SYNTHESIS AND SPECTROSCOPIC STUDIES OF MANGANESE(II), COBALT(II), NICKEL(II), COPPER(II), ZINC(II) AND CADMIUM(II) COMPLEXES WITH SCHIFF BASE DERIVED FROM 1,2-DIPHENYL -3-METHYL-4-AMINO-5-OXO-PYRAZOLE WITH BENZALDEHYDE

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Abstract

The synthesis and characterization of new complexes of Mn(II), Co(II), Ni(II), Cu(II) ,Zn(II) and Cd(II) ions with bidentate Schiff base 1,2-diphenyl-3-methyl-4-benzaladene-5-oxo-pyrazole ligand which was prepared via the condensation reaction of both benzaldehyde with 1,2-diphenyl-3-methyl-4-amino-5-oxo-pyrazole in acidic medium. The complexes were synthesized by treating an ethanolic solution of the ligand with appropriate amount of metal salts [1:2] [M:L] ratio. The complexes were characterized by metal and elemental analysis, FTIR, electronic spectra, molar conductivity, magnetic susceptibility and mole ratio. According to the obtained data the probable coordination geometries of manganese, cobalt, nickel, copper, zinc and cadmium ions in these complexes with nitrogen and oxygen as donor atoms are octahedral. All complexes were found to be non-electrolyte systems in absolute ethanol, and the complexes were formulated as $[ML_2Cl_2]n\ H_2O$.

Keywords:Benzaldelyde,Cobalt,Nickel,Copper,Zinc and Complexes.

تشخيص ودراسة طيفية لمعقدات المنغنيز والكوبلت والنيكل والنحاس والخارصين والكادميوم ثنائية التكافؤ مع قاعدة شف المشتقة من ١,٢- ثنائي فنيل-٣- مثيل-٤- أمينو-٥- أوكسو- بايرازول مع البنزالديهايد

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الخلاصة

تم وصف تحضير وتشخيص معقدات جديدة لكل من Mn(II) و Co(II) و Ni(II) و Cu(II) Zn(II) و Cd(II) مع الليكاند ١,٢- ثنائي فنيل-٣- مثيل-٤- بنزيليدين-٥-اوكسو- بايرازول الذي تم تحضيره من تفاعل بنزالديهايد مع ١,٢- ثنائي فنيل-٣- مثيل- ٤-أمينو-٥- اوكسو- بايرازول في وسط حامضي. تم تحضير المعقدات بمعاملة محلول كحولي لليكاند مع كمية مناسبة من املاح الفلزات وبنسبة [M:L] [1:2]. شخصت المعقدات بواسطة تحليل العناصر و الفلزات واطياف الاشعة تحت الحمراء واطياف الانتقالات الالكترونية والتوصيلية المولارية والحساسية المغناطيسية وطريقة النسبة المولية. طبقاً الى البيانات المستحصلة فالاشكال

الفراغية المحتملة للتناسق لكل من معقدات المنغنيز والكوبلت والنيكل والنحاس والخارصين والكادميوم مع ذرات النتروجين والاوكسجين الواهبة هي ثمانية السطوح. لقد تبين ان جميع المعقدات المحضرة غير الكتروليتية في مذيب الايثانول المطلق وتمتلك الصيغة العامة $[ML_2Cl_2\ ]XH_2O$.

Introduction:

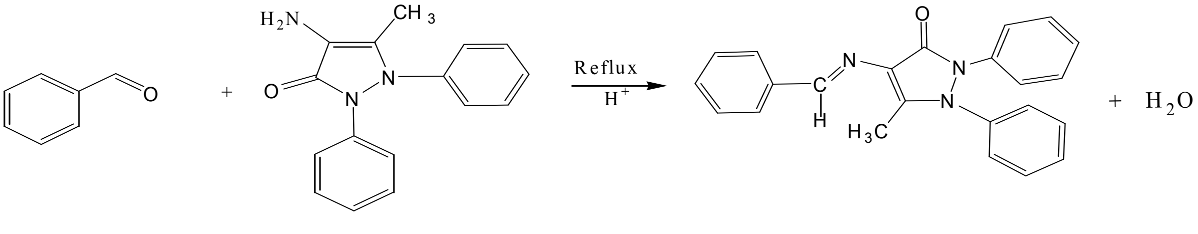
Schiff bases have often been used as chelating ligands in the field of coordination chemistry and their metal complexes are of great interest for many years[1,2]. Chelating ligands containing N, S and O donor atoms show broad biological activity and are of special interest because of the variety of ways in which they are bonded to metal ions[2]. It is well known that N and S atoms play a key role in the coordination of metals at the active sites of numerous metallo biomolecules [3,4]. It is known that the existence of metal ion bonded to biologically active compounds may enhance their activities [5-7]. Schiff base ligands with nitrogen donor atoms of the azomethine group and oxygendonor atoms of the carbonyl group afforded stable complexes with various transition metals[8]. The importance of the coordination compound has been appeared in the biological structures[9]. The increasing proportion of the application and utilization of these compounds as agents have given rise to an intensification into the investigations of the complexes[9]. In the present work bidentate Schiff base ligand has been prepared via the reaction of 1,2-diphenyl-3-methyl-4-amino-5-oxo-pyrazole with benzaldehyde in order to prepare the complexes with Mn, Co, Ni, Cu, Zn and Cd divalent transition metals. The complexes were separated and characterized by elemental analysis, infrared electronic and the reaction chloride spectra, molar conductivity, magnetic susceptibility and mole ratio method.

Materials and Methods:

All the chemicals and solvents which are used for the synthesis were of reagent grade and obtained commercially from British Drug House (BDH) with the exception of manganese, cobalt, nickel, copper, zinc and cadmium chlorides, which were obtained from Fluka company. The solvents were purified by standard methods[10]. The infrared spectra of the ligand and its complexes were recorded in the range (4000-200) cm^{-1} on a Shimadzu (8300) FTIR Spectrophotometer, using CsI pellets. Electronic absorption spectra were recorded in the range (200-1100) nm on a Shimadzu (160) Spectrophotometer in freshly prepared (10^{-3}M) solutions in absolute ethanol at room temperature using quartz cell (1.00) cm. Atomic absorption technique was used to determine the metal contents of the complexes using (GBC933 plus) flame atomic absorption Spectrophotometer. Molar conductivity was used to measure the conductivity of the complexes at room temperature in freshly prepared (10^{-3} M) solutions in absolute ethanol using a (PW9625) digital conductivity meter. Elemental analysis for carbon, hydrogen and nitrogen elements were carried out at the Euro vecter-EA3000A C. H. N. Analyzer, Al al-Bayt University (Jordan). Melting point apparatus of Gallen Kamp was used to measure melting points of all prepared compounds. Also the chlorine content was determined Gravimetrically[11].

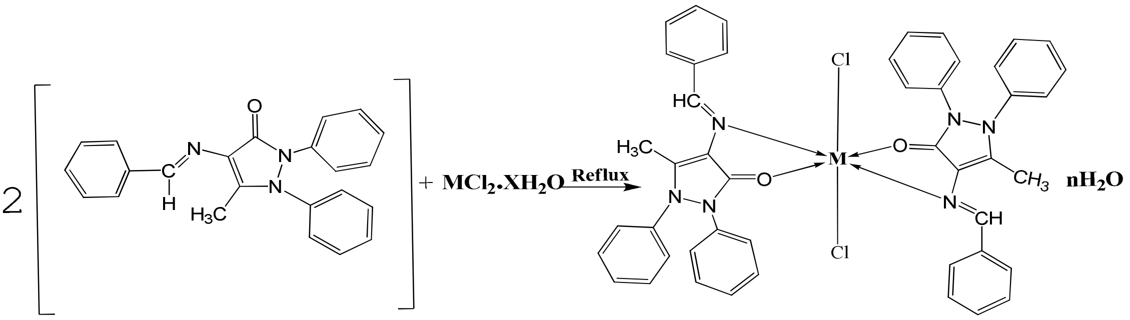
Synthesis of Ligand [L][12]

A solution of benzaldehyde (0.106gm., 1mmole) was added to (10 ml) of methanol, this solution was added to another solution which was consisted of (1,2-diphenyl-3-methyl-4-amino-5-oxo-pyrazole) (0.265gm. 1mmole) dissolved in (10 ml) of methanol. Then 3 drops of glacial acetic acid were added to the reaction mixture. The mixture was refluxed in water bath for 6 hours. The completion of the reaction was confirmed by the TLC. Then the solution was filtered and the solvent was evaporated to dryness. The product was light green crystals and the yield was 86.32% , the melting point was (198 °C). The reaction is clarified bellow



General procedure for the synthesis of metal complexes

The complexes have been prepared by the reaction of (0.706gm. 2mmol) of (L) with (1mmol) of metal chloride (0.198mg., 0.238gm., 0.234gm., 0.171gm., 0.136gm, and 0.220gm. $MnCl_2.4H_2O$, $CoCl_2.6H_2O$, $NiCl_2.6H_2O$, $CuCl_2.2H_2O$, $ZnCl_2$ and $CdCl_2.2H_2O$, respectively) dissolved in (10ml) absolute ethanol and refluxed with stirring under anhydrous conditions using Na_2SO_4 (anhydrous) for 24 hours. The obtained complexes were collected after evaporation of ethanol and triturated with petroleum ether (60-80^{0}C) then filtered and the products were dried at 50^{0}C for 1hour.The general reaction is clarified:



Results and Discussion

All the complexes have been prepared according to the above general equation :
M = Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) [X = 3 for Mn(II), X=2 for Co(II) and Ni(II) and X=1 for Cu(II), Zn(II) and Cd(II)] complexes. The synthesized Schiff base ligand and its complexes are stable at room temperature in the solid state. The complexes were decomposed without melting between (276-315^{o}C), and are soluble in most common organic solvents. Elemental analysis data confirm that the complexes have (1:2) (M:L) ratio confirm the general formula $[ML_2Cl_2]nH_2O$ [n = 3, 2 or 1] for all metal complexes. The physical properties and the elemental analysis data of the ligand and the complexes were clarified in **(Table-1)**

(Table -1) Some physical properties and elemental analysis of the ligand and the complexes

Compound Mwt	Color	M.P. ^{o}C	Yield %	Elemental Analysis Calculated (Found)				
				C%	H%	N%	M%	Cl%
L	Light green	198	86.32	78.19	5.38	11.90	-----	-----
353				(78.88)	(5.54)	(11.75)		
$[CoL_2Cl_2]2H_2O$	Dark green	300d	84.95	63.31	4.82	9.63	6.76	8.14
871.93				(63.20)	(4.63)	(9.03)	(7.85)	(9.88)
$[NiL_2Cl_2]2H_2O$	Light yellow	282d	73.72	63.33	4.82	9.36	6.73	8.15
871.69				(63.87)	(4.89)	(9.63)	(6.86)	(8.83)
$[CuL_2Cl_2]$ H_2O	Green	315d	78.59	64.29	4.66	9.78	7.40	8.27
858.55				(64.67)	(4.87)	(9.55)	(7.19)	(8.78)
$[ZnL_2Cl_2]$ H_2O	Light yellow	276d	85.44	64.16	4.65	9.67	7.60	8.25
860.38				(64.01)	(4.80)	(9.49)	(7.95)	(8.76)
$[CdL_2Cl_2]$ H_2O	Light brown	305d	82.72	60.83	4.41	9.26	12.38	7.82
907.4				(60.55)	(4.55)	(9.02)	(12.12)	(7.69)
$[MnL_2Cl_2]3H_2O$	Green yellow	309d	74.62	62.31	4.97	9.48	6.20	8.01
885.94				(60.92)	(4.88)	(9.58)	(6.45)	(8.33)

d=decomposition point ^{0}C

Infrared Spectroscopy

The FTIR spectrum of the ligand [L] and $[NiL_2Cl_2]2H_2O$ complex are shown in**(figure-1)**. The most important FTIR bands are shown in **(Table-2)**. Two bands appeared at 1670 and 1607 cm^{-1} in the free ligand (L) spectrum were assigned to the stretching vibration modes υC=0 and υC=N respectively[13-15]. The spectrum revealed υC=0 band has the value at 1670 cm^{-1} in the free ligand (L) which was shifted to lower wave number in the complexes spectra. This shift indicates the implication of carbonyl oxygen in the coordination at the metallic center[16]. Another band was appeared at 1607 cm^{-1} in the free ligand was assigned to the υC=N vibration mode, which was shifted to lower wave number in the complexes spectra, as shown in **(Table -2).** In the complexes spectra, this indicates the participation of nitrogen atom of azomethine group in the coordination[17]. The most important conclusion drawn from discussion is that the Schiff base ligand (L) was coordinated to the central metal ion from nitrogen and oxygen atoms and behaves as bidentate ligand. The presence of υM-O and υM-N bands are further support for the coordination of the ligand with the metal ion[18]. The presence of lattice water molecule in all complexes **(Table- 2)** was supported by the presence of broad band in 3433-3379 cm^{-1} region of infrared spectra[19].

(Table -2) The characteristic bands of FTIR spectra of the ligand and its complexes (cm^{-1})

Compound	υO-H cm^{-1} Lattice water	υC=N cm^{-1}	υC=O cm^{-1}	υM-N cm^{-1}	υM-O cm^{-1}
L	--------	1607	1670	--------	--------
$[MnL_2Cl_2]3H_2O$	3379	1581	1630	595	519
$[CoL_2Cl_2]2H_2O$	3417	1587	1605	580	510
$[NiL_2Cl_2]2H_2O$	3413	1572	1622	600	545
$[CuL_2Cl_2]H_2O$	3397	1576	1612	593	480
$[ZnL_2Cl_2]H_2O$	3433	1555	1628	585	470
$[CdL_2Cl_2]H_2O$	3398	1560	1620	582	485

Molar Conductance Data

The recorded conductivity values for the complexes in absolute ethanol 10^{-3} M at room (10.50-18.30 S. $cm^2.mol^{-1}$) which indicate the non-electrolytic nature of the complexes[13]

Magnetic Moments Studies

The Mn(II) complex shows magnetic moment corresponding to five unpaired electrons 5.85 BM at room temperature, close to the spin-only value of 5.92 BM(20). Co(II) complex has magnetic moments value 5.15 BM[21], which agreed with the expected value for the high spin cobalt (II) ion in octahedral environmental. The magnetic moment value of the nickel (II) complex of the Schiff base ligand at room temperature was found to be 3.15 BM[22,23]. The magnetic moment value of Cu(II) complex (d^9) configuration is 1.85 BM[24]. This value refers to distorted octahedral copper(II) complex[24]. As expected, the Zn(II) and Cd(II) complexes are diamagnetic in nature[21].

Electronic Spectral Studies

The electronic absorption spectra are often very helpful in the evaluation of results furnished by other methods of structural investigation. The electronic spectral measurements were used to assign the stereo chemistries of the metal ions in the complexes based on the positions and number of d-d transition peaks. Electronic spectra of the ligand (L) and all its metal complexes were taken in absolute ethanol (10^{-3}M) solutions. The electronic absorption spectra together with the suggested structures are listed in **(Table-3)**. The UV-Vis spectrum of the ligand showed two bands at 257nm (38910cm^{-1}) and 336nm (29762cm^{-1}) as shown in**(figure-2)**, assigned to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions respectively within the molecule, these bands were slightly shifted to blue or red regions for the complexes due to (d-d) transitions. The electronic spectrum of manganese (II) complex showed only the charge transfer transition at 373nm (26809cm^{-1}) which can be assigned to charge transfer from the metal to the ligand $(M \rightarrow L)$ and no $(d \rightarrow d)$ transition are expected for (d^5) (half filled) manganese (II) complex because its Term-symbols is [^{6}**S**][25,26]. The electronic spectrum of cobalt (II) complex showed two main bands at 567nm (17636cm^{-1}) and 445nm (22471cm^{-1}).These bands are assigned to $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ (υ_2) and $^4T_{1g}(F) \rightarrow {}^4T_{2g}(P)$ (υ_3) transitions respectively[27]. The (υ_1) transition is expected to appear at large wavelength[22,28]. Therefore it could not be observed, it will be calculated theoretically through the Tanabe-Sugano diagram[21]. By using this diagram for (d^7) and for υ_3/υ_2 (1.27) ratio, the values of 10Dq, B$^-$, Dq/B$^-$ and β(0.826) can be calculated, this value indicates that the complex has covalent character[23]. While the observed transitions are consistent with an octahedral geometry(28,29). The electronic spectra of Ni(II) complex showed two bands at 689nm(14513cm^{-1}) and 438nm (22831cm^{-1}), these have been assigned to the transitions $^3T_{2g}(F) \rightarrow {}^3T_{1g}(F)$ (υ_2) and $^3T_{2g}(F) \rightarrow {}^3T_{1g}(P)$ (υ_3) respectively[27]. The (υ_1) transition is expected to appear at large wavelength[22], therefore it could not be observed, it will be calculated theoretically through the Tanabe-Sugano diagram[22,30], by using this diagram for (d^8) and for υ_3/υ_2 (1.57) ratio, the values of 10Dq, B$^-$, Dq/B$^-$ and β(0.804) were calculated, this value indicates that the complex has covalent character[24,27]. The spectrum of Cu(II) complex displayed a band at 672 nm (14880 cm^{-1}) that can be assigned to $^2E_{1g} \rightarrow {}^2T_{2g}$ transition, indicating the Cu(II) complex has distorted octahedral geometry[21,31]. The electronic spectrum of zinc (II) complex as shown in **(figure-2)** and cadmium (II) complex showed only the charge transfer transition of 376 nm (26595cm^{-1}) and 365nm (27397 cm^{-1}) respectively, which can be assigned to charge transfer from the metal to the ligand $(M \rightarrow L)$(32). No d-d transitions are observed for the complexes consistent with(d^{10}) configuration(32)

(Table-3) Electronic spectral data in absolute ethanol of L and its metal complexes with their conductivity values

Compound	λ nm	υ cm^{-1}	Transition	B	B$^-$	Dq/B$^-$	10Dq cm^{-1}	B	15 B$^-$ cm^{-1}	S.cm^2.mole^{-1}	Suggested structure
L	257 336	38910 29762	$\pi \rightarrow {}^*\pi$ $n \rightarrow {}^*\pi$	----	-----	-----	-----	-----	-----	-----	-----
[MnL_2Cl_2]$3H_2O$	275 360 373	36363 27777 26954	Ligand Field Ligand Field C.T	----	-----	-----	-----	-----	-----	15.20	O.h
[CoL_2Cl_2] $2H_2O$	285 344 390 1001 567 445	35087 29069 25641 9982* 17624 22471	Ligand Field Ligand Field C.T $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$	971	802	1.21	9704	0.826	112030	14.90	O.h
[NiL_2Cl_2] $2H_2O$	289 342 380 1206 689 438	34602 29239 26178 8289* 14513 22831	Ligand Field Ligand Field C.T $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$	1030	828	0.75	6216	0.804	12420	18.30	O.h
[CuL_2Cl_2]H_2O	277 335 390 672	36101 29850 25641 14880	Ligand Field Ligand Field C.T $^2E_{1g} \rightarrow {}^2T_{2g}$	----	-----	-----	----	-----	-----	14.20	Distorted O.h
[ZnL_2Cl_2]H_2O	240 340 376	416667 29411 26595	Ligand Field Ligand Field C.T	----	-----	-----	-----	-----	-----	10.50	O.h
[CdL_2Cl_2]H_2O	270 345 365	37037 28985 27397	Ligand Field Ligand Field C.T	----	-----	-----	-----	-----	-----	12.35	O.h

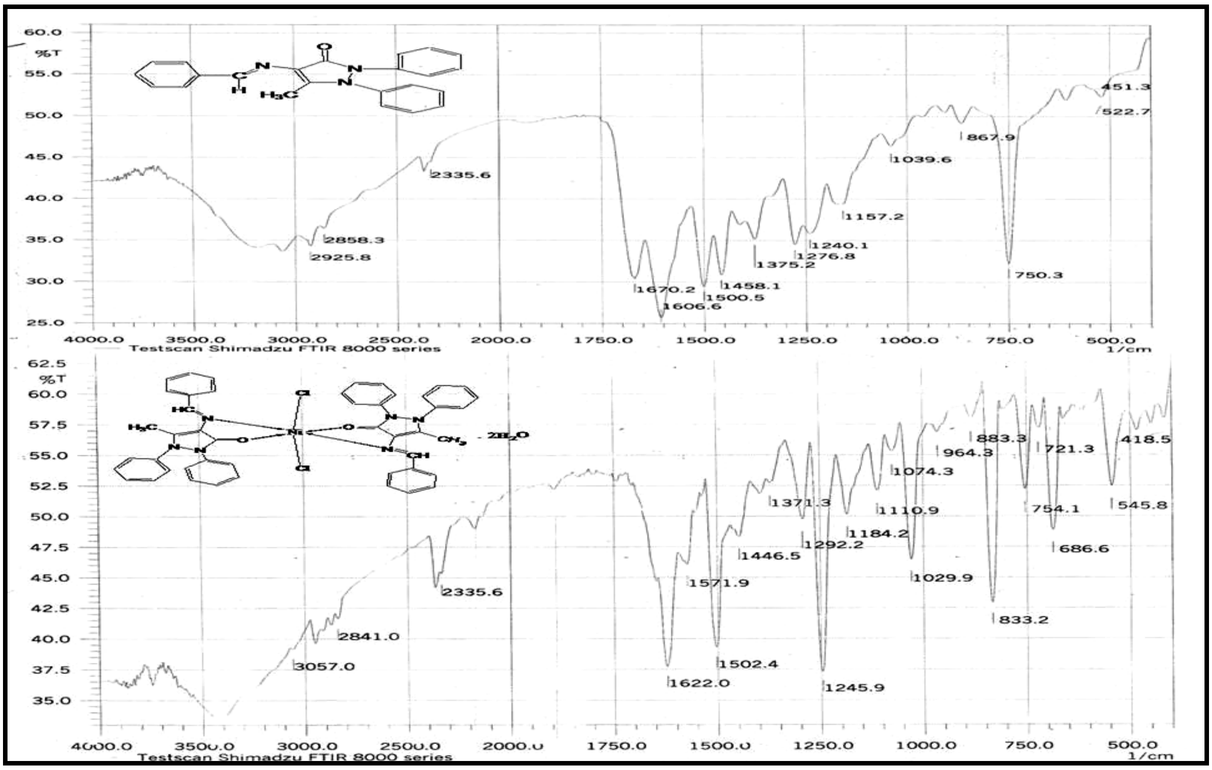
*calculated value

Mole ratio method

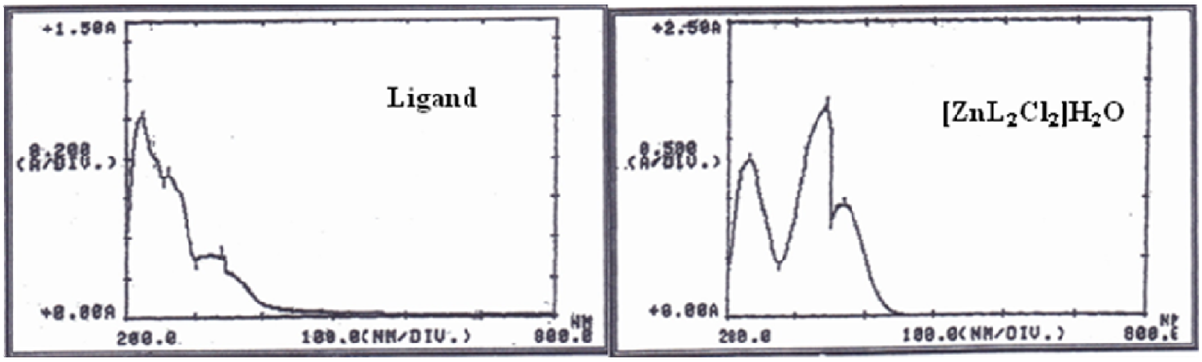
The plots of the ratio method for all the prepared complexes showed that the M:L ratio are 1:2 as shown in **(figure-3)** which represents examples of the prepared complexes [CoL_2Cl_2]$2H_2O$ and [CuL_2Cl_2] H_2O. **(Table -4)** represents the absorption at λ_{max} and the molar concentration of the [L]/[M] of the previous two examples

(Table- 4) [L]/[M] concentration and absorbance data of [CoL_2Cl_2]$2H_2O$ and [CuL_2Cl_2]H_2O complexes

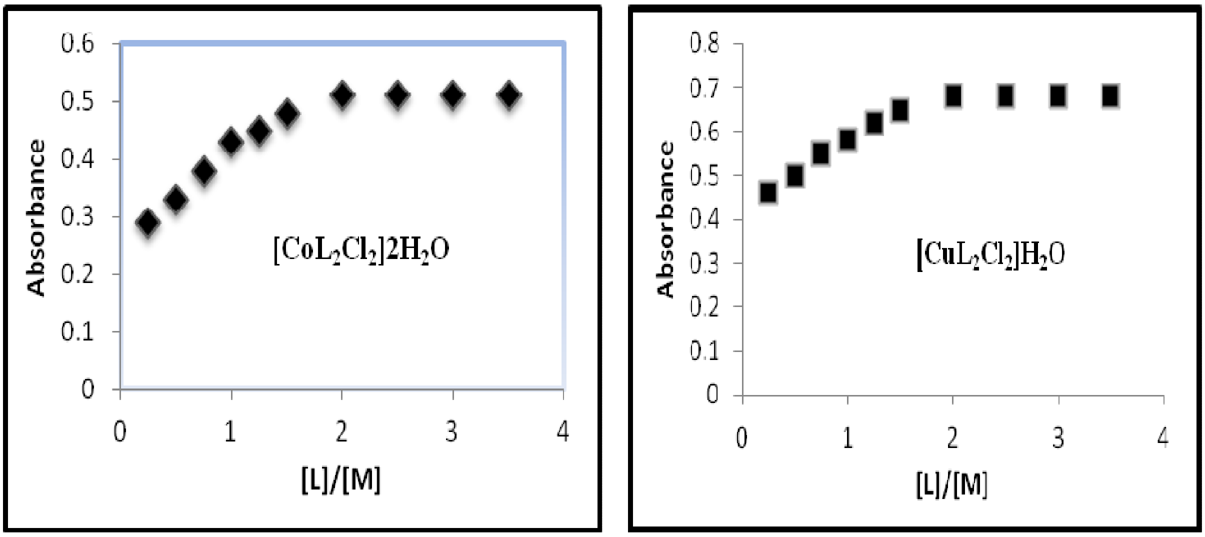
[L]/[M] o f [CoL_2Cl_2]$2H_2O$	Abs.λ_{max} at 567nm	[L]/[M] o f [CuL_2Cl_2]H_2O	Abs.λ_{max} at 672nm
o.25	0.29	o.25	0.46
0.50	0.33	0.50	0.50
0.75	0.38	0.75	0.55
1.00	0.43	1.00	0.58
1.25	0.45	1.25	0.62
1.50	0.48	1.50	0.65
2.00	0.51	2.00	0.68
2.50	0.51	2.50	0.68
3.00	0.51	3.00	0.68
3.50	0.51	3.50	0.68



(Figure -1) FTIR spectrum of the ligand [L] and [NiL_2Cl_2]$2H_2O$ complex



(Figure -2) Electronic spectrum of the ligand [L] and $[ZnL_2Cl_2]H_2O$ complex in absolute ethanol



(Figure -3) Mole ratio method plots of $[Co L_2Cl_2]2H_2O$ and $[CuL_2Cl_2]H_2O$ complexes

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