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Synthesis, Crystal Structures, and Antibacterial Property of Tris[2-(5-Bromosalicylideneamino)ethyl]amine and Its Manganese(III) Complex[1]

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Abstract—A tripodal Schiff base tris[2-(5-bromosalicylideneamino)ethyl]amine (H_3L) was prepared by the reaction of 5-bromosalicylaldehyde with tris(2-aminoethyl)amine. Reaction with the Schiff base with manganese perchlorate in methanol resulted a mononuclear manganese(III) complex (**I**). The crystal structures of the Schiff base and the complex have been determined by single crystal X-ray diffraction (CIF files CCDC nos. 1007902 (H_3L); 1007983 (**I**)). The Schiff base coordinates to the Mn atom through all the phenolate O and imino N atoms. The Mn atom of the complex is in octahedral coordination. The antibacterial properties have been tested on some bacteria and yeast.

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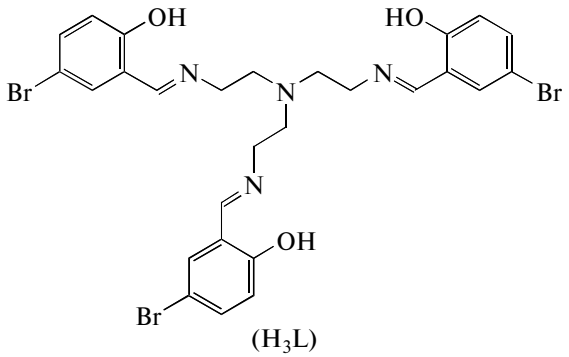
INTRODUCTION

Schiff bases have been extensively used as ligands to construct complexes with various metal ions. In the last decades, numerous Schiff bases and their complexes have been prepared and studied their properties, such as magnetic [1–5], catalytic [6–10], luminescence [11], as well as biological applications [12–15]. Among the complexes, most are derived from mono- or bis-Schiff bases. Tris(2-aminoethyl)amine is an interesting primary amine, which can react with aldehydes to form tripodal Schiff bases. During the search of literature, we find that the complexes derived from tri-Schiff bases are very rare. In this paper, a tripodal Schiff base tris[2-(5-bromosalicyideneamino)ethyl]amine (H_3L) and its manganese complex (**I**) were prepared, and studied on their antibacterial properties.



(H_3L)

[1] The article is published in the original.

EXPERIMENTAL

Materials and methods. Tris(2-aminoethyl)amine, 5-bromosalicylaldehyde, and manganese perchlorate were obtained from commercial sources and were used as received without further purification. Elemental analyses of C, H, and N were performed using a PerkinElmer 240C elemental analyzer. IR spectra were recorded as KBr pellets using a Magna 750 FTIR spectrophotometer. ^{1}H NMR was recorded on a Bruker 300 instrument.

Caution! Although we did not experience any problem with the compounds reported in this work, perchlorate salts are potentially explosive. Only a small amount of material should be prepared, and it should be handled with care.

Synthesis of the tripodal Schiff base (H_3L). 5-Bromosalicylaldehyde (6.03 g, 0.3 mol) was dissolved in 30 mL methanol, to which was added dropwise a methanolic solution (20 mL) of tris(2-aminoethyl)amine (1.46 g, 0.1 mol). The color changed from colorless to orange during the reaction procedure. The reaction was continued for 30 min, and the solvent was allowed to slow evaporate in air. Yellow single crystals were obtained in 5 days. The yield was 73%. IR (KBr; ν, cm^{-1}): 1645 ν (C=N). ^{1}H NMR data (300 MHz; DMSO; δ, ppm): 13.61 (s., 3H), 8.37 (s., 3H), 7.73 (s, 3H), 7.38 (d.d., J = 8.8, 2.4 Hz, 3H), 6.77 (d., 3H), 3.62 (t., 6H), 2.76 (t., 6H).

For $C_{27}H_{27}N_4O_3Br_3$			
anal. calcd., %:	C, 46.64;	H, 3.91;	N, 8.06.
Found, %:	C, 46.83;	H, 4.00;	N, 7.95.

Table 1. Crystallographic data and refinement parameters for the Schiff base (H_3L) and complex **I**

Parameter	Value	
	H_3L	**I**
Fw	695.26	747.17
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a, Å	9.8562(3)	9.5479(5)
b, Å	11.9170(5)	11.7796(6)
c, Å	13.2324(4)	13.3841(8)
α, deg	89.269(3)	79.750(2)
β, deg	77.229(3)	78.680(2)
γ, deg	67.500(3)	88.647(2)
V, Å^3	1395.94(8)	1452.4(1)
Z	2	2
ρ_{calcd}, g cm^{-3}	1.654	1.709
μ, mm^{-1}	4.370	4.616
λ, Å	0.71073	0.71073
F(000)	692	736
Measured reflections	22872	13153
Unique reflections	5720	5112
Observed reflections	4790	3786
GOOF (F^2)	1.017	1.049
Parameters	343	343
Restraints	0	0
R_1, wR_2 (all data)	0.0271, 0.0544	0.0865, 0.2141
R_1, wR_2 ($I \geq 2\sigma(I)$)	0.0376, 0.0583	0.0624, 0.1958

Synthesis of I. Manganese perchlorate hexahydrate (1.81 g, 0.05 mol) and the tripodal Schiff base (3.48 g, 0.05 mol) were mixed in methanol, and stirred at room temperature for 30 min to give brown solution. The solution was kept still to slow evaporate in air for several days, to form well block-shaped single crystals. The yield was 41%. IR (KBr; ν, cm^{-1}): 1615 ν(C=N).

For $C_{27}H_{24}N_4O_3Br_3Mn$			
anal. calcd., %:	C, 43.40;	H, 3.24;	N, 7.50.
Found, %:	C, 43.23;	H, 3.31;	N, 7.62.

X-ray crystallography. Single crystal X-ray data for the tripodal Schiff base and the manganese complex were collected on a Bruker SMART APEX CCD diffractometer using the SMART/SAINT software [16]. Intensity data were collected using graphite-monochromatized MoK_α radiation (0.71073 Å) at 293(2) K. The structures were solved by direct methods using the SHELX-97 program [17]. Empirical absorption corrections were applied with SADABS [18]. All non-hydrogen atoms were refined with anisotropic displacement coefficients. The hydrogen atoms bonded to carbon and nitrogen were included in geometric positions and given thermal parameters equivalent to 1.2 times those of the atom to which they were attached. Crystallographic data and refinement parameters are given in Table 1, and important interatomic distances and angles are given in Table 2.

Supplementary material for structures H_3L and **I** have been deposited with the Cambridge Crystallographic Data Centre (nos. 1007902 (H_3L); 1007983 (**I**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Biological assay. The antibacterial property of the Schiff base and the complex was evaluated by a macrodilution method using *Staphylococcus aureus*, *Escherichia coli*, and the yeasts *Candida parapsilosis*. The cultures of bacteria and yeasts were incubated under vigorous shaking. The compounds were dissolved in small amount of DMSO. Concentration of the tested compounds ranging from 0.01 to 2.50 mmol L^{-1} for the bacteria and yeasts was used in all experiments. The antibacterial activity was characterized by IC_{50} and MIC values. MIC experiments on subculture dishes were used to assess the minimal microbicidal concentration (MMC). Subcultures were prepared separately in Petri dishes containing competent agar medium and incubated at 30°C for 48 h. The MMC value was taken as the lowest concentration, which showed no visible growth of microbial colonies in the subculture dishes.

RESULTS AND DISCUSSION

The tripodal Schiff base H_3L was obtained from the reaction of 1 : 3 molar quantities of tris(2-aminoethyl)amine and 5-bromosalicylaldehyde in methanol. Complex **I** was prepared by the reaction of the Schiff base with manganese perchlorate in methanol. The Schiff base H_3L is soluble in DMSO, but not very soluble in methanol and ethanol. The complex is soluble in methanol, ethanol, and DMSO.

Table 2. Selected bond distances (Å) and angles (deg) for the Schiff base (H_3L) and complex **I**

Bond	*d*, Å	Bond	*d*, Å
H_3L			
C(7)–N(1)	1.279(3)	C(16)–N(2)	1.275(3)
C(25)–N(3)	1.274(3)	C(9)–N(4)	1.466(3)
C(18)–N(4)	1.469(3)	C(27)–N(4)	1.464(3)
I			
C(7)–N(1)	1.283(9)	C(16)–N(2)	1.283(9)
C(25)–N(3)	1.282(8)	C(9)–N(4)	1.468(10)
C(18)–N(4)	1.442(9)	C(27)–N(4)	1.438(9)
Mn(1)–O(1)	1.908(5)	Mn(1)–O(2)	2.098(5)
Mn(1)–O(3)	1.882(4)	Mn(1)–N(1)	2.355(6)
Mn(1)–N(2)	2.068(5)	Mn(1)–N(3)	2.069(5)
Angle	ω, deg	Angle	ω, deg
I			
O(3)Mn(1)O(1)	89.5(2)	O(3)Mn(1)N(2)	169.6(2)
O(1)Mn(1)N(2)	84.2(2)	O(3)Mn(1)N(3)	88.7(2)
O(1)Mn(1)N(3)	171.3(2)	N(2)Mn(1)N(3)	98.8(2)
O(3)Mn(1)O(2)	86.8(2)	O(1)Mn(1)O(2)	100.8(2)
N(2)Mn(1)O(2)	86.3(2)	N(3)Mn(1)O(2)	87.6(2)
O(3)Mn(1)N(1)	83.7(2)	O(1)Mn(1)N(1)	82.5(2)
N(2)Mn(1)N(1)	103.6(2)	N(3)Mn(1)N(1)	88.8(2)
O(2)Mn(1)N(1)	169.9(2)		

Table 3. Geometrical parameters for hydrogen bonds for H_3L and **I***

D–H···A	Distance, Å			Angle D–H···A, deg
	D–H	H···A	D···A	
H_3L				
O(1)–H(1)···N(1)	0.80(3)	1.81(3)	2.553(2)	153(3)
O(2)–H(2)···N(2)	0.82(3)	1.84(3)	2.593(3)	151(3)
O(3)–H(3)···N(3)	0.78(3)	1.91(3)	2.611(2)	150(3)
I				
C(16)–H(16)···O(1)^{i}	0.93	2.51	3.338(5)	148

* Symmetry transformation used to generate the symmetry related atoms: ^{i} $-x, -y, -z$.

The molecule of the Schiff base is shown in Fig. 1a. The bond lengths and angles related to the N(4), C(9), C(18) and C(27) atoms indicate that the apical N4 atom is sp^3-hybridized. The bond lengths of C(7)–N(1), C(16)–N(2), and C(25)–N(3) in the Schiff base are in the range of 1.27–1.28 Å, indicates they are typical double bonds. The intramolecular O–H···N hydrogen bonds (Table 3) in the Schiff base molecule make *S*(6) ring motifs [19]. Moreover, there exists π···π interactions (Table 4) in the crystal packing (Fig. 2a).

The Schiff base coordinates to the Mn atom through the three phenolate O and three imino N atoms, while the tertiary amine group does not take place in the coordination (Fig. 1b). The central Mn atom is in an octahedral coordination. The bond lengths of C(7)–N(1), C(16)–N(2), and C(25)–N(3) in the complex are about 1.28 Å, which are longer than those in the free Schiff base. The coordination through the

Table 4. Parameters between the planes for the Schiff base*

Cg	Distance between ring centroids, Å	Dihedral angle, deg	Perpendicular distance of *Cg*(*I*) on *Cg*(*J*), Å	β angle, deg	γ angle, deg	Slippage	Perpendicular distance of *Cg*(*J*) on *Cg*(*I*), Å
Cg(1)–*Cg*(1)$^{\#1}$	4.645	0	–3.540	40.4	40.4	3.007	–3.540
Cg(1)–*Cg*(3)	3.746	9	–3.339	18.6	27.0		3.552
Cg(2)–*Cg*(2)$^{\#2}$	4.319	0	–3.352	39.1	39.1	2.723	–3.352

* Symmetry codes: $^{\#1}$ $1-x, 1-y, 1-z$; $^{\#2}$ $1-x, 1-y, -z$. *Cg*(1), *Cg*(2), and *Cg*(3) are the centroids of C(1)–C(2)–C(3)–C(4)–C(5)–C(6), C(10)–C(11)–C(12)–C(13)–C(14)–C(15), and C(19)–C(20)–C(21)–C(22)–C(23)–C(24), respectively.

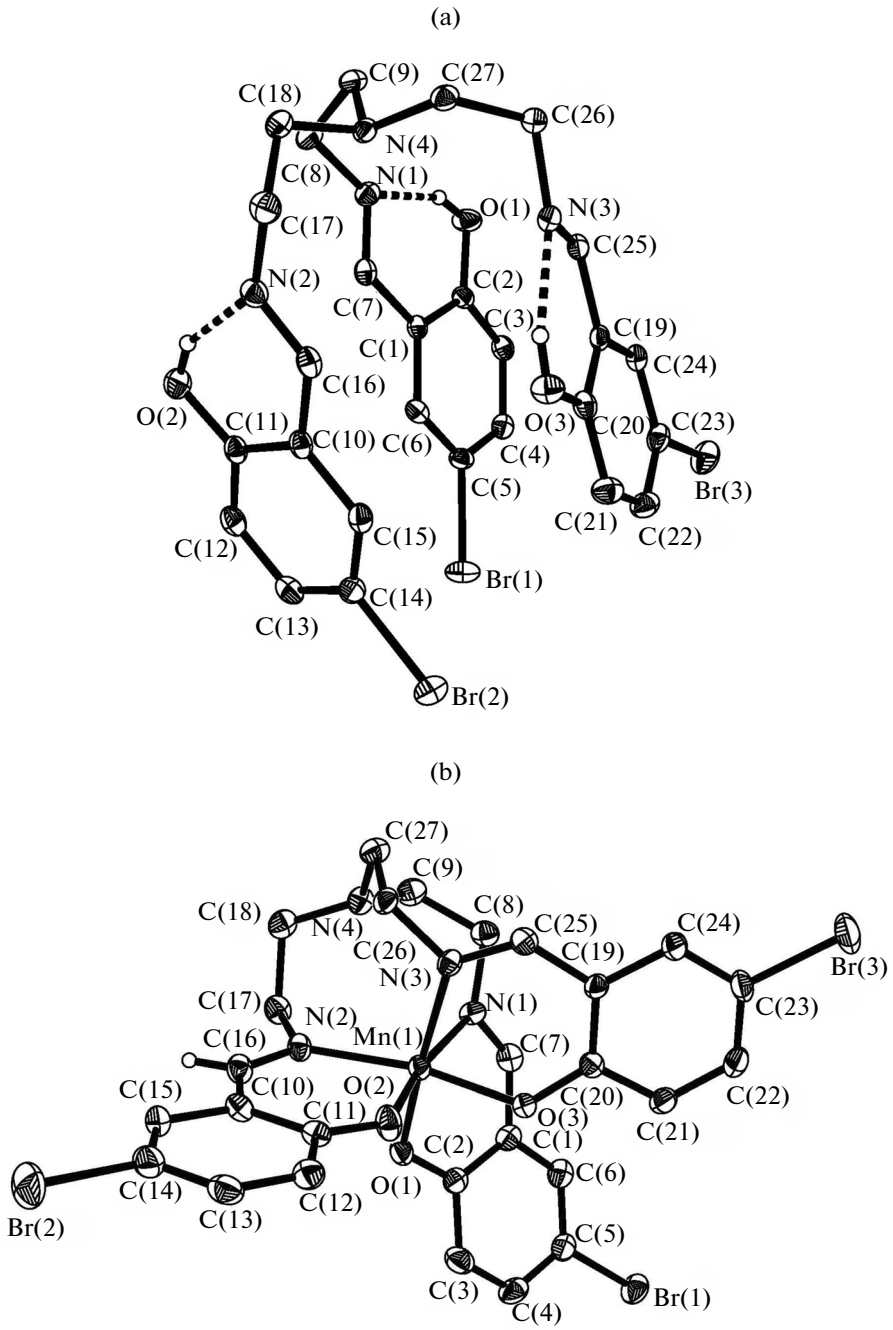


Fig. 1. ORTEP view of the Schiff base (H_3L) (a) and compound **I** (b). Thermal ellipsoids are at the 30% probability level.

Table 5. Antibacterial property of H_3L and **I**

Compound	*S. aureus*		*E. coli*		*C. parapsilosis*	
	IC_{50}^{*}	MIC*	IC_{50}	MIC	IC_{50}	MIC
H_3L	0.77	>2.5	1.26	>2.5	1.50	>2.5
I	0.20	0.31	0.53	1.25	0.87	>2.5

* mmol L^{-1}.

imino N atoms decreased the electron density of the C=N bonds, thus lengthened the bonds. The coordinate bonds related to the Mn atoms are similar to those observed in the literature [20, 21]. The axial O(1)Mn(1)N(3), O(2)Mn(1)N(1) and O(3)Mn(1)N(2) bond angles are 171.3(2)°, 169.9(2)° and 169.6(2)°, respectively. In the crystal structure of the complex, two molecules are linked through intermolecular C–H···O hydrogen bonds, to form dimers (Fig. 2b).

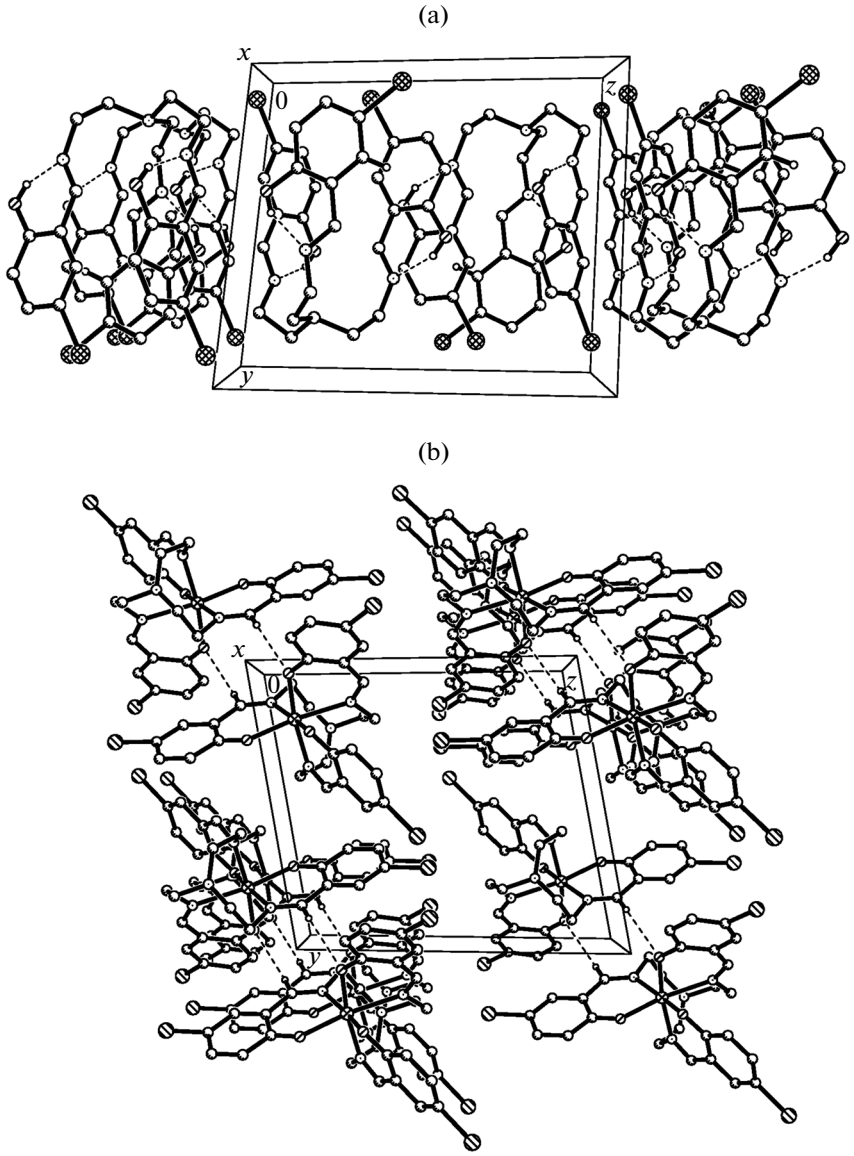


Fig. 2. Molecular packing diagram of the Schiff base (H_3L) (a) and compound **I** (b). Hydrogen bonds are shown as dashed lines.

The antibacterial results are summarized in Table 5. The Schiff base showed strong activity against *S. aureus*, and medium activity against *E. coli* and *C. parapsilosis*. The manganese complex showed strong activity against *S. aureus* and *E. coli*, and medium activity against *C. parapsilosis*. It is obvious that the manganese complex is more effective than the free Schiff base. The complex has the most activity against *S. aureus*, with IC_{50} and MIC values of 0.20 and 0.31 mmol L^{-1}, which deserve further study.

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