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SYNTHESIS, CHARACTERIZATION, AND BIOLOGICAL APPLICATIONS OF 2- HYDROXY-3-METHOXY BENZALDEHYDE SEMI AND THIOSEMI CARBAZONE COMPLEXES OF THE Co (II) & Ni (II) METAL IONS

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ABSTRACT

Four complexes, $[Co(L1)_2Cl_2]$ (1), $[Ni(L1)_2(H_2O)_2)]$ (2), $[Co(L2)_2Cl_2]$ (3), $[Ni(L2)_2(H_2O)_2]$ (4), were prepared by reacting 2-hydroxy-3-methoxy benzaldehyde semicarbazone and thiosemicarbazone ligands with $CoCl_2.6H_2O$ and $NiSO_4.6H_2O$. The infrared, UV, EPR, mass and ^1H NMR spectra of the complexes have been assigned. Thermogravimetric analyses (TGA, DTA) were also carried out. The data agree quite well with the proposed structures and show that the complexes were finally decomposed to the corresponding ligands. The ligands and their metal complexes were screened for antimicrobial activities by the disc diffusion technique using DMSO as solvent. The minimum inhibitory concentration (MIC) values for 1–4 were calculated at 30^0C for 24–48 h. The activity data show that the semicarbazone metal complexes are more potent antimicrobials than the thiosemicarbazone metal complexes. The complexes were also screened for their anti oxidant properties, which are comparatively lesser for nickel complexes than for cobalt complexes.

Key Words: 2-hydroxy-3-methoxybenzaldehyde; semicarbazone; metal complexes; IR; ^1H NMR; Antimicrobial activity

1. INTRODUCTION

Semicarbazones and thiosemicarbazones present a wide range of bioactivities, and their chemistry and pharmacological applications have been extensively investigated. The literature contains reviews on many aspects of the chemistry of these interesting compounds, such as preparative methods, stereochemistry, bonding in metal complexes, spectral characteristics and crystal structures [2-6]. Schiff base metal complexes have been widely studied because of their industrial,

antifugal and biological applications [7-12]. The biological properties of semicarbazones and thiosemicarbazones are often related to metal ion coordination. Firstly, lipophilicity, which controls the rate of entry into the cell, is modified by coordination [13]. Also, the metal complex can be more active than the free ligand, and some side effects may decrease upon complexation. In addition, the complex can exhibit bioactivities which are not shown by the free ligand. The mechanism of action can involve binding to a metal *in vivo* or the metal complex may be a vehicle for activation of the ligand as the cytotoxic agent. Moreover, coordination may lead to significant reduction of drug-resistance [5]. Given these appreciable biochemical applications, as well as the diverse stereochemistry of semicarbazone metal complexes [8-13], this group of ligands deserve further investigations.

2. EXPERIMENTAL

2.1. Materials and spectral measurements

All chemicals used were of analar grade. The Infrared spectra of complexes were recorded on a Bruker-Tensor 27 FT-IR spectrophotometer using KBr pellets in the range of 4000-400 cm^{-1}. Electronic spectra of the complexes were recorded in DMSO on Perkin-Elmer spectrophotometer in the range of 800-200 nm. EPR spectra were recorded on a Varian model E112 EPR spectrometer. The ^1H NMR spectra were recorded in DMSO-d_6 with JEOL 400 MHz instrument using TMS as internal reference. Mass spectra were recorded on JEOL GC mate mass spectrometer. Thermal analyses (TGA, DTA) were carried out using a Shimadzu TGA Q50 V20.5 Build 30 computerized thermal analysis system. The system includes a program which processes data from the thermal analyzer with the ChromotPac C-R3A. The rate of heating of the samples was kept at $10^0C\ min^{-1}$. Alumina powder was used as DTA standard material.

2.2 Synthesis of metal complexes

A solution (0.002mol; 200mL MeOH) of the respective ligand (2-hydroxy-3-methoxy benzaldehyde semicarbazone / thiosemicarbazone) was added to the solution of (0.002mol; 20 mL H_2O) of Cobaltous chloride, $CoCl_2.\ 6H_2O$ and the reaction mixtures were refluxed for 3h.

A solution (0.002mol; 200mL MeOH) of the respective ligand (2-hydroxy-3-methoxy benzaldehyde semicarbazone / thiosemicarbazone) was added to the solution of (0.002mol; 20 mL H_2O) of Nickel chloride, $NiCl_2.\ 6H_2O$. A pinch of sodium acetate was added and the reaction mixtures were refluxed for 3h.

The obtained precipitates were removed by filtration, washed several times with water, MeOH and recrystallized from EtOH. Finally, all the obtained complexes were dried under vacuum over P_4O_{10}.

$[Co(L_1)_2Cl_2]$ (1): Yield: 238.0 mg (96%). Color: light yellow. Anal. Found 552.23(Calcd for $C_{18}H_{22}N_6O_6CoCl_2$, 548.3): C, 51.65 (51.25); H, 5.95 (5.85); N, 18.99 (18.68); Co, 8.20 (8.10)

$[Ni(L_1)_2(H_2O)_2]$ (2): Yield: 210.0 mg (85%). Color: light blue. Anal. Found 510.64 (Calcd for $C_{18}H_{22}N_6O_6Ni(H_2O)_2$, 511.14): C, 51.44 (51.32); H, 5.26 (5.25); N, 19.32 (19.18); Fe, 9.20 (9.54)

$[Co(L_2)_2Cl_2]$ (3): Yield: 166.0 mg (72%). Color: dark brown. Anal. Found 584.68 (Calcd for $C_{18}H_{22}N_6O_4S_2CoCl_2$, 581.70): C, 53.45 (53.25); H, 5.85 (5.85); N, 18.98 (18.78); Mn, 8.21 (8.10)

$[Ni(L_2)_2(H_2O)_2]$ (4): Yield: 173.4 mg (65%). Color: brown. Anal. Found 550.19 (Calcd for $C_{18}H_{22}N_6O_4S_2Ni(H_2O)_2$, 546.98): C, 52.35 (52.20); H, 5.75 (5.65); N, 19.80 (19.32); Fe, 9.26 (9.75)

2.3. Antimicrobial activity

The ligands and corresponding complexes were evaluated for their in-vitro antibacterial activity against Methicillin drug resistant Staphylococcus aureus, Micrococcus luteus, Staphylococcus aureus, Salmonella paratyphi- B, Salmonella typhimurium, and Proteus vulgaris and anti fungal activity against *Klebsiella pneuomoniae* ,

Enterococcus aerogens, Shigella flexneri by the disc diffusion method. Bacteria inoculums were prepared by growing cells in Mueller Hinton Broth for 24 h at 37°C. These cell suspensions were diluted with sterile MHB to provide initial cell counts of about 10^{-4} CFU/ml. Yeast was grown on Sabouraud Dextrose Broth (SDB) at 28°C for 48 h. The studied bacteria and fungi were incubated into Nutrient Broth for 24 h. After incubation period the culture was diluted. In this method, Petri plates were prepared with 20 ml of sterile Agar. The test cultures (100µl of suspension containing 10^8 CFU/ml bacteria) were swabbed on the top of the solidified media and allowed to dry for 10 min. The tests were conducted at 1000 µg/disc concentration of the compounds. The loaded discs were placed on the surface of the medium and left for 30 min at room temperature for compound diffusion. Negative control was prepared using DMSO. Streptomycin (25µg /disc) was used as positive control. The plates were incubated at 37°C for bacteria (24 h) and (72 h) for fungi. Zone of inhibition was recorded in millimeters and the antimicrobial tests were calculated as a mean of three replicates and the SD was calculated using the software SPSS.

2.4. Determination of minimal inhibitory concentration (MIC)

Nutrient agar and Sabouraud Dextrose Broth are employed as basal medium for the growth of bacteria and fungi, respectively, during the test of 1, 2, 3 and 4. The culture medium (20 mL) was poured into Petri dishes (9mm in diameter) and maintained at 37^0C until the samples were incorporated into the agar. The samples were added as 1mL using an automatic micropipette while constantly stirring to assure a uniform distribution. Each sample was tested at 25, 50, 75, 100, 125, 150, 175, and 200 mmolmL^{-1} in DMSO. The different bacterial strains were layered to place 30 mL over the surface of the solidified culture medium containing a sample. After the bacteria were absorbed into the agar, the plates were incubated at 30^0C for 24–48 h. Bacterial growth was monitored visually and the MIC was determined [20, 22].

2.5. Antioxidant activity:

The antioxidant activity was measured by the method of Mensor *et al* (2001). Different concentration of each sample (5, 10, 20, 40, 60, 80, 100µg/ml) were prepared. To each of this solution 1 ml of methanolic solution of DPPH was added, and then the tubes were made up to 3ml using methanol. The tubes were incubated at room temperature for 30 min. After 30 min of incubation, the decolourisation of the purple colour was measured at 518nm using UV spectrophotometer. The antioxidant activity was measured using the formula,

$$\% \text{ of Scavenging} = \frac{A_0 - A_S}{A_0} \times 100$$

A0 = Absorption of DPPH solution without the sample
As = Absorption of DPPH solution with the sample

3. RESULTS AND DISCUSSION

3.1. Synthesis of the metal complexes

Metal complexes 1–4 were obtained during the reaction of Cobaltous chloride, $CoCl_2$. $6H_2O$ / Nickel sulphate, $NiSO_4.6H_2O$ with 2-hydroxy-3-methoxy benzaldehyde semicarbazone / thiosemicarbazone (L1and L2). The complexes were obtained in good yields (67–96%). The structures of complexes were verified by elemental analyses, spectroscopic methods, and
confirmed by thermal analysis (TGA, DTA). The metal complexes are in 1:2 stoichiometry.

3.2. Vibrational spectra

The most characteristic IR bands of the ligands (L1 and L2) and their metal complexes (1-4) are summarized in Table 1. The ligand L1 shows sharp absorption band at 1688 cm^{-1} corresponding to >C=O frequency, and the presence of band in the region 1680-1687 cm^{-1} supports the keto form of the ligand in the metal complexes. Similarly, the ligand L2 shows a sharp absorption band at 1596 cm^{-1} corresponding to >C=S frequency, and

the presence of band in the region 1590-1600 cm^{-1} supports the existence of >C=S stretching in the metal complexes. A sharp band at 1604 cm^{-1} corresponds to >C=N stretching frequency for L1 and 1515 cm^{-1} for L2. On coordination of the azomethine nitrogen, the IR stretching frequency of >C=N shows a shift and is observed in the region 1594-1602 cm^{-1} in 1 and 2 and 1500-1520 cm^{-1} in 3 and 4. The strong bands at 3465 cm^{-1} and 3436 cm^{-1} in the spectra have been assigned to -NH_2 cm^{-1}. The bands at 3196 cm^{-1} and 3175 cm^{-1} in ligands are due to NH vibration. In all the complexes, the presence of a band in this region corresponds to NH vibration which indicates that the ligand is coordinated in the neutral form. In the case of metal complexes, the appearance of bands in the region of 418-442 cm^{-1} and 438-510 cm^{-1} correspond to the M-N and M-O vibrational frequencies respectively. The appearance of the band around 1106-1194 cm^{-1} corresponds to N-N stretching frequency both in ligands and in metal complexes. Aromatic ν(C=C) value appears around 1381-1462 cm^{-1} and the aromatic ν(C-H) stretching value appears in the region 3036-3182 cm^{-1} both in ligands and metal complexes.

3.3. UV spectra

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 for assigning the stereochemistry of metal ions in the complexes based on the positions and number of d–d transition peaks. The electronic absorption spectra of the ligands and its Co (II) and Ni (II) complexes were recorded at room temperature using DMSO as solvent. The electronic spectra of Co(II) complexes showed two spin-allowed transitions at 17080cm^{-1}, 17290cm^{-1} and 21390cm^{-1}, 21383cm^{-1}assignable to $^4T_1g(F)\rightarrow{}^4A_2g(F)$ and$^4T_1g(F)\rightarrow{}^4T_1g(P)$ transitions respectively, are in conformity with octahedral arrangements for Co(II) ion[13].The appearance of a band at 19290cm^{-1} & 19887cm^{-1} due to $^3A_2g(F)\rightarrow{}^3T_1g(P)$ transition favours an octahedral geometry[14] for the Ni(II)complexes. The absence of any band below 10,000cm^{-1} eliminates the possibility of a tetrahedral environment in this complex.

3.4. EPR spectra

The g-value calculated for the $[Co(L1)_2Cl_2]$ (1), $[Ni(L1)_2(H_2O)_2)]$ (2), $[Co(L2)_2Cl_2]$ (3), $[Ni(L2)_2(H_2O)_2]$ (4), using EPR spectroscopy are given in Table 3. $[Co(L1)_2Cl_2]$ (1) complex shows hyperfine splitting. Since the measurements are made at room temperature the fine splitting was not observed in the EPR spectra of other metal complexes, as the spin lattice relaxation time is shorter that makes EPR hyperfine splitting possible only at liquid nitrogen temperature.

3.5. ^{1}HNMR spectra

^{1}H NMR values (ppm) of L^1, L^2 and metal complexes (1–4) in DMSO-d6 are summarized in Table 4.

3.5.1. $[Co(L1)_2Cl_2]$ (1). Deuterated DMSO provided adequate solubility [27] for recording 1H NMR signals of L1, L2 and 1,2,3,4 (table 4). The complex $[Co(L1)_2Cl_2]$ (1) shows signal at 1.9 δ has been assigned to –C-H proton and the signals at 2.5 δ and 3.8 δ due to NH2 and NH protons respectively. The signal at 6.8– 8.8 δ is due to aromatic protons.

3.5.2. $[Ni(L1)_2(H_2O)_2)]$ (2). The complex shows signal at 1.9 δ have been assigned to –C-H proton and the signals at 2.5 δ and 3.4 δ due to NH2 and NH protons respectively. The signal at 6.7-8.9 δ is due to aromatic protons.

3.5.3. $[Co(L2)_2Cl_2]$ (3). The complex shows signal at 2 δ have been assigned to –C-H proton and the signals at 2.3 δ and 3.4 δ due to NH2 and NH protons respectively. The signal at 7-8.8 δ is due to aromatic protons.

3.5.4. $Ni(L2)_2(H_2O)_2]$ (4). The complex shows signal at 2.3 δ have been assigned to –C-H proton and the signals at 2.3 δ and 3.5 δ due to NH2 and NH protons respectively. The signal at 6.9-8 δ is due to aromatic protons.

3.6. Mass spectra

The mass spectrum of the ligand L1 (C9H11O3N3) shows a molecular ion [M+] peak at m/z 209 amu corresponding to the species [C9H11O3N3]+, which confirms the proposed formula. It also shows a series of peaks at 175, 161, 158, 143, 132, 115, 103, 97, 91, 86, 75, 72, 61 amu corresponding to various fragments (Figure 5).

The mass spectrum of the ligand L2 (C9H11O2N3S) shows a molecular ion [M+] peak at m/z 225 amu corresponding to the species [C9H11O2SN3]+, which confirms the proposed formula. It also shows a series of peaks at 179, 168, 161, 148, 137, 121, 109, 102, 91, 76, 65 amu corresponding to various fragments (Figure 6).

The mass spectrum of $[Co(L1)_2Cl_2]$ (1) $[C_{18}H_{22}N_6O_6CoCl_2]$ shows a molecular ion [M+] peak at m/z 552.23 amu corresponding to the species) $[C_{18}H_{22}N_6O_6CoCl_2]^+$, which confirms the proposed formula.

The mass spectrum of $[Ni(L1)_2(H_2O)_2)]$ (2), $[C_{18}H_{22}N_6O_4S_2Ni(H_2O)_2]$ shows a molecular ion [M+] peak at m/z 550.19 amu corresponding to the species) $[C_{18}H_{22}N_6O_4S_2Ni(H_2O)_2]^+$, which confirms the proposed formula.

The mass spectrum of $[Co(L2)_2Cl_2]$ (3) $[C_{18}H_{22}N_6O_4S_2CoCl_2]$shows a molecular ion [M+] peak at m/z 584.68 amu corresponding to the species) $[C_{18}H_{22}N_6O_4S_2CoCl_2]^+$, which confirms the proposed formula.

The mass spectrum of $[Ni(L2)_2(H_2O)_2]$ (4) $[C_{18}H_{22}N_6O_6CoCl_2]$shows a molecular ion [M+] peak at m/z 552.23 amu corresponding to the species) $[C_{18}H_{22}N_6O_6CoCl_2]^+$, which confirms the proposed formula.

3.7. Thermal analysis

To confirm the proposed structures for the complexes, thermogravimetric analyses TGA and DTG are measured under nitrogen. The thermal data for L1, L2, 1, 2, 3 and 4 are summarized in table 5. The decomposition reactions of $[Co(L1)_2Cl_2]$ (1) occur in three steps from 229^0C to 536^0C. The first and second steps of decomposition proceed at 229^0C and 342^0C, respectively associated with the loss of co-ordinated chlorine. The third step of decomposition proceeds at maximum temperature of 536^0C, attributed to the loss of $C_9H_{11}O_3N_3$ of L1. The total weight loss associated with these steps (74.99%) is in good agreement with the calculated value of 74.97%. The decomposition reaction of $[Co(L2)_2Cl_2]$ (3) also occurred in three steps in a similar manner to 1 (Table 5).

Decomposition of $[Ni(L1)_2(H_2O)_2)]$ (2) occurred in four steps. Coordinated water is lost at 311^0C with 4.35% weight loss (calculated 4.26%). The third and fourth degradation steps were observed as two consequent decomposition peaks at 452, and 569^0C. The total weight loss value was 71.49% associated with the loss of $C_9H_{11}O_3N_3$ of L2, which agrees with the theoretical value of 71.21%. The decomposition reaction of $[Ni(L2)_2(H_2O)_2]$ (4) also occurred in four steps in a similar manner to 2 (Table 5).

3.8. Antimicrobial activity

The results of antibacterial and antifungal studies were given in Table 6. The complexes were tested against MIC- *Micrococcus luteus* , MRSA- Methicillin resistant *Staphylococcus aureus,* SPB- *Salmonella paratyphi*- B, SA- *Staphylococcus aureus* MTCC 96, KP- *Klebsiella pneuomoniae* , EA- *Enterococcus aerogens,* ST- *Salmonella typhimurium,* SF- *Shigella flexneri,* PV- *Proteus vulgaris.* The semicarbazone metal complexes $[Co(L1)_2Cl_2]$ (1) and $[Ni(L1)_2(H_2O)_2)]$ (2) show better activity than the corresponding thiosemicarbazone metal complexes $[Co(L2)_2Cl_2]$ (3), $[Ni(L2)_2(H_2O)_2]$ (4).

3.9. Antioxidant activity:

The antioxidant activities of tested compounds are listed in Table-7. The result shows that the activity increases with increase in concentration. At concentration 10 µg/ml, the ligand L1 shows 54.05% activity, and when the concentration increases to 100 µg/ml, it shows 99.46% activity.

The ligands have very good antioxidant property, such as 99.6%, 98.92% respectively at 100 µg/ml concentration, in comparison to the cobalt and nickel complexes. Nickel complexes show lesser activities, 28.11% and 41% respectively at the concentration 100 µg/ml.

The result shows that the ligands have more activity towards DPPH free radical, than the standard (L) - ascorbic acid, which has a activity of 93.51% at 100 µg/ml concentration. Thio semicarbazone metal complexes show greater antioxidant property compared to the corresponding semicarbazone complexes.

4. CONCLUSION

The Cobalt (II) and Nickel (II) metal complexes of 2-hydroxy-3-methoxy benzaldehyde semi and thiosemicarbazones were synthesized using 2-hydroxy-3-methoxy benzaldehyde semicarbazone / thiosemicarbazone ligands and they were characterized using IR, UV, Mass, NMR, EPR and thermal analysis. The spectral studies indicate neutral, bidentate nature of the ligands (L1 and L2), which undergo coordination to metal ions with NO or NS donor atom sets. Such metal complexation with metal/ligand stoichiometry of 1:2 leads to octahedral geometry for the metal complexes.

Antimicrobial studies confirmed that ligands are biologically active and their semicarbazone metal complexes show enhanced activity. The examined semicarbazone metal complexes show significant differences for their antimicrobial activities in comparison with the corresponding free ligands and the thiosemicarbazone metal complexes.

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Tubular Data:

Table 1: IR frequencies (cm^{-1}) and assignments for L^1, L^2 and their corresponding complexes (1-4)

Complexes	ν (C=O)	ν (C=S)	ν (C=N)	ν (N-H)	ν (NH_2)	ν (M-N)	ν (OH)	ν (M-O)	Aromatic ν (C=C)	ν (N-N)	Aromatic ν (C-H)
L^1	1688	-	1604	3196	3465	-	3295	-	1438	1190	3073
L^2	-	1596	1515	3175	3436	-	3276	-	1462	1114	3036
1	1687	-	1602	3194	3460	442	3293	503	1444	1194	3072
2	1684	-	1594	3200	3424	418	3290	446	1384	1120	3100
3	-	1600	1500	3182	3440	438	3308	510	1426	1133	3182
4	-	1598	1520	3190	3430	420	3283	438	1381	1106	3040

Table 2: Electronic absorption spectral bands for L^1, L^2 and their corresponding complexes (1-4)

Compound	n→π*	π→π*	CT	d-d
L^1	31,250	40,000		
L^2	37,736	42,373		
1	33,708	39,523	21, 390	17,080
2	33,679	39,356		16,077, 27,108, 28,194
3	26, 728	43, 472	21,383	19,290
4	35, 400	44, 625	27, 098	19, 887

Table 3: EPR g-values of metal complexes (1–4)

S.No	g-value
1	1.9671
2	1.9736
3	1.9736
4	1.9843

Table 4: ^1H NMR values (ppm) of L1, L2 and metal complexes (1–4) in DMSO-d6

S.No	**C-H (δ)**	**OH**	**OCH_3**	**NH_2 (δ)**	**NH (δ)**	**Aromatic protons (δ)**
L^1	2	9.9	2.4	3.8	3.9	6.8-8.5
L^2	3.2	9.8	2.5	3.8	4.5	6.9-8.8
1	1.9	9.5	1.8	2.5	3.8	6.8-8.8
2	1.9	9.6	1.7	2.5	3.4	6.7-8.9
3	2	9.7	1.5	2.3	3.4	7-8.8
4	2.3	9.5	1.9	2.3	3.5	6.9-8

Table 5: Maximum temperature values for decomposition along with the species lost in each step of the decomposition of the complexes

Compound	Decomposition	Tmax (^{0}C)	Lost species	% Weight loss	
				Found	Calcd
L1	First step Second step Third step Fourth step Total loss Residue	95 151 231 419	H_2O H_2O $C_9H_{11}O_3N_3$	2.65 5.39 75.51 83.55 16.45	2.62 5.37 75.32 83.31 16.69
L2	First step Second step Third step Fourth step Total loss Residue	82 134 235 437	H_2O H_2O $C_9H_{11}O_2N_3S$	3.40 5.74 69.87 79.01 20.99	3.31 5.72 69.85 78.88 21.12
1	First step Second step Third step Total loss Residue	229 342 536	Cl Cl $C_9H_{11}O_3N_3$ CoO	1.00 52.79 68.01 74.99 25.01	1.57 52.65 67.75 74.97 25.03
2	First step Second step Third step Fourth step Total loss Residue	150 311 452 569	H_2O H_2O $C_9H_{11}O_3N_3$ NiO	1.30 4.35 59.88 71.49 73.08 26.92	1.20 4.26 59.68 71.21 72.97 27.03
3	First step Second step Third step Total loss Residue	232 367 558	Cl Cl $C_9H_{11}O_2N_3S$ CoO	1.75 52.25 69.78 74.95 25.05	1.47 51.95 69.52 74.57 25.43
4	First step Second step Third step Fourth step Total loss Residue	158 342 478 587	H_2O H_2O $C_9H_{11}O_2N_3S$ NiO	1.32 5.69 57.76 71.74 78.75 21.25	1.25 5.53 57.48 71.49 78.27 21.73

Table 6: Antimicrobial activity of 2-hydroxy-3- methoxy benzaldehyde semi and thio semi carbazone ligands and their metal complexes (diameter of inhibition in mm)

Tested Compounds	**Tested organisms (Zone of inhibition in mm)**								
	MIC	**MRSA**	**SPB**	**SA**	**KP**	**EA**	**ST**	**SF**	**PV**
1	8	7	5	12	13	12	6	11	15
2	9	6	5	10	12	10	9	13	16
3	5	-	-	7	6	11	-	10	-
4	5	-	-	8	6	12	-	11	-
STD	26	19	17	24	25	22	26	29	31

Table 7: Determination of Antioxidant using DPPH scavenging effect:

S.No	Compound	Concentration	Optical density	% of scavenging
1	Blank	-	0.185	-
2	Standard Ascorbic acid	5µg	0.093	49.73%
		10 µg	0.062	58.92%
		20 µg	0.058	68.65%
		40 µg	0.039	78.92%
		60 µg	0.031	83.24%
		80 µg	0.023	87.57%
		100 µg	0.012	93.51%
3	L1	10 µg	0.085	54.05%
		20 µg	0.054	70.81%
		40 µg	0.036	80.54%
		60 µg	0.018	90.27%
		80 µg	0.011	94.05%
		100 µg	0.001	99.46%
4	L2	10 µg	0.076	58.92%
		20 µg	0.052	71.89%
		40 µg	0.035	81.08%
		60 µg	0.021	88.65%
		80 µg	0.014	92.43%
		100 µg	0.002	98.92%
5	$[Co(L1)_2Cl_2]$	10 µg	0.123	38.90%
		20 µg	0.113	40.02%
		40 µg	0.107	41.00%
		60 µg	0.094	49.74%
		80 µg	0.075	58.89%
		100 µg	0.056	68.89%
6	$[Ni(L1)_2(H_2O)_2)]$	10 µg	0.187	1.08%
		20 µg	0.176	4.86%
		40 µg	0.159	14.05%
		60 µg	0.142	23.24%
		80 µg	0.139	24.86%
		100 µg	0.133	28.11%
7	$[Co(L2)_2Cl_2]$	10 µg	0.108	40.81%
		20 µg	0.089	52.75%
		40 µg	0.071	60.21%
		60 µg	0.049	72.17%
		80 µg	0.038	80.24%
		100 µg	0.027	85.03%
8	$[Ni(L2)_2(H_2O)_2]$	10 µg	0.186	0.00%
		20 µg	0.152	17.84%
		40 µg	0.113	32.97%
		60 µg	0.124	38.92%
		80 µg	0.111	40%
		100 µg	0.109	41%