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Synthetic, spectroscopic and Antimicrobial activity of mixed ligand of some complexes of symmetrical Schiff base and Nicotinamide

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Abstract

New symmetrical Schiff base ligand (H_2L) is prepared via condensation of hydrazine hydrate and 4-hydroxy-3-methoxybenzaldehyde in ethanol solution at room temperature is reported .

Polydentate mixed ligand complexes were obtained from 1:1:1 molar ratio reactions with metal ions and H_2L, NA on reaction with MCl_2 .nH_2O salt yields complexes corresponding to the formulas

$[M(L)(NA)_2]$.

All the complexes are air stable and soluble in water and common organic except benzene .All complexes are soluble in dimethyl formamide (DMF)and dimethyl sulfoxide (DMSO) solvent. Comparison of the IR spectra of ligands(H_2L) and (NA) and there metal complexes confirm that Schiff base behave as a dibasic tetradentate ligand towards the central metal ion with an ONNO donor sequence and nicotinamid . behave as unidentate **.**

The ligands and their metal complexes were screened for their antimicrobial activity against four bacteria(gram +ve) and (gram -ve).

Keywords: Complexes; Spectral; symmetrical Schiff base Metal complexes ; Antimicrobial activities.

1. Introduction

Metal ions play a vital role in a vast number of widely different biological processes. The interaction of these ions with biologically active ligands, for example in drugs, is a subject of considerable interest. Some of the biologically active compounds act via chelation [1], but for most of them little is known about how metal binding influences their activity. Therefore we have been interested in studying the complexing ability of biologically active ligands. The Schiff base compounds constitute an important class of ligands which have been extensively studied in coordination chemistry. The nature of the effect of one ligand and its transmission to another ligand through the central metal ion is very important in coordination chemistry. [2-3], Antipyrine Schiff base derivatives can serve as antiparasitic agents and their complexes with platinum (II) and cobalt(II) ions have been shown to act as antitumour substances [4]. Nicotinamide is known as a component of the vitamin B complex as well as a component of the coenzyme, nicotinamide adenine dinucleotide (NAD). These are more important for transfer of hydrogen in the cell breath. The presence of ,pyridine ring in numerous naturally abundant compounds

adducts of nicotinamide are also scientific interest. Therefore, the structure of nicotinamide has been the subject of many studies [5-8]

In the area of bioinorganic chemistry the interest in the Schiff base complexes lies in that they provide synthetic models for the metal-containing sites in metalloproteins/enzymes and also contributed enormously to the development of medicinal chemistry, radio immunotherapy, cancer diagnosis and

treatment of tumor [9] and [10]. In addition, some of the complexes containing N and O donor atoms are effective as stereo specific catalysts for oxidation [11] eduction, hydrolysis, biocidal activity and other transformations of organic and inorganic chemistry. [12]

2.Materials and Methods

a- All the chemicals and solvents were of analytical grade (supplied by either Merck or Fluka) received. All the metal ions Mn(II), Co(II),Ni(II), Fe(II) and Cd(II) were of (BDH). They were used in the form of chlorides without further purification.

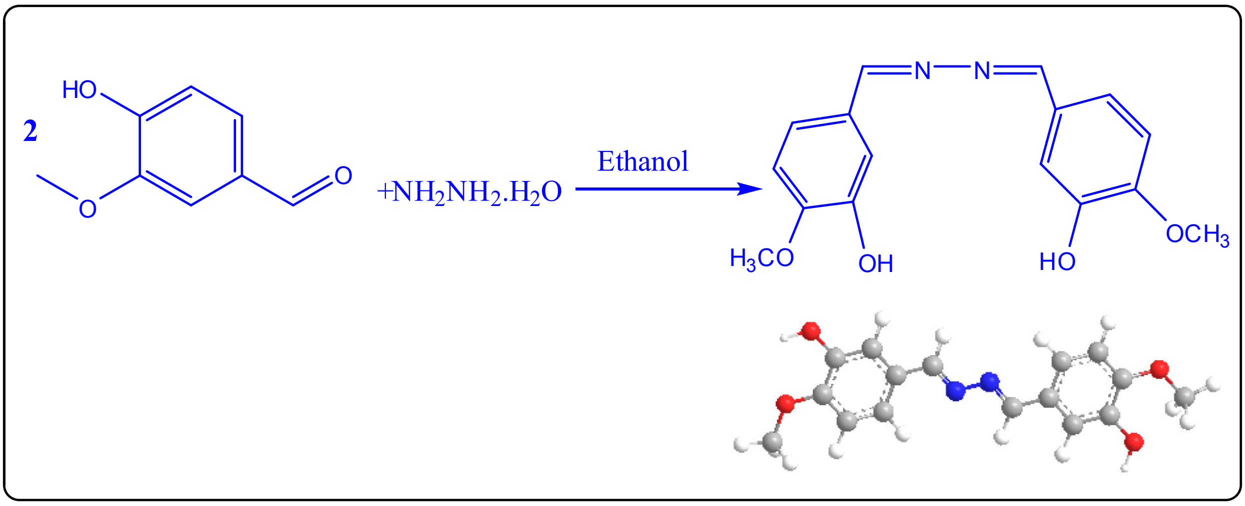
b- Instruments: FTIR spectra were recorded as KBr discs using Fourier transform Infrared Spectrophotometer Shimadzu 24 FTI.R 8400s. Electronic spectra of the prepared complexes were measured in the region (200- 1100) nm for 10^{-3} M solutions in DMF at 25ºC using shimadzu-U.V-160.A Ultra Violet Visible- Spectrophotometer with 1.000 ± 0.001 cm matched quartz cell. While metal contents of the complexes were determined by Atomic Absorption(A.A)Technique using Japan A.A-67G Shimadzu. Electrical conductivity measurements of the complexes were recorded at room temperature for 10-3 M solutions of the samples in DMF using pw9527 Digital conductivity meter (Philips). Melting points were recorded by using Stuart melting point apparatus . The Chloride contents of complexes were determined by potentiometric titration method using (686-Titro processor-665. Dosimat Metrohn Swiss). Magnetic susceptibility measurements were measured using Bruker magnet BM6 instrument at 298°K following the Faraday's method. The proposed molecular structure of the complexes were determinated by using chem. office program, 3DX (2006).

C- General procedure for the formation of 4,4'-(hydrazine-1,2-diylidenebis(methan-1-yl-1-ylidene))bis(2-methoxyphenol)

A solution of hydrazine hydrate(0.833gm,0.5mol) in ethanol 10ml was added dropwise to a stirred solution of 4-hydroxy-3-methoxybenzaldehyde(5gm,1mol) and the mixture was refluxed for 4h the reaction mixture was distilled under reduced pressure .The solid obtained was recrystallized from ethanol.

m .p=158 ^{o}c , The color of the product is orange. yield 85.10 %. Anal. Calcd for ligand(H_2L)

C = 63.99%, H = 5.37%, N = 9.33%. = Found: C = 61.59%, H = 6.2%, N = 9.78%.



Scheme (1) : Schematic representation of synthesis of the ligand(H_2L)

Antibacterial Activities: [12]

The antibacterial activity of the ligands and some there complex were tested on Gram positive bacteria, Staphylococcus , and Gram negative, Bacillus , Pseudomonas, and Bacillus. The solvent used was di methyl form amid(DMF) and sample from 1 to 200 µg/ml were used. Ant bactericidal activities of each compound were evaluated by the well-diffusion method. 1 cm^3 of a 24 h broth culture containing 106 CFU/cm^3 was placed in sterile Petri-dishes. Molten nutrient agar(15 cm^3) kept at ca.45°C was then poured in the Petri-dishes and allowed to solidify. Then holes of 6 mm diameter were punched carefully using a sterile cork borer and these were completely filled with the test solutions. The plates were incubated for 24 h at 37°C.

3. Results and discussion

3.1. Characterization of ligand(H_2L)

New symmetrical Schiff base ligand (H_2L) is prepared via condensation of hydrazine hydrate and 4-hydroxy-3-methoxybenzaldehyde.The physical characterization and micro analytical data of ligand(H_2L) ligand Is given in Table(1), The purity of the Schiff base as formulated, was established by microanalyses.

3.2. Characterization of mixed ligand complexes:

Generally, the complexes were prepared by reacting the respective metal salts with the ligands using 1:1:2 mole ratio, i.e. one mole of metal salt : one mole of (H_2L) and two moles of nicotinamide . The formula weights and melting points , are given in (Table 1).Based on the physicochemical characteristics, it was found that all the complexes were non-hygroscopic, stable at room temperature. The molar conductance values of the complexes in solvent at 10^{-3} M concentration The observed molar conductance (Table-1) values measured in DMF 10^{-3}M solution lie in the (4.80-15.92) Ω^{-1} cm^2 mol^{-1} range, indicating their nonelectrolytic nature[13].The atomic absorption measurements and chloride ion content (Table-1) for all complexes gave approximated values for theoretical values. **Figure.** 1

Fourier-transform infrared spectra and mode of coordination :

The most important infrared spectral bands that provide conclusive structural evidence for the coordination of the ligands to the central metal ions. The important IR peaks of the complexes are shown in Table 2. IR spectra of the complexes were interpreted by comparing the spectrum with that of the free ligand as shown in Table 2. The comparison of the IR spectral bands of the free ligand (H_2L) and its metal complexes indicate that the band at 2993 cm^{-1} due to intramolecular hydrogen bonded υ (OH) group in the free ligand spectrum disappeared in all complexes and the υ (CO) (phenolic) band at 1261 cm^{-1}, [14].shifted to a higher frequency, suggesting the coordination of ligand through phenolic oxygen via deprotonation. Besides, the bands at 1600 cm^{-1} (azomethine C=N) shifted its position on complexation [15]. In addition to the above bands all the complexes display the new bands in the far-infrared region (518-617) cm^{-1} and (418-445) cm^{-1} were assigned to υ (M–O) and υ (M–N) vibrations, respectively [16-18].

The UV-Visible Spectroscopy and Magnetic measurements:

The electronic spectra of the ligands and there complexes were recorded in DMF and their assignments are given in Table (3). The free ligand H_2L spectral data display two bands at 342 nm (29230cm^{-1}) 357 nm (28011 cm^{-1})) attributed to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions and the spectrum of the free ligand (NA), exhibits absorption peak at (271 nm)(36900 cm^{-1}) which assigned to ($\pi \rightarrow \pi^*$), [17] .

The electronic spectrum of the Mn(II) complex exhibited three spin allowed bands in the region 14749cm^{-1}, 27932cm^{-1} and 29239 cm^{-1} assigned to the transitions 6A 1g 4T1g (4G)(υ1), 6A1g 4T2g (4G) (υ2) and LMCT respectively, indicating octahedral geometry [19-20].The observed magnetic moment of the Mn(II) complex are 5.041 B.M. corresponding to five unpaired electrons indicates high spin octahedral environment [20].The electronic spectra of the Fe(II) complex exhibited three bands at 342nm (29239cm^{-1}), 358 nm (27932 cm^{-1}) and 672nm(14880cm^{-1}) due to the presence of a charge transfer (LMCT) and $5T_{2g} \rightarrow 5E_{2g}$. The magnetic moment value of this complex was found 5.05 BM which was very close to the value of octahedral environment.The electronic spectra of Co(II) complex displayed three bands at 669nm(14947 cm^{-1}) ,357nm (28011 cm^{-1}) and 342 nm (29239 cm^{-1}) corresponding to the transitions 4T1g →4T2g(F), due to the presence of a charge transfer (LMCT)respectively[21]. These transitions as well as the measured value of magnetic moment 4.12 BM suggested the octahedral geometry for this complex. The electronic spectrum of Ni(II)- complex exhibited three bands in the region 19880, 29239 and 36630 cm^{-1} corresponding to the transitions 3A2g →3T2g,

3A2g→3T1g and (LMCT) respectively for octahedral geometry[22]. The magnetic moment value of this complex was found 3.23 BM which was very close to the value of a distorted octahedral environment. [21-22] .The electronic spectrum of Cd (II) complex exhibited two bands in the region 271nm(36900cm^{-1}) and 344nm(29069 cm^{-1}) corresponding to the Cd (II) complex is diamagnetic in nature and its electronic spectra do not furnish any characteristic d-d transitions except charge transfer (CT) bands as expected for d^{10} systems. [21-22]

Antibacterial Activities:

The zone inhibition of bacterial growth were measured in mm depending upon the diameter as shown in Table (4) Figure. (2)The antibacterial activity results revealed that the ligands and there complexes shown weak to good activity when compared to the Control (DMF) . [21-22]

It is evident from the above data that the antibacterial activity significantly increased on coordination. This enhancement in the activity may be rationalized on the basis of their structures mainly possessing an additional azomethine bond. It has been suggested that the ligand with nitrogen and oxygen donor

systems inhibit enzyme activity. Coordination reduces the polarity of the metal ion mainly because of the partial sharing of its positive charge with the donor groups within the chelate ring system..[23- 24]

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able (1) The physical properties of the compounds

Compounds	M .wt	Color	M .p (de) °	Λm ohm^{-1} cm^{2} mol^{-1}	Cl%	%Metal Theory	% Metal Experiment
$H_2L= C_{16}H_{12}N_2O_4$	300.3092	yellow	180	o.78	-	-	-
$NA= C_6H_6N_2O$	122	white	132	0.70	-	-	-
$[Mn(L)(NA)_2]$ $C_{28}H_{26}MnN_6O_6$	597.48	green	162(de)	9.06	Nil	9.19	9.7
$[Fe(L)(NA)_2]$ $C_{28}H_{26}MnN_6O_6$	598.38	Deep brown	146(de)	15.92	Nil	9.33	10.3
$[Co(L)(NA)_2]$ $C_{28}H_{26}CoN_6O_6$	601.47	green	174(de)	7.96	Nil	9.80	10.1
$[Ni(L)(NA)_2]$ $C_{28}H_{26}NiN_6O_6$	601.23	green	132 (de)	7.76	Nil	9.76	10.1
$[Cd(L)(NA)_2]$ $C_{28}H_{26}CdN_6O_6$	654.95	yellow	154(de)	4.80	Nil	7.16	7.90

Table (2) FTIR spectral data of the Ligands and there complexes

Compound	**NH $_{sym}$**	**(CH)$_{cyclic}$**	**υ (C=N)**	**C=O**	**C–O**	**N–N**	**M- O**	**M-N**
ligand	3132br-s	2939	1625vs	1716m	1266s	986 s	-	-
NA	3323br -vs	2969	1634s	-	-	-	-	-
[Mn(L) $(NA)_2$]	3190	2943	1624vs	1716m	1282vs	1020s	555	430
[Fe(L) $(NA)_2$]	3361vs	2937	1593s	1716m	1286vs	1029m	617	445
[Co (L) $(NA)_2$]	3190vs	2941	1618vs	1734m	1280vs	1022s	607	433
[Ni (L) $(NA)_2$]	3190vs	2945	1618vs	1734m	1288vs	1020s	518	418
[Cd (L) $(NA)_2$]	3190vs	2943	1624vs	1780m	1282vs	1024s	603	433

Sym: symmetric, asy: asymmetric, str: stretching, v .s: very strong, s: strong, m: medium, w:week, sh: shoulder

Table (3) Electronic Spectral data, magnetic moment, of the studied complexes and two ligands

Compounds	**λ_{max}(nm)**	**υ′(cm^{-1})**	**Assignments**	**μ_{eff} (BM)**
ligand	342 357	2923 28011	n→π* n→π*	-
NA	271	36900	π→π*	-
[Mn(L) (NA)$_2$]	678 358 342	14749 27932 29239	6A 1g 4T1g (4G) 6A1g 4T2g (4G) LMCT	5.041
[Fe(L) (NA)$_2$]	672 358 342	14880 27932 29239	$5T_{2g} \rightarrow 5E_{2g}$ LMCT LMCT	5.05
[Co (L) (NA)$_2$]	669 357 342	14947 28011 29239	4T1g →4T2g(F) LMCT LMCT	4.12
[Ni (L) (NA)$_2$]	503 342 273	19880 29239 36630	3A2g →3T2g 3A2g→3T1g LMCT	3.23
[Cd (L) (NA)$_2$]	271 344	36900 29069	CT CT	0.00 Diamag

Table (4) Showed the inhibition circle diameter in millimeter for the bacteria after24 hour incubation paid and 37°C for complexes

Compounds	*E .coli*	*Pseudomonas*	*Staphylococcus*	*Bacillus*
Control(DMF)	5	5	5	5
Ligand (N_o-1)	8	8	7	10
NA(**N_o -2)**	10	9	12	12
$[Mn(L)(NA)_2]$	7	8	10	7
$[Fe(L)(NA)_2]$	11	15	23	14
$[Co(L)(NA)_2]$	14	12	12	13
$[Ni(L)(NA)_2]$	13	13	15	14
$[Cd(L)(NA)_2]$	17	17	18	16

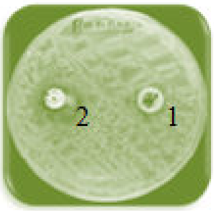
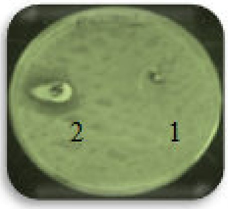
E .coli			
Pseudomonas			
Staphylococcus			
Bacillus			

Figure.2 : Shows the antimicrobial activity of Ligands (No1=NA,No2=H_2L appear the inhibition zones against pathogenic bacteria (*Bacillus, Escherichia coli , Pseudomonas , and Staphylococcus*

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