Synthesis and Characterization Complexes of Zn(II),Cd(II),Hg(II) With New Schiff Base Derivative of 4-Amino Antipyrine With Ethylene Diamine

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Abstract:

Anew metal complexes of Zn(II), Cd(II) and Hg(II) were synthesized from the Schiff base derived from 4-amino antipyrine, 3- hydroxyl benzaldehyde and ethylene diamine in alcohol medium. All the complexes were characterized on the basis of their elemental analysis, molar conductance, in addition FTIR and electronic spectra. The result show that the functional groups was (-C=N). It has been found that the Schiff base ligand behaves as atridentate ligand forming chelates with 1:2 (metal : ligand) stoichiometry. The suggest geometry of the complexes appears to be octahedral.

Key words: ethylene diamine, 4- amino antipyrine; Schiff base Complexes.

الخلاصة :-

تضمن البحث تحضير المعقدات لايونات الخارصين (II) والكادميوم (II) والزئبق(II) مع ليكاند قاعدة شف المشتقة من ٤- امينو انتيبيرين و٣- هيدروكسي بنزلديهايد واثلين ثنائي الامين. شخصت المعقدات بوساطة التحليل الدقيق للعناصر وطيف الاشعة تحت الحمراء بالاضافة الى التوصيلية المولارية والاطياف الالكترونية. بينت نتائج الدراسة ان الليكاند يسلك كليكاند ثلاثية المخلب من خلال مجموعة (C=N) وترتبط مع الايونات الفلزية بنسبة مولية (2:1). تم اقتراح الصيغة التركيبية ثمانية السطوح.

فلز: ليكاند

Introduction

Schiff bases on important of ligands in coordination chemistry and find extensive application in different fields (Tarafder et al.,2001). The magjority of Schiff base usually acts as multidentate N,N and N,O donors with the formation of mono or polynuclear complexes (Shaker et al.,2009). In addition to their interesting ligational properties, both Schiff bases and their complexes have important biological, industrial applications (Singh et al.,2007; Jain et al., 2003; Kumar et al ., 2009) and several azomethines have been reported to possess remarkable anti bacterial (Halli et al., 2011) Antifungal, anticancer (Raman et al ., 2007) and diuretic activities (Raman et al ., 2009). Pyrazoline and its derivatives are agroup of antibiotics that have been extensively used in treating several bacterial diseases (Chandra et al ., 2009) .

The aim of the present research in the synthesis and physicochemical study of new Zinc(II), Cadmium(II) and Mercury(II) coordination complexes with new Schiff base ligand.

Experimental

Materials and measurements

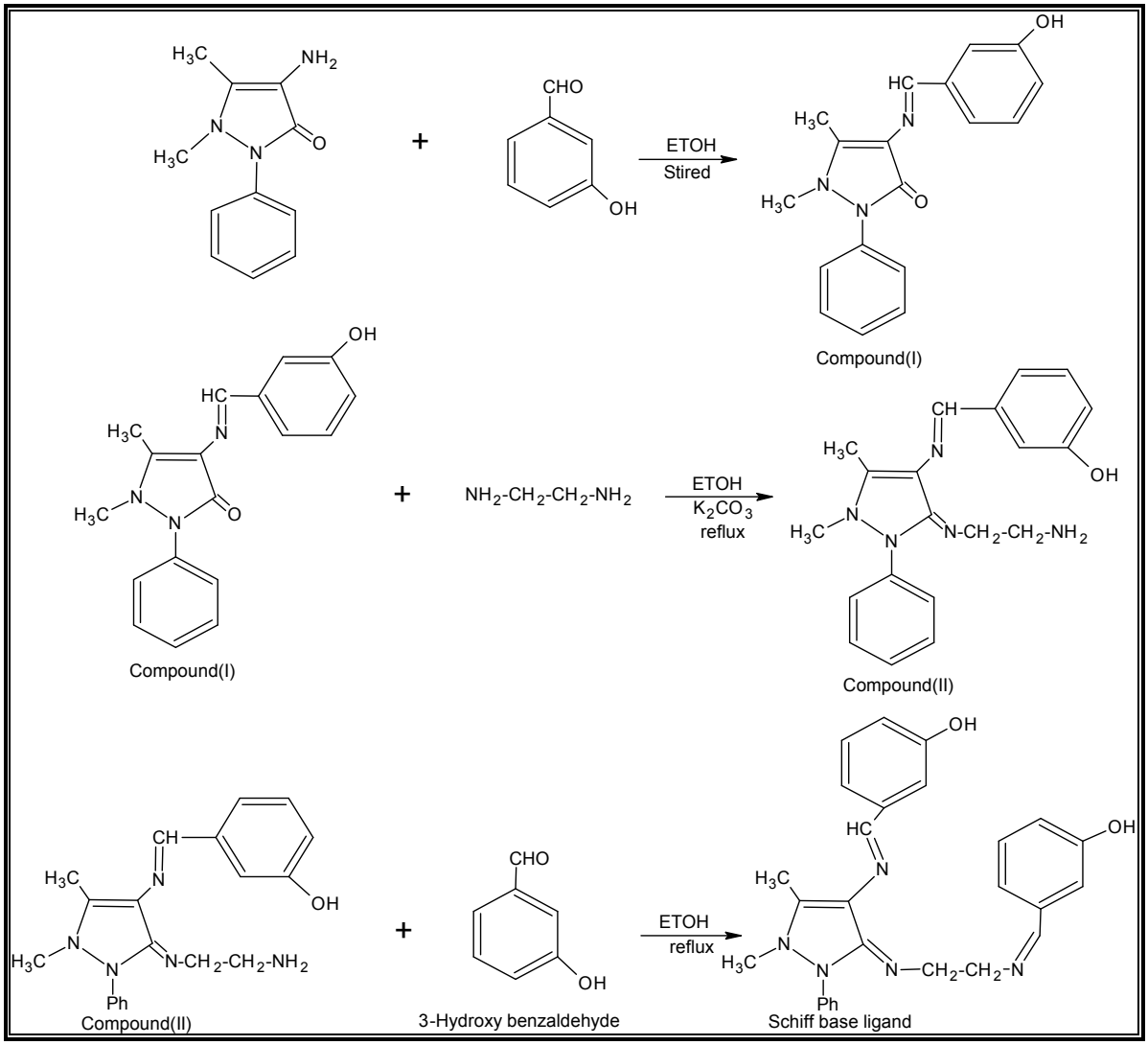
All chemicals are of highest purty and used as supplied. All metal (II) salts were used as chlorides. Elemental Microanalysis (C.H.N) performed using EA 300a C.H.N Elemental analyzer. IR spectra were recorded using KBr discs 4000-400 cm^{-1} on FT-IR Tectscan Shimadzu model 8000. Uv-Visible spectra were recorded in ethanol on shimadzu model 1700 Uv-Visible spectrophotometer. Molar conductance measurements were determine in DMSO by using Alpha Digital conductivity meter

model 800. Electro thermal malting point model 9300 was used to measure the melting points of the ligand and its complexes.

Preparation of Schiff base ligand

The new Schiff base was prepared by condensation of 3-hydroxy benzaldehyde with 4-amino antipyrine was performed by heating eqimolar amounts (10mmol) under reflux in 50ml ethanol, in the presence of 5 drops of acetic acid as acatalyts for not less than 5h. The solution was then cooled and the condensed solid product and isolated by filtration and recrytallised from ethanol. Compound (I).

An ethanolic solution (50ml) of compound (I) (10mmol) and ethylene diamine (5mmol) was boiled under reflux for about 5h. The yellow solid formed was filtered and recrystallised from hot ethanol and dried over anhydrous $CaCl_2$ (Raman et al., 2007). compound(II).



Scheme 1: preparation of the ligand

Compound (II) was reacted with 3-hydroxy benzaldehyde in ethanolic solution (50ml) was under reflux for 3h. The dark yellow solid fromed was filtered and recrystallised from hot ethanol and dried. Yield 60% (m.p 194 - 196C°) Scheme1.

Preparation of complexes

Asolution of metal chloride in ethanol (1mmol) was refluxed with an ethanolic solution of the Schiff base (2mmol) for about 3h. Then the solution was decant and filtered. The solid complex precipitated was washed thoroughly with hot ethanol and dried over anhydrous $CaCl_2$.

Results and Discussion

The analytical data for the ligand and complexes together with some physical properties are summarized in Table1. The complexes are quiet air-stable, insoluble in water, but its soluble in most common organic solvents. The complexes. In all cases (1:2) (metal:ligand) solid complexes are isolated, that is agreement with the stoichiometric ratio found using molar ratio method. Based on the elemental analysis data, the formulas $[ML_2]$ Cl_2 are assigned for all complexes. The molar electric conductivities showed that the complexes are electrolytes. Attempts to propose the structure of the complexes come from full investigation using the following studies.

Metal : ligand ratio

The metal : ligand ratio of chelates were deterimined of molar ratio method at the wavelength of maximum absorption . The ligand was found to form 1:2 chelates with metal ions under studies.

Infrared spectra

The IR spectra of the Schiff base ligand and its complexes are listed in Table 2. The IR spectra of the complexes are compared with those of the free ligand in order to determine the coordination sites that may be involved in coordination. The spectrum of free ligand shows two weak band 3062 cm^{-1} and 2993 cm^{-1} which due to (C-H) aromatic and aliphatic respectively. These band are in stable in postion in both ligand and chelate complexes. The IR spectrum of the ligand shows band in the region. 3178 cm^{-1} assignble to –OH group. The appearance of this peak in the all the spectra of the complexes indicate that –OH group is free from the complexation (Raman et al., 2008). Upon comparison it was found the (C=N) stretching vibration from the azomethine group is found in the Schiff base at 1647cm^{-1}, 1627cm^{-1} and 1593cm^{-1} (El-ajailyet al., 2007). This bands are shifted to lower (10-25cm^{-1}) wave numbers in the complexes, indicating the participation of the azomerthine nitrogen in coordination (Montazerozohori et al., 2011) Accodingly the ligand acts as atridetate chelating agent, bonded to the metal ion via the three nitrogen (C=N) atoms of the Schiff base. The spectra of chelate complexes showed new weak band in the region (450-400) cm^{-1} these band did not present in the spectrum of ligand may be attributed to vibration (M-N) (Suresh et al .,2011; Suresh et al.,2010) provide evidences concerning the bonding of nitrogen atoms of azomethine group to the metal ion. Representative example for their spectra is give in Fig1.

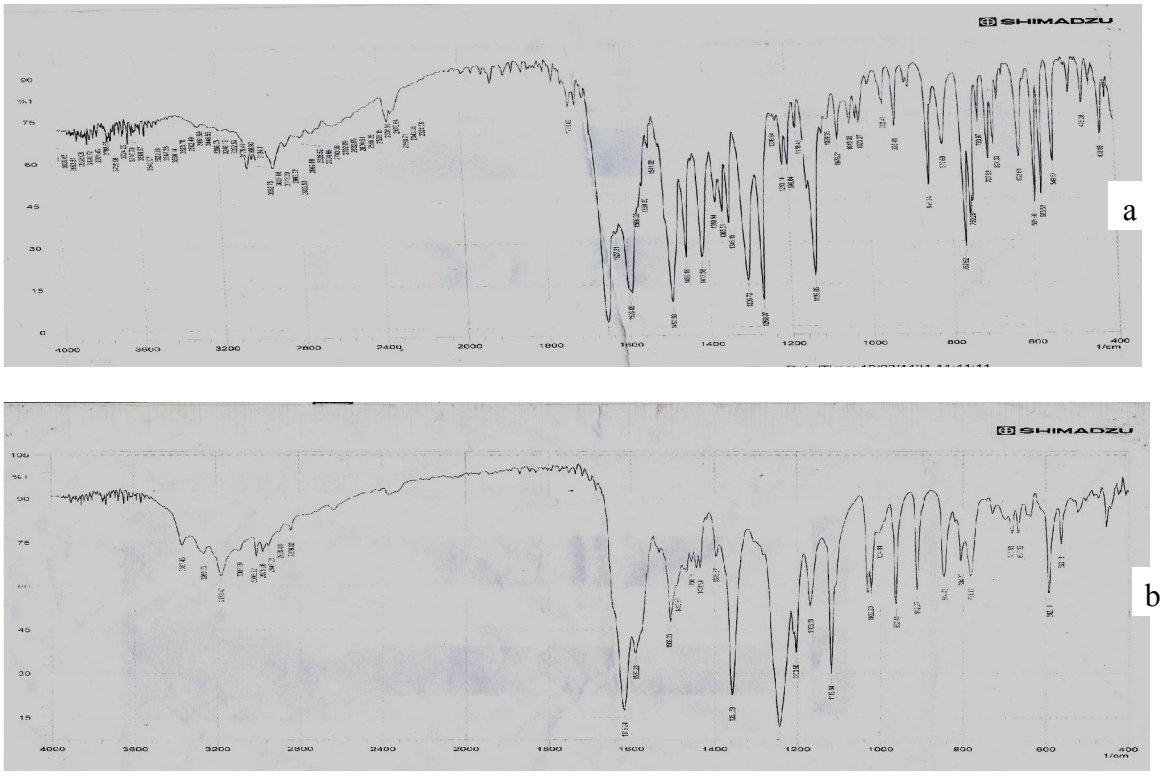


Fig .(1): IR spectra of : (a) the ligand & (b) [Zn L_2] Cl_2

1: Physical data and analysis of ligand and its complexes Table

No.	Compound	Colour	M.P °C	Formula	Found,(calc.)%			
					C	H	N	M
1	L	Dark yellow	194-196	$C_{27}H_{27}N_5O_2$	71.32 (71.52)	5.54 (5.96)	15.32 (15.45)	---
2	$[ZnL_2]Cl_2$	yellow	184-186	$[Zn(C_{54}H_{54}N_{10}O_4)]Cl_2$	62.03 (62.18)	5.42 (5.18)	13.20 (13.43)	6.18 (6.27)
3	$[CdL_2]Cl_2$	yellow	176-178	$[Cd(C_{54}H_{54}N_{10}O_4)]Cl_2$	59.32 (59.48)	4.72 (4.95)	12.62 (12.85)	10.14 (10.31)
4	$[HgL_2]Cl_2$	brown	178-180	$[Hg(C_{54}H_{54}N_{10}O_4)]Cl_2$	55.13 (55.02)	4.23 (4.58)	11.62 (11.88)	17.21 (17.03)

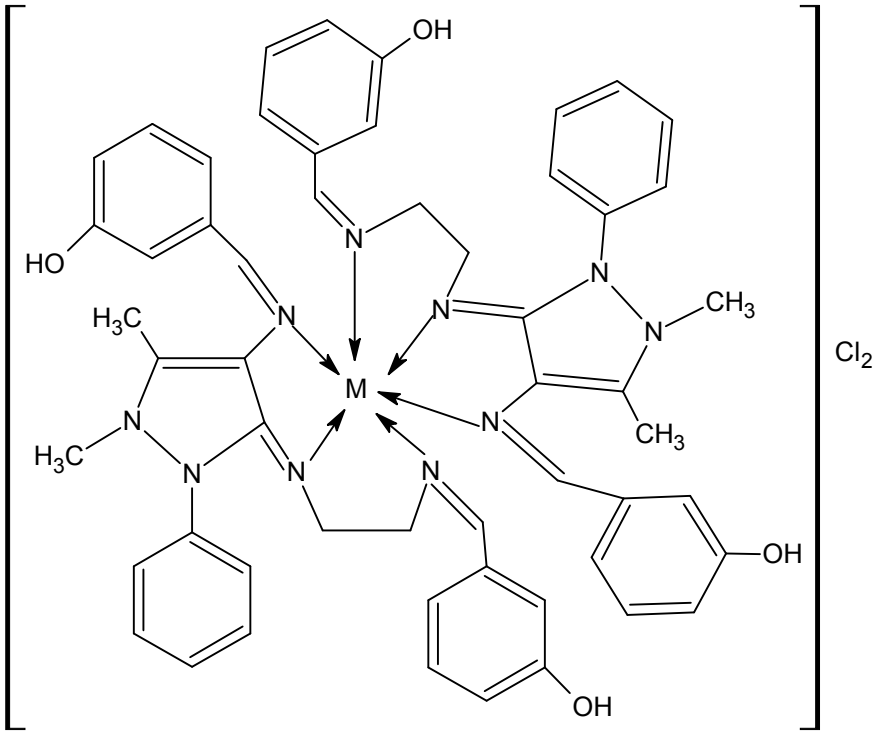
Table.2 : IR spectra frequencies for the ligand and its metal complexes in cm^{-1} units

Compound	υ (OH)	υ(C-H) aromatic	υ(C-H) aliphatic	υ(C=N)	(M-N)
L	3178m	3062w	2993w	1647s	----
$[ZnL_2]$	3175w	3040w	2990w	1630m	445 w
$[CdL_2]$	3170w	3055w	2989wbr	1620m	440 w
$[HgL_2]$	3177m	3059w	2995w	1595s	447 w

L= ligand, s = strong, w = weak, m = medium, br = broad

Conductivity measurement

All chelate complexes prepared in the work showed conduyctivity values ranged between (84-130) $S.mol^{-1}cm^2$ in DMSO at room temperature these values indicating that conductive species exist(Raman et al., 2008). According to these results the structural formulas of thses complexes may be proposed in Fig2.



M= Zn(II), Cd(II), and Hg(II)

Fig. 2: The proposed structural formula of the metal chelate complexes.

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