Preparation and characterization of Some Metal Ions Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) Complexes With New Schiff Bases and Evaluation of Their Biological Activities

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الخلاصة

يتضمن البحث تحضير مجموعة من المعقدات الجديدة ذات الصيغة العامة $[M(L)_2]Cl_2$ و $[M(L)_2]$ Co(II), Ni(II), Cu(II), Zn(II), Cd(II) إذ أن M تمثل ايونات L_1, L_2, L_3=L، وان L_1 تمثل (Z)-3-(4-ميثوكسي فينايل ايمينو) اندولين-2-اون وان L_2 تمثل (Z)-1-((4-ميثوكسي فينايل ايمينو) مثيل) نفثالين-2-اول وان L_3 تمثل (Z)-2-(4-ميثوكسي فينايل ايمينو) -2- فينايل ايثانول. تكونت المعقدات بنسبة 2:1 (فلز: ليكاند). تم دراسة وتشخيص هذه المعقدات المحضرة باستخدام التحليل الدقيق للعناصر وقياس الحساسية المغناطيسية والتوصيلية المولارية الكهربائية وطيف الأشعة تحت الحمراء والأطياف الالكترونية. أظهرت قياسات الأشعة تحت الحمراء ارتباط الليكاند من خلال ذرة النيتروجين لمجموعة الازوميثاين وذرة الأوكسجين لمجموعة الكاربونيل لليكاند الاول أو ذرة الأوكسجين لمجموعة الهيدروكسي بالنسبة لليكاند الثاني والثالث لجميع المعقدات وأظهرت قياسات المغناطيسية والأطياف الالكترونية بنية رباعي السطوح لجميع المعقدات ودلت قياسات التوصيلية الكهربائية لهذه المعقدات بأنها ذات طبيعة الكتروليتية بنسبة 2:1 لليكاند الأول وذات طبيعة متعادلة غير الكتروليتية لليكاندين الثاني والثالث.

أظهرت اختبارات الفعالية البايولوجية لمعظم المعقدات المحضرة قدرتها العالية لتثبيط نمو نوعين من البكتريا *Staphylococcus aureus* و *Escherichia coli*.

Abstract

Metal complexes of general formula $[M(L)_2]Cl_2$ and $[M(L)_2]$, L=L_1, L_2, L_3 have been prepared where M is Co(II), Ni(II), Cu(II), Zn(II)

and Cd(II), L_1 is (Z)-3- (4-methoxyphenylimino) indolin-2-one, L_2 is (Z) -1- ((4-methoxyphenylimino) methyl) naphthalene-2-ol, L_3 is (Z)-2-(4-methoxyphenylimino) -2-phenylethanol. The complexes which have the molar ratio of 1:2 (metal to ligand). The complexes were characterized by elemental analyses, magnetic and conductance measurements infrared absorpation spectra and electronic spectra. IR spectra showed that the nitrogen of the azomethine group, carbonyl oxygen of L_1 or the oxygen hydroxy group for the L_2 and L_3 take part in coordination. Magnetic susceptibility measurements and electronic spectra studies suggested a tetrahedral structure for all complexes. Conductance measurements indicating the 1:2 electrolytic nature for L_1 and non electrolyte for L_2 and L_3. The biological activity testes indicate that most of the prepared complexes posses high ability to inhibit growth *Staphylococcus aureus* and *Escherichia coli* bacteria.

Introduction

Schiff base and their metal complexes have important and popular area of research due to their liquid crystal complex formation tendencies[1], simple synthesis, diverse range of application[2-4] and played a central role in the development of coordination chemistry[5,6]. The presence of azomethine group in these molecules made them acting as suitable ligands towards metal ions and forming different coordination compounds[7,8].

The complexes make these compound effective and stereospecific catalysts for oxidation, electroreduction, decomposition, hydrolysis, reaction on oxygenation. It is well known that some drug have higher activity when administered as metal complexes than as free ligands[9-11]. p-anisidine as apart in ligand which is aniline derivative have been found to be biologically interesting compound for many years and show antibacterial activity[12,13]. Also, compounds containing isatin, naphthyl groups derived Schiff bases has been studies and has attacked great attention for long time showed that possess anti HIV activity, antibacterial, enhance fungicidal activity[14-16]. In this work we described and prepared Schiff base from anisidine and isatin, 2-hdroxy-1-naphthaldehyde and *o*-hydroxyacetophenone and its mononuclear complexes with Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) ions.

Experimental

A-Preparation of Schiff bases:

An ethanolic solution (20 ml) of isatin (0.01 mole, 1.47 g) or 2-hydroxy-1-naphthaldehyde (0.01 mole, 1.72 g) or o-hydroxy acetophenone (0.01 mole, 1.36 g) were added to an ethanolic solution (10 ml) of p-anisidine (0.01 mole, 1.23 g) and this mixture was refluxed for 2 hr. The reaction mixture was then cooled in an ice bath which

immediately gave a precipitated product then was separated by filtration, washed with the cold ethanol and ether and then air dried.

B-Preparation of the Complexes:

A hot ethanolic solution (20 ml) of metal(II) chloride (0.01 mole) was added to an ethanolic solution (10 ml) of Schiff base (0.02 mole) and this mixture was refluxed for 3 hr. The reaction mixture was concentrated to half its volume by evaporation. On cooling the complexes which precipitated, filtered off, washed with ethanol and ether and then air dried.

Analysis and Physical measurements:

Elemental analysis was carried out on a Costech instruments (Element combustion system, International Sp.A., Model 4010, Italia). The metal content were determined according to the standard procedure[17]. Analysis of ligands and complexes were carried out using standard method of analysis. The metal contents were estimated spectrometrically using (SP6-350 atomic absorption spectrophotometer, Pye – Unicam, England). Molar conductivities of the complexes have been measured in an electrolytic conductivity measuring PCM3 (Jenway) conductivity using 10^{-3} M of the complexes in N,N-dimethylformamide (DMF) solution at room temperature. Infrared spectra in the range 400-4000 cm^{-1} were recorded on a Perkin-Elmer 580 B spectrophotometer, as KBr disc. Electronic spectra were obtained with Shimadzu UV/Vis, recording UV160 spectrophotometer in DMF at room temperature for 10^{-3} M solution of the compounds using a 1 cm quartz cell. The magnetic measurements were carried out at 25ºc on the solid by a Faraday's method using Bruker BM6 apparatus and melting points were determined by using Electrothermal 9300 Engineering LTD apparatus.

Biological activity

Preliminary biological activity screening of the synthesized compounds has been performed at 100 µg /ml DMF against microorganisms representing Gram-positive bacteria (*Staphylococcus aureus*) and Gram-negative bacteria (*Escherichia coli*), using nutrient agar medium. By pouring the sterile agar into Petri dishes in aseptic conditions, 0.1ml of each standardized test organism culture was spread onto agar plates[18]. The sensitivity of a microorganism to antimicrobial agents was determined by the assay plates, which were incubated at 37 ◦C for 1 day.

Results and discussion

The metal complexes of the Schiff bases were prepared by reacting the metal (II) chloride and the Schiff base in the molar ratio M:L = 1:2.

All the complexes are stable solids and colored at room temperature. The values of molar conductivities for these complexes in DMF expected for 1:2 electrolytes (Table 1) indicating the ionic nature[19] and consistent with given formula $[M(L)_2]\ X_2$, $L=L_1$ for the complexes (1-5) while complexes of the type $[M(L)_2]$, $L= L_2, L_3$ are nonelectrolyte (Table 1).

IR Spectra

The IR spectra of the Schiff bases showed characteristic absorption bands at the ranges (3271-3298, 1641-1643, 1739 and 3230 cm^{-1}) due to υ(O-H), *υ*(C=N), *υ*(C=O) and *υ*(NH) stretching vibrations respectively (Table 2).

The azomethine bands at 1739 and (1641-1643 cm^{-1}) due to *υ*(C=O) and *υ*(C=N) stretching frequencies respectively in the free ligands shift towards lower values in all complexes (1690-1712 cm^{-1}) and (1610-1628 cm^{-1}) indicating that the carbonyl oxygen atom of the isatin residue and the azomethine nitrogen atom are coordinated for L_1[20-22]. However, the band at 3230 cm^{-1} due to *υ*(NH) of isatin remained unchanged indicating that it is not involved in the coordination[23]. On the other hand the (C-O phenolic) band of the L_2, L_3 at (1248-1252 cm^{-1}) in the free ligand was moved to a higher frequency (1281-1304 cm^{-1}) after complexation which means that the shifts are due to coordination of ligand to metal atom by phenolic oxygen[24]. Moreover, the new bands appearing in the spectra of the metal complexes and not observed in the spectra of the free Schiff bases with in 459-472 cm^{-1} and 416-426 cm^{-1} [25,26] assigned to M-O and M-N modes conclusively indicated that the ligands are coordinated to the metal ions through these groups.

Electronic Spectra and magnetic moments

For tetrahedral cobalt(II) complexes, three bands can be observed these are assigned to the transitions: $^4A_2(F) \longrightarrow {}^4T_2(F)\ \upsilon_1$ 3000-4000 cm^{-1}

$^4A_2(F) \longrightarrow {}^4T_1(F)\ \upsilon_2$ 6000-8000 cm^{-1}

$^4A_2(F) \longrightarrow {}^4T_1(P)\ \upsilon_3$ 13250-16600 cm^{-1}

The electronic spectra bands for Co(II) complexes are given between (14836-16447 cm^{-1}), assigned to the transition electron. $^4A_2(F) \longrightarrow {}^4T_1(P)$ (υ_3). The other two bands υ_1 and υ_2 (due to $^4A_2(F) \longrightarrow {}^4T_2(F)$ and $^4A_2(F) \longrightarrow {}^4T_1(F)$ transition) were absence because they fall below the limit of our instrument[25] and bands at (30303-32894cm^{-1}) assigned to the charge transferee which also supported a tetrahederal arrangement around Co(II) ion[27,28] (Table 3).

The magnetic moments obtained for Co(II) complexes (3.97-4.40 B.M) suggesting a tetrahedral geometry.

For tetrahedral nickel(II) complexes, three spin allowed transitions are expected these are: $^3T_1(F) \rightarrow {}^3T_2(F)\ \upsilon_1$ 5000-7000 cm^{-1}

$^3T_1(F) \rightarrow {}^3A_2(F)\ \upsilon_2$ 7000-9000 cm^{-1}

$^3T_1(F) \rightarrow {}^3T_1(P)\ \upsilon_3$ 11000-15000 cm^{-1}

and υ_1 and υ_2 usually located bellow the instrumental limit.

The electronic spectra of Ni(II) complexes showed strong band between (14450-14880 cm^{-1}) region assignable to the transitions $^3T_1(F) \rightarrow {}^3T_1(P)\ \upsilon_3$ which are assigned as d-d transition for $Ni(L)_2$ Transition of tetrahedral geometry[29,30] and bands at (31055-33334 cm-1) assigned to the charge transferee the position of the band indicated that these complexes exhibited tetrahedral geometry.

The Ni(II) complexes gives magnetic moments between (3.25-3.65 B.M.) supporting tetrahedral geometry (Table 3).

Three bands were observed at (31055-33334 cm^{-1}) assigned to the charge transferee. The position of the bands indicated these complexes exhibited tetrahedral geometry.

The copper (II) complex display broad band at (9803-14925 cm^{-1}) Corresponding to $^2T_1 \rightarrow {}^2E$ transition, and band at (29239-32679 cm^{-1}) which might be assigned to the charge transferee transition supporting tetrahedral geometry of the Cu(II) complexes[31]. The magnetic moment of the Cu(II) complexes has been found between (1.91-2.09 B.M.), this corresponds to the presence of one unpaired electron in the complexes.

For the Zn(II) and Cd(II) ions have no unpaired electrons and given an intense band situated at (28409-32894 cm^{-1}) which can be assigned to the charge transfer transition[32] from M to L and π to π^* transitions, on complex formation this bands may be shifted to lower wave length from ligands spectra. These observations represented a further indication about the coordination of the ligands with the metal ions[33,34].
Therefore Zn(II) and Cd(II) complexes are expected diamagnetic whether they have tetrahedral structures[35].

From this study, it can be concluded that the ligands acted as bidentate chelating ligand coordinated to the metal ions through azomethine nitrogen atom, carbonyl oxygen atom of the isatin residue for L_1 and hydroxyl-1-naphthaldehyde oxygen for L_2 and hydroxy acetophenone oxygen for L_3 and azomethine nitrogen atoms. As a result tetrahedral structure was suggested for all the complexes as shown in Figure (1,2 and 3).

Biological activity

As shown in the Table (4) of the compounds (1, 2, 4 and 15) have the higher inhibition effect on bacterial cultures gram-positive bacteria (*Staphylococcus aureus*) (12, 13, 14 and 12 mm) (Figure 4). While, compounds (13 and 15) have the higher inhibition effect on bacterial cultures gram-negative bacteria (*Escherichia coli*) (14 mm and 13 mm)(Figure 5).

Table 1: Analytical and some physical properties of the ligand and complexes.

No.	Compounds	Color	M.P (°C)	Yield (%)	Molar conductance Λ_M in DMF (Ω^{-1} cm^2 mol^{-1})	Element analysis data found (calculated)(%)			
						C	H	N	M
	L_1	**Yellow**	230	83	-----				-----
1	$[Co(L_1)_2]Cl_2$	Dark-brown	> 330	73	136				9.77(9.29)
2	$[Ni(L_1)_2]Cl_2$	Brown	> 330	79	147				9.81(9.26)
3	$[Cu(L_1)_2]Cl_2$	Black	274	77	169	56.13(56.37)	3.46(3.75)	8.33(8.76)	10.45(9.95)
4	$[Zn(L_1)_2]Cl_2$	Orange	262	93	132				10.76(10.20)
5	$[Cd(L_1)_2]Cl_2$	Orange	> 330	73	146				------
	HL_2	Yellow	122	77	-----				------
6	$[Co(L_2)_2]$	Green	244	75	16				9.97(9.64)
7	$[Ni(L_2)_2]$	Dark-green	254	56	29				10.03(9.61)
8	$[Cu(L_2)_2]$	Dark-green	236	73	27				10.71(10.32)
9	$[Zn(L_2)_2]$	Yellow	268	92	14	69.58(69.97)	4.18(4.53)	4.20(4.53)	10.88(10.58)
10	$[Cd(L_2)_2]$	Yellow	214	80	18				------
	HL_3	Yellow	116	74	-----				------
11	$[Co(L_3)_2]$	Blue	238	60	18				11.29(10.93)
12	$[Ni(L_3)_2]$	Green	242	68	28				11.16(10.89)
13	$[Cu(L_3)_2]$	Brown	160	71	16				11.94(11.69)
14	$[Zn(L_3)_2]$	Yellow	234	73	22				12.35(11.98)
15	$[Cd(L_3)_2]$	Yellow	216	71	24	60.29(60.76)	4.43(4.72)	4.35(4.72)	------

Table 2: Characteristic I.R. bands of the ligand and complexes in cm^{-1}.

No.	Compounds	υ(O-H)	υ(C = N)	υ (C = O)	υ(M – N)	υ(M – O)	υ(-NH)	υ(C-O)
	L_1		1643	1739			3230	
1	$[Co(L_1)_2]\ Cl_2$		1622	1695	416	465	3230	
2	$[Ni(L_1)_2]\ Cl_2$		1614	1697	416	461	3228	
3	$[Cu(L_1)_2]\ Cl_2$		1610	1690	418	465	3228	
4	$[Zn(L_1)_2]\ Cl_2$		1610	1712	418	464	3230	
5	$[Cd(L_1)_2]\ Cl_2$		1612	1705	420	461	3228	
	HL_2	3271	1641					1248
6	$[Co(L_2)_2]$		1626		420	459		1284
7	$[Ni(L_2)_2]$		1616		418	467		1300
8	$[Cu(L_2)_2]$		1626		418	461		1294
9	$[Zn(L_2)_2]$		1624		418	459		1281
10	$[Cd(L_2)_2]$		1628		418	469		1304
	HL_3	3298	1643					1252
11	$[Co(L_3)_2]$		1620		418	466		1296
12	$[Ni(L_3)_2]$		1616		417	465		1288
13	$[Cu(L_3)_2]$		1623		418	472		1300
14	$[Zn(L_3)_2]$		1618		426	459		1302
15	$[Cd(L_3)_2]$		1621		417	465		1300

Table 3: The electronic spectra and magnetic moments of the complexes.

No.	Compounds	Absorption region cm^{-1}	Possible assignments	μeff Magnetic moment(B.M.)	Geometry
1	$[Co(L_1)_2]\ Cl_2$	14836,16447 30303	$^4A_2(F) \longrightarrow {}^4T_1(P)(\nu_3)$ Charge transfer	4.40	Td
2	$[Ni(L_1)_2]\ Cl_2$	14880 33334	$^3T_1(F) \longrightarrow {}^3T_1(P)\ (\nu_3)$ Charge transfer	3.65	Td
3	$[Cu(L_1)_2]\ Cl_2$	10183 32051	$^2T_2 \longrightarrow {}^2E$ Charge transfer	2.09	Td
4	$[Zn(L_1)_2]\ Cl_2$	28409	Charge transfer	---	Td
5	$[Cd(L_1)_2]\ Cl_2$	29940	Charge transfer	---	Td
6	$[Co(L_2)_2]$	14839,16447 31847	$^4A_2(F) \longrightarrow {}^4T_1(P)$ Charge transfer	3.97	Td
7	$[Ni(L_2)_2]$	14450 31055	$^3T_1(F) \longrightarrow {}^3T_1(P)$ Charge transfer	3.25	Td
8	$[Cu(L_2)_2]$	9803 32679	$^2T_2 \longrightarrow {}^2E$ Charge transfer	1.91	Td
9	$[Zn(L_2)_2]$	32894	Charge transfer	---	Td
10	$[Cd(L_2)_2]$	29411	Charge transfer	---	Td
11	$[Co(L_3)_2]$	14836,16441 32894	$^4A_2(F) \longrightarrow {}^4T_1(P)$ Charge transfer	4.01	Td
12	$[Ni(L_3)_2]$	14836 32051	$^3T_1(F) \longrightarrow {}^3T_1(P)$ Charge transfer	3.56	Td
13	$[Cu(L_3)_2]$	14925 29239	$^2T_2 \longrightarrow {}^2E$ Charge transfer	2.02	Td
14	$[Zn(L_3)_2]$	29239	Charge transfer	---	Td
15	$[Cd(L_3)_2]$	30303	Charge transfer	---	Td

Td = tetrahedral

Table 4: Biological activity of metal complexes.

No.	Compounds	Dimension inhibition zone (mm)	
		Gram-positive bacteria (*Staphylococcus aureus*)	Gram-negative bacteria (*Escherichia coli*)
1	$[Co(L_1)_2]\ Cl_2$	R	13
2	$[Ni(L_1)_2]\ Cl_2$	R	14
3	$[Cu(L_1)_2]\ Cl_2$	R	9
4	$[Zn(L_1)_2]\ Cl_2$	R	15
5	$[Cd(L_1)_2]\ Cl_2$	12	6
6	$[Co(L_2)_2]$	6	3
7	$[Ni(L_2)_2]$	3	R
8	$[Cu(L_2)_2]$	R	6
9	$[Zn(L_2)_2]$	3	R
10	$[Cd(L_2)_2]$	12	10
11	$[Co(L_3)_2]$	3	3
12	$[Ni(L_3)_2]$	7	6
13	$[Cu(L_3)_2]$	16	7
14	$[Zn(L_3)_2]$	9	R
15	$[Cd(L_3)_2]$	15	14
Control	**Amp.**	R	R
	Cipro.	10	9
	Ceph.	R	12
	Tetra.	R	R

R = resistance.

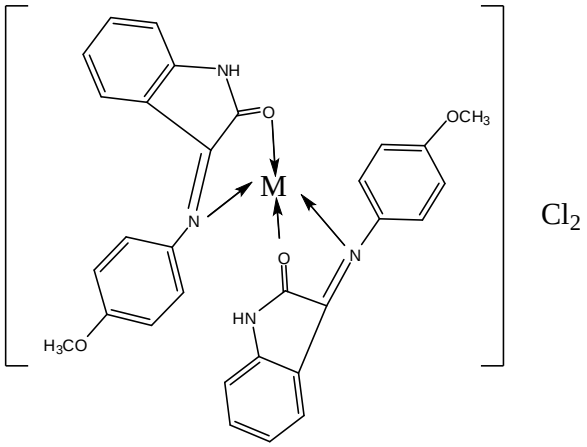

Fig.1: The proposed structure of the complexes $[M(L_1)_2]\ Cl_2$.

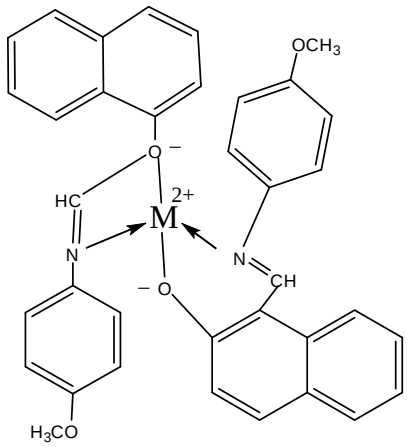

Fig.2: The proposed structure of the complexes $[M(L_2)_2]$.

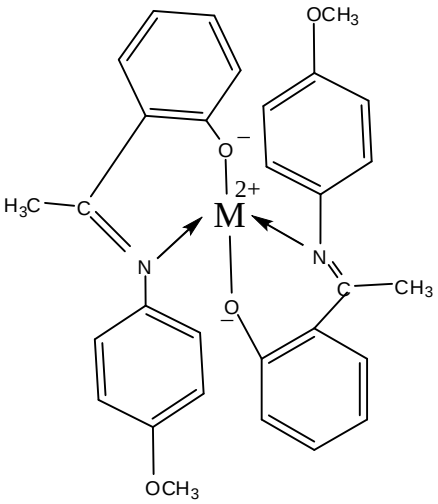

Fig.3: The proposed structure of the complexes $[M(L_3)_2]$.
M= Co(II),Ni(II),Cu(II),Zn(II),Cd(II).

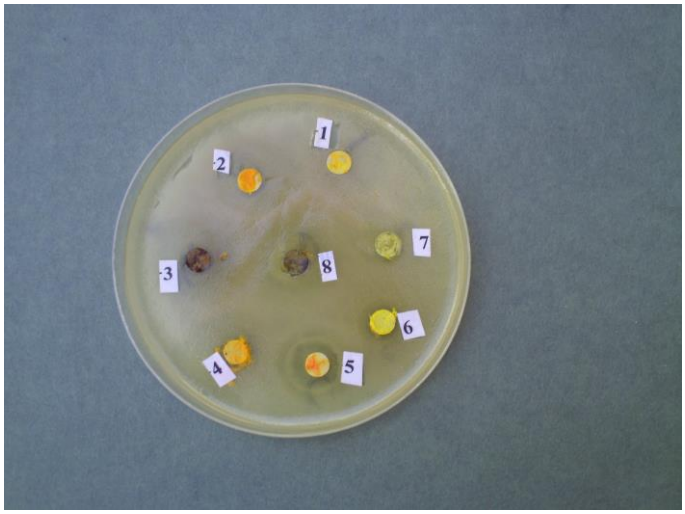

Fig. 4: Biological effects for (1-8) compounds to gram-positive bacteria (*Staphylococcus aureus*).

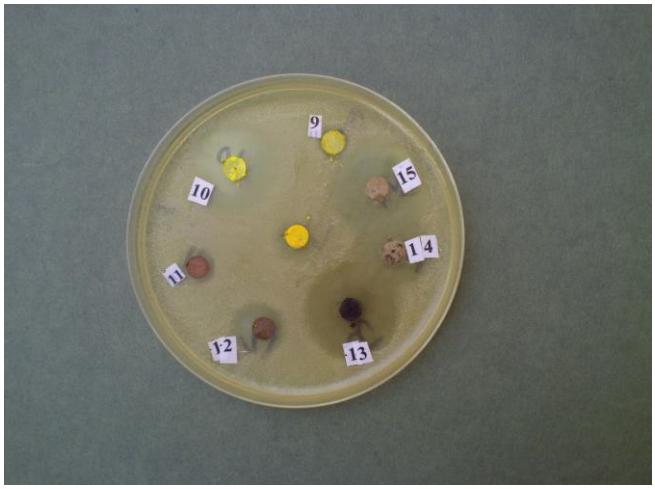

Fig. 5: Biological effects for (9-15) compounds to gram-negative bacteria (*Escherichia coli*).

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