using the program SHELXS-97 and refined by full-matrix least-squares techniques on F^2 using anisotropic displacement parameters [15]. 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.

Supplementary material has been deposited with the Cambridge Crystallographic Data Centre (nos. 997243 (**I**) and 995896 (**II**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

The Schiff bases H_2L^a and H_2L^b were readily prepared by the condensation of 1:2 molar ratio of ethane-1,2-diamine with 5-fluorosalicylaldehyde, and pyridine-3,4-diamine with salicylaldehyde,

Table 2. Selected bond distances (Å) and angles (deg) for **I*** and **II**

Bond	*d*, Å	Bond	*d*, Å
		I	
Mn(l)–O(1)	1.876(1)	Mn(l)–O(2)	1.888(1)
Mn(l)–N(1)	1.988(2)	Mn(l)–N(2)	1.983(2)
Mn(l)–N(3)	2.280(2)	Mn(l)–N(5*A*)	2.319(2)
		II	
Mn(l)–O(1)	1.862(2)	Mn(l)–O(2)	1.873(2)
Mn(l)–N(1)	1.986(2)	Mn(l)–N(2)	1.996(2)
Mn(l)–O(3)	2.363(2)	Mn(l)–N(4)	2.271(2)
Angle	ω, deg	Angle	ω, deg
		I	
O(l)Mn(l)O(2)	94.31(6)	O(1)Mn(1)N(2)	173.54(6)
O(2)Mn(l)N(2)	92.01(6)	O(l)Mn(l)N(l)	91.57(6)
O(2)Mn(l)N(l)	173.61(6)	N(2)Mn(l)N(l)	82.17(6)
O(l)Mn(l)N(3)	92.03(6)	O(2)Mn(l)N(3)	89.76(6)
N(2)Mn(l)N(3)	86.70(6)	N(l)Mn(l)N(3)	92.53(6)
O(1)Mn(1)N(5*A*)	91.30(6)	O(2)Mn(1)N(5*A*)	89.52(6)
N(2)Mn(1)N(5*A*)	90.04(6)	N(1)Mn(1)N(5*A*)	87.85(6)
N(3)Mn(1)N(5*A*)	176.64(6)		
		II	
O(l)Mn(l)O(2)	93.04(7)	O(1)Mn(1)N(1)	92.38(8)
O(2)Mn(l)N(l)	173.06(8)	O(l)Mn(l)N(2)	173.97(8)
O(2)Mn(l)N(2)	92.20(8)	N(l)Mn(l)N(2)	82.17(8)
O(l)Mn(l)N(4)	93.86(8)	O(2)Mn(l)N(4)	94.15(8)
N(l)Mn(l)N(4)	89.81(8)	N(2)Mn(l)N(4)	88.73(8)
O(l)Mn(l)O(3)	90.99(8)	O(2)Mn(l)O(3)	86.98(7)
N(l)Mn(l)O(3)	88.59(8)	N(2)Mn(l)O(3)	86.31(8)
N(4)Mn(l)O(3)	174.95(8)		

* Symmetry code for *A*: $1/2 - x, y, -1/2 + z$.

respectively, in methanol at ambient temperature. The Schiff bases were not isolated and used directly to the synthesis of the complexes with sodium azide and manganese perchlorate. The complexes are very stable at room temperature in the solid state and soluble in common organic solvents, such as methanol, ethanol, chloroform, and acetonitrile. The results of the elemental analyses are in accord with the composition suggested for the complexes.

In order to compare the IR spectra of the complexes with the free Schiff bases, small quantities of H_2L^a and H_2L^b were prepared. The IR spectra of the Schiff bases contain strong C–O absorption bands in the region 1245–1253 cm^{-1}. The bands disappeared on complexation, and new C–O absorption bands appeared in the region 1080–1100 cm^{-1} in the spectra of the complexes, indicating that the Schiff bases coordinate to the metal atoms through deportonated form. The infrared spectra of the complexes display intense absorption bands in the region 1626–1632 cm^{-1}, which can be assigned to the C=N stretching frequencies of the Schiff base ligands, whereas for the free Schiff bases the corresponding absorption bands are observed at higher wave numbers, 1640–1655 cm^{-1}. The shift of these bands on complexation towards lower wave number indicates coordination of the imine nitrogen to the metal center [16]. In the spectra of complexes **I** and **II**, very strong bands observed at 2027 and 2071 cm^{-1}, respectively, are assigned to the absorption of the azide ligands [17].

The molecular structure of complex **I** is shown in Fig. 1a. Selected bond distances and angles are listed in Table 2. The complex is an end-to-end azido-bridged polynuclear manganese species with Mn···Mn separation of 5.556(2) Å. The Mn atom in the complex is coordinated by two phenolate O and two imine N

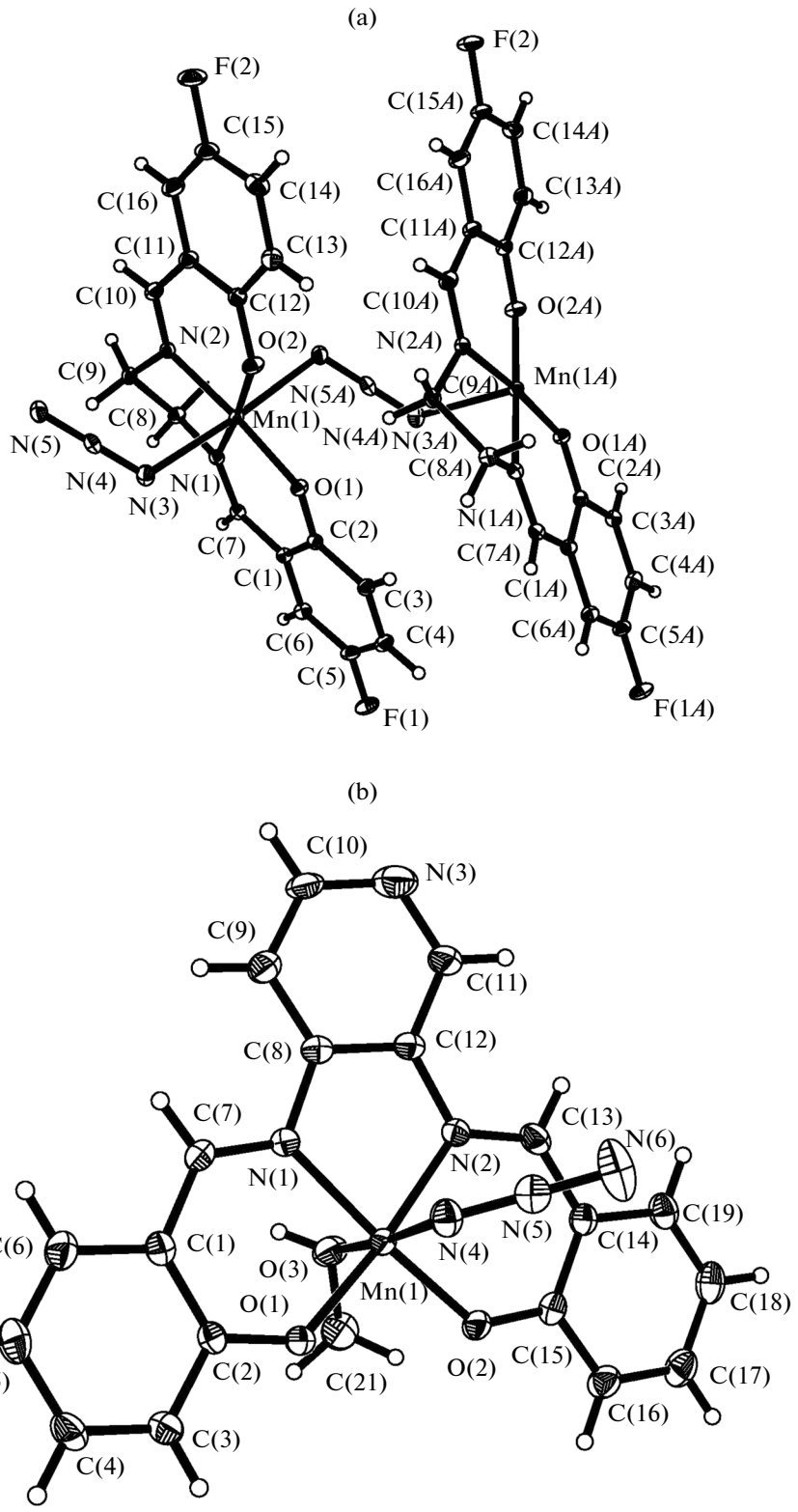

Fig. 1. Perspective view of complexes **I** (a) **II** (b) and with 30% probability thermal ellipsoids.

atoms of L^a, defining the equatorial plane, and by two N atoms from two azido ligands, occupying the two axial positions, generating an octahedral 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 metal atoms are com-

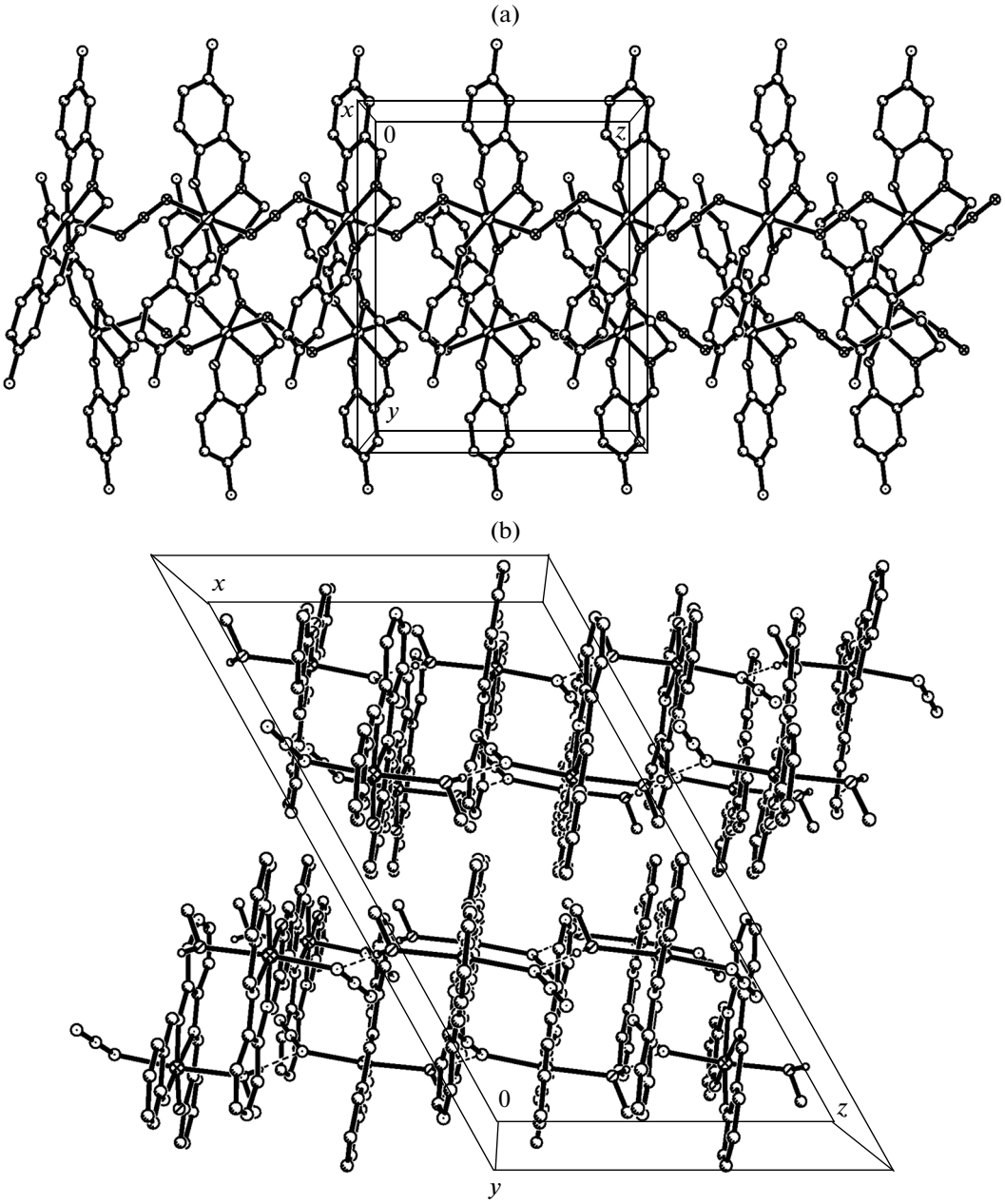

Fig. 2. Molecular packing structure of complexes **I** (a) **II** (b). Hydrogen bonds are drawn as dashed lines.

parable to those observed in similar manganese(III) complexes with Schiff bases [18–20]. In the crystal structure of complex **I**, the [MnL^a] moieties are linked through end-to-end azido bridges, generating 1D chains along the *z* axis direction (Fig. 2a).

The molecular structure of complex **II** is shown in Fig. 1b. Selected bond distances and angles are listed in Table 2. The complex is a terminal azido-coordinated mononuclear manganese species. The Mn atom in the complex is coordinated by two phenolate O and two imine N atoms of L^b, defining the equatorial plane, and by one N atom of an azido ligand and one O atom of a methanol ligand, occupying the two axial positions, generating an octahedral 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 metal atoms are comparable to those observed in similar manganese(III) com-

Table 3. MIC values (μg/mL) for the antimicrobial activities of the tested compounds

Compound	*Staphylococcus aureus*	*Escherichia coli*	*Candida albicans*
H_2L^a	16	64	256
H_2L^b	128	256	>1024
I	4	8	128
II	16	64	512
Tetracycline	0.30	2.15	>1024

plexes with Schiff bases [21–23]. In the crystal structure of complex **II**, the [MnL^b] moieties are linked through intermolecular O–H···N hydrogen bond: O(3)–H(3*A*)···N(4) (x, $-y$, $-1/2 + z$) (O–H 0.85(1), H···N 2.01(1), O···N 2.853(3) Å, angle OHN 171(4)°), generating 1D chains along the z axis direction (Fig. 2b).

Qualitative determination of antimicrobial activity was done using the disk diffusion method [24, 25]. The results are summarized in Table 3. A comparative study of minimum inhibitory concentration (**MIC**) values of the Schiff bases and the complexes indicate that the two complexes have more effective activity than the free Schiff bases. Generally, this is caused by the greater lipophilic nature of the complexes than the ligands. Such increased activity of the metal chelates can be explained on the basis of chelating theory [26]. 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 3, it can be seen that in general complex **I** shows greater antibacterial and antifungi activities against *Staphylococcus aureus*, *Escherichia coli*, and *Candida albicans* when compared to complex **II**. And, it is obvious that H_2L^a has also greater antibacterial and antifungi activities against *Staphylococcus aureus*, *Escherichia coli*, and *Candida albicans* when compared to H_2L^b. This phenomenon obvious indicates that the fluoro-substitute groups are essential for the biological activity. For *Staphylococcus aureus* and *Escherichia coli*, the activities of the complexes are less than the control drug Tetracycline. But for *Candida albicans*, the complexes have stronger activities than Tetracycline. Further work needs to be carried out to investigate the structure-activity relationship.

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