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Research Article

Synthesis, characterization and antibacterial Evaluation for mixed-ligand Complexes of Nickle (II), Manganese(II), Copper(II),Cobalt(II) and Mercury(II) with Tetradentate Schiff base and 1,10-phenanthroline

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Abstract

An abstract is a brief summary of a research article, thesis, Schiff base ligand (L) was prepared by the reaction of 4-aminantipyrine with o-phenylenediamine, the prepared ligand characterized by Micro elemental Analysis, FT. IR, UV-Vis, and ^{1}H,^{13}C-NMR spectroscopy.complexes of Mn(II), Co(II), Ni(II), Cu(II) and Hg(II) with Schiff base and 1,10-phenanthroline (Phen) have been investigated in aqueous ethanol with (1:1:1) (M:L:Phen). The prepared complexes were characterized using flame atomic absorption, (C. H. N) Analysis, FT. IR and UV-Vis spectroscopic methods as well as magnetic susceptibility and conductivity measurements. From the obtained data the octahedral structure was suggested for all complexes. The biological screening effects of the investigated compounds were tested against the bacterial species *(Staphylococcus aureus*), (*Escherichia coli*), (*Bacillus*) and *(Pseudomonas)* by the good diffusion method.

Keywords: Schiff base, 1, 10-phenanthroline, 4-aminoantipyrine, Mixed ligand complexes.

الخلاصة

تم تحضيرليكاند قاعدة شف من تفاعل 4-امينوانتيبيرين مع اورثوفنيلين ثنائي الأمين، شخصت الليكاند المحضرة بواسطةاطياف الأشعة تحت الحمراء وفوق البنفسجية – المرئيةوالرنين النووي المغناطيسي للكاربون والهيدروجين والتحليل الدقيق للعناصر(C. H. N). حضرت معقدات المنغنيز(II) ، الكوبلت (II) ، النيكل(II) ، النحاس (II) والزئبق(II) مع قاعدة شف و1,10-فينانثرولين في وسط ايثانول- ماء وبنسبة (1:1:1)(فلز:ليكاند:فينانثرولين). شخصت المعقدات المحضرة بوساطة التحليل الدقيق للعناصر(C. H. N)؛ تقنية الإمتصاص الذري اللهبي وأطياف الأشعة تحت الحمراء وفوق البنفسجية - المرئية، فضلا عن قياسات التوصيلية الكهربائية والحساسية المغناطيسية، ومن النتائج المحصول عليها تم اقتراح الشكل ثماني السطوح للمعقدات المحضرة. كما تمت دراسة الفعالية البكتيرية لليكاند والمعقدات المحضرة تجاه انواع مختلفة من البكتريا.

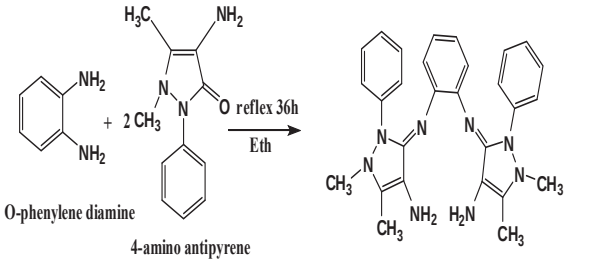
Introduction

One of the most important derivatives is 4-aminoantipyrine which is deemed from remarkable reagents as its significance in biological [1], pharmacological [2], clinical and analytical applications [3]. Further, they have been investigated due to their diverse biological properties as sedative [4], antifungal [5], ability anti-inflammatory [6], analgesic [7], antibacterial [8], greater DNA binding [9], and antipyretic agents [10]. Amino group in antipyrine as a site of chelation shows highlighting behavior with transition metal ions through covalent or coordinate [11]. In this work, we are interested to explore preparation and structural design of 4-aminoantipyrine based Schiff base having nitrogen donors, derived from a 4-aminoantipyrine and o-phenylene diamine, and its complexes with Hg (II), Ni (II), Mn (II), Co (II) and Cu (II) metal ions. The antibacterial evaluation of present complexes is also researched against the bacterial types such as *(Staphylococcusaureus*), (*Escherichia coli*), (*Bacillus subtilis*) and *(Pseudomonas aeruginosa)*.

Materials and Methods

Preparation of the ligand (L)

Ethanolic solution of 4-aminoantipyrine (4.06g, 0.02mmol) was added to ethanolic solution of o-phenylenediamine (1.08g,0.01mmol) with 2 drop glacial acetic acid[8]. The solution mixture was stirred and refluxed for 36 hours, yellow crystalline precipitate observed. The resulting precipitate as filtered off recrystallized from menthol and dried at 50°C. The preparation method of the ligand (L) is represented inScheme 1.

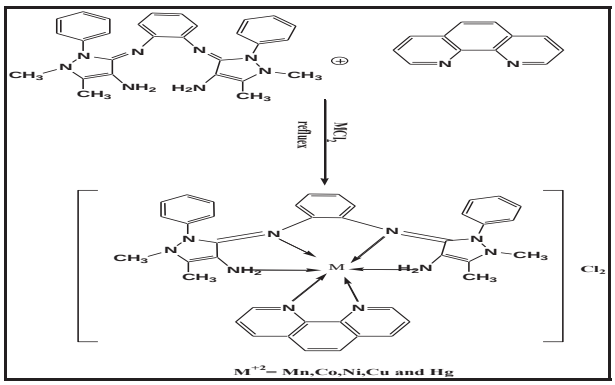


(N^1Z,N^2Z)-N^1,N^2-bis(4-amino-1,5-dimethyl-2-phenyl-1*H*-pyrazol-3(2*H*)-ylidene)benzene-1,2-diamine

Scheme 1: Preparation method of ligand.

Preparation of Metal Complexes

A aqueous solution of the metal salts containing 0.198g, 0.2388g, 0.238g, 0.170 g and 0.271g (1mmole) of $MnCl_2.4H_2O$, $CoCl_2.6H_2O$, $NiCl_2.6H_2O$, $CuCl_2.2H_2O$, and $HgCl_2$ respectively was added gradually with stirring toethanolic solution (0.29g, 1mmol, the complexes precipitate of the ligand, an ethanolic solution of (0.18g, 1mmol) of 1, 10-phenanthroline added in each case by using stoichiometric amount (1:1:1) Metal to ligands molar ratio. The mixture was refluxed with constant stirring for 2 hours. The mixture was cooled at room temperature dark precipitate was formed, filtered and recrystallized from ethanol. The preparation method is shown in Scheme 12.



Scheme 2: The expected structure of the metal (II) complexes.

Instrumentation

Melting points were determined on "Gallenkamp melting point Apparatus". Elemental microanalysis C. H. N. was carried out using Euro Vector EA 3000A Elemental Analysis (Italy). FT-IR measurements were recorded on Shimadzu-8300 Spectrophotometer in the range of (4000-400cm^{-1}) as KBr disc. Electronic spectra were recorded using U. V-Vis. Spectrophotometer type (CECIL, England, with quartz cell in rang (200-1000) nm which path length (1cm) atroom temperature in ethanol.1H and^{13}C-NMRspectra were recorded by using a [Bruker 300 MHZ (Switzerland), Chemical shift of were recorded in δ(ppm) unit downfield internal reference (TMS)], using DMSO. Conductivity measurements were obtained from (WTW conductivity meter)by using ethanol of 10^{-3} M concentration at room temperature. The chloride content determined using potentiometric titration method on 686–Titro Processor–665 Dosim A–Metrohm/Swiss. Magnetic properties were performed by usingAuto Magnetic Susceptibility Balance Sherwood Scientific instrument at 25C^{o}. Metal analysis of complexes was determined by Atomic Absorption (A. A.) technique. Using a shimadzu PR-5. Oraphic Printer atomic absorption spectrophotometer.

Results and Discussion

The ligand was prepared by condensation reaction between 4-amino antipyrine and o-pheylene diamine. Synthesized ligand (L) was characterized by FT-IR, Elem. Anal (C, H, N) and UV-Vis, ^{1}H,^{13}C-NMR spectroscopic technique. [1] The solid complexes were prepared by reaction of alcoholic solution of the ligands with the aqueous solution of the metal ions in a (M:L) of (1:1:1). The (C. H. N) analysis with metal contents of these complexes was in good agreements with the calculated values Table 6 includes some physical properties and elemental analysis [2]. Conductivity measurements of complexes were carried out in (10^{-3} M) in dimethylsulphoxide (DMSO) solvent. The molar conductance values are listed in the Table-5. The table reveals that the conductance values of all the metal complexes supporting their 1:2 electrolytic behavior.

NMR Spectra

The ^{1}H NMR spectrum of ligand Figure 14 in DMSO-d_6 solution shows the following signals:

=C-CH_3 at δ_H 2.15, DMSO at δ_H 2.49, N-CH_3 at δ_H 3.31, NH_2at δ_H 4.78, C_6H_5 as multiple at δ_H6.66 ~7.08, Ph-NH- at δ_H 7.82, the data recorded in Table 1[3]. The ^{13}C NMR spectrum of ligand Figure-2 in DMSO-d_6 solution shows the signals at: (8.82 for =C-CH_3 group);(34.96 for N-CH_3 group); (40.52 for DMSO);(75.12 attributed to -C-OHgroup); (109.82for=C-N);(123.10~135.86) to 4 benzene rings) and (139.90 for C=C in antipyrine). The peak observed at 164.50 is due to the C=N imine groups for Schiff base[4]. The data tabulated in Table 2:13 CNMR chemical shifts for the ligand (ppm in DMSO-d6).

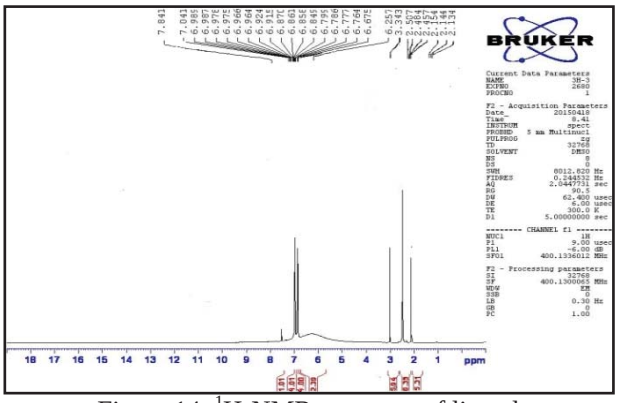


Figure 14: ^{1}H-NMR spectrum of ligand

Table 1: ^{1}H NMRchemical shifts for ligand (ppm in DMSO-d_6).

DMSO	CH_3-N	CH_3-C=	NH_2	C =C	Ph-NH
2.5	2.16	3.33	4.79	6.67-7.07	7.84

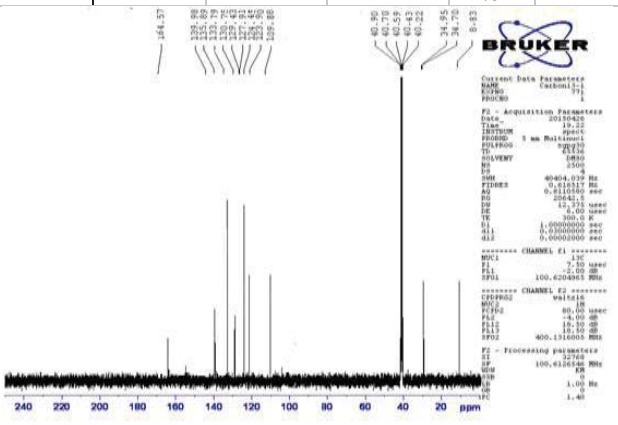


Figure 15:^{13}C-NMR of the ligand.

Table 2: ^{13}CNMR chemical shifts for the ligand (ppm in DMSO-d_6).

Compound	NH_2	$\upsilon(C=N)_{imine}$	M–N
L	3428 3343	1624	-
[Co(phen)(L)]Cl_2	3339 3261	1615 1608	597
[Ni(phen)(L)]Cl_2	3350 3272	1614 1607	588
[Cu(phen)(L)]Cl_2	3377 3265	1618 1610	547
[Mn(phen)(L)]Cl_2	3348 3274	1616 1608	553
[Hg(phen)(L)]Cl_2	3381 3251	1617 1610	545

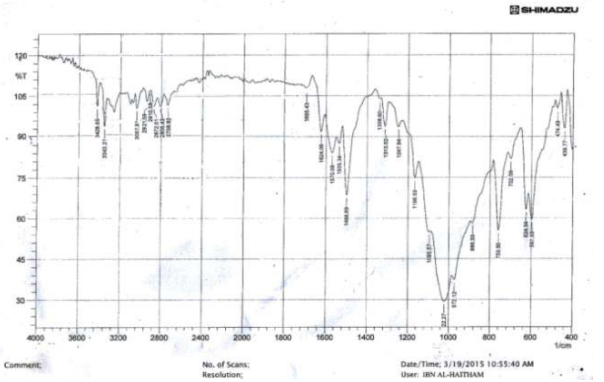


Figure 16:FT-IR spectrum of the lignd

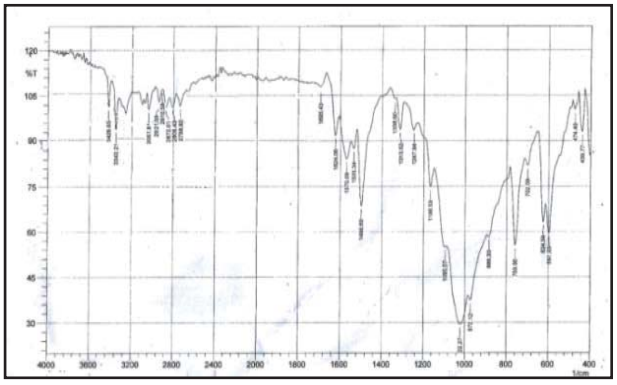


Figure 17:FT-IR spectrum of [Hg(phen)(L)]Cl2 complexes

Table 1:Diameter of zone of inhibition (mm)

Compound.	*Staphylococcus aurous*	*Escherichia. Coli*	*Pseudomonas*	*Bacillus*
L	6	7	9	10
[Co(phen)(L)]Cl_2	12	15	15	11
[Ni(phen)(L)]Cl_2	14	10	13	10
[Cu(phen)(L)]Cl_2	13	11	10	15
[Mn(phen)(L)]Cl_2	18	17	16	12
[Hg(phen)(L)]Cl_2	15	12	10	19

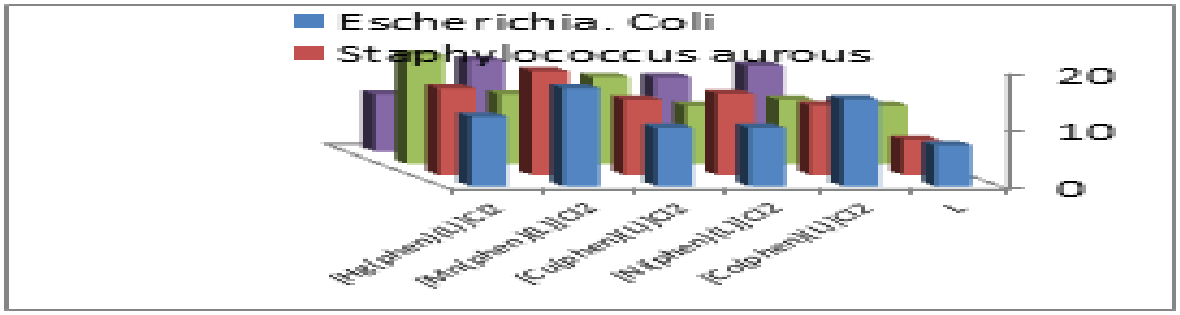


Figure 5: Difference between the antimicrobial activity of ligand and its complexes.

Table 5:Some physical prepared ligand and its complexesand weight of metal salts

Compounds	Formula	Molecu-lar Weight	Colour	Yeild%	M. P. ˚C	%Elemental Analysis Found % (Calculated)			
						C	H	N	M
L	$C_{28}H_{30}N_8$	478.59	pale yellow	65	178	70.00 (70.27)	6.07 (6.32)	23.70 (23.41)	-
$[Co(phen)(L)]Cl_2$	$C_{40}H_{38}Cl_2CoN_{10}$	788.64	Brown	74	210	61.20 (60.92)	4.76 (4.86)	17.53 (17.76)	7.64 (7.47)
$[Ni(phen)(L)]Cl_2$	$C_{40}H_{38}Cl_2N_{10}Ni$	788.40	Brown	76	231	59.52 (60.94)	4.84 (4.86)	17.77 (8.68)	7.29 (7.44)
$[Cu(phen)(L)]Cl_2$	$C_{40}H_{38}Cl_2CuN_{10}$	791.20	Deep brown	82	236	60.56 (59.07)	4.37 (4.83)	17.41 (17.66)	8.46 (8.01)
$[Mn(phen)(L)]Cl_2$	$C_{40}H_{38}Cl_2MnN_{10}$	784.64	Light brown	72	227	59.87 (61.23)	4.87 (4.88)	17.73 (17.85)	6.88 (7.00)
$[Hg(phen)(L)]Cl_2$	$C_{40}H_{38}Cl_2HgN_{10}$	930.24	Off-White	72	227	50.87 (51.64)	4.23 (4.12)	14.73 (15.06)	21.13 (21.56)

Table 6: Electronic spectral data of the ligand and its metal complexes

Compound	**μ_{eff}**	**Λ_m ohm. $cm^2 mole^{-1}$**	**λnm**	**υ' wave number cm^{-1}**	**(εmax $molar^{-1}$ cm^{-1}**	**Assign-ments**	**Proposed structure**
L	-	-	243 312	41152 32051	2278 1245	π→π* n→π*	-
1,10-phenan-throline	-	-	202 228 264	49504 43859 37878	2469 2281 1456	π→π* π→π* n→π*	-
$[Co(phen)(L)]Cl_2$	4.65	77.4	330 519 654 824	30303 19267 15933 12135	1402 615 209 148	C. T $^4T_1g_{(F)} \rightarrow {}^4T_1g_{(P)}$ $^4T_1g \rightarrow {}^4A_2g$ $^4T_1g \rightarrow {}^4T_2g_{(F)}$	octahedral

[Ni(phen)(L)]Cl_2	2.47	73.6	333 827	27700 12091	734 213	C. T $^3A_2g_{(F)} \rightarrow {}^3T_2g_{(F)}$	octahedral
[Cu(phen)(L)]Cl_2	1.85	70.9	338 855	29585 11687	1517 318	C. T $^4B_1g \rightarrow {}^4B_2g$	octahedral
[Mn(phen)(L)]Cl_2	5.43	81.0	328 805	30487 12422	1236 436	C. T $^6A_1g_{(F)} \rightarrow {}^4T_1g_{(G)}$	octahedral
[Hg(phen)(L)]Cl_2	-	71.6	331 407	30211 24570	1271 629	C. T C. T	octahedral

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