

Synthesis and Characterization of Mn(II) ,Co(II) ,Ni(II) ,Cu(II) ,Zn(II) and Cd(II) Complexes with Di-Schiff Bases Derived from o- or m- Phenylenediamine and 9,10-Phenanthrenequinone

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الخلاصة

حضرت سلسلة جديدة من المعقدات من نوع $[MLCl_2]$ حيث $Cd(II), Zn(II), Cu(II), Ni(II), Co(II), Mn(II) = M$ وان $L^1 = L$ أو L^2 تمثل ليكندي قواعد شيف الثنائية $\{L^1 = (EN', N, EN', N) =$ فيناثرين - 9, 10 - داي يلدين) بس (بنزين 1, 2 - داي امين)

$\{L^2 = (EN', N, EN', N) =$ فيناثرين - 9, 10 - داي يلدين) بس (بنزين 1, 3 - داي امين)

بنسبة مولية (1:1) (L:M) وتم تشخيصها من خلال التوصيلية الكهربائية ، العزوم المغناطيسية و اطيف IR والاطيف الالكترونية وتعيين المحتوى الفلزي .

اوضحت دراسة التوصيلية المولارية بمذيب DMSO و DMF ان جميع المعقدات غير الكتروليتية . كما بينت العزوم المغناطيسية والاطيف الالكترونية ان بعض المعقدات تمتلك شكل رباعي السطوح والبعض الآخر يمتلك ترتيب مربع المستوي .

اوضحت نتائج الفعالية المضادة للبكتريا من نوع *E.coli* و *S.aureus* لليكند L^1 والليكند L^2 وبعض من معقداتها مع $Cu(II)$ و $Zn(II)$ بان المعقدات تمتلك فعالية اعلى من الليكند العضوي .

ABSTRACT

A series of new complexes of the type $[MLCl_2]$ where $M = Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II)$ $L = L^1$ or L^2 represents di-Schiff base ligands: $\{L^1 = (N, N'E, N, N'E) - N, N' - (phenanthrene-9, 10 - diylidene) bis (benzene-1, 2 - diamine)$. $L^2 = (N, N'E, N, N'E) - N, N' - (phenanthrene-9, 10 - diylidene) bis (benzene-1, 3 - diamine)\}$ have been prepared in (1:1)(M:L) molar ratio and characterized by electrical conductivity, magnetic moment, IR, UV-VIS and metal content analysis.

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Conductivity data in DMF and DMSO solution showed that all complexes are non-electrolytes. Magnetic moment and electronic spectra indicate that some of the complexes have a tetrahedral geometry and the others have an square planar environment. The antibacterial activity against *E.coli* and *S.aureus* of L¹ and L² and some of their complexes derived from Cu(II) and Zn(II) illustrates that the complexes have higher activity than the corresponding organic ligand.

INTRODUCTION

Particular attention has recently been paid to the synthesis and study of the di-Schiff bases derived from diamine and quinones and their complexes. This is due to a variety of reasons, Schiff bases of phenylene diamine and its complexes have a variety applications including biological⁽¹⁻⁴⁾, Clinical⁽⁵⁾ and analytical⁽⁶⁾. Earlier work has shown that some drugs showed increased activity when administered as metal chelates rather than as organic compounds^(1,5), and that the coordinating possibility of phenylene diamine has been improved by condensing with a variety of carbonyl compounds.

On the other hand quinones are known to play an important role in photosynthesis in plants and bacteria as well as for blood clotting in animals^(7,8), quinone structure exists in some vitamins, which are necessary to maintain life as vitamins (K), which take part in the blood clot action and have a naphthoquinone structure⁽⁹⁻¹¹⁾, Trimethyl-p-benzoquinone is a key compound in the vitamin (E) synthesis, and 2-methyl-1,4-naphthoquinone is used as blood coagulating agent and as supplement in animal food⁽¹²⁾.

Some drugs have quinone structures, such as daunorubicin and doxorubicin, which are used as anti-tumor drugs⁽¹³⁾. So mass screening programs of natural products by the (National Cancer Institute) have identified the quinone as an important pharmacophoric moiety for cytotoxic activity⁽¹⁴⁾, therefore, synthesised some Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) complexes with symmetric Schiff base ligands derived from 9,10-phenanthraquinone and o- or m- phenylene diamine. The structure of Schiff base ligands is shown in fig1.

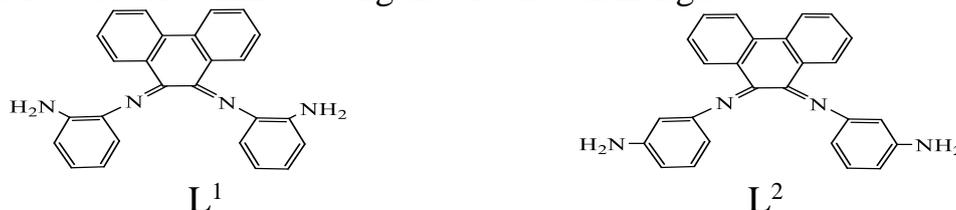


Fig 1: suggested structures of the ligands

EXPERIMENTAL

Materials and Methods:

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

Melting points were obtained on electrothermal 9300 melting point apparatus in open capillaries. Infrared spectra were recorded as KBr disc using Tensor 27 Bruker FT-IR spectrophotometer (400-4000 cm^{-1}). Electronic absorption spectra were recorded in DMSO (10⁻³M) solution on Shimadzu U.V- 1650PC- spectrophotometer at room temperature using 1 cm quartz cell. Molar conductance were measured at room temperature using PCM3- Jenway conductivity meter. Magnetic susceptibility measurements of the complexes were carried out using Bruker BM6 instrument at ambient temperature. The metal content of complexes were determined spectrophotometrically using Shimadzu AA670 atomic absorption spectrophotometer, chloride was determined volumetrically using standard AgNO_3 solution⁽¹⁵⁾, after acid digestion with conc. HNO_3 .

Synthesis of (N,N'E,N,N'E)-N,N'-(phenanthrene-9,10-diylidene) bis (benzene-1,2-diamine) (L¹)⁽¹⁶⁾

A clear solution of (1,2-phenylene diamine) (2.16g, 0.02mole) in absolute ethanol (10ml) was added slowly and drop wise to a solution of (9,10-phenanthrenequinone) (2.08g, 0.01mole) in absolute ethanol (50ml), the mixture was stirred about (30min). Two drops of (2M) hydrochloric acid were added. The resultant solution was refluxed for (7h), after cooling, pale-yellow precipitate was filtered off, washed with cold absolute ethanol (5 ml) then with ether (5 ml) and dried under vacuum.

Synthesis of (N,N'E,N,N'E)-N,N'-(phenanthrene-9,10-diylidene) bis (benzene-1,3-diamine) (L²)⁽¹⁶⁾

It was prepared by using (2.16g, 0.02mol) of (1,3-phenylene diamine) and (2.08g, 0.01mole) of (9,10-phenanthrenequinone) then applied the above procedure.

Preparation of [MLCl₂] complexes

A solution of (0.001mole) of metal salt [$\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (0.197g); $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.237g); $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (0.238g); $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.170g) and ZnCl_2 (0.136g) and CdCl_2 (0.183g)] in (10ml) absolute ethanol was added drop wise for (10 min) with continuous stirring to a hot solution of the L¹ (0.001mole, 0.388g) or L² (0.001mole, 3.88g), in (20 ml) absolute ethanol. The mixture were refluxed for (4-5 h), then it was filtered off, washed with cold absolute ethanol then with ether and dried.

Antibacterial activity

Antibacterial activity was evaluated using agar diffusion method⁽¹⁷⁻¹⁹⁾. Gram-positive bacteria *Staphylococcus aureus* and Gram-negative bacteria *Escherichia coli* were cultivated in nutrient agar on petri dishes. The test solution were prepared by weighing (10mg) of all tested substance then dissolved in (1ml) DMSO. A (6mm) diameter filter paper discs were soaked in the tested solutions . after (24 h.) cultivation at (37 °C) ,diameter of zones of inhibition were determined . DMSO was inactive under applied conditions .

RESULTS AND DISCUSSION

Direct reaction of ligand L¹ or L² with absolute ethanol solution of metal(II) chloride in (1:1) molar ratio (L:M) gave (12) complex. The chemical analysis and physical properties of the ligand and their complexes are given in (Table 1) . All the complexes were solids , stable in air and decomposed at a degree above(149 °C) , they are insoluble in most organic solvent but soluble in DMF and DMSO .

The molar conductance values of (10⁻³ M) solution of metal complexes in DMF and DMSO were in the range(3.97-28.88)ohm⁻¹ cm² mol⁻¹ and (2.55-21.20) ohm⁻¹ cm² mol⁻¹ respectively indicating non electrolytic nature of these complexes ^(20,21).

Infrared spectra:

The most important IR assignment of the ligands and their complexes are listed in (Table 2) . the ligands L¹ and L² show an intense band due to $\nu(\text{C}=\text{N})$ of azomethine group at 1602 cm⁻¹ and 1610 cm⁻¹ of free Schiff bases ^(22,23) . In all complexes this band undergoes a shift to higher frequencies and observed (1618-1637cm⁻¹) ^(22,24) ; it may be due to increasing band order of the C=N double bond on coordination with the metal ions as a result of electron donating of other attached groups or due to strain that occurred on the coordinating site on coordination ⁽²⁵⁻²⁷⁾.

The IR spectra of L¹ and L² show bands at 3350 cm⁻¹ and 3338 cm⁻¹ respectively due to $\nu(\text{NH}_2)$ ⁽²⁸⁾ , the spectra of all complexes show very slight shift (1-3) cm⁻¹ or no shift in the position of $\nu(\text{NH}_2)$ band indicating that the (NH₂) group do not shared in coordination . The ligands coordination is substantiated by new band appearing at the ranges (415-474 cm⁻¹) for the complexes , these are mainly attributed to $\nu(\text{M}-\text{N})$ ^(29,30). All complexes show no band for (M-Cl) because it is below the spectrophotometer limits . (Fig.2) and (Fig.3)

Electronic spectra and magnetism:

The magnetic moment and the electronic spectral data at 25 °C of the ligands and their complexes were listed in (Table3) .The electronic spectra of L¹ and L² in (Table3) show the aromatic intenses bands at

30769 cm^{-1} and 32894 cm^{-1} is attributed to benzene $\pi \rightarrow \pi^*$ transition and at 27777 cm^{-1} and 28571 cm^{-1} due to the $n \rightarrow \pi^*$ transition of non-bonding electrons present on the nitrogen of the azomethine group, these transition are also found in spectra of complexes but they were shifted, confirming the coordination of ligands to metal ions⁽³¹⁾.

The Mn(II) complexes (1,7) show magnetic moments of (5.67 B.M) and (6.10 B.M) respectively, which were appreciably close to the calculated spin-only value, for five unpaired electrons, and reveals high spin state. The Mn(II) complexes (1,7) and diamagnetic Zn(II), Cd(II) complexes (5,6,11,12) has no spin allowed d-d transition, therefore, structures of the prepared Mn(II), Zn(II) and Cd(II) were proposed depending on the data of other measurements⁽³²⁾. namely metal content and IR spectra.

The magnetic moment value of Co(II) complex (2) was (4.07 B.M) indicating tetrahedral geometry⁽³³⁾, their electronic spectra exhibits one transition V_3 , ${}^4A_2(F) \rightarrow {}^4T_1(P)$ consisting of two humps located at (14836-16447 cm^{-1}), the splitting of this band was expected due to distortion of Jahn-Teller type of tetrahedral structure in the excited state⁽³⁴⁾, the other two bands V_1 and V_2 are below the spectrophotometer limits. (Fig.4) and (Fig.5) The magnetic moment of Co(II) complex (8) were found to be (2.03 B.M)⁽³⁵⁾, the electronic spectra of this complex shows absorption band at 16778 cm^{-1} attributed to the ${}^2A_{1g} \rightarrow {}^2E_g$ transition which is compatible with this complex having a low spin square-planar structure⁽³⁶⁾.

The magnetic moment value of Ni(II) complex (3) found to be (3.86 B.M) and its electronic spectra show a band V_3 at 14792 cm^{-1} due to ${}^3T_1(F) \rightarrow {}^3T_1(P)$ transition in tetrahedral geometry⁽³³⁾. The Ni(II) complexes (9) show a diamagnetic moment⁽³⁷⁾ and the electronic spectra show two bands at 16666 cm^{-1} and 26315 cm^{-1} due to ${}^1A_{1g} \rightarrow {}^1A_{2g}$ and ${}^1A_{1g} \rightarrow {}^1B_{2g}$ which is consistent with square planar geometry⁽³⁸⁾.

The Cu(II) complex (4) show magnetic moments of (2.65 B.M) corresponds to the presence of unpaired electron⁽³⁹⁾. The electronic spectra of this complex showed a broad band at 10869 cm^{-1} attributed to ${}^2T_2 \rightarrow {}^2E$ transition which is comparable with complex having tetrahedral structure⁽⁴⁰⁾, while complex (10) show magnetic moment (1.98 B.M) and electronic spectrum showed a broad band at 17301 cm^{-1} which is assigned to combination of transition ${}^2B_{1g} \rightarrow {}^2A_{1g}$ and ${}^2B_{1g} \rightarrow {}^2E_g$ transition which is consistent with square planer geometry around Cu(II) complex⁽⁴¹⁾. Proposed structure for the prepared complexes (Fig.6 and 7)

ANTIBACTERIAL ACTIVITY

The ligands and four of their complexes (4,5,10,11) were tested against Gram - positive bacteria *S. aureas* and Gram - negative bactria *E.*

coli⁽¹⁷⁻¹⁹⁾ (Table 4). The antibacterial activity of the tested complexes was higher than the organic ligand which seems to be inert toward both type of bacteria at the used concentration but it was less toward both types of bacteria as compared with Erythromycin and Amoxicillin (Fig.8).

(Table 4) : Antibacterial effects of the investigated compound

Complex No.	Compound	Inhibition zone diameter* (mm) <i>S. aureus</i>	Inhibition zone Diameter* (mm) <i>E. coli</i>
L ¹	C ₂₆ H ₂₀ N ₄	6.0	7.0
L ²	C ₂₆ H ₂₀ N ₄	9.0	6.0
4	[CuL ¹ Cl ₂]	10.0	11.0
5	[ZnL ¹ Cl ₂]	11.0	9.0
10	[CuL ² Cl ₂]	12.0	10.0
11	[ZnL ² Cl ₂]	13.0	9.0
E	Erythromycin	20.0	12.0
AX	Amoxicillin	15.0	20.0

*Including diameter of disc (6mm)



Fig 8:Antibacterial effectes of L² and complex (11)

Table1: Some physical properties and analytical data of the ligands and their complexes

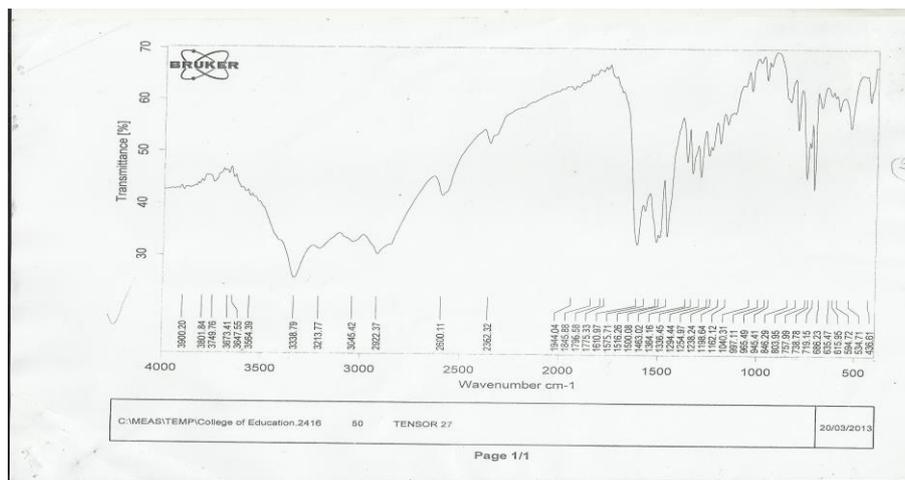
No.	Complexes	Colour	m.p (°c)	Cl%Calc. (Found)	M%Calc. (Found)	Am	
						OHm ⁻¹ DMF	OHm ⁻¹ DMSO
L ¹	C ₂₆ H ₂₀ N ₄	Pale yellow	224-226	-----	-----		
1	[MnL ¹ Cl ₂]	Dark yellow	190-192	13.80(14.20)	-----	26.17	12.90
2	[CoL ¹ Cl ₂]	Blue green	182-185	13.69(12.78)	11.36(11.49)	23.13	10.37
3	[NiL ¹ Cl ₂]	Pale green	215-217	13.70(14.20)	11.32(11.50)	6.51	6.17
4	[CuL ¹ Cl ₂]	Dark green	215-218	13.57(14.20)	12.14(12.43)	18.60	9.29
5	[ZnL ¹ Cl ₂]	Pale brown	239-241	13.52(12.78)	12.45(12.75)	3.97	2.55
6	[CdL ¹ Cl ₂]	Milky white	240-242	12.41(12.67)	-----	8.08	6.34
L ²	C ₂₆ H ₂₀ N ₄	Dark yellow	185-187	-----	-----		
7	[MnL ² Cl ₂]	Yellow	160-162	13.80(14.20)	-----	28.88	20.01
8	[CoL ² Cl ₂]	Dark blue	230-233	13.69(14.20)	11.36(11.63)	25.11	21.20
9	[NiL ² Cl ₂]	Dark brown	150-152	13.70(12.78)	11.32(13.35)	28.15	19.19
10	[CuL ² Cl ₂]	Dark green	250-253	13.57(12.78)	12.14(12.40)	17.15	8.11
11	[ZnL ² Cl ₂]	Pale brown	165-168	13.52(14.20)	12.45(12.71)	16.34	6.67
12	[CdL ² Cl ₂]	Dark yellow	170-173	12.41(12.78)	-----	11.22	7.79

Table2: Characteristic Infrared spectral data of the ligands and their complexes

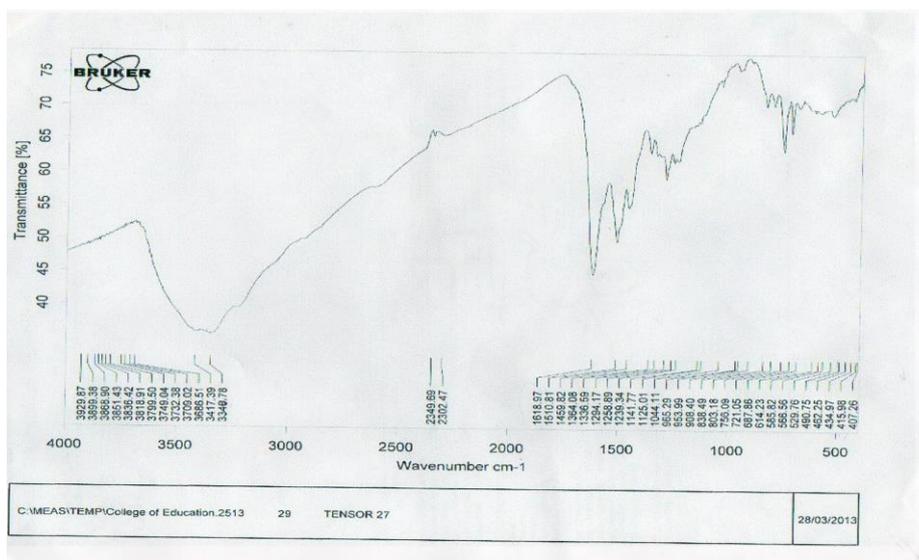
NO.	Complexes	IR spectral bands (cm ⁻¹)		
		ν (C=N _{imin})	ν (NH ₂)	ν (M-N)
L ¹	C ₂₆ H ₂₀ N ₄	1602	3415	-----
1	[MnL ¹ Cl ₂]	1637	3414	450
2	[CoL ¹ Cl ₂]	1637	3415	449
3	[NiL ¹ Cl ₂]	1637	3412	425
4	[CuL ¹ Cl ₂]	1618	3415	420
5	[ZnL ¹ Cl ₂]	1618	3416	440
6	[CdL ¹ Cl ₂]	1620	3414	445
L ²	C ₂₆ H ₂₀ N ₄	1610	3338	-----
7	[MnL ² Cl ₂]	1628	3340	436
8	[CoL ² Cl ₂]	1626	3336	420
9	[NiL ² Cl ₂]	1625	3340	435
10	[CuL ² Cl ₂]	1619	3339	414
11	[ZnL ² Cl ₂]	1618	3340	415
12	[CdL ² Cl ₂]	1620	3335	433

Table3: Magnetic moments and the electronic spectral data of the ligands and their complexes

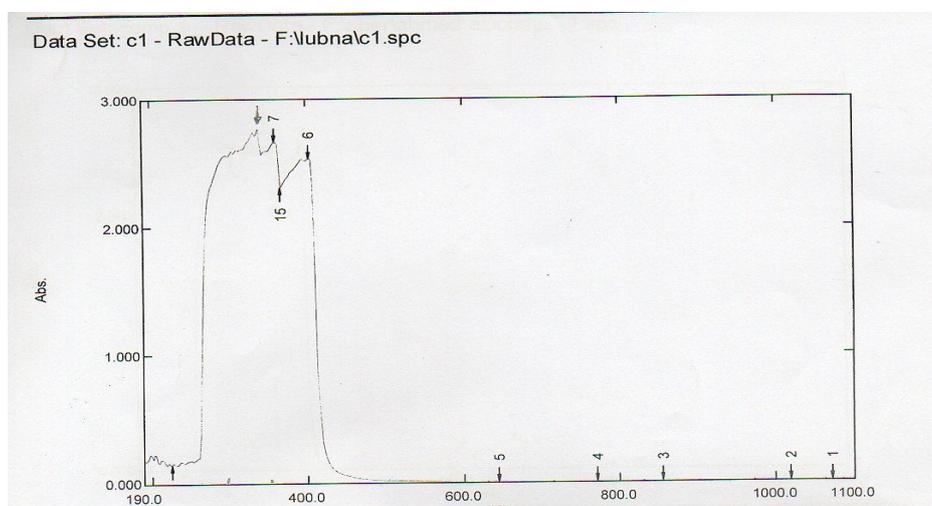
NO.	Complexes	μ^{eff} (B.M)	Electronic Spectra(cm ⁻¹)
L ¹	C ₂₆ H ₂₀ N ₄	-----	27777,30769
1	[MnL ¹ Cl ₂]	5.67	29239,31645
2	[CoL ¹ Cl ₂]	4.07	28571,31645,14836,16447
3	[NiL ¹ Cl ₂]	3.86	29850,31750,14792
4	[CuL ¹ Cl ₂]	2.65	28571,30303,10869
5	[ZnL ¹ Cl ₂]	Dia	29411,31864
6	[CdL ¹ Cl ₂]	Dia	28571,29940
L ²	C ₂₆ H ₂₀ N ₄	-----	28571,32894
7	[MnL ² Cl ₂]	6.10	29585,31894
8	[CoL ² Cl ₂]	2.03	29761,33112,16778
9	[NiL ² Cl ₂]	Dia	29940,33894,16666,26315
10	[CuL ² Cl ₂]	1.98	27777,30864,17301
11	[ZnL ² Cl ₂]	Dia	33120,30555,
12	[CdL ² Cl ₂]	Dia	29409,31800



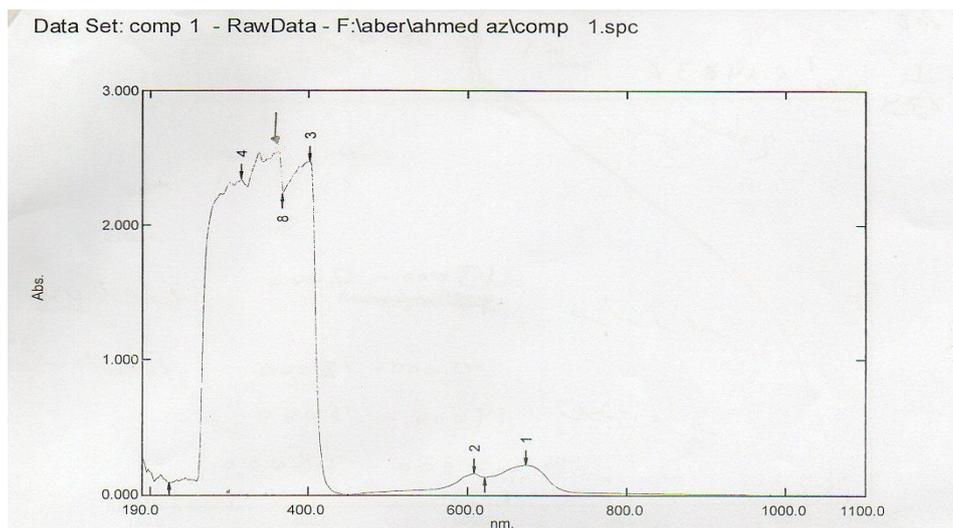
(Fig .2) IR. Spectra for L²



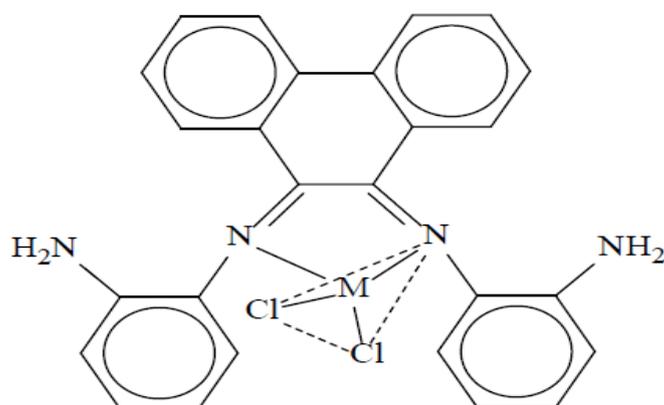
(Fig . 3) IR. Spectra for complex 11



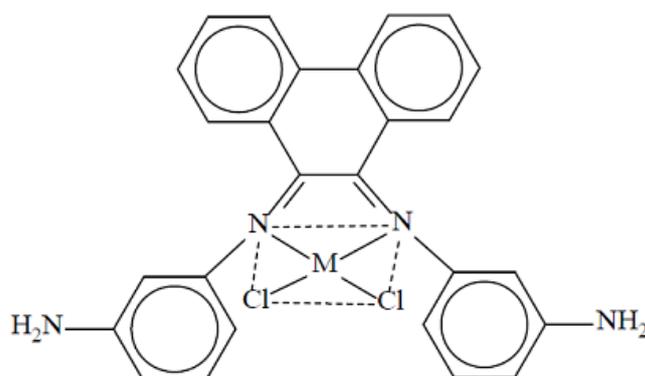
(Fig . 4) UV. Spectra for L¹



(Fig .5) UV. Spectra for complex (2)



(Fig:6) Proposed structures for (1-6) complexes



(Fig:6) Proposed structures for (7-12) complexes

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