Pak. J. Chem. 4(2): 67-71, 2014 Full Paper
ISSN (Print): 2220-2625
ISSN (Online): 2222-307X DOI: 10.15228/2014.v04.i02.p03

Synthesis and Characterization of New Schiff Base and Its Metal (Cu, Ni, Co, Zn, Mn) Complexes

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ABSTRACT
Many chemists have reported on the chemical, structural and biological properties of Schiff bases. In this study, ([(2-hydroxybenzylidene)-3methylurea]) Schiff base derivative and ıts metal (Cu, Co, Ni, Mn, Zn) complexes have been synthesized and characterized. From the elemental analyses date we found that the complexes have general formula $[Mn](L)_2]$, $[Co](L)_2].H_2O$, $[Zn](L)_2].3H_2O$, $[Cu](L)_2].4H_2O$, $[Ni](L)_2].2H_2O$. From the magnetic moment and UV-Vis spectral studies, the geometrical shape for the complexes of Mn (II), Co (II) and Zn (II) are octahedral, for the complexes of Ni (II) it is tetrahedral. While it is square-planar for the complexes of Cu (II).

Keywords: Schiff base and metal complexes, ([(2-hydroxybenzylidene)-3methylurea]).

1. INTRODUCTION
Schiff bases, aldehyde or ketone compounds are achieved from the reaction with the primary amine condensation products. They contain carbon-nitrogen double bond, as a functional group[1]. General formula is $R_1CH=NR_2$. This definition, Schiff base is synonymous with azomethine[2]. Schiff bases are common ligands in coordination chemistry. The ligands are typically derived from alkyl diamines and aromatic aldehyde[3]. Schiff base ligands are able to coordinate many different metals, and they tend to stabilize them in various oxidation states, enabling the use of Schiff base metal complexes for a large variety of useful catalytic transformations. Schiff bases and their coordination compounds are well known to be biologically important. The presence of nitrogen and other donor atoms in its structure makes it biologically active[4]. Recent literature has explored the biological importance of various structural derivatives of heterocyclic compounds. Schiff's bases, the condensed products of aromatic amines with aromatic aldehydes, have been known to possess a wide variety of biological applications like antibacterial, antifungal, antitumor, analgesic and anti-inflammatory activities[5-6]. Moreover, Schiff's bases obtained from various heterocyclic scaffolds cover a wide range of pharmacological potential such as antimicrobial[7], anthelmintic, analgesic[8], anti-inflammatory, allergic inhibitors reducing activity[9], antipyretic[10], diuretic[11], hypoglycemic[12], anticonvulsant[13], anti-HIV[14], cytotoxic[15], anticancer[16], antitumor[17], activities. Also determined that radical scavenging[18] anti-oxidative action[19]. In a recent report published in 2013; Schiff base derivative of Cu complexes were found to exhibit a strong pro-oxidant property[20].

This present work was performed using to salicylaldehyde with ([(2-hydroxybenzylidene)-3methylurea]). For the metal complexes Cu, Ni, Zn, Mn, Co were selected. Because they are biologically very important.
This work is focused on the synthesis, characterization and determination of biological activity of a new Schiff base derivative.

2. MATERIAL AND METHOD
2.1 *Materials and instrumentation*
All solvents were of analytical-grade reagents. The metal salts, $CuCl_2.2H_2O$, $CoCl_2.6H_2O$, $NiCl_2.6H_2O$, $ZnCl_2$, $MnCl_2.2H_2O$ and starting materials for the ligand were purchased from Merck Sigma-Aldrich. Elemental analyses were carried out on a LECO CHNS-O model 932 elemental analyzer, ^{1}H-NMR spectra were recorded using a model Broker GmbHDPX-300 MHz, Spectrophotometer, Infrared (IR) spectra were recorded with a Perkin Elmer, Precisely Spectrum One spectrometer on KBr discs in the wave-number range of 400 - 4000cm$^-$. Electronic spectral studies were conducted on a Shimadzu model UV-1700 spectrometer in the wavelength of 200-1100 nm. Magnetic susceptibility measurement were performed using the standard Gouy tube technique, using Hg $[CoSCN)_4]$ as a calibrate. Thermal analyses (TGA and DTA) were carried out in a nitrogen atmosphere with a heating rate of 10°C/min, using Shimadzu Dtg-60 Ah (DSC 60A; Shimadzu, Kyoto, Japan) thermal analyzers.

2.2 *Method*
2.2.1 *Synthesis of ligand (L)*
0.1 mole ([(2-hydroxybenzylıdene)-3methylurea]) was dissolved in 10 ml methanol. Then; it was added to 0.1 mole salicyladehyde (its 2 ml created in 10 ml hot methanol). 5drops of acetic acid solution were added to the above mentioned solution to keep ~ 5.30. The resultant solution was heated on a electromagnetic stirring apparatus to reflux for 5 hours. After evaporation a dark red solid was obtained. The product was dried in air for 48 hours.

*Corresponding Author Received 21st May 2014, Accepted 21st July 2014

2.2.2 *Synthesis of [Cu (L)$_2$]. 4H$_2$O*

A solution of salicylaldehyde prepared in methanol (2ml salicylaldehyde created in10 ml methanol). Was added to (1g) 0,1 mole ([(2-hydroxybenzylıdene)-3methylurea]) which created in 10 ml hot methanol. 5 drops of acetic acid solution were added to the above mentioned solution to keep ~ 5.30. 1 gram $CuCl_2$ was dissolved in hot methanol and was added to reaction mixture. The resultant solution was heated on an electromagnetic stirring apparatus to reflux for 4 hours, consequently the green solid complex was precipitated. The solid complex that separated out at room temperature was filtered and dried.

2.2.3 *Synthesis of [Ni] (L)$_2$]. 2H$_2$O*

A solution of salicylaldehyde which (2ml in 10 ml methanol) added to $NiCl_2$ solution which 1 gram salt created hot in methanol, and the reaction continued, 0.1 mole ([(2-hydroxybenzylıdene)-3methylurea]) in 10 ml hot methanol, was added to reaction mixture. 5 drops of acetic acid solution were added to the above mentioned solution to keep ~ 5.30. The mixture was left for reflux, with continuous stirring for 4 hours, and brown solid complex was obtained. The solid complex, which separated out at room temperature, was filtered and oven dried.

2.2.4 *Synthesis of [Co] (L)$_2$]. H$_2$O*

A solution of salicylaldehyde in methanol added to $CoCl_2$ solution (1 gram salt created hot in methanol), and the reaction continued. 0,1 mole ([(2-hydroxybenzylıdene)-3methylurea]) in 10 ml hot methanol was added to reaction mixture. 5 drops of acetic acid solution were added to the above mentioned solution to keep ~ 5.30. The mixture was left under reflux, with continuous stirring for 6 hours. and black solid complexes was obtained. The solid complex, which separated out at room temperature, was filtered and oven dried.

2.2.5 *Synthesis of [Mn](L)$_2$]*

A solution of salicylaldehyde (2ml salicyaldehyde in 10 ml methanol), added to 0.1 mole ([(2-hydroxybenzylıdene)-3methylurea]) (1 gram in 10 ml hot methanol). 5 drops of acetic acid solution were added to the above mentioned solution to keep ~ 5.30. and the reaction continued. $MnCl_2$ solution (1 gram salt dissolved in 10 ml hot methanol) was added to in reaction mixture. The result in solution was heated on a electromagnetic stirring apparatus to reflux for 6 hours, consequently the green solid complexes was formed. The solid complexes that separated out at room, temperature, were filtered and dried.

2.2.6 *Synthesis of [Zn (L)$_2$]. 3H$_2$O*

A solution of salicyladehyde (1 gram in methanol) added to 0.1 mole ([(2-hydroxybenzylıdene)-3methylurea]) solution (1g / 10 ml hot methanol). 5 drops of acetic acid solution were added to the above mentioned solution to keep ~ 5.30. $ZnCl_2$ solution (1 gram salt dissolved hot in methanol) was added to in reaction mixture. The resultant solution was heated on an electromagnetic stirring apparatus to reflux for 6 hours, until solid complex was precipitated. The product was precipitated with diethyl ether and the resulting dark-yellow solid was obtained.

3. RESULTS

All date present in a table-3

Table-1: Characteristic IR bands cm^{-1} of ligand (L) and its metal complexes in the KBr pellets.

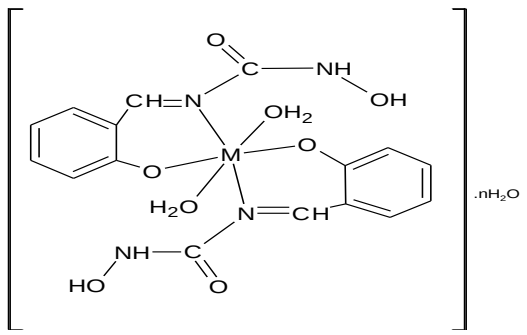
Assignment	Ligand	Cu	Co	Mn	Zn	Ni
ν (OH)	*3379*	_	_	_	_	_
ν phenolic C-O	1297-1253					
ν CH=N	1636	1647	1649	1654	1654	1621
ν M-O	_	466	474	472	463	467
ν M-N	_	570	581	530	533	520
ν phenolic O-H	1371	_	_	_	_	_

Table-2: Characteristic UV of ligand (L) and its metal complexes

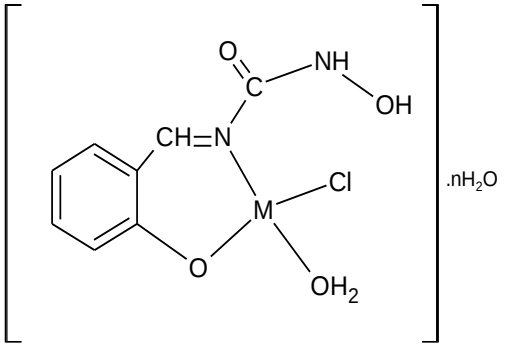
COMPUNDS		Wavelength in nm
Ligand(L)		
[Co](L)$_2$].H$_2$O	301 and 436 nm $\pi\rightarrow\pi^*$ transition	479-500 nm $^4T_{1g}(F)\rightarrow {}^4T_{1g}(P)$ and 703-710nm $^4T_{1g}(F)\rightarrow {}^4A_{2g}(F)$ transitions
[Ni](L)$_2$]. 2H$_2$O	328-354 nm $\pi\rightarrow\pi^*$, $n\rightarrow\pi^*$ transition	600 nm $^3T_1(F)\rightarrow {}^3T_{1g}(P)$, transitions
[Cu](L)$_2$].4H$_2$O	641-450 nm region absorption	$^2B_1\rightarrow {}^2A_1$ and $^2B_1\rightarrow {}^2E$ transition
[Mn](L)$_2$	280 nm $\pi\rightarrow\pi^*$	377-460 absorption band L→M

Table-3: Colors, formula, formula weight (FW), magnetic moments and elemental analyses results of the ligand (L) and the complexes

Compound	Colors	Formula	Formula weight(FW) (g/mol)	magnetic moment (B.M)	Elemental analyses (%) C	N	H	O
Ligand	Dark red	$C_8H_{14}N_2O_3$	186	_	53.6	15.05	7.52	25.80
$[Cu](L)_2].4H_2O$	green	$C_{16}H_{36}CuN_4O_{10}$	507,5	1.53	37.83	11.03	7.09	31.52
$[Ni](L)_2].2H_2O$	brown	$C_{16}H_{32}NiN_4O_8$	466	2.35	41.20	12.01	6.86	27.46
$[Co](L)_2].H_2O$	black	$C_{16}H_{30}CoN_4O_7$	448	3.30	42.85	12.50	6.69	25.00
$[Mn](L)_2]$	green	$C_{16}H_{30}MnN_4O_7$	444	5.80	43.24	12.61	6.75	25.22
$[Zn](L)_2].3H_2O$	Dark yellow	$C_{16}H_{34}ZnN_4O_9$	491	_	39.10	11.40	6.92	29.32



M:	Mn(II)	Co(II)	Zn(II)
n:	-	1	3



M:	Cu(II)	Ni(II)
n:	4	2

Figure-1.1: Suggested structure of metal complexes

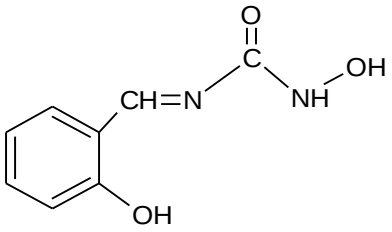


Figure-1.2: Ligand structure

4. DISCUSSION

In the IR spectrum of ([2-hydroxyureabenzylidene-3methylurea]), characteristic band of ligand is at 1636 cm^{-1} which is assigned to (CH=N) vibration band. The solid- state IR spectra of the complexes were compared with that of the ligand. It was found that CH=N band vibration in these complexes is 1647 cm^{-1} for Cu(II) complex, 1621 cm^{-1} for Ni(II) complexes, 1649 for Co(II) and 1654 cm^{-1} for both the Zn(II) and Mn(II) complexes. Reason of this shifting is that the nitrogen atom of azomethine (CH=N) groups is involved in Metal-Nitrogen bond formation. Schiff base ligands show OH stretching vibration in IR spectrum at 3379 cm^{-1}, which was not observed in IR spectra of complexes.

The IR spectral bands of ligand and its complexes are listed in Table1, together preferment for most of the important peaks. The position and complex 467 or intensities of these peaks are expected to change upon chelation. New peaks are also quite peaks as well as water in chelation.

Further evidence of the metal ions was shown by the appearance of weak low frequency new bands which can be designated as M-O and M-N bond. This M-O band is in the Co(II) complex 474 c^{-1} Ni(II) complex 466 cm^{-1} Cu(II) complex 466 cm^{-1}, Zn(II) complexes 463 cm^{-1}, :Mn (II) 472 cm^{-1} [5]. M-N bond is in the Co(II) complex 581 cm^{1}, Ni(II) complex 520 cm^{-1}, Cu(II) complex 570 cm^{-1}, Zn(II) complex 533 cm^{-1}, Mn (II) complex 530 cm^{-1} [21].

According to a study published in 2013; Yellow-orange crystals have IR (cm-1): 3434, 1615, 1591, 1281, 1257, 1151, 996, 916, 846, 792, 736, 581. ^{1}HNMR: 6.91-8.51(m, 8H), 9.41(s, 1H), 13.41(s, 1H). Also, in analytic calculated determinate that C, 72.72, H, 5.02, N, 14.10. Yellow solid; 178-1800°C. IR (cm-1): 3050, 1612, 1582, 152\57, 1430, 1291, 1105, 1090, 990, 892, 830, 784, 705, 640. 1HNMR 7.11 to 8.55 (m, 7H), 9.50 (s, 1H), 14.53 (s, 1H). Anal. calc. for $C_{12}H_9N_3O_3$: C, 59.24, H, 3.68, N, 17.25[22].

The ^{1}HNM-R spectra of the free ligand appear that 9.80 ppm phenolic-O-H proton, 8.10 ppm azomethine protons, 6.98-7.39 ppm aromatic proton and 2.74 ppm –CH_3 group's proton[23].

The UV-Vis spectra of ligand and complexes were recorded in the DMF solution in the wavelength range from 200 to 1100nm. The UV-Vis spectra of ligand and its complexes are listed in table2. The corresponding magnetic susceptibility measurement and elemental analysis are presented in table3.

In a study published in 2010; done for salicylidene glycine, the IR band of OH 3443.62 cm^{-1}, C = N 1618 cm^{-1}, UV bands λ 255-327nm , m.p or B.p* 180 ˚C colour: yellow, for salicylidene DL-alanine at IR band OH 3443.83 cm^{-1}, C=O 1681.97, C=N 1602.02, UV bands 247-327, m.p or B.p* 195 ˚C, color: orange, for salicylidene ß–alanine IR band OH 3424.33, C=O 1637.89,C=N 1612.17, UV band 250-326, m.p or B.p* 120 C, colour: Faint yellow, for salicylidene L- methionine IR band OH 3385.41,C=O 1633.20, C=N 1625.00, UV band 251-328, m.p or B.p* 100-120 C, color: Brown[24].

The electronic spectra of Co (II) complexes show two bans at 301 and 436 nm. This value in 301-436 nm are attribute to the $\pi\rightarrow\pi^*$ transition. 479 - 500nm $^4T_{1g}$ (F) → $^4T_{1g}$ (P) and 703-710nm $^4T_{1g}$ (F) → $^4A_{2g}$ (F) transitions, respectively, and their octahedral geometry round the cobalt ion[25]. The electronic spectra of Ni (II) complex showed bands in the region of 328-354 nm , which are attributed to $\pi\rightarrow\pi^*$, $n\rightarrow\pi^*$ transition. The band at 600 nm might be due to $^3T_1$ (F)→ $^3T_{1g}$(P) transition. Tetrahedral geometry was proposed[26]. The electronic spectra of Cu (II) complex showed absorption bands at 641-450 nm region and are due to $^2B_1\rightarrow{}^2A_1$ and$B_1\rightarrow{}^2E$ transition[27].

In this study the electronic spectra of Mn(II) complex observed 280 nm $\pi\rightarrow\pi^*$ transition and about 377-460 nm absorption band due to L→M load transfer transition. All this transition showed that Mn (II) complex octahedral geometry.

According to the magnetic susceptibility measurement found for Co (II) complex magnetic moment value 3.30 B.M and it has paramagnetic structure[28]. Cu (II) complex magnetic moment value 1.53 B.M and it has paramagnetic structure[29]. Ni (II) complex magnetic moment value 2.35 B.M and it has paramagnetic structure[30], Mn (II) complex magnetic moment value 5.80 B.M and it has paramagnetic structure[31], Zn (II) complex diamagnetic structure.

In this study; according to the magnetic susceptibility measurement and elemental analysis value it was found that L, Cu (II) and Ni (II) complexes form square planar and tetrahedral molecules[32]. While, Co (II), Mn (II), Zn (II) complexes octahedral structure.

5. CONCLUSION

The importance of Schiff bases is increasing day by day because; has the ability to act on the various groups (catalytic, oxygen binding, the amino group transfer, etc.). With this capability is increasing in importance, we believe that will contribute to; both for us and in all other work substances synthesized in this study

6. DECLARATION OF INTEREST

This study was financially supported by Firat university scientific research unit (Project no: 1700). The authors would also like to thanks.

7. CONFLICT OF INTEREST

We have no conflict of interest

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