

Synthesis And Characterization of New Complexes of 2(Benzo[d]Thiazol-2-Ylamino)-2-(2-Hydroxy-Phenyl) Acetonitrile Ligand with Some Divalent Transition Metal Ions

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Abstract

A series of metal complexes of some divalent transition metal ions having the general composition $[ML_2Cl_2].nH_2O$ with bidentate 2(benzo[d]thiazol-2-ylamino)-2-(2-hydroxy-phenyl)-acetonitrile ligand which was prepared from 2-hydroxy-benzaldehyde and benzo[d]thiazol-2-amine in the presence of KCN and acidic medium have been prepared and characterized by (1H -NMR of the ligand) elemental chemical analysis, molar conductance, magnetic susceptibility measurements, FTIR, electronic spectral studies and mole ratio method. 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(benzo[d]thiazol-2-ylamino)-2-(2-hydroxy-phenyl) acetonitrile, bidentate, divalent, transition metals.

INTRODUCTION

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 leukemia[1]. The classical Strecker reaction provides one of the most efficient methods for the synthesis of cyanide, α -amino nitriles since 1850 when Adolph Strecker interact an aldehyde, an amine and hydrogen cyanide[2]. 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-phenyl-naphthalene-2-carbonitrile have been postulated to have high fungistatic activity even stronger than the activity of the commercial fungicide – Kaptan [3]. 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 nystatin [6-8]. 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 -trimethylsilyloxynitriles 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 activity [13], antibacterial activity [14] and antiviral activity in agriculture field [15]. α -amino nitriles have often been used as chelating ligands through two nitrogen atoms in the field

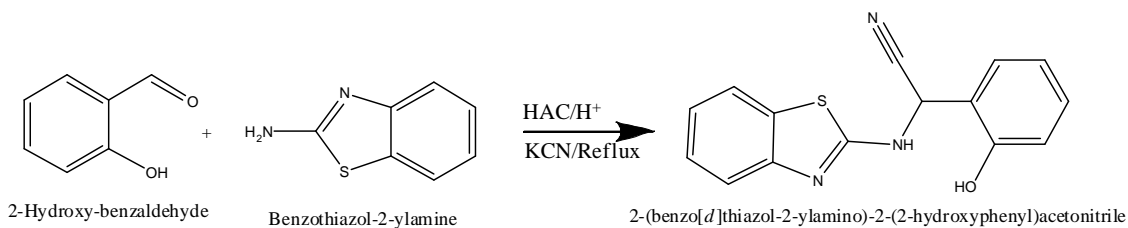
of amino coordination chemistry. This is one of the first studies to reveal a new coordination field of α -amino nitrile compounds as ligands and their interactions with transition metal ions.

EXPERIMENTAL

All the chemicals and solvents used for the synthesis were of reagent grade and were obtained commercially from British Drug House (BDH) with the exception of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, ZnCl_2 , $\text{CdCl}_2 \cdot 2\text{H}_2\text{O}$ and HgCl_2 salts were obtained from Fluka Company. The prepared ligand 2(benzo[d]thiazol-2-ylamino)-2-(2-hydroxy-phenyl) acetonitrile was synthesized and characterized according to published work. The infrared spectra of the ligand and the complexes were recorded on a Shimadzu (8300) FTIR Spectrophotometer, as CsI disk. 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. Atomic Absorption technique was used to determine the metal contents of the complexes using a Shimadzu (A.A 680G) Atomic Absorption Spectrophotometer. 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. Elemental analysis for carbon, hydrogen nitrogen and sulfur elements were carried out at the Euro vector-EA3000A C. H. N. Analyzer, Italy. Gallen Kamp apparatus was used to determine the melting points of the ligand and the prepared complexes. Also the chlorine content was determined gravimetrically [16].

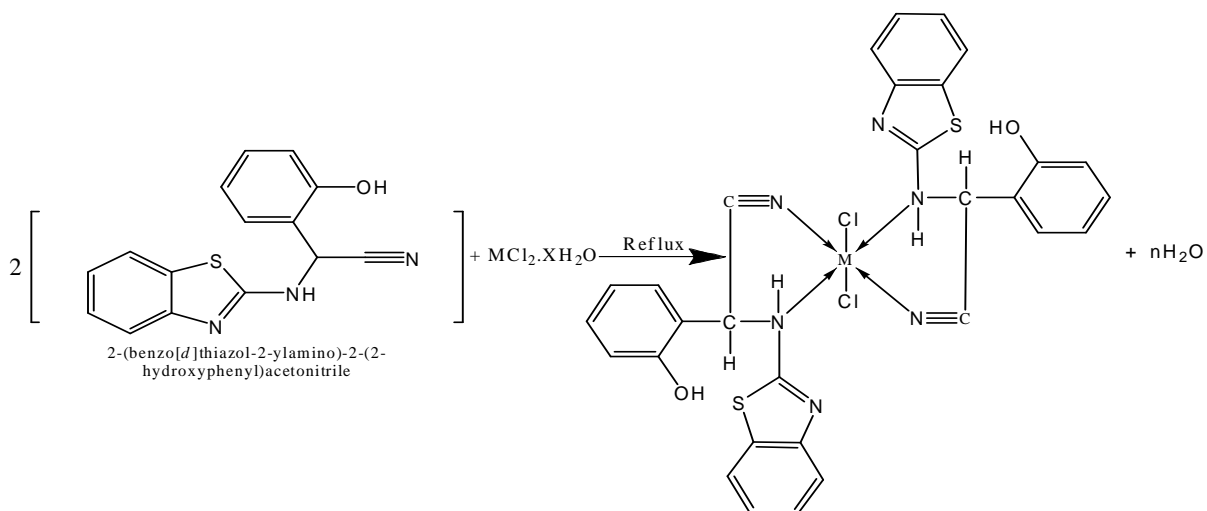
Preparation method of 2(benzo[d]thiazol-2-ylamino)-2-(2-hydroxy-phenyl) acetonitrile:

A general method [17-19] can be adopted for [L] preparation which can be described as follows: The 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) benzothiazol-2-ylamine. 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 (88.25 %) and the melting point was (93-94 $^{\circ}\text{C}$). The condensation reaction to prepare the new ligand was clarified below:



Preparation method of metal complexes:

The complexes $[\text{ML}_2\text{Cl}_2] \cdot n\text{H}_2\text{O}$ have been prepared by the reaction of (0.628 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:



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(benzo[d]thiazol-2-ylamino)-2-(2-hydroxy-phenyl) acetonitrile was prepared as reported in literature [18]. 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 ion [20]. 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 amide [21]. 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 (8-16) indicating that the non-electrolytic nature of the complexes [22]. Mole ratio method was used to determine the ratio of metal ion to the ligand for the complexes at λ_{max} [$\lambda_{\text{max}}=495\text{ nm}$ for $[\text{CoL}_2\text{Cl}_2] \cdot 5\text{H}_2\text{O}$ and $\lambda_{\text{max}}=486\text{ nm}$ for $[\text{CuL}_2\text{Cl}_2] \cdot 2\text{H}_2\text{O}$] in alcoholic solutions.

¹H-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, respectively [23].The ¹³C-NMR spectrum shows result was listed in table (3).

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 2120-2196 cm^{-1} which could be attributed to $\text{C}\equiv\text{N}$ group [24]. A shift of the range 65-117 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 15-28 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 582-606 cm^{-1} due to $\nu_{\text{M-N}}$ [25, 26].The $\nu_{\text{M-Cl}}$ however could not be ascertained due to non-availability of far infrared data. 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 3500-3150 cm^{-1} region of infrared spectrum [25] and by its metal and elemental analysis data in table (1).

Molar Conductance Data:

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 $^{\circ}\text{C}$ possible. The data in Table (1) showed that the molar conductance values of the manganese (II), cobalt (II), nickel (II), copper (II), zinc (II) cadmium (II) and mercury (II) complexes were relatively low, indicating the non-electrolytic nature of these complexes.

Magnetic studies:

The Zn (II), Cd (II) and Hg (II) complexes are diamagnetic as expected for the d^{10} configuration [27]. Cu (II) complex shows a normal magnetic moment of 1.78 B.M. observed for the d^9 system with an unpaired electron [28]. The Ni (II) complex with a magnetic moment of 3.05 B.M. reveals a spin free octahedral configuration [28]. The magnetic moment of 4.75 B.M. for the Co (II) complex suggest a high spin octahedral configuration [27, 28]. The Mn (II) complex has a magnetic moment of 5.45 B.M. as expected for high spin octahedral geometry [29].

Ultra violet – visible spectroscopy:

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. The electronic absorption spectra of the ligand and its 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 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. The electronic spectrum of six coordinated Cu (II) complex displays three bands at 14684 , 23095 and 25316 cm^{-1} corresponding to the following transitions: ${}^2B_{1g} \rightarrow {}^2A_{1g} (d_{x^2-y^2} \rightarrow d_z^2)$, (ν_1) , ${}^2B_{1g} \rightarrow {}^2B_{2g} (d_{x^2-y^2} \rightarrow d_{zy})$, (ν_2) ${}^2B_{1g} \rightarrow {}^2E_g (d_{x^2-y^2} \rightarrow d_{zy}d_{yz})$, (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 envelope [31]. 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 15410 cm^{-1} . These two d-d bands are attributed to the ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ (ν_3) and ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ (ν_2) transitions, respectively, in an octahedral geometry around the Co (II) ion [26]. The (ν_1) ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ transition is expected to appear at large wavelength, therefore it could not be observed, it will be calculated theoretically through the Tanabe-Sugano diagram [32]. 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 ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ (ν_3) , ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ (ν_2) transitions, respectively, indicating in an octahedral geometry around the Ni (II) ion. The (ν_1) ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$, transition is expected to appear at large wavelength, therefore it could not be observed, it will be calculated theoretically through the Tanabe-Sugano diagram [32]. 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, respectively [27]. Various ligand field parameters table (5), such as the Racah inter-electronic repulsion parameter (B'), ligand field 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 equation [27]:

$$B' = 1/510 \{7 (v_3 - 2 v_2) + 3 [81 v_3^2 - 16 v_2 (v_2 - v_3)]^{1/2}\}$$

In case of the Ni (II) complex, (B') is given by the following equation [26]:

$$B' = v_2 + v_3 - 3 v_1/15$$

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

For the Co (II) complex,

$$10Dq = 1/3 (v_2 - v_3) + 15B'$$

For the Ni (II) complex, $10Dq = v_1$

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

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

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

$$LFSE = 12Dq$$

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}	Magne tic mome nt BM
	C%	H%	N%	S%	M%	Cl%					
L 281	64.06 (63.8 7)	3.91 (3.75)	14.95 (14.7 7)	11.39 (11.1 7)	-----	-----	Orang	93-94	88.25	-----	-----
[MnL ₂ Cl ₂]3 H ₂ O 741.94	48.52 (48.3 3)	3.77 (3.58)	11.32 (11.1 3)	8.63 (8.40)	7.40 (7.15)	9.57 (9.38)	Dark orang	202- 204	78.32	13.7 7	5.45
[CoL ₂ Cl ₂]5 H ₂ O 781.93	46.04 (45.8 2)	4.09 (5.51)	10.74 (10.6 6)	8.18 (8.07)	7.54 (7.47)	9.08 (8.95)	Dark brown	188- 190	81.66	12.6 8	4.75
[NiL ₂ Cl ₂]5H ₂ O 781.69	46.05 (45.8 9)	4.09 (3.93)	10.75 (10.5 8)	8.19 (8.03)	7.51 (7.35)	9.08 (8.88)	Greeni sh yellow	221- 223	79.32	13.0 9	3.05
[CuL ₂ Cl ₂]4 H ₂ O 768.55	46.84 (46.6 5)	3.90 (3.78)	10.93 (10.7 0)	8.33 (8.17)	8.27 (8.02)	9.24 (9.03)	Dark green	195- 197	77.45	11.8 9	1.78
[ZnL ₂ Cl ₂]H ₂ O 716.38	50.25 (50.0 6)	3.35 (3.15)	11.73 (11.6 1)	8.93 (8.84)	9.13 (9.03)	9.91 (9.83)	yellow orang	178- 180	76.89	15.7 6	Dia

[CdL ₂ Cl ₂] 2H ₂ O 781.41	46.07 (46.15)	3.33 (3.12)	10.75 (10.58)	8.19 (8.01)	14.39 (14.18)	9.09 (8.88)	Light green	181-183	83.21	10.65	Dia
[HgL ₂ Cl ₂] H ₂ O 851.60	42.27 -----	2.82 -----	9.86 -----	7.52 -----	23.56 -----	8.34 -----	Brown	232-235	74.56	14.63	Dia

Table (2) ¹H-NMR data for the 2(Benzo[d]thiazol-2-ylamino)-2-(2-hydroxy-phenyl) acetonitrile in DMSO solution (ppm)δ – H

C ₁₅ H ₁₁ N ₃ SO	Aromatic protons	Phenolic OH proton	NH proton	CH proton
	7.0 - 7.7	5.6	9.8	4.8

Table (3): ¹³C- NMR data for 2(Benzo[d]thiazol-2-ylamino)-2-(2-hydroxy-phenyl) acetonitrile

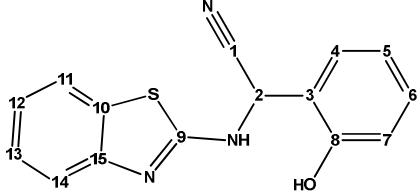
Structure	C ₁	C ₂	C ₈	C ₉	C of all aromatic
	117.5	56.5	155.5	168.5	120-130

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

Compound	νO-H cm ⁻¹ Lattice water	νN-H cm ⁻¹	νC-H cm ⁻¹ Aromatic	νC-H cm ⁻¹ Aliphatic	νC≡N Nitrile	δN-H	νM-N
L	-----	3232	3063	2237	2237	1616	-----
[MnL ₂ Cl ₂] 5H ₂ O	3385	3005	3005	2160	2160	1600	606

[CoL ₂ Cl ₂]5H ₂ O	3425	3030	3030	2168	2168	1601	598
[NiL ₂ Cl ₂]H ₂ O	3400	3017	3017	2172	2172	1595	590
[CuL ₂ Cl ₂]2H ₂ O	3357	3018	3018	2145	2145	1597	593
[ZnL ₂ Cl ₂]H ₂ O	3422	3032	3032	2196	2196	1588	585
[CdL ₂ Cl ₂]2H ₂ O	3375	3011	3011	2136	2136	1592	588
[HgL ₂ Cl ₂]H ₂ O	3410	3022	3023	2120	2120	1590	582

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

Compound	λ_{nm}	$\nu_{cm^{-1}}$	Transition	B^{-1} cm^{-1}	Dq/ B^{-1}	β	$15B^{-1}$ cm^{-1}	Suggested structure
L	251 276	3984 1 3623 2	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$	-----	-----	-----	-----	-----
[MnL ₂ Cl ₂] 5H ₂ O	242 262 467	4132 2 3816 8 2141 3	Ligand Field Ligand Field C.T	-----	-----	-----	-----	O.h
[CoL ₂ Cl ₂] 5H ₂ O	245 291 402 ---- 649 398	4081 6 3436 4 2487 6 9625 * 1541 0 2512 6	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	3921 6 3484 3 2531 6	Ligand Field Ligand Field C.T ${}^3A_{2g}(F)$ $\rightarrow {}^3T_{2g}(F)$ ${}^3A_{2g}(F)$	621	1.572	0.603	9315	O.h

	413	9760 * 1439 5 2420 0	$\rightarrow^3T_{1g}(F)$ $^3A_{2g}(F)$ $\rightarrow^3T_{1g}(P)$					
[CuL ₂ Cl ₂] 2H ₂ O	258 283 398 681 433 395	3876 0 3533 6 2512 6 1468 4 2309 5 2531 6	Ligand Field Ligand Field C.T $^2B_{1g} \square \square \square \square \square_g$ $^2B_{1g} \rightarrow ^2B_{2g}$ $^2B_{1g} \rightarrow ^2E_g$	-----	-----	-----	-----	O.h
[ZnL ₂ Cl ₂] H ₂ O	258 272 383	3876 0 3676 5 2611 0	Ligand Field Ligand Field C.T	-----	-----	-----	-----	O.h
[CdL ₂ Cl ₂] 2H ₂ O	253 267 394	3952 6 3745 3 2538 1	Ligand Field Ligand Field C.T	-----	-----	-----	-----	O.h
[HgL ₂ Cl ₂] H ₂ O	248 265 376	4032 3 3773 6 2660 0	Ligand Field Ligand Field C.T	-----	-----	-----	-----	O.h

*Calculated value

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