Synthesis and Characterization of New Metal Ions Mn(II),Co(II),Ni(II),Cu(II),Zn(II) and Cd(II) Complexes With (*E*)-1-

(1-(furan-2-yl)ethylideneamino)anthracene-9,10-dione Ligand and Evaluation of Their Biological Activities

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Abstract:Metal complexes of the general formula $[MLCl_2]$ and $[ML_2Cl_2]$, L= (*E*)-1-(1-(furan-2-yl)ethylideneamino)anthracene-9,10-dione and M = Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) in (1:1) and (1:2) metal to ligand malor ratio have been prepared and characterized by molar conductance, magnetic measurement, FT- IR, UV-visible spectral studies and metal content analysis, Conductivity measurements indicates that all complexes were non electrolytes and the ligand. Schiff base behaves as a bidentate chelating ligand. Magnetic moment and electronic spectra indicates that the complexes have either tetrahedral or octahedral geometry. Beside of, the biological activity testes indicate that some of the prepared complexes posses ability to inhibit growth *Staphylococcus aureus* and *Escherichia coli* bacteria.

الملخص: يَضمن البحث تحضير مجموعة من المعقدات الجديدة ذات الصيغة العامة [MLCl] و [ML2Cl] و ان لم يمثل (ع)-1-(1-فيوران-2-إلى) اثيليدين امينو) انثراسين-10،9 دايون، إذ أن M تمثل ايونات (Mn(II)، (Mo(II)، (Ni(II)، (Cu(II)، (Cu(II)، (Cu(II))، (Cu(II))) و(2:1) و(2:1) و(2:1) و(2:1) و(1:2) والن : ليكاند) . تم تشخيص المعقدات المحضرة بوساطة قياسات التوصيلية الكهربائية المولارية وقياسات الحساسية المغناطيسية واطياف الاشعة تحت الحمراء وفوق البنفسجية-المرئية وتعيين الحتوى الفلزي. دلت قياسات التوصيلية الكهربائية بأن هذه المعقدات غير موصلة، وإن الليكاند يسلك سلوك ليكاند ثنائي السن. أظهرت قياسات الحساسية المغناطيسية والاطياف الالكترونية بأن قسماً من المعقدات تمتلك بنية رباعية السطوح او ثمانية السطوح . فضلا عن ذلك فقد أظهرت اختبارات الفعالية البايولوجية لبعض المعقدات المحضرة قدرتها لتثبيط غو نوعين من البكتريا Staphylococcus aureus والعواد عالم عن ذلك فقد

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⁻ 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 $^{(7,8)}$.

Metal complexes of Schiff bases have attracted considerable attention due to their remarkable importance in medicinal and pharmaceutical field. They show biological including activities antibacterial, antifungal, anticancer and herbicidal activities⁽⁹⁾. Similarly 9,10anthracenediones are a very important of compounds having some class remarkable in vivo biological activities, antibacterial, antifungal, such as antimalarial. antioxidant. antileukemic. hypotensive, mutagenic functions, and analgesic activity⁽¹⁰⁻¹⁴⁾.

In this work, the synthesis and characterization of the new Schiff base

(*E*)-1-(1-(furan-2-

yl)ethylideneamino)anthracene-9,10dione ligand and its complexes Mn(II), Co(II), Ni(II) Cu(II),Zn(II) and Cd(II) in (1:1) and (1:2) metal to ligand molar ratio had been described in details.

Experimental

Material and Methods

All chemicals used were reagent grade from Fluka or B.D.H. companies, used as supplied.

The metal of the content complexes determined was volumetrically (Ni, Cu, Zn) against standard EDTA using suitable indicator⁽¹⁵⁾. Cobalt was determined spectrophotometerically⁽¹⁶⁾ . chloride content was estimated by Mohr's method⁽¹⁵⁾. The IR spectra of the ligand and its complexes were recorded on an spectrophotometer bruker Infrared (Tensor 27) in the 200-4000 cm⁻¹ range discs. Conductivity CsI using measurements were performed on 10⁻³ M solutions of the complexes in DMF 25°C, using PMC3 Jeneway and Terminal 740 wtw conductivity meters. Electronic spectra were recorded on Shimadzu UV -

1650 PC spectrophotometer for 10⁻³ M solutions of the ligand and complexes in DMF or acetonitrile solvents at 25°C. Magnetic susceptibility measurements of the complexes were carried out using Bruker BM6 instrument at ambient temperature. Melting points were determined using electrothermal 9300 apparatus.

Preparation of the Schiff base:

An ethanolic solution (20 ml) of 2acetyl furan (0.01 mole, 1.10 g) were added to an cold ethanolic solution (20 ml) of 1-amino anthraquinone (0.01 mole, 2.2 g) and this mixture was refluxed for 4 hr. The precipitate was obtained after evaporation of solution to about 1/3 of its volume, which was filtered off, washed with cold ethanol then ether and recrystallized from cold ethanol and then air dried. This ligand synthesis is shown in the following equation:



Preparation of the Complexes:

Preparation of [MLCl₂] (1-6) (M=Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II)): Ethanolic solution (20 ml) of Schiff base (0.001 mol, 0.315 g) was added to An ethanolic solution of $MnCl_2.4H_2O$ metal (0.001 mole, 0.19 gm) then the mixture was refluxed for 2 hr with continuous stirring. The mixture was cold to room temperature and the solid formed was filtered off, washed with cold ethanol and with diethyl ether then air dried. Similar procedure were used for the preparation of Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) complexes. The same technique was also followed to prepare the next complexes (2-6) as shown as in table (1).

Salt	Wight (gm) of metal salt	Weight (gm) of ligand
CoCl ₂ .6H ₂ O	0.24	0.315
NiCl ₂ .6H ₂ O	0.24	0.315
CuCl ₂ .6H ₂ O	0.17	0.315
ZnCl ₂	0.137	0.315
CdCl ₂ .2(1/2)H ₂ O	0.228	0.315

Table (1) : The weight of metal salt and ligand used.

Preparation of [ML₂Cl₂] (7-12) (M=Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II)):

Ethanol solution (20 ml) of Schiff base (0.002 mole, 0.63 gm) was add to an ethanolic solution of MnCl₂.4H₂O metal (0.001 mole, 0.19 gm) then the mixture was refluxed for 2 hr with continuous stirring. The precipitates were obtained after evaporation of solution to about 1/3of its volume, which was filtered out, washed with ethanol and diethyl ether, then dried under air. Similar procedure were used for the preparation of Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) complexes.

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⁽¹⁷⁾. The sensitivity of a microorganism to antimicrobial agents was determined by the assay plates, which were incubated at $37 \circ C$ for 1 day.

Results and discussion

All the prepared complexes are stable at room temperature. The values of molar conductivities for these the complexes in DMF are within the range of (6-18) (ohm⁻¹.cm².mol⁻¹) and it indicated that all complexes are nonelectrolyte⁽¹⁸⁾. Some physical properties of the ligand and its complexes are listed in Table (2).

Table 2: Some physical properties and analytical data of ligand and its
complexes .

No.	Compounds	Color	M.P (°C)	Yield (%)	Molarconductance $\Lambda_{\rm M}$ in DMF $(\Omega^{-1} {\rm cm}^2 {\rm mol}^{-1})$	M% Found (Calculated)	Cl% Found (Calculated)
L	$C_{20}H_{13}O_{3}N$	Brown	216-218	79.18			
1	[MnLCl ₂]	Purple	244-246	64.9	18		16.10 (15.94)
2	[CoLCl ₂]	Green	238-240	67.6	9.6	13.24 (13.62)	15.95 (15.99)
3	[NiLCl ₂]	Orang	240-242	63.0	10.8	13.20 (13.10)	15.96 (16.17)
4	[CuLCl ₂]	Brown	248-250	69.8	13.7	14.13 (14.17)	15.79 (15.53)
5	[ZnLCl ₂]	Orang	248-250	67.8	9.9	14.48 (15.05)	15.72 (16.02)
6	[CdLCl ₂]	Red-Purple	254-256	87.7	15.3		14.24 (14.22)

7	[MnL ₂ Cl ₂]	Purple	240-242	62.2	10.3		9.39 (9.54)
8	[CoL ₂ Cl ₂]	Dark Green	260-262	89.1	14.1	7.75 (7.38)	9.34 (9.30)
9	[NiL ₂ Cl ₂]	Orang	269-271	85.6	10.3	7.72 (7.75)	9.34 (9.0)
10	[CuL ₂ Cl ₂]	Brown	258-260	77.5	7.9	8.31 (8.27)	9.28 (9.29)
11	[ZnL ₂ Cl ₂]	Orang	268-270	79.2	6.0	8.52 (8.41)	9.26 (9.29)
12	[CdL ₂ Cl ₂]	Purple	262-264	69.9	12.4		8.72 (8.45)

FT-IR Spectra

The most important IR assignment of ligand and its complexes are listed in Table (3).

The ligand show bands at 1731 and 1649 cm⁻¹ due to v(C=O) and v(C=N)stretching frequencies respectively which shifted towards lower values in all complexes (1688-1709 cm⁻¹) and (1600-1618 cm⁻¹) indicating that the carbonyl oxygen atom and the azomethine nitrogen atom are coordinated to the metal ion ^{(19,} ²⁰⁾. And notice the starching vibration for (C-O-C) for the furan in ligand spectra at (1155-1159 cm⁻¹) and when formation the complexes appear the band in the same site, that indicating that it is not involved in the coordination between oxygen atom for furan group with the metals and that agreement with the others prepares⁽²¹⁾.

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 (458-483 cm⁻¹) and (418-428 cm⁻¹)^(22, 23) assigned to M-O and M-N modes conclusively indicated that the ligands are coordinated to the metal ions through the azomethine nitrogen and the carbonyl oxygen.

Furthermore the IR spectra of all complexes showed a new band in the region (334-340) cm⁻¹ which may be due to v(M-Cl) vibration ⁽²⁴⁾.

No.	Compounds	$\mathbf{U}(\mathbf{C} = \mathbf{N})$	v (C = O)	U (C-O-C)	U (M – O)	$\upsilon(M-N)$	V(M – Cl)
	L	1649	1731	1158			
1	[MnLCl ₂]	1612	1600	1156	465	426	336
2	[CoLCl ₂]	1607	1703	1156	464	420	340
3	[NiLCl ₂]	1600	1688	1159	459	418	334
4	[CuLCl ₂]	1605	1695	1159	472	418	335
5	[ZnLCl ₂]	1618	1700	1158	458	427	340
6	[CdLCl ₂]	1607	1693	1156	466	428	335
7	$[MnL_2Cl_2]$	1605	1709	1156	483	421	340
8	[CoL ₂ Cl ₂]	1618	1703	1156	467	418	336
9	[NiL ₂ Cl ₂]	1611	1697	1158	459	426	340
10	[CuL ₂ Cl ₂]	1610	1705	1159	466	417	340
11	$[ZnL_2Cl_2]$	1608	1695	1156	480	428	334
12	$[CdL_2Cl_2]$	1603	1704	1158	472	420	336

Table 3: IR Spectra data of the ligand and the complexes in cm⁻¹.

Magnetic measurements and Electronic Spectra

The magnetic moment of the complexes and the electronic spectra data at 25°C of the ligand and its complexes are listed in Table (4). The electronic spectra of the ligand L show bands at the region (34482-36642 cm⁻¹) and at 27777 cm⁻¹ attributed to benzene $\pi \rightarrow \pi^*$ and n π transition of the non-bonding electrons present on the nitrogen of the azomethine group respectively, these bands were shifted in the spectra of the complexes towards lower or higher frequencies confirmed the coordination between ligand and metal ion.

The Mn(II) complexes (1,7) show a magnetic moments (5.63 and 5.87) B.M which are appreciably close to the calculated spin only value for five unpaired electrons . The electronic spectra of Mn (II) complexes (1, 7) show no prominent absorption that could be assigned for d-d transition but the electronic spectra showed bands attributed to the charge transfer transition , then the structures of the prepared Mn(II) complexes (1, 7) were proposed depending on the data of other measurements namely metal content and IR spectra⁽²⁵⁾.

The magnetic moment of Co(II) complexes (2, 8) were (4.41, 5.11) B.M (26, 27) indicating a tetrahedral and octahedral geometry respectively ⁽²⁸⁾, the electronic spectra of the complex (2) exhibit band in the visible region (14920 cm^{-1}), which correspond to transition. ${}^{4}A_{2}(F) \longrightarrow {}^{4}T_{1}(P) (v_{3})$ in the tetrahedral geometry. The other two bands v_1 and v_2 \rightarrow ⁴A₂(F) ⁴T₂(F) and (due to ${}^{4}A_{2}(F) \longrightarrow {}^{4}T_{1}(F)$ transition) and band at (27770-32899 cm⁻¹) assigned to the charge transferee which also supported a tetrahedral arrangement around Co(II) ion^(29, 30) (Table 4).

Cobalt (II) complex (8) gave three bands at (10162, 14987, 20325) cm^{-1}

which were attributed to transitions ${}^{4}T_{1}g(F) \longrightarrow {}^{4}T_{2}g(F), {}^{4}T_{1}g(F) \qquad {}^{4}A_{2}g(F)$ and ${}^{4}T_{1}g(F) \longrightarrow {}^{4}T_{1}g(P)$ respectively. These values indicated that the geometry for this complex is octahedral^(31, 32). The magnetic moment of Ni(II) complexes (3, 9) were (3.65, 3.21) B.M indicating a tetrahedral⁽³³⁾ and octahedral geometry⁽³⁴⁾ respectively.

The electronic spectra of the Ni(II) complex (3) showed strong band at (14266) cm⁻¹ region assignable to the transition ${}^{3}T_{1}(F)$ ${}^{3}T_{1}(P)$ v3 in tetrahedral geometry⁽³⁵⁾ and bands at (24334, 37055) cm⁻¹which could be assigned as charge transfer the position of the band indicated that these complexes exhibited tetrahedral geometry, whereas the Ni(II) complex (9) showed the presence of three transition bands at (10162, 15409, 27624) cm⁻¹ regions assignable to transitions ${}^{3}A_{2}g(F)$ ${}^{3}T_{2}g(F)$ and ${}^{3}A_{2}g(F) \longrightarrow {}^{3}T_{1}g(F)$ and $^{3}A_{2}g(F)$ $^{3}T_{1}g(P)$ respectively $^{(36)}$. These bands are consistent with the octahedral geometry of the complex.

The magnetic moment of the Cu(II) complexes (4, 10) has been found between (2.17-1.78) B.M supporting tetrahedral and octahedral environment respectively⁽³⁷⁾.

The copper (II) complex (4) display broad band at (9615 cm⁻¹)

Corresponding to ${}^{2}T_{1}$ ²E transition. and band at (22770-32796 cm⁻¹) which might be assigned to the charge supporting transferee transition geometry of the Cu(II) tetrahedral complexes⁽³⁸⁾. Cu(II) complexes (10) exhibit a single broad a symmetric band in the region 13019 cm⁻¹. The broadness of the band indicates the three transitions $^{2}B_{1}g$ $^{2}A_{1}g$, $^{2}B_{1}g$ $^{2}B_{2}g$ $^{2}B_{1}g$ ²Eg in the eleetronic and spectra, point →out the octahedral geometry while other transition (32809 cm⁻¹) could be due to charge transfer transition⁽³⁹⁾.

For the Zn(II) and Cd(II) complexes (5, 6, 11, 12) have no unpaired electrons and given an intense band situated at $(28877-32682 \text{ cm}^{-1})$ which can be assigned to the charge transfer transition $^{(40)}$ from M to L and π to π^* transitions, on complex formation this bands may be shifted to the other values compared with the corresponding bands in the spectrum of the free ligand. These observations represented a further indication about the coordination of the ligands with the metal ions⁽⁴¹⁾.

Table 4: Magnetic measurements and Electronic Spectra of ligand and its
complexes.

No.	Compounds	µeff Magnetic moment(B.M.)	Absorption region cm ⁻¹	Geometry
	L		27777($n \rightarrow \pi^*$), 34482-36642 ($\pi \rightarrow \pi^*$)	
1	[MnLCl ₂]	5.63	20762, 24875, 32360	Td
2	[CoLCl ₂]	4.41	14920, 22770, 32899	Td
3	[NiLCl ₂]	3.65	14266, 24334, 37055	Td
4	[CuLCl ₂]	2.17	9615, 22770, 32796	Td
5	[ZnLCl ₂]	(dia)	28877, 31605	Td
6	[CdLCl ₂]	(dia)	30103, 31037	Td
7	[MnL ₂ Cl ₂]	5.87	21195, 24534, 32250	Oh
8	[CoL ₂ Cl ₂]	5.11	10162, 14987, 20325	Oh
9	[NiL ₂ Cl ₂]	3.21	10162, 15409, 27624	Oh
10	[CuL ₂ Cl ₂]	1.78	13019, 32809	Oh
11	[ZnL ₂ Cl ₂]	(dia)	29923, 32069	Oh
12	$[CdL_2Cl_2]$	(dia)	29764, 32682	Oh

Td = tetrahedral

Oh= Octahedral

From the above discussion the following structure in figure 1 and 2, can be suggested for the prepared complexes in this work.



Figure 1: The proposed structure of the complexes No.(1-6).

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Figure 2: The proposed structure of the complexes No. (7-12).

Antibacterial activity

The antibacterial activity of the newly synthesized Schiff base and its Co(II), Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) complexes against Gram positive *Staph. aureus* and Gram negative *E. coli* organism have been studied by the disk diffusion method⁽⁴²⁾.

The antibacterial results suggest that the complexes Table 5 show a moderate activity against both type of bacteria . They show higher antibacterial activity than the ligand, specially Zn(II) and Cd(II) complexes which show the highest activity . The solvent DMSO was inactive against any bacterial strain.

Comp.		Staph. aureus	E. coli	
No.	Empirical formula	Diameter of inhibition	Diameter of	
		zone (mm)	inhibition zone (mm)	
L	$C_5H_{10}N_2O$	R	R	
1	[Mn(L)Cl ₂]	R	R	
2	[Co(L)Cl ₂]	R	R	
3	[Ni(L)Cl ₂]	R	R	
4	[Cu(L)Cl ₂]	R	R	
5	$[Zn(L)Cl_2]$	9	R	
6	$[Cd(L)Cl_2]$	8	R	
7	$[Mn(L)_2Cl_2]$	R	R	
8	$[Co(L)_2Cl_2]$	R	R	
9	$[Ni(L)_2Cl_2]$	R	R	
10	$[Cu(L)_2Cl_2]$	R	R	
11	$[Zn(L)_2Cl_2]$	15	9	
12	$[Cd(L)_2Cl_2]$	11	R	

Table 5: Antibacterial activity of the ligand and its complexes.

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