RESEARCH ARTICLE

Microwave Preparation, Spectroscopic Investigation, and Anticorrosion Evaluation of Bidentate N, O-Doner Schiff bases and its Complexes with Cu (II) and Co (II) Ions

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ABSTRACT

A new ligand (LH) and its complexes with Cu (II) and Co (II) were prepared. The purity of the new synthesized compound was checked by performing TLC using appropriate solvent and the spots visualized in the UV light. Ligand (LH) is characterized by using Fourier-transform infrared spectroscopy (FTIR), ultraviolet-visible (UV-vis), Proton nuclear magnetic resonance (^{1}H-NMR) spectra, and Mass spectrum. Metal ion complexes with Cu (II) and Co (II) were prepared in a M:L (1:1) ratio and characterized by the same spectrophotometric techniques, magnetic susceptibility and molar conductivity. The new ligand showed a reasonable amount of anti-corrosion activity. It was observed that the corrosion rate (CR) in the presence of the inhibitor decreased with the increase of the inhibitor concentration at a constant temperature.

Keywords: Anticorrosion activity, Bidentate Schiff base, Metal complexes Spectral Studies.

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INTRODUCTION

A large number of Schiff bases and their complexes have been studied for their interesting and important properties.[1] Schiff bases derived from aromatic aldehyde and diamine compounds have been widely used as ligand to synthesize transition metal complexes. Schiff bases or their complexes have many applications in different fields,[2] and forms stable complexes with transition metal ions.[3] Schiff base complexes having N, O donor atoms are very important because of their significant medical[4] such as antifungal,[5] antibacterial,[5] and anticancer.[6] In organic preparations, Schiff base reactions are useful in making azomethine group (C=N) and serve as intermediate in enzymatic reaction (involving interaction NH_2 of amine or C=O of aldehyde) with an enzyme.[7] Schiff base (LH) derived from 3-ethoxy-salicylaldehyde with 4, 4'-diamino-diphenylethane, and their Co(II) and Cu(II) complexes were characterized by FTIR, ^{1}H-NMR, UV-visible mass spectra(UV-VMS), Thermogravimetric – TGA, and anticorrosion activity.

Instrumentation

The UV-Vis spectrophotometer model T 60, PG Instruments Ltd, (Germany). The FT-infrared measurements were recorded using FTIR affinity Spectrophotometer (Shimadzu) Japan; Mass spectra are recorded of compounds using Agilent Technology (HP)/MS Model 5973 Network Mass Selective Detector. The ^{1}H-NMR with using Dimethyl sulfoxide (DMSO) as a solvent in Tehran, Iran.

Chemistry the Synthesis of Ligand (LH)

3-ethoxysalicylaldehyde (1.66 g, 0.01 mol) in absolute EtOH (20 mL) were added to hot solution 4, 4'-diamino-diphenylethane (2.12 g, 0.01 mol) in the same solvent in an equimolar ratio for 15 mL followed 4 drops wise of glacial acitic acid. Then the reaction Irradiated in microwave for (2–5) minutes. Then allowed to cool, the precipitated orange powder has been filtered and recrystallization from absolute EtOH. Scheme 1 Yield: 90%. F.W.: 360.3 $C_{23}H_{24}N_2O_2$.

Synthesis of Metal Complexes

(0.36 g, 0.001 mol) of Schiff base (LH) was dissolved in 15 mL hot absolute ethanol. Solution of metal salts $[Co(Cl)_2]$ H_2O (0.237 g, 0.001 mol) $[Cu(Cl)_2]2H_2O$ (0.134g, 0.001 mol) in

Scheme 1: Structure of the ligand

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15 mL of absolute hot ethanol were added dropwise to the solution and the ligand. The mixture was stirred for 15 minutes, and Irradiated in microwave for 1 to 3 minutes, The precipitated complexes were filtered off after overnight, washed with water and cold ethanol and dried at room temperature. yield: 68%. Color: black. F.W.: 597, μeff (B.M.): 4.02. For Cu(II) complex, yield: 65%. Color: dark green. F.W.: 494. μeff (B.M.): 0.5.

RESULT AND DISCUSSION

The formation of the complexes may be represented as follow.

$$Co(Cl)_2.6H_2O + LH \rightarrow [ML(Cl)_2(H_2O)_2].nH_2O + CH_3COOH$$
n=4
$$Cu(Cl)_2.2H_2O + LH \rightarrow [ML(Cl)_2(H_2O)_2].nH_2O + CH_3COOH$$
n= 0

IR Spectra

The FTIR spectrum of the Schiff bases Figure 1 showed bands υ (C=N), υ (O-H) and υ ($C\text{-}NH_2$) respectively, which absorbed at 1623 cm^{-1}, 3430–3550 cm^{-1} and 3200–3390 cm^{-1}.[8,9] Band at 1623 cm^{-1} has shifted in $Co(L)(Cl)_2(H_2O)_2$ 15 cm^{-1} to lower wave numbers and band has shifted $Cu(L)(Cl)_2(H_2O)_2$ 8 cm^{-1} to high wave numbers due to coordination in the IR spectra of the complexes. The band at (3430–3550) cm^{-1} of υ (O-H) in spectra of ligand remained in spectra of both complexes because of coordination of oxygen atom.[10] The band at (3430–3550) cm^{-1} may be due to the bending modes of lattice and coordinated water.[11] The band at 509 cm^{-1}, 430 cm^{-1} and 374 cm^{-1} assigned to the stretching vibrations of the υ (M-O), υ (M-N), and υ (M-Cl), respectively.[12]

Mass Spectra

The mass spectrum of the prepared Schiff bases shows a peak for the molecular ion, which agrees with the proposed molecular formula for these bases. Where we notice the appearance of a molecular ion peak in the Schiff base L at (M/S) =m/s calcd for $C_{23}H_{24}N_2O_2$ =360 ; M^+ ; found: 360, (M/S) $(Cu(LH)(H_2O)_2(Cl)_2)$ =529 and $(Co(LH)(H_2O)_2(Cl)_2)$ = 525.

UV-vis Spectra

The absorptions and assignments related to the ligand and their complexes are listed in Table 1, absorption band for the ligand exhibited at wavelength (300 nm) attributed to n→π*. The spectrum Cu(II) gave two bands at 405 nm and 500 nm, which may be attributed to (C-T) and ^2Eg – ^2T_2g when the spectrum of Co(II) Complex exhibited absorption at 414 nm, which may be attributed to (C-T).[14]

Magnetic Susceptibility Measurements

The low value of the magnetic moment 1.02 B.M. for Co(II) complex confirms that to strong ligand Capable of pairing electron (low spin–complex) lies in the range expected for a d^7 system, agreement with mononuclear octahedral geometry.[15] When Cu(II) complex gave very low magnetic moment 0, 5 B.M. agreement with diamagnetic ajative for complex or maybe to the mononuclear octahedral geometry.[15]

Thermal Analysis

The thermal stability of the ligand and complexes were studied by TGA analysis with a heating rate of 10°C/min, the thermograms of LH, Cu(II), and Co(II) complexes exhibited

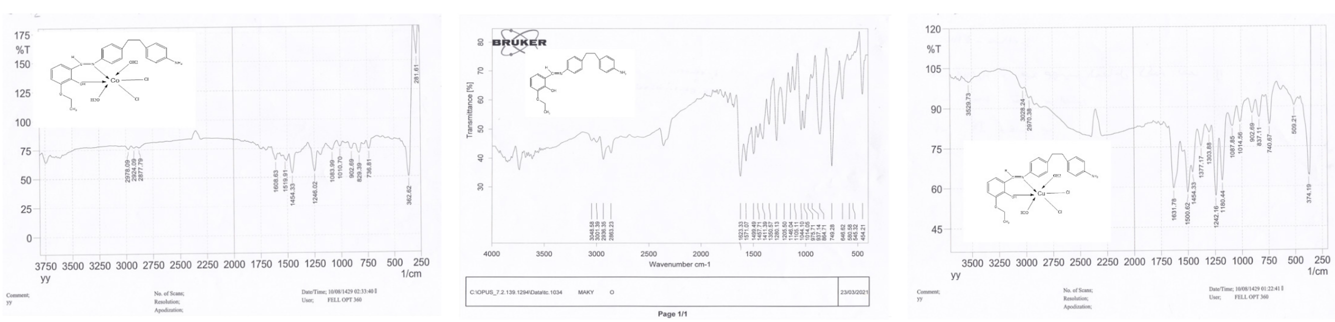
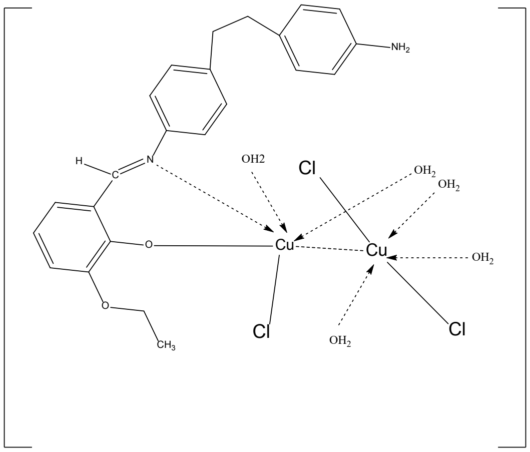


Figure 1: IR spectrum of ligand and complexes

Table 1: Spectroscopic data for ligand and its complexes

Compound	*IR C=N (cm)$^{-1}$*	*H1-NMR &(ppm)*	*Mass spectra*	*UV. –Vis (nm)*
Ligand	1623	-N=CH- = (8.8) -OH = (13.4) -CH3 = (1.4) $-NH_2$= (4.2) -CH2 = (3.3) -Ar-H = (6.6 – 7.4)	m/s; 360 M^+	302 n—π* 228 π---π* 270 π---π*
A	16O8	—	m/s; 597 M^+	200 π-π* 414 C-T
B	1631	—	m/s; 494 M^+	336 n—π* 405 C-T 500 d-d

$(Co(LH)(H_2O)_2(Cl)_2)$ b- $(Cu(LH)(H_2O)_2(Cl)_2)$ *Charge Transfer two steps at temperature (300–399, 399–650), (270–407, 407–602), (250–401, 401–650), respectively, by using thermogravimetric techniques in the temperature range from ambient to 800°C. The results agree the absence of the lattice water molecules in the complexes.[16,17] Suggested structure of the dimeric Cu(II) complex (Table 2). (36)



Anticorrosion Activity

Table 2: TGA data of Ligand and the complexes

Compounds Temperature range (°C) Weight loss (%) (ligand and complexes)	
Ligand 300–399	64% M. wt
399–650	42% M. wt
$[Cu(L_{H)}\ (Cl)_2.\ (H_2O)_2]$ 270–407 57% M.wt	
407 - 602	42% M. wt
$[Co(L_{H)}\ (Cl)_2.(H_2O)_2]$ 250–401	57.9% M. wt
401–650	42% M. wt

Weight Loss Measurements

The weight loss data and the rate of corrosion of Stainless Steel 410 in 0.1 M HCl in the absence and presence of various concentrations of inhibitors at 303 K after 4 hours immersed period were obtained and are given in Tables 3 to 5. The results show that the weight loss data and the rate of corrosion decrease with increasing inhibitor concentration (Figures 6 and 7). The corrosion rate (CR), the percentage inhibition efficiency (IE%), and the degree of surface coverage (θ) were calculated using the following equations.[19]

$$CR=\frac{W.K}{A.D.t} \quad (2)$$

Where:
WL is the weight loss (g)
CR is the corrosion rate
A is the area of the specimen $(Inch)^2$
D is the density of the alloy in $g.cm^{-3}$
K is a constant (543) (giving rate in mpy) and t is immersion time (hours).
The inhibition efficiency (IE%)was computed using the following Equation

$$E\% = CR\ uninh - CR\ inh / C\ Runih \times 100 \quad (3)$$

Where:
CR uninh and CR inh are the corrosion rates in the absence and presence of the inhibitor, respectively θ is the surface coverage of the metal surface covered by the adsorbed inhibitor, was evaluated from weight loss measurements using the following equation.

$$\theta = CR_{uninh} - CR_{inh} / CR_{unih} \quad (4)$$

The amount of weight loss is less compared to the absence of inhibitors. We also find that at a temperature of 303 K and

Table 3: Weight loss, Rcorr (mpy), %IE and Θ for stainless steel 410 in (0.1) M HCl in the absence and presence of various concentrations of inhibitor at 303 K after 4 hours immersed Period

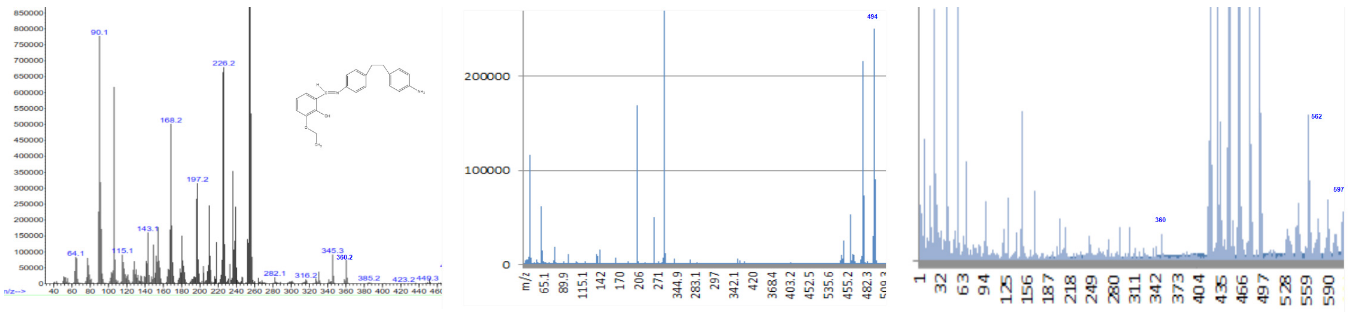
	303k درجة حرارة																
	time (hr)	*1*				*2*				*3*				*4*			
	cone (ppm)	*Wt.loss gm*	*Rcarr (mpy*	*%IE*	*Θ*	*Wt.loss gm*	*Rcorr (mpy)*	*%NE*	*Θ*	*Wt.loss gm*	*Rcarr (mpy*	*%IE*	*Θ*	*Wt.loss gm*	*Rcorr (mpy)*	*%NE*	*Θ*
ligand (5)	blank	0.0082	492			0.0185	559			0.0285	570			0.0394	591		
	25 ppm	0.0064	384	23	0.23	0.0077	231	59	0.59	0.0109	218	62	0.62	0.0123	184	69	0.69
	50 ppm	0.005	300	40	0.4	0.0062	186	55	0.55	0.0089	178	58	0.58	0.0109	153	72	0.72
	100 ppm	0.0031	186	63	0.63	0.0044	132	76	0.76	0.0072	144	75	0.75	0.008	120	80	0.8

Table 4: Weight loss for stainless steel 410 in 0.1 M HCl in the absence and presence of various concentrations of inhibitor at 303 K after 4 hours immersed period

Time	*Wt-loss HCl*	*Wt-loss HCl+ inhibit*	*Wt-loss HCl+ inhibit*	*Wt-loss HCl+ inhibit*
(hours)	*Gm*	*25 PPM*	*50 PPM*	*100 PPM*
1	0.0082	0.0064	0.005	0.0031
2	0.0185	0.0077	0.0062	0.0044
3	0.0285	0.0109	0.0089	0.0072
4	0.0394	0.0123	0.0109	0.008

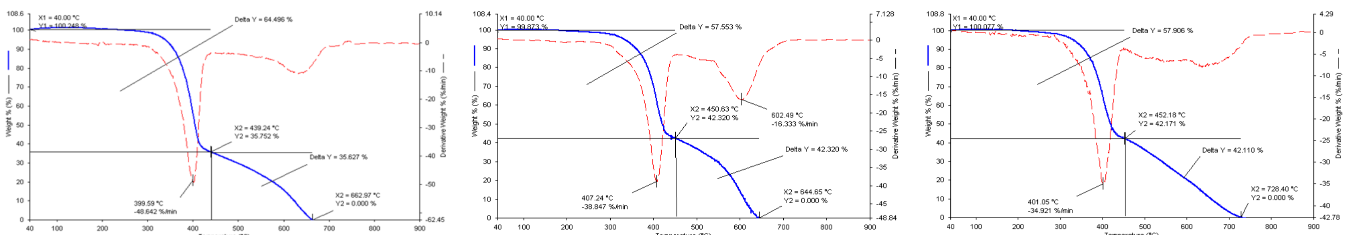
Table 5: Corrosion rate for stainless steel 410 in (0.1) M HCl in the absence and presence of various concentrations of inhibitor at 303 K after 4 hours immersed period

Time	*Rcorr HCl (mpy)*	*Rcorr (mpy) inhibit*	*Rcorr (mpy) inhibit*	*Rcorr (mpy) inhibit*
(hours)	*gm*	*25 PPM*	*50 PPM*	*100PPM*
1	492	384	300	186
2	559	231	186	132
3	570	218	178	144
4	591	184	163	120



Ligand $[Cu(L)CL_2(H_2O)_2]$ $[Co(L)CL_2(H_2O)_2]$

Figure 2: Mass spectrum of ligand and complexes



Ligand $[Cu(L_H)Cl)_2\ (H_2O)_2]$ $[Co(L_H)Cl)_2\ (H_2O)_2]$

Figure 3: TGA spectrum of ligand and complexes

Figure 4: ^{1}H-NMR spectrum of ligand

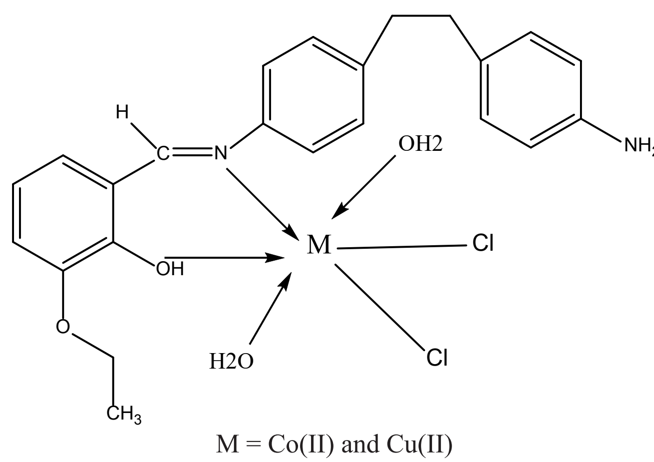


Figure 5: Suggested structure of the Co(II) and Cu(II) complexes.

Table 6: The relationship between the Rcorr (mpy) in the absence and presence of the inhibitor in time one for the ligand at a temperature of 303 K

Time	*Rcorr HCl (mpy)*	*Rcorr (mpy) inhibit*	*Rcorr (mpy) inhibit*	*Rcorr (mpy) inhibit*
(hr)	Gm	25 PPM	50 PPM	100 PPM
1	390	105	143	78

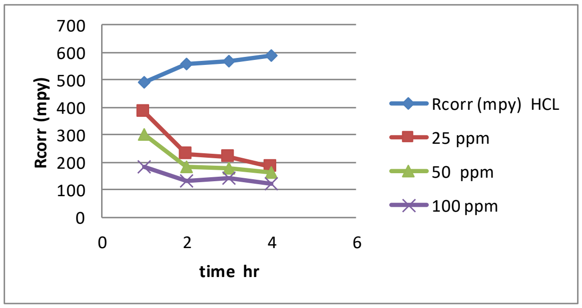


Figure 7: The relationship between the Rcorr (mpy) with time for the ligand at a temperature of 303 k

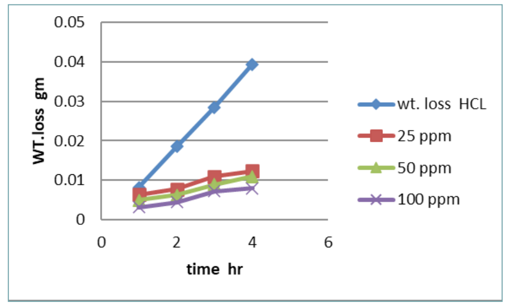


Figure 6: The relationship between weight loss with time for Ligand at a temperature of 303 K

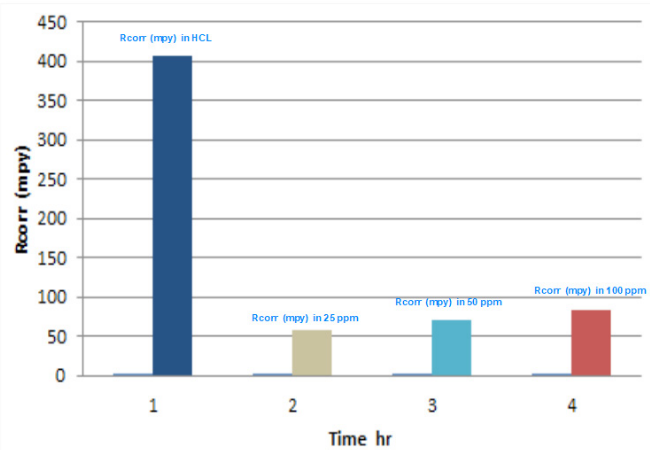


Figure 8: The relationship between the electrochemical Rcorr(mpy) with time for the ligand at a temperature of 303 K

with a constant concentration and a change in time, the amount of weight loss increases with the increase in time, but when the concentration changes and the time and temperature are constant, the amount of weight loss decreases with the increase in concentration.

Through the above results, we find that at one temperature, with constant concentration and time change, the rate of corrosion speed increases with the increase of time in the absence of inhibitors. In the presence of inhibitors, the rate of corrosion speed decreases with the increase of time. When the concentration is changed and time and temperature are fixed, the rate of corrosion rate decreases with the increase in the concentration of the inhibitor.

Study of Corrosion of Stainless Steel 410 in Aqueous Solution of HCl at a Concentration of 0.1 M by Electrochemical Method (Potentio-dynamic Polarization).

This electrochemical method (polarization technique) proves and enhances the results of measurements of the method by weight loss in terms of the rate of corrosion velocity Rcorr (mpy), where the two methods were identical and the results were good as in Table 6 and Figure 8.[19,20]

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