Synthesis, Characterization and Biological Study of Cr(III), Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) Complexes with a New Tetradentate Schiff Base Ligand

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Abstract

At this paper we describe the synthesis of new Schiff Base (L) : 3,3`-(benzene-1,4-diyldinitrilo) bis (1,3-dihydro-2*H*-indol-2-one).

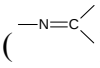
The product (L) was characterized by (FT-IR), (UV-Vis) spectroscopy and elemental analysis (C. H. N). (L) has been used as aligand to prepare a number of metal complexes with Cr(III), Mn(II, Co(II), Ni(II), Cu(II) and Zn(II). The prepared complexes were isolated and characterized by (FT-IR) and (UV-Vis) spectroscopy, elemental analysis (C. H. N) flame atomic absorption technique, as well as magnetic susceptibility and conductivity measurement. The Schiff base (L) and its complexes, with different concentration, have been screened for their (***In-Vitro***) antibacterial on (***E. coli***) and (***Bacillusubtilis***) and antifungal (***A. niger***) and (***P. chrysogenum***) activities by using different concentration.

الخلاصة

يتضمن هذا البحث تحضير ليكاند قاعدة شف الجديدة
3,3`-(benzene-1,4-diyldinitrilo)bis (1,3-dihydro-2*H*-indol-2-one) (L)
جرى تشخيص (L) بطرائق تحليل طيف الأشعة تحت الحمراء (FT-IR) وطيف الأشعة فوق البنفسجية المرئيـة والتحليل الدقيق للعناصر (C. H. N). وتم إستخدام (L) كاليكاند فـي تحـضير معقـدات الأيونـات الفلزيـة : الكروم(III) والمنغنيز(II) والكوبلت(II) والنيكل(II) والنحاس(II) والخارصين(II).
عزلت المعقدات الجديدة وتم تشخيصها بإستخدام طيف الأشعة الحمراء وطيف الأشعة فـوق البنفـسجية المرئيـة وتقنية التحليل الدقيق للعناصر (C. H. N) وتقنية الإمتصاص الذري اللهيبي للعناصـر إضـافةً إلـى قياسـات الحساسية المغناطيسية والتوصيلية الكهربائية.

تم إجراء التقويم الحيوي لليكاند قاعدة شف(L) ومعقداتها وبإستخدام تراكيز مختلفة ضد البكتريـا (***E. coli***) و (***Bacillussubtilis***)، كما وتم إجراء التقويم الحيوي للمركبات ضد الفطريات بإستخدام (***A.niger***) و (***P.chrysogenum***)

Introduction

Isatin derivatives have been shown to exhibit a wide range of biological activity like anti-bacterial[1], anti-inflammatory[2], analgesic[3], anti-viral[4], antifungal[5], anti-tubercular[6] and anti-depressant[7]. Schiff bases are important class of ligands due to their synthetic fleribility, selectivity and sensitivity towards the central metal atom, structural similarities with natural biological substances, and also, due to presence of imine group () which imports in elucidating the mechanism of transformation and rasemination reaction in biological system[8]. Metal complexes with Schiff base of isatin derivatives exhibited remarkable biological activity[9-11]. The present paper describes the preparation of a new Schiff base (L) derived from the reaction of isatin and P-phenylenediamine to be used as a ligand that provide four potential donor sites to form complexes with some metal ions. The ligand (L) and its complexes have been fully characterized.

Experimental

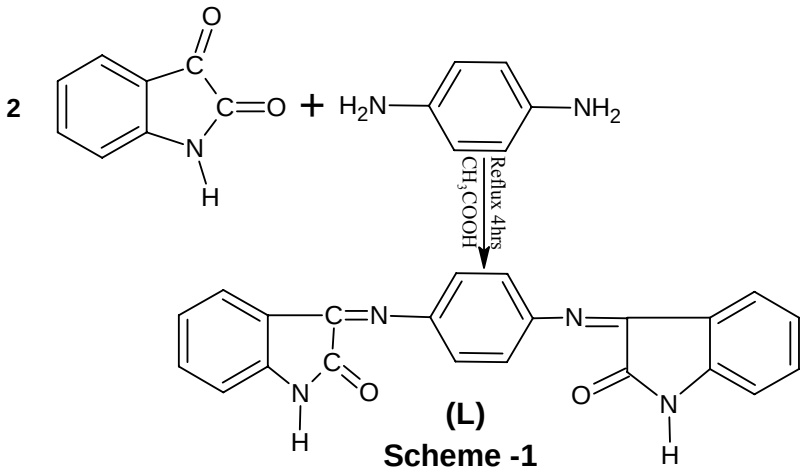
All chemicals were of highest purity and used as received.

Physical measurement and analysis :

Melting points were recorded on Gallenkamp melting point apparatus and were uncorrected. FT-IR spectra were recorded using FT-IR 8300 Shimadzu at range (4000-200)cm^{-1} as CSI disc. Electronic spectra were obtained using UV-1650 PC. Shimadzu spectrophotometer at room temperature. The measurements were recorded using concentration (10^{-3}M) of the complex in chloroform as a solvent. Micro analytic data for (C. H. N) were obtained by EA-034, mth. Conductivity measurements were obtained by corning conductivity meter 220. These measurements were obtained in (DMF) as a solvent using concentration (10^{-3}M) at 25^{o}C.Magnetic susceptibility measurements were obtained at 25^{o}Con the solid state applying Faraday's method by using Bruker BM6 instrument.

Synthesis of Schiff base Ligand (L)

The synthesis of Schiff base is schematically presented at scheme (1). Schiff base has been synthesized by refluxing the reaction mixture of hot ethanolic solution of isatin (0.294g, 2mmole) and hot ethanolic solution of P-phenylenediamine (0.11g, 1mmole) for 4hrs with few of glacial acetic acid. The product obtained after the evaporation of the solvent was filtered and recrystallized from ethanol. Some of the physical and chemical properties of the prepared ligand arelisted at table (1)



(L)

Scheme -1

formation in solution were listed at table (1).

***In-Vitro* antibacterial and antifungal assay :**

The biological activities of synthesized Schiff base and its Cr(III), Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) metal complexes have been studies for their antibacterial and antifungal activities by agar and potato dextrose agar diffusion methods respectively[13]. The antibacterial and antifungal activities were done at 100, 200 and 500 mg/ml concentrations in DMF solvent by using two kinds of bacteria (***E. coli*** and ***Bacillus subtilis***) and tow kinds of fungi (***A. niger*** and ***P. chrysogenum***). These bacterial strains were incubated for 24hr at 37°C and fungi strains were incubated for 48hr at the same temperature.

Results and Discussion

A- Elemental Analysis :

The analytical data of Schiff base ligand (L) and its metal complexes are given at table (1), in a satisfactory agreement with the calculated values. The suggested molecular which are formulated and supported by subsequent spectral and molar ratio as well as magnetic moment.

Synthesis of Schiff base complexes (A_1-A_6)

Ethanolic solution (20ml) of each one of the following metal chloride (1mmole), $CrCl_3.6H_2O$, $MnCl_2.4H_2O$, $CoCl_2.6H_2O$, $NiCl_2.6H2O$, $CuCl_2.2H_2O$ and $ZnCl_2$ was added to an ethanolic solution (20ml) of (0.366g, 1mmole) of (L) with stirring. The mixture was heated under reflux for 2 hrs during this time a precipitate was formed. The product was isolated by filtration, washed several times with hot ethanol and then dried under vacuum. Some of the physical and chemical data of the prepared complexes are shown at table (1).

Study the complexes formation is the solution :

Complexes of (L) with metal ions were studied in the solution using the ethanol as a solvent in order to determine [M:L] ratio in the complex following molar ratio method[12]. A series of solutions were prepared having a constant concentration [10^{-3}M] of the metal ion and (L). The [M:L] ratio was determined from the relationship between the absorption of the absorbed light and the mole ratio of [M:L]. The results of complexes

Table -1 : Physical data of (L) and Schiff base complexes (A_1-A_6)

Comp. No	Color	M. P. °C	%Elemental analysis found (calc.)			Metal M% found (calc.)	M:L in EtOH	Suggested Formula
			C	H	N			
(L)	Orange	290-292	71.69 (72.13)	3.55 (3.825)	16.12 (15.30)	-	-	$C_{22}H_{14}N_4O_2$
A_1	Brown	325d*	51.27 (50.61)	3.58 (4.22)	10.02 (9.08)	8.85 (8.43)	1:1	$[Cr(C_{22}H_{14}N_4O_2)Cl_2]Cl(C_2H_5OH)_2$
A_2	Dark Orange	310d*	50.89 (50.09)	3.31 (3.41)	11.04 (10.62)	11.6 (11.16)	1:1	$[Mn(C_{22}H_{14}N_4O_2)Cl_2(H_2O)_2]$
A_3	Brownish-red	320d*	50.11 (49.64)	3.94 (3.38)	10.63 (10.62)	12.73 (11.7)	1:1	$[Co(C_{22}H_{14}N_4O_2)Cl_2(H_2O)_2]$
A_4	Light brown	300d*	60.83 (61.27)	3.41 (3.25)	13.52 (12.99)	7.64 (7.3)	1:2	$[Ni(C_{22}H_{14}N_4O_2)]Cl_2$
A_5	Brown	330d*	44.32 (44.56)	3.17 (2.36)	8.86 (9.45)	10.1 (10.72)	1:1	$[Cu(C_{22}H_{14}N_4O_2)Cl_2(C_2H_5OH)_2]$
A_6	Orange	310d*	50.31 (49.07)	3.24 (3.34)	10.68 (10.40)	12.89 (13.00)	1:1	$[Zn(C_{22}H_{14}N_4O_2)(H_2O)_2]Cl_2$

d* = decomposed

B- Infrared Spectroscopic Study :

The reaction of isatin with P-phenylenediamine produced Schiff base (L). this reaction was followed by disappearance of absorption bands at (3420-3365)cm^{-1} due to νNH_2 and characteristic new band at 1653cm^{-1} of azomethine group νC=N are utilized to confirm the structure of (L)[14, 15], table (2).

A comparison of the infrared spectra of the free ligand and metal complexes reveal that table (2) behaves as a four dentate coordinating with ions metal by oxygen of carbonyl and nitrogen of the azomethine groups, therefore, the bands due to νC=O and νC=N were shifted to lower frequencies[16]. These observations were further indicated by the appearance of νM-O, νM-N and νM-Clrespectively[16], as well as υ-OH for some complexes between (3400-3450)cm^{-1}, table (2).

Table -2 : characteristic stretching vibration frequencies (cm^{-1}) located at FT-IR of (L) and their metal complexes

Comp. No.	νC=O	νC=N	νM-N	νM-O	νM-Cl
L	1741	1653	-	-	-
A_1	1714	1647	500	420	387
A_2	1729	1616	550	455	383
A_3	1705	1647	530	443	366
A_4	1699	1655	515	493	-
A_5	1697-1728	1631	539	491	380
A_6	1722	1633	535	445	-

[A_2] : The spectrum of dark orange Mn(II) complex showed two band at (12562, 263158)cm^{-1} due to the transitions $^6A_1g \rightarrow {}^4T_2g$ and $^6A_1g \rightarrow {}^4E_1g$, these assignmentswhen compared with those published for octahedral geometry[21]. In addition to the measured magnetic moment of this complex which was found to be (5.19B.M), this value refers to high-spin (d^5) complex[22], table (3). Conductivity measurement in (DMF) showed a non-conductive behavior of this complex.

[A_3] : The solution spectrum of the brownish-red Co(II) complex showed three bands at (8930, 18588 and 30697)cm^{-1} due to $^4T_1g \rightarrow {}^4T_2g_{(F)}$, $^4T_1g \rightarrow {}^4A_2g_{(F)}$, $^4T_1g \rightarrow {}^4T_1g_{(P)}$ these bands correspond to those of octahedral geometry[8], magnetic moment of the solidcomplex (4.81 B.M) showed a high-spin Co(II)

C- Electronic spectra, magnetic moment and conductance studies :

The UV spectrum of Schiff base (L) showed intense bands at 295nm and at 426 which belong to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$respectively[14, 17], table (3).

The electronic spectra of the Schiff base and metal complexes were recorded for their solution in chloroform at range (200-1100)nm, while the molar conductance were measurement in (DMF) as solvent.

[A_1] : The solution of brown chromium complex show three absorption bands appeared at (21739, 22172 and 34722)cm^{-1}, following octahedral field with (d^3) configuration[18]. The effective magnetic moment at room temperature was found to be (3.83 B.M) revealing to octahedral stereo chemistry of the ligand around Cr(III) metal ion[19,20]. Conductivity in (DMF) showed that complex was due to be ionic, table (3).

that the complex was to be ionic, table (3).

[A_5] : The electronic spectrum of this complex showed one band at (16129cm^{-1}) attributable to $^2Eg \rightarrow {}^2T_2g$ transition in the octahedral geometry[28,29]. The magnetic moment value was (1.82 B.M) corresponds to one unpaired electron, table (3). The low conductivity value in DMF showed a non-conductive behavior.

[A_6] : Zn(II) complex show no absorption peak to rang (380-1000)nm that is indicated no (d-d) electronic transition happened (d^{10}-system) in visible region that is a good result for Zn(II) tetrahedral complex[30,31].

complex[23,24]. Conductivity measurement in (DMF) showed a non-conductive behavior of the complex, table(3).

[A_4] : The solution of Ni(II) complex gave a light brown colour, which refers to the presence of vaccant coordination site on the metal ion.The new weak bands in the visible region of Ni(II) complex at (18867, 22271 and 24390)cm^{-1} are assigned as ligand field bands due to the transitions $^1A_1g \rightarrow {}^1A_2g$, $^1A_1g \rightarrow {}^1B_1g$ and $^1A_1g \rightarrow {}^1Eg$ respectively[18, 27]. Moreover, the magnetic moment of the solid complex (0.00 B.M) indicating a square planer geometry [25, 26] and the conductivity in (DMF) showed

Table -3 : Electronic Spectra, Conductance in (DMF) and Magnetic Moment (B.M) of (L) and its metal complexes

Comp. No.	Bands cm^{-1}	Assignment	Molar cond. MS.cm^{-1}	μeff B.M	Suggested Structure
(L)	23474 33898	$n \rightarrow \pi^*$ $\pi \rightarrow \pi^*$	-	-	-
[A_1]	21739 22172 34722	$^4A_2g \rightarrow {}^4T_2g$ $^4A_2g \rightarrow {}^4T_1g_{(F)}$ $^4A_2g \rightarrow {}^4T_1g_{(P)}$	78.68	3.83	O.h
[A_2]	12562 263158	$^6A_1g \rightarrow {}^4T_2g$ $^6A_1g \rightarrow {}^4Eg$, $^4A_1g_{(G)}$	13.62	5.19	O.h
[A_3]	8930 18588 30697	$^4T_1g \rightarrow {}^4T_2g_{(F)}$ $^4T_1g \rightarrow {}^4A_2g_{(F)}$ $^4T_1g \rightarrow {}^4T_1g_{(P)}$	16.33	4.81	O.h
[A_4]	18867 22271 24390	$^1A_1g \rightarrow {}^1A_2g$ $^1A_1g \rightarrow {}^1B_1g$ $^1A_1g \rightarrow {}^1Eg$	62.91	Zero	S.q
[A_5]	16129	$^2Eg \rightarrow {}^2T_2g$	16.02	1.82	O.h
[A_6]	229886 317460	$L \rightarrow M_{(C.T)}$	168.93	Zero	T.h

D- *In-Vitro* antimicrobial assay :

The antimicrobial results are systemized at table (4). From antibacterial studies it is inferred that Schiff base (L) was found to be potentially activity against ***Bacillus subtilis***. In case of antifungal activity Schiff base and its complexes were found to be active, table (4). It is evident from the results that the biological activity of some of the metal complexes is higher than the ligand. It is, however, known that the chelating tends to make Schiff base act as more powerful and potent bacterostaticagent, thus, inhibiting the growth of bacteria and fungi more than the parent Schiff base.

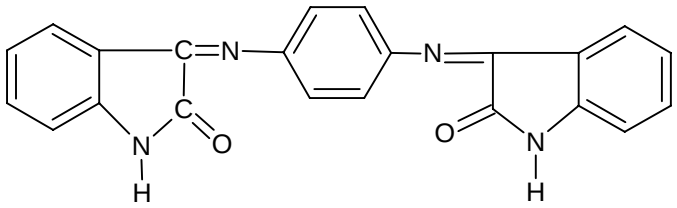
Table -4 : Antimicrobial results of Schiff base and its metal complexes

Comp. No.	Conc ($mg.ml^{-1}$)	*E. coli*	*B. subtilis*	*A. niger*	*P. crysogenum*
(L)	100	8	11	10	7
	200	9	14	10	8
	500	11	18	12	10
[A_1]	100	5	14	7	5
	200	10	10	10	8
	500	13	8	10	10
[A_2]	100	8	12	9	8
	200	8	9	7	8
	500	7	10	10	8
[A_3]	100	10	14	7	9
	200	12	12	8	10
	500	11	10	10	8
[A_4]	100	8	10	9	7
	200	10	12	10	5
	500	8	10	10	9
[A_5]	100	9	16	8	6
	200	12	11	5	8
	500	12	14	7	6
[A_6]	100	5	14	7	7
	200	12	16	7	6
	500	14	18	6	9

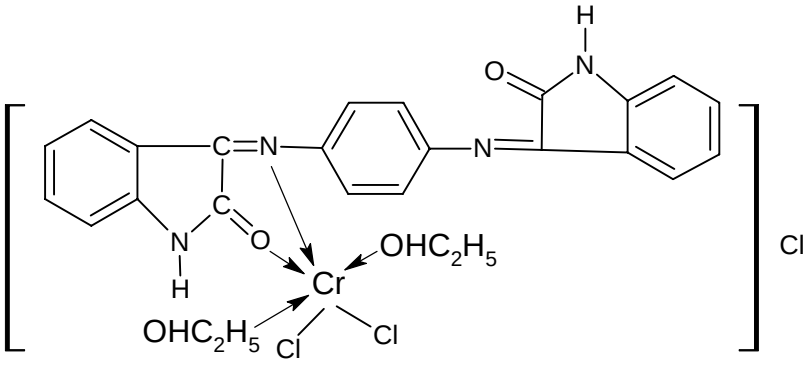
Suggested stereo chemistry structure of Schiff base (L) and its metal complexes [A_1-A_6]

According to the results obtained from elemental and spectral analysis as well as magnetic moment and conductivity measurements, the suggested structure of the above mentioned compounds can be illustrated as follows :

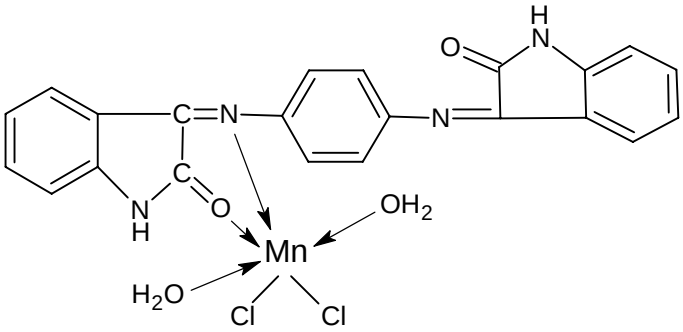
(L)



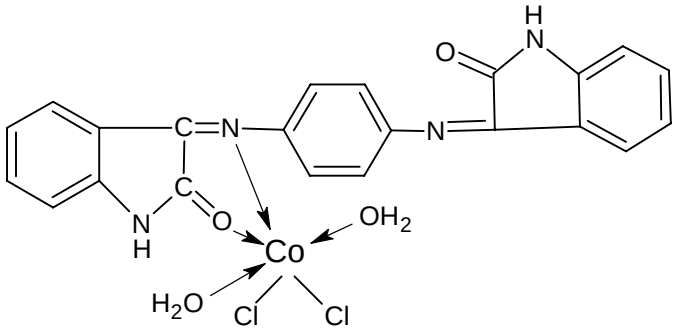
[A_1]



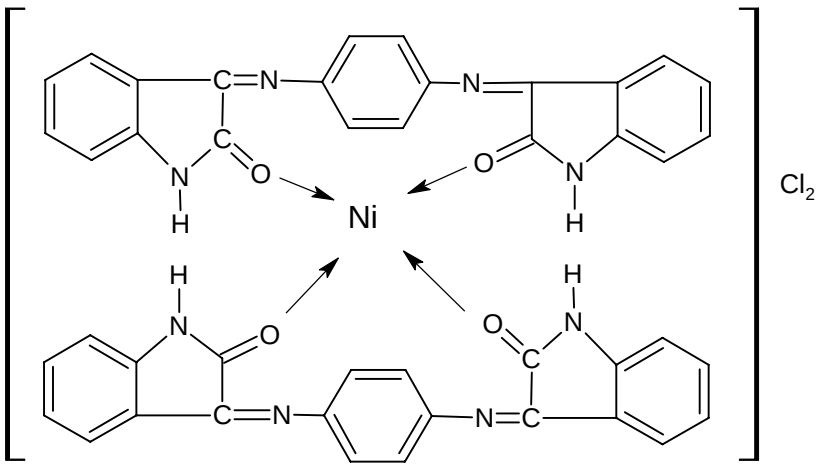
[A_2]



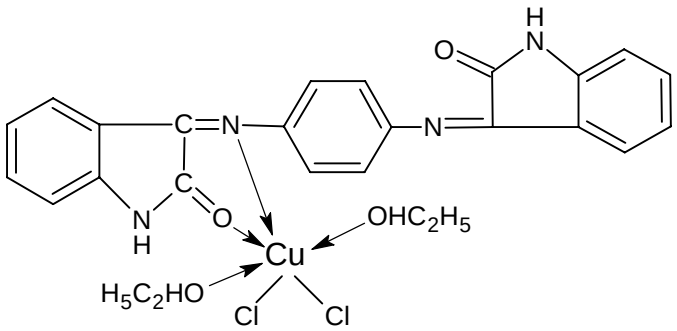
[A_3]



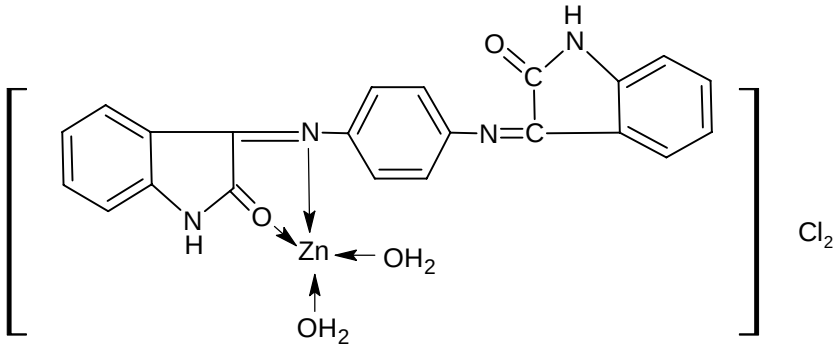
[A_4]



[A5]



[A6]



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