RESEARCH ARTICLE

Microwave Assisted Synthesis of Schiff base derived from Salicyldehyde and 1, 4- butane diamine and Complexes with Transition Metal (Sm^{+3}, Cu^{+2})

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ABSTRACT

Schiff base as ligands and their complexes have been synthesized from 1, 4- butane diamine and salicyldehyde. The ligand and its transition metal complexes of Cu(II) and Sm (III) are characterized by ultraviolet-visible (UV-Vis), Fourier transform infrared spectroscopy (FTIR) Proton nuclear magnetic resonance (^{1}H-NMR), mass, molar conductance and magnetic susceptibility measurements. The antibacterial activity of the synthetic organic compounds was tested. For both complexes, The stoichiometry has been found to be (metal : ligand) is 1:1.

Keywords: 1, 4- butane diamine, Schiff base, Transition metal complexes.

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Conflict of interest: None

INTRODUCTION

Schiff bases are Chemical compounds prepared by multi-methods. The first method condenses reactions of a carbonyl compound (aldehyde or ketone) with primary amines (first amine or diamine).[1,2] Second method by irradiated in the microwave as green chemistry method in the synthesis of Azomethines.[3,4] The compounds include good biological activity, clinical, medicinal, pharmacological, and analytical[5] such as anticancer.[6] Antifungal,[7] antibacterial,[8,9] antiviral.[10] Because the Schiff bases their high solubility in common solvents, are used as molecules donated of electrons as ligands to obtain metal complexes. The complexes of ligands can serve as models of understanding bio-systems.[11,12] In our previous studies, we investigated the synthesis and characterization of Cu(II), Sm(II) complexes of novel Schiff base.[13] In present paper, the ligand (LH) and Cu(II), Sm(III) complexes) have prepared by microwave method from aromatic aldehyde and diamine.

Instrumentation

The UV-Vis spectrophotometer model T 60, PG instruments Ltd, (Germany). The FT-infrared measurements were recorded by using FTIR affinity Spectrophotometer (Shimadzu) Japan; Mass spectra are recorded of compounds using Agilent Technology (HP)/MS Model 5973 Network Mass Selective Detector, Tehran, Iran. The ^{1}H-NMR with using dimethylsulfoxide (DMSO)-d^6 as solvent in Tehran, Iran. Magnetic susceptibility instrument (μeff. B.M).

Synthesis

Preparation of the Ligand (LH)

To a solution of Salicylaldehyde (1.22 g, 0.01 mol) in 25 mL absolute EtOH, 1, 4- butane diamine (0.88 g, 0.01 mol) dissolved in 15 mL absolute EtOH were added dropwise at room temperature with continuous stirring 5 minutes irradiated by microwave technique for 2 to 5 minutes.

The precipitate was filtered of after 24 hours, washed with hot absolute EtOH and dried at room temperature. Yield: 88%. Color: yellow. F.W.:192 $C_{11}H_{16}N_2O_1$. FT-IR:υmax cm^{-1} (KBr): 1623(C=N), 1279 (C–O), 3340-3570 (O-H), UV–Vis: υ_{max} (nm): 307 (n→π*) (azomethine).^{1}H-NMR (DMSO-d^6, 500 MHz): 6.72-7.4 (Ar-H), 8.60 (s, H, CH=N), 13.3 (s, H, OH).

Preparation of the Ni(II), Sm(III) Complexes

Two solutions of the ligand LH (0.192 g, 0.001 mol) were dissolved in 20 mL hot ethanol. A solutions of $Cu(Cl)_2.2H_2O$ (0.129 g, 0.001 mol), $Sm(Cl)_3.6H_2O$ (0.364 g, 0.001 mol) in 20 mL of hot ethanol was added dropwise at room temperature with stirring 5 minutes irradiated by microwave technique for 2 to 5 minutes.

The change of the local of (C=N) band and the appearance of the (O-H) band through the reaction was monitored by the infrared (IR) spectrum, including implication the nitrogen atom for azomethine group and oxygen atom of hydroxyl group in coordination with metal ion in complexes. The precipitated complexes were filtered off after 24 hours, washed with water and cold methanol and dried at room temperature.

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For Cu(II) complex, yield: 78%. Color: green. F.W.: 326 FTIR: υ_{max} cm^{-1} (KBr): 1620 (C=N), 420 (cl), 1238 (C–O), 3450-3550 (O-H), UV–vis: υ_{max} 3 cm: 300 (nm) (n→π*) (azomethine)), 421 (nm) (Charge- Transfer), μeff (B.M): 1.2 For Sm(III) complex, yield: 69%. Color: orange F.W.: 556. FTIR: υ_{max} cm^{-1} (KBr): 1631 (C=N), 4 59 (M-Cl), 1284 (C–O), 3430-3550 (H_2O), μeff (B.M): Dia.

RESULT AND DISCUSSION

The synthesis of the complexes may be represented as following equation:

$$Cu(Cl)_2.2H_2O+LH\rightarrow[Cu(LH)(Cl)_2.(H_2O)_2[+CH_3COOH.$$

$$Sm(Cl)_3.6H_2O+LH\rightarrow[Sm(LH)(Cl)_2.(H_2O)_2[n\ H_2O+CH_3COOH.$$

n = 4

FT-IR Spectra

The stretching vibration for υ (C=N) group in ligand at (1623) cm^{-1} in the IR spectrum. This band in Cu(II) complex changed [3-4]cm^{-1} to lower wave numbers, when in Sm(III) complex, the same band shifted (8–10) cm^{-1} to high wave numbers due to coordination in the complexes. This change in the local of stretching vibrations of the band suggests the coordination of the ligand through their azomethine nitrogen atom. The stretching vibration of υ(OH) in the spectra of the free ligand around (3340–3570) cm^{-1}.[14] This band in Sm(III) complex deprotonation of ligand to coordination through oxygen atom of hydroxyl group by equivalent bond, while in Cu(II) complex coordination the oxygen atom by coordinated bond. Because of the coordination of oxygen atom in coordination of the complexes, the phenolic bond (C-O) shifted to higher frequency due to the coordinated water (Figure 1).[15]

UV-vis Spectra

Table 1 results of UV-vis spectrum for synthesized compounds in DMF solution show band of n→π* transition around (305–307) nm due to nonbonding electrons on nitrogen the (C=N) group in the ligand molecule. Both the complexes Cu(II) and Sm(III) complexes show an intense band at (300–307) nm indicated the n →π* transition through the azomethine linkage.[16]

Magnetic Susceptibility Measurements

For Sm(III) complex, the magnetic moment value 1.12 BM contains unpaired electrons in the low spin complex with strong ligand (bidentate ligand) mononuclear octahedral geometry for Sm (III) complex. because of the dimeric structure of Cu(II) complex,[17] the magnetic moment value 0.5 B. M, the complex is Dia.

^{1}H-NMR Spectra

The ^{1}H-NMR spectrum of LH has been analyzed in DMSO-d^6, and data are given in Table 1, Figure 2.

Mass Spectra

The mass spectra of the prepared LH and complexes show a peak for the molecular ion, which agrees with the molecular formula for the synthesized compounds. The mass spectra of ligand appeared molecular ion peak at 192 m/z which conforms with the molecular formula. for $C_{11}H_{16}N_2O;M^+$; found: 192, (M/S) $Cu(LH)(Cl)_2(H_2O)_2$ =326M^+; found: 326 and Sm (LH) $(Cl)_2(H_2O)_2$= 556 M^+; found: 556 (Figure 3).

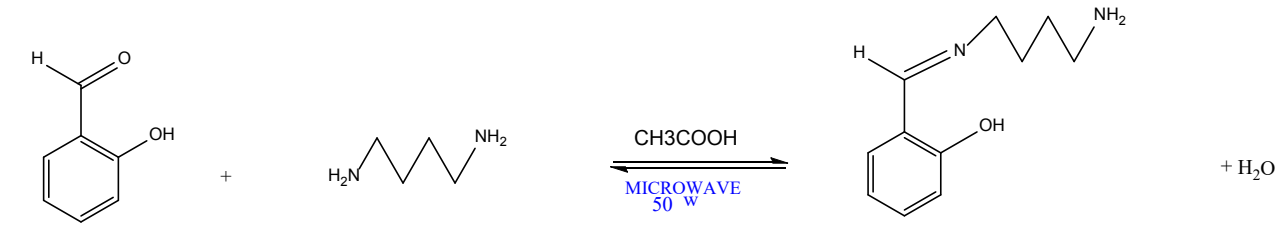
Molar Electrical Conductivity:

One from multi method and simple means for diagnosis of the nature the complex (ionic or non-ionic) formula by measuring the electrical conductivity).[18] Molar conductivity measured

Table 1: Spectroscopic data for ligand and its complexes

Compound	*IR C=N (cm)$^{-1}$*	*^{1}H-NMR & (ppm)*	*Mass spectra*	*UV–vis (nm)*
Ligand	1623	-N=CH- = (8.6) -OH =(13.6) -CH_2 =(3.7) -OCH_3=(1, 7) -CH_2 =(2.6) -Ar-H =(6.7 – 8.6)	m/s; 192]M+H	307 n—π* 259 π—π*
A	1620	—	m/s; 326]M+H	300 n—π* 260 π-π* 421 C-T
B	1631	—	m/s; 556]M+H	

[a][$(Cu(LH)(CL)_2(H_2O)_2$[[b]]$Sm(LH)(H_2O)_2CL_2$] *Charge Transfer



2-hydroxybenzaldehyde butane-1,4-diamine (E)-2-(((4-aminobutyl)imino)methyl)phenol

Scheme 1: Structure of the ligand (LH).

for solid complexes solutions of ions [Sm^{+3}, Cu^{+2}] with (LH) solution (10^{-3}) M uses DMSO as solvent and a distilled water as a reference at 25°C (Figure 4). The measured results of the electrical conductivity indicated in Table 2. The values of conductivity for the complexes have non-electrolytic neutral compounds.[18]

Biological Study

Gram Positive Bacteria as *Staphylococcus aureus* and Gram Negative Bacteria as *Escherichia coli*, as two Species from bacteria, tested the antibacterial efficiency of LH and complexes by using agar spread method Ciprofloxacin as standard drug and evaluate tested. Nutrient agar was used as culture medium, DMSO as a solvent, and the efficacy of DMSO was tested against the bacteria. Inhibition of the bacteria was calculated in millimeter. 10 mg.m/L concentrations of prepared compounds, agar spread method, indicated the exposure of the zone of inhibition toward the spread of bacteria on agar dish (Figure 5).[20,21]

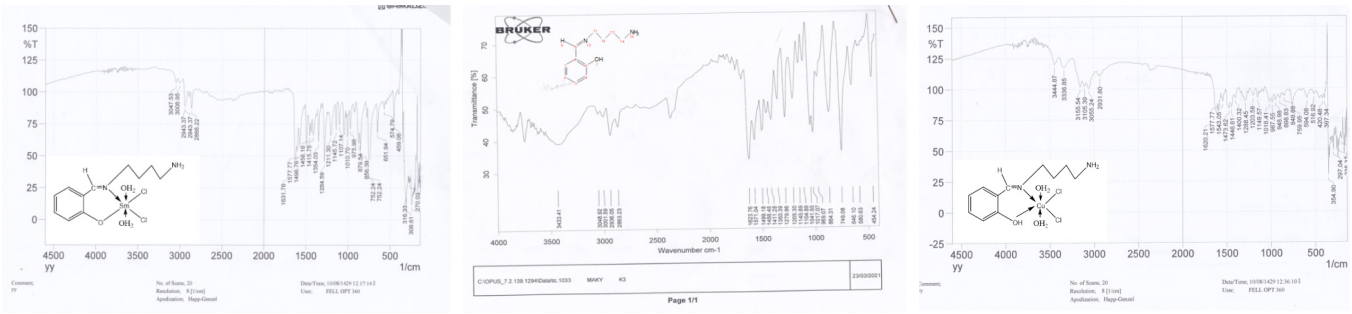
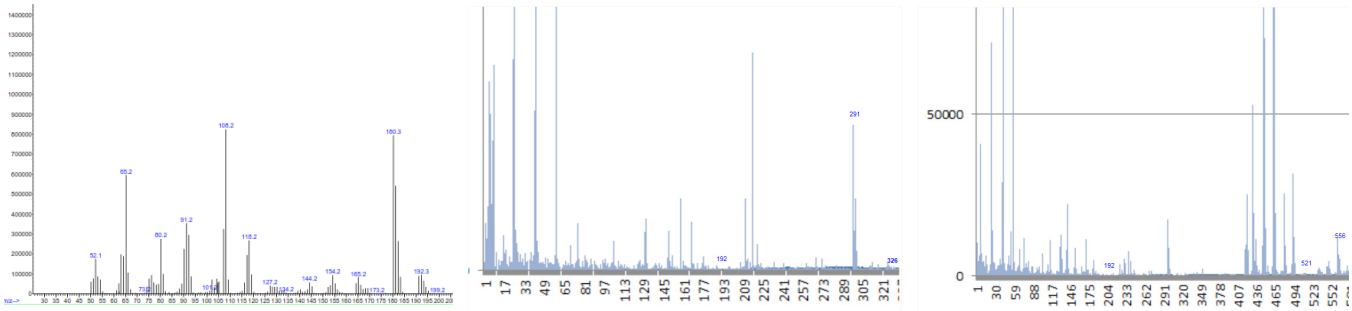


Figure 1: IR spectrum of ligand and complexes.



Ligand **$Cu(LH)(H_2O)_2(Cl)_2$** **$]Sm(LH)(H_2O)_2(Cl)_2[$**

Figure 3: Mass spectrum of ligand and the complexes

Table 2: Molar electrical conductivity of (LH) complexes

Complex no.	*Complexes*	*Λm (S.cm².mole⁻¹)*	*Electrolyte type*
1	[Cu (L_H) $(Cl)_2(H_2O)_2$]	13	Non-electrolyte
2	[Sm(L_H) $(Cl)_2(H_2O)_2$]	18	Non-electrolyte

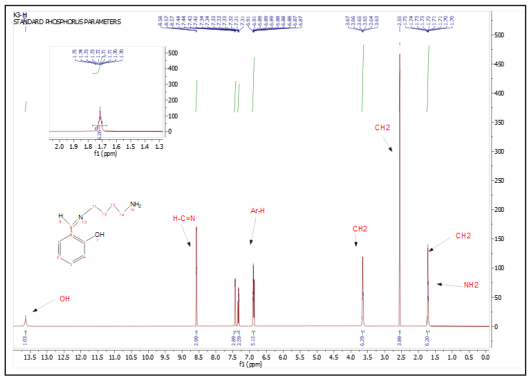


Figure 2: ^{1}H-NMR spectrum ligand

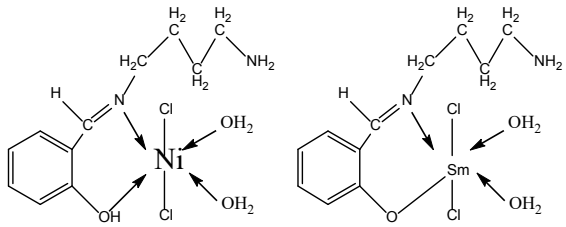


Figure 4: Suggested structure of the Sm(III) and Cu(II) complexes

Table 3: Biological activity of the prepared compounds against bacteria *E. coli* and *S. aureus*

No.	*Compounds*	*S. aureus inhibition zone (mm)*	*E. coli inhibtion zone (mm)*
1	$C_{11}H_{16}N_2O$	17	19
2	$[Cu(L_3)_2\ Cl_2]$	8	10
3	$[Sm(L_3)_2\ Cl_2]$	24	20
4	DMSO	—	—
5	Cipro	30	26

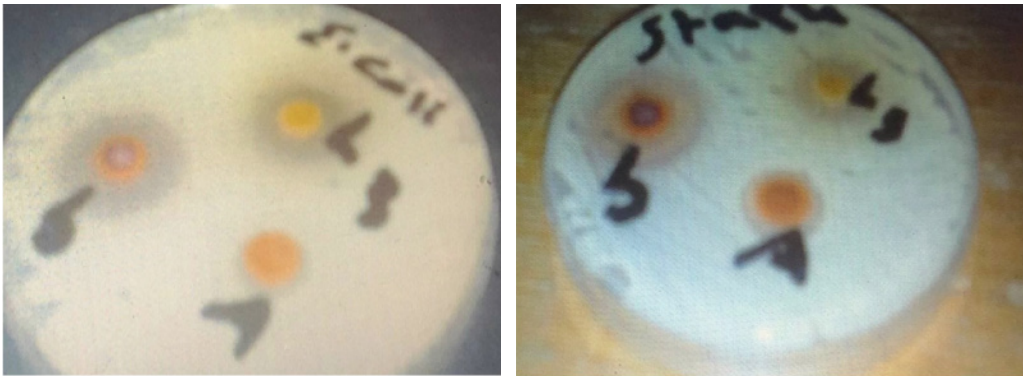


Figure 5: A=Cu, B=Sm

- The LH showed high activity against *E. coli* and *Staph* bacteria.
- The complexes showed high activity against *E. coli* bacteria and lower activity against *Staph* bacteria

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