

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 2145-2237 cm^{-1} which could be attributed to $\text{C}\equiv\text{N}$ group²⁴. 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 555-595 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 3425-3357 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} mol dm^{-3} solution at 25 $^{\circ}\text{C}$ 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), ${}^2\text{B}_{1g} \rightarrow {}^2\text{B}_{2g}$ ($d_{x^2-y^2} \rightarrow d_{zy}$), (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:

$$LFSE = 12Dq$$

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%					
C ₁₅ H ₁₀ N ₃ 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	-----	-----
[MnL ₂ Cl ₂].3H ₂ 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
[CoL ₂ Cl ₂].2H ₂ 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
[NiL ₂ Cl ₂].H ₂ 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
[CuL ₂ Cl ₂].3H ₂ 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
[ZnL ₂ Cl ₂].H ₂ 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
[CdL ₂ Cl ₂].2H ₂ 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
[HgL ₂ Cl ₂].2H ₂ 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) $\delta - H$

C ₁₅ H ₁₀ N ₃ SOCl	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-(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
C ₁₅ H ₁₀ N ₃ SOCl	-----	3232	3041	2237	1616	-----
[MnL ₂ Cl ₂].3H ₂ O	3385	3205	3029	2160	1600	595
[CoL ₂ Cl ₂].2H ₂ O	3425	3240	3030	2198	1601	569
[NiL ₂ Cl ₂].H ₂ O	3400	3217	3065	2192	1595	590
[CuL ₂ Cl ₂].3H ₂ O	3357	3218	3078	2145	1597	573
[ZnL ₂ Cl ₂].H ₂ O	3422	3252	3042	2226	1588	585
[CdL ₂ Cl ₂].2H ₂ O	3375	3251	3045	2196	1592	588
[HgL ₂ Cl ₂].2H ₂ 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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