

Synthesis and Characterization of New Complexes of 2- (2-Hydroxy Phenyl)-2-N-Amino (4-Chloro-Benzothiazol-2-Yl) Acetonitrile Ligand with Some Divalent Transition Metal Ions

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Abstract: A series of metal complexes of some divalent transition metal ions [Mn^{II} , Co^{II} , Ni^{II} , Cu^{II} , Zn^{II} , Cd^{II} , Hg^{II}] having the general composition $[ML_2Cl_2].nH_2O$ with bidentate 2-(2-hydroxy phenyl)-2-N-amino (4-chloro- benzothiazol-2-yl) acetonitrile ligand which was prepared from 2-hydroxy-benzaldehyde and 5-chlorobenzo[d]thiazol-2-amine in the presence of KCN and acidic medium have been prepared and characterized by elemental chemical analysis (CHNS), molar conductance, magnetic susceptibility measurements, 1H -NMR spectra, FTIR electronic spectral studies and Atomic Absorption Technique. The FTIR spectral data suggest the involvement of amino and acetonitrile nitrogen in coordination to central metal ion. On the basis of spectral studies, an octahedral geometry has been assigned for the divalent transition metal complexes.

Keywords: 2-(2-hydroxy phenyl)-2-N-amino (4-chloro-benzothiazol-2-yl) acetonitrile, bidentate, divalent, transition metals

1. Introduction

α -Aminonitriles are important intermediates for the synthesis of a wide variety of amino acids, amides, diamines and nitrogen-containing heterocycles. ligands and its transition metal complexes have been of great interest to research workers since seventies of the last century. At that time it was found that pyridine complexes show activity against leukemia¹. Three-component reaction of aldehydes, amines and cyanide, known as the Strecker reaction. The classical Strecker reaction provides one of the most efficient methods for the synthesis of α -amino nitriles since 1850 when Adolph Strecker interact an aldehyde, an amine and hydrogen cyanide². The addition of cyanide to imines provides a direct route for the synthesis of α -amino nitriles. Some of the α -amino nitrile derivatives like 1-amino-4-phenylnaphthalene-2-carbonitrile have been postulated to have high fungistatic activity even stronger than the activity of the commercial fungicide – Kaptan³. α -amino nitriles are useful intermediates for the synthesis of amino acids^{4,5} and nitrogen-containing heterocyclic such as thienopyrimidine derivatives which have antibacterial and antifungal activities higher than the corresponding antibacterial ampicillin and antifungal nystatin⁶⁻⁸. Moreover, among many other applications, they are readily hydrolyzed to diamines, which are of interest as ligands for Platinum (II) complexes with potential antitumor properties^{9, 10}. Several modifications of the Strecker reaction have been reported using a variety of cyanating agent such as α -trimethylsiloxynitriles and under various reaction conditions^{11,12}. Complexes with dinitrogen N_2 ligand are of interest not only in theoretically but also from a practical point of view. They have found application as antitumor activity¹³, antibacterial activity¹⁴ and antiviral activity in agriculture field¹⁵. α -amino nitriles have often been used as chelating ligands through two nitrogen atoms in the field of amino coordination chemistry. This is one of the second studies to obtain a new coordination field of α -

amino nitrile compounds as ligands and their interactions with transition metal ions.

2. Experimental

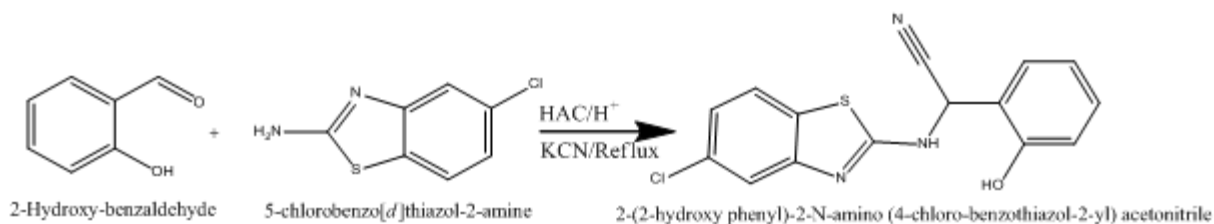
All reagents were of commercial quality and reagent quality solvents were used without further purification. They obtained from British Drug House (BDH). Elemental analysis for carbon, hydrogen nitrogen and sulfur elements were carried out at the Euro vector-EA3000A C. H. N. S. Analyzer, Italy. Molar conductivity was used to measure the conductivity of the complexes at room temperature in freshly prepared ($10^{-3}M$) in absolute ethanol using (PW9526) Digital conductivity meter. The infrared spectra of the ligand and the complexes were recorded on a Shimadzu (8300) FTIR Spectrophotometer, as KBr disk. Atomic Absorption Technique was used to determine the metal contents of the complexes using a Shimadzu (A.A 680G) Atomic Absorption Spectrophotometer. Electronic absorption spectra were recorded in the range (190 –1100) nm on a Shimadzu (160 A) Spectrometer in freshly prepared ($10^{-3}M$) in absolute ethanol at room temperature using quartz cell (1.00) cm. Gallen Kamp apparatus was used to determine the melting points of the ligand and the prepared complexes. TLC was carried out on aluminum sheet precoated with silica gel. Also the chlorine content was determined gravimetrically¹⁶.

3. Preparation of ligand (L)

The ligand (L) was prepared as follows¹⁷⁻¹⁹: 2-hydroxy-benzaldehyde (1 mmol) was added to (20 ml) glacial acetic acid, p-toluene sulphonic acid was added in very small portion as catalyst, followed by addition of (1 mmol) 5-chlorobenzo[d]thiazol-2-amine. The pH was adjusted to about 4 by addition of concentrated sulfuric acid drop wise to obtain Schiff base which stirred for 30 min. Potassium cyanide (2 mmol) was added to the mixture and kept under

stirring for 4 days. The reaction mixture was poured into ice and then made slightly alkaline with ammonium hydroxide solution. The solid precipitate which formed was filtered, washed with water and air dried. The presence of nitrile group in the prepared α -amino nitrile was indicated by treating few amount of the sample with 10% sodium hydroxide solution, the liberation of ammonia after

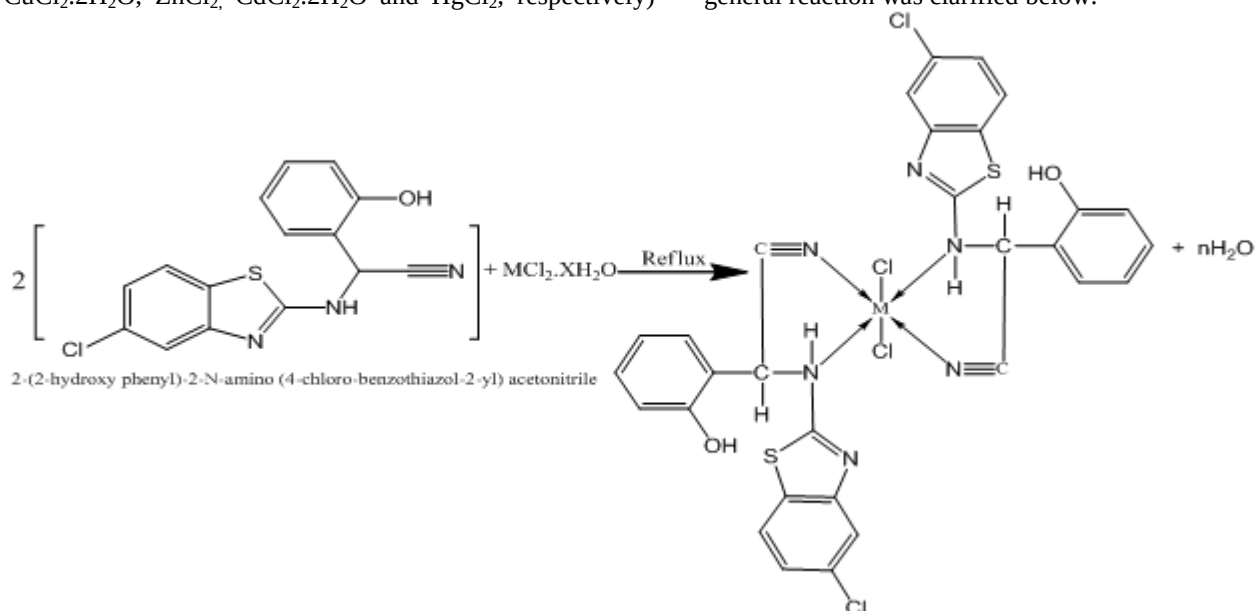
hydrolysis of nitrile group, which was detected by wet red litmus paper, indicating the presence of nitrile group. Purity of the obtained compound was checked by TLC, using chloroform and ethyl acetate (1:1) as eluent. The product color was orange and the yield percentage was (85.73 %) and the melting point was (153-155 °C). The condensation reaction to prepare the new ligand was clarified below:



3.1 Preparation of Complexes

All complexes were prepared by the reaction of (0.633 gm) (2 mmol) of (L) with (1mmol) of metal chloride (0.198 gm, 0.238 gm, 0.238 gm, 0.171 gm, 0.136 gm, 0.220 gm and 0.272 gm for $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, ZnCl_2 , $\text{CdCl}_2 \cdot 2\text{H}_2\text{O}$ and HgCl_2 , respectively)

dissolved in (20 ml) 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 °C) then filtered and the products were left in the desiccators to be dried under P_2O_5 . The general reaction was clarified below:



4. Results and Discussion

All the compounds reported in this work are presented in table (1) which illustrated physical properties, along with their molar conductivity at room temperature. Metal and elemental analysis of all compounds is represented in Table 1 as well. The ligand 2-(2-hydroxy phenyl)-2-N-amino (4-chloro-benzothiazol-2-yl) acetonitrile was prepared as reported in literature¹⁷⁻¹⁹. It was characterized by elemental analysis and infrared spectral data. The complexes have been prepared under anhydrous conditions to avoid any hydrolysis of nitrile group to amide due to the presence of water molecules and metal ion²⁰. In addition to that when organic molecules are coordinated to metal cations in organo-metallic or coordination compounds, they become susceptible to nucleophilic attack like water molecules which cause hydrolysis of nitrile into amide²¹. These complexes were stable in the solid state and were characterized by the usual methods; FTIR, UV- Visible spectroscopy, metal and elemental analysis, molar

conductivity, mole ratio, chloride content and magnetic susceptibility. On the basis of the characterization methods it's suggested that all complexes probably have octahedral structure with coordination number 6 that includes two atoms of coordinated chlorides. The conductivity values for the complexes of (10^{-3}M) in absolute ethanol were recorded in the rang (12-15) indicating that the non-electrolytic nature of the complexes²². Mole ratio method was used to determine the ratio of metal ion to the ligand for the complexes at λ_{max} [$\lambda_{\text{max}} = 575 \text{ nm}$ for $[\text{CoL}_2\text{Cl}_2] \cdot 2\text{H}_2\text{O}$ and $\lambda_{\text{max}} = 695 \text{ nm}$ for $[\text{NiL}_2\text{Cl}_2] \cdot \text{H}_2\text{O}$] in alcoholic solutions.

¹H-NMR and ¹³C-NMR:

The ¹H-NMR spectra of the free ligand [L] in DMSO solution with assignments are collected in Table 2. The ¹H-NMR spectra of the free ligand showed besides the aromatic proton signals appearing at 7.0-7.7 ppm. The phenolic OH proton has a signal at 5.6 ppm and the signals due to NH and CH 9.8 and 4.8 ppm, respectively²³. The ¹³C-NMR spectrum shows result was listed in Table 3.

4.1 Infrared Spectroscopy

The significant infrared bands of the ligand and its metal complexes and their assignments are given in Table 4. The infrared spectral data of [L] and all complexes in Table 3 showed some characteristic bands related to α -amino nitriles; like $2145\text{--}2237\text{ cm}^{-1}$ which could be attributed to $\text{C}\equiv\text{N}$ group²⁴. A shift of the range $65\text{--}117\text{ cm}^{-1}$ was observed for $\text{C}\equiv\text{N}$ stretching vibration on coordination due to the decrease of bond order as result of metal nitrogen bond formation. The next characteristic band near 1606 cm^{-1} which could be attributed to $\delta(\text{N-H})$ group. A red shift of the range $15\text{--}28\text{ cm}^{-1}$ was observed in N-H bending frequency on complexes indicating the coordination on nitrogen to metal ion. On the other hand the spectrum of the complexes showed new bands around $555\text{--}595\text{ cm}^{-1}$ due to $\nu_{\text{M-N}}$ ²⁵⁻²⁶. The presence of these bands supported the formation of complexes under investigations. The presence of lattice water molecule in all complexes Table 4 was supported by the broad band in $3425\text{--}3357\text{ cm}^{-1}$ region of infrared spectrum²⁵ and by its metal and elemental analysis data in Table 1.

4.2 Molar Conductance Data

The data in Table 1 showed that the molar conductance values of the Mn^{II} , Co^{II} , Ni^{II} , Cu^{II} , Zn^{II} , Cd^{II} and Hg^{II} complexes were relatively low, indicating the non-electrolytic nature of these complexes. The molar conductance of the solid complexes ($\Omega^{-1}\cdot\text{cm}^2\cdot\text{mole}^{-1}$) was calculated. Absolute ethanol solubility of the above complexes made calculations of the molar conductivity (λ_{max}) dm^{-3} of $10^{-3}\text{ mol dm}^{-3}$ solution at 25°C possible.

4.3 Mole Ratio Method

The absorption spectra were measured for many mixed solutions containing (1 ml) of the metal ion salt in the optimum concentration, and variable volumes of the ligand solution in the same concentration. M:L ratio was obtained by plotting the relation between the mole ratio in the X-axis and absorbance in the Y-axis. The intercept of the two straight lines represent the M:L ratio, it was (1:2).

4.4 Magnetic Studies

The Cu^{II} complex shows a normal magnetic moment of 1.72 B.M. observed for the d^9 system with an unpaired electron²⁷. The Ni^{II} complex with a magnetic moment of 3.24 B.M. reveals a spin free octahedral configuration²⁸. The magnetic moment of 4.33 B.M. for the Co^{II} complex suggest a high spin octahedral configuration^{27, 28}. The Mn^{II} complex has a magnetic moment of 4.95 B.M. as expected for high spin octahedral geometry²⁹. Zn^{II} , Cd^{II} and Hg^{II} complexes are diamagnetic as expected for the d^{10} configuration²⁸.

4.5 UV – Visible Spectroscopy

The preparation of all metal complexes is essentially the same and a generic description will be presented. 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. The electronic absorption spectra of the ligand and its metal complexes were recorded at room temperature using absolute ethanol as the solvent. The ligand showed two absorption bands in the region 39841 cm^{-1} and 36232 cm^{-1} corresponding to $(\pi \rightarrow \pi^*)$ and $(n \rightarrow \pi^*)$ transitions respectively. On complexation, these bands are shifted to higher wavelengths, suggesting coordination of the uncharged dinitrogen N_2 of the ligand to the metal ion. The electronic spectrum of six coordinated Cu^{II} complex displays three bands at 14684 , 23095 and 25316 cm^{-1} corresponding to the following transitions: ${}^2\text{B}_{1g} \rightarrow {}^2\text{A}_{1g} (d_{x^2-y^2} \rightarrow d_z^2)$, (ν_1), ${}^2\text{B}_{1g} \rightarrow {}^2\text{B}_{2g} (d_{x^2-y^2} \rightarrow d_{yz})$, (ν_2) ${}^2\text{B}_{1g} \rightarrow {}^2\text{E}_g (d_{x^2-y^2} \rightarrow d_{zy}d_{yz})$, (ν_3), respectively. Therefore, the Cu^{II} complex may be considered to possess a tetragonal geometry around the copper ion^{30, 31}. Though three transitions are expected in this case, they are very close in energy and often appear in the form of one broad band envelope³¹. The spectrum also exhibits a band at 25126 cm^{-1} , which is assigned to a charge transfer band. The electronic spectrum of Co^{II} complex showed two main bands are at 25126 cm^{-1} and 17391 cm^{-1} . These two d-d bands are attributed to the ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$ (ν_3) and ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{2g}(\text{F})$ (ν_2) transitions, respectively, in an octahedral geometry around the Co^{II} ion [26]. The (ν_1) ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})$ transition is expected to appear at large wavelength, therefore it could not be observed, it will be calculated theoretically through the Tanabe-Sugano diagram³². The Co^{II} complex displays a charge transfer band at 24876 cm^{-1} ³³. The electronic spectrum of Ni^{II} complex exhibits two bands in the region 24200 and 14395 cm^{-1} which are assigned to the ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{P})$ (ν_3), ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{F})$ (ν_2) transitions, respectively, indicating in an octahedral geometry around the Ni^{II} ion. The (ν_1) ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{2g}(\text{F})$, transition is expected to appear at large wavelength, therefore it could not be observed, it will be calculated theoretically through the Tanabe-Sugano diagram³². The spectrum of Ni^{II} complex also exhibits a charge transfer band at 25316 cm^{-1} . The octahedral geometry of Co^{II} and Ni^{II} complexes are further supported by the value of the ν_2/ν_1 ratio, which are 1.60 and 1.48, respectively²⁷. The Mn^{II} , Zn^{II} , Cd^{II} and Hg^{II} complexes do not show any d-d transitions but display charge transfer bands at 21413 , 26110 , 25381 and 26600 cm^{-1} , respectively. Various ligand field parameters Table 5, such as the Racah inter-electronic repulsion parameter (B'), ligand filed splitting energy ($10Dq$), covalency factor (β) and ligand field stabilization energy (LFSE) have been calculated for Co^{II} and Ni^{II} complexes^{27, 34}.

In case of the Co^{II} complex, the Racah inter-electronic repulsion parameter (B') is given by the following equation²⁷:

$$B' = 1/510 \{ 7 (\nu_3 - 2 \nu_2) + 3 [81 \nu_3^2 - 16 \nu_2 (\nu_2 - \nu_3)]^{1/2} \}$$

In case of the Ni^{II} complex, (B') is given by the following equation²⁶:

$$B' = \nu_2 + \nu_3 - 3 \nu_1/15$$

The ligand field splitting energy ($10Dq$) is calculated as follows:

For the Co^{II} complex,

$$10Dq = 1/3 (\nu_2 - \nu_3) + 15B'$$

For the Ni^{II} complex, $10Dq = \nu_1$

The covalence factor (β) is obtained in the following manner:

$$\beta = B'/B \quad (B \text{ is the free ion value})$$

The ligand field stabilization energy (LFSE) is expressed by the equation:

$$\text{LFSE} = 12Dq$$

The (B') values for the complexes are lower than that of the free ion, which is an indication of orbital overlap and delocalization of the d-orbitals. The obtained (β) values are less than unity, suggesting the metal–ligand bonds have a considerable amount of covalent character. The (β) value for the Ni^{II} complex is less than that for the Co^{II} complex, indicating the greater covalent nature of the former.

Table 1: Analytical data and Physical properties of [L] and its metal complexes with their conductivity values

Formula M.wt. (gm/mole)	Elemental Analysis Calculated (Found)						Color	M.P. °C (Dec.)	Yield %	$\Omega^{-1}\text{cm}^2$ mol^{-1}	Magnetic moment BM
	C%	H%	N%	S%	M%	Cl%					
$\text{C}_{15}\text{H}_{10}\text{N}_3\text{SOCl}$ 315.5	57.05 (56.87)	3.17 (3.05)	13.31 (13.07)	10.14 (10.01)	-----	11.25 (10.98)	Orang	153-155	85.73	-----	-----
$[\text{MnL}_2\text{Cl}_2] \cdot 3\text{H}_2\text{O}$ 810.94	44.39 (42.33)	3.21 (2.92)	10.36 (9.63)	7.89 (7.40)	6.77 (6.15)	17.51 (16.38)	white orang	215-217	72.96	11.92	4.95
$[\text{CoL}_2\text{Cl}_2] \cdot 2\text{H}_2\text{O}$ 796.93	45.17 (43.82)	3.01 (3.31)	10.54 (9.66)	8.03 (7.02)	7.39 (6.47)	17.82 (15.95)	Dark brown	175-177	88.06	12.44	4.33
$[\text{NiL}_2\text{Cl}_2] \cdot \text{H}_2\text{O}$ 778.69	46.23 (45.89)	2.83 (2.63)	10.79 (10.58)	8.22 (8.03)	7.54 (7.35)	18.24 (17.88)	Greenish yellow	205-207	73.55	13.19	3.24
$[\text{CuL}_2\text{Cl}_2] \cdot 3\text{H}_2\text{O}$ 819.55	43.93 (44.65)	3.77 (2.78)	10.25 (9.49)	7.81 (7.57)	7.75 (7.02)	17.33 (16.03)	Dark green	189-192	74.76	11.89	1.72
$[\text{ZnL}_2\text{Cl}_2] \cdot \text{H}_2\text{O}$ 785.38	45.84 (45.06)	2.80 (2.65)	10.70 (10.61)	8.15 (7.84)	8.33 (8.03)	18.08 (17.83)	yellow orang	188-191	86.45	15.76	Dia
$[\text{CdL}_2\text{Cl}_2] \cdot 2\text{H}_2\text{O}$ 850.41	42.33 (42.15)	2.82 (2.72)	9.88 (9.58)	7.53 (7.01)	13.22 (13.18)	16.70 (15.88)	Light green	181-183	83.21	10.65	Dia
$[\text{HgL}_2\text{Cl}_2] \cdot 2\text{H}_2\text{O}$ 956.60	37.63 -----	2.51 -----	8.78 -----	6.69 -----	20.97 -----	14.84 -----	Brown	278-281	83.76	13.88	Dia

Table 2: ^1H -NMR data for the 2-(2-hydroxy phenyl)-2-N-amino (4-chloro-benzothiazol-2-yl) acetonitrile in DMSO solution (ppm) $\delta - \text{H}$

$\text{C}_{15}\text{H}_{10}\text{N}_3\text{SOCl}$	Aromatic protons	Phenolic OH proton	NH proton	CH proton
	7.0 - 7.7	5.6	9.8	4.8

Table 3: ^{13}C - NMR data for 2-(2-hydroxy phenyl)-2-N-amino (4-chloro-benzothiazol-2-yl) acetonitrile

Structure	C_{13}	C_1	C_2	C_8	C_9	C of all aromatic
	135.6	117.5	56.5	155.5	168.5	120-130

Table 4: The characteristic bands of FTIR spectra of the ligand and its metal complexes in (cm^{-1})

Compound	$\nu\text{O-H cm}^{-1}$ Lattice water	$\nu\text{N-H cm}^{-1}$	$\nu\text{C-H cm}^{-1}$ Aromatic	$\nu\text{C}\equiv\text{N cm}^{-1}$ Nitrile	$\delta\text{N-H cm}^{-1}$	$\nu\text{M-N cm}^{-1}$
$\text{C}_{15}\text{H}_{10}\text{N}_3\text{SOCl}$	-----	3232	3041	2237	1616	-----
$[\text{MnL}_2\text{Cl}_2] \cdot 3\text{H}_2\text{O}$	3385	3205	3029	2160	1600	595
$[\text{CoL}_2\text{Cl}_2] \cdot 2\text{H}_2\text{O}$	3425	3240	3030	2198	1601	569
$[\text{NiL}_2\text{Cl}_2] \cdot \text{H}_2\text{O}$	3400	3217	3065	2192	1595	590
$[\text{CuL}_2\text{Cl}_2] \cdot 3\text{H}_2\text{O}$	3357	3218	3078	2145	1597	573
$[\text{ZnL}_2\text{Cl}_2] \cdot \text{H}_2\text{O}$	3422	3252	3042	2226	1588	585
$[\text{CdL}_2\text{Cl}_2] \cdot 2\text{H}_2\text{O}$	3375	3251	3045	2196	1592	588
$[\text{HgL}_2\text{Cl}_2] \cdot 2\text{H}_2\text{O}$	3410	3222	3053	2180	1590	555

Table 5: Electronic spectra in absolute ethanol for the (L) and its metal complexes

Compound	λ nm	ν cm ⁻¹	Transition	B ⁻ cm ⁻¹	Dq/ B ⁻	β	15B ⁻ cm ⁻¹	Suggested structure
C ₁₅ H ₁₀ N ₃ SOCl	251 276	39841 36232	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$	-----	-----	-----	-----	-----
[MnL ₂ Cl ₂].3H ₂ O	242 262 467	41322 38168 21413	Ligand Field Ligand Field C.T	-----	-----	-----	-----	O.h
[CoL ₂ Cl ₂].2H ₂ O	245 291 402 ---- 575 398	40816 34364 24876 9625* 17391 25126	Ligand Field Ligand Field C.T ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$	777	2.14	0.801	11660	O.h
[NiL ₂ Cl ₂].H ₂ O	255 287 395 --- 695 413	39216 34843 25316 9760* 14395 24200	Ligand Field Ligand Field C.T ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$	621	1.572	0.603	9315	O.h
[CuL ₂ Cl ₂].3H ₂ O	258 283 398 681 433 395	38760 35336 25126 14684 23095 25316	Ligand Field Ligand Field C.T ${}^2B_{1g} \rightarrow {}^2A_{1g}$ ${}^2B_{1g} \rightarrow {}^2B_{2g}$ ${}^2B_{1g} \rightarrow {}^2E_g$	-----	-----	-----	-----	O.h
[ZnL ₂ Cl ₂].H ₂ O	258 272 383	38760 36765 26110	Ligand Field Ligand Field C.T	-----	-----	-----	-----	O.h
[CdL ₂ Cl ₂].2H ₂ O	253 267 394	39526 37453 25381	Ligand Field Ligand Field C.T	-----	-----	-----	-----	O.h
[HgL ₂ Cl ₂].2H ₂ O	248 265 376	40323 37736 26600	Ligand Field Ligand Field C.T	-----	-----	-----	-----	O.h

*Calculated value

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