

Synthesis, and spectroscopic characterization of copper(II) metal complexes of salicyldehyde thiosemicarbazone (L₁) and 4-hydroxy acetophenone Thiosemicarbazone(L₂)

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ABSTRACT

New Cu(II) metal complexes containing ligands Salicyldehyde thiosemicarbazone (L₁), and 4- hydroxyacetophenone thiosemicarbazone(L₂), have been synthesized. These ligands were characterized on the basis of elemental analyses, IR, ¹H NMR and mass spectral studies while that of the complexes were characterized by elemental analyses, molar conductance, magnetic moment, IR, electronic and EPR spectral studies. The IR spectral data for ligand L₁ indicated involvement of phenolic oxygen, sulphur and azomethine nitrogen in coordination to the central metal ion and L₁ act as tridentate ligand and ligand L₂ indicated involvement of sulphur and azomethine nitrogen in coordination to the central metal ion and act as bidentate ligand. On the basis of elemental analyses and molar conductance data the complexes were found to have general composition [Cu(L₁)(X)(H₂O)₂] and [Cu(L₂)₂X₂] [(where X = Cl⁻, NO₃⁻ and CH₃CO⁻). On the basis of IR, electronic and EPR spectra of complexes, tetragonal geometry has been assigned for all the complexes were found with planar coordination of the ligand around Cu²⁺ ion and the anions occupies axial position.

Keywords: Salicyldehyde thiosemicarbazone, 4-hydroxyacetophenone thiosemicarbazone, Cu(II) complexes. Spectral studies.

1. INTRODUCTION

Thiosemicarbazones are a family of compounds with beneficial biological activity. Thiosemicarbazones and their metal complexes have been widely explored for nearly 50 years [1-2] because of their versatile biological activity and prospective use as drugs, A large number of authors were interested in investigating the biological and medicinal properties of transition metal complexes of thiosemicarbazones in recent years [3]. Owing to the interest they generate through a variety of biological properties ranging from anticancer [4-6], antitumour [7-9], antifungal [10], antibacterial [11-12], antimalarial [13], antifilarial [14], antiviral [15-17] and anti-HIV [18] activities.

They are very good ligands, and it has been shown that their biological activity is related to their ability to coordinate to metal centre in enzymes. One interesting thing is that the more pharmaceutically promising thiosemicarbazone derivatives possess additional functional groups that are not coordinated to their "primary" metal

ion, suggesting that the biological activity may also depend on the non-coordinating groups [19]. Particularly first row of transition metal complexes with such ligands have a wide range of biological applications [20-22].

In view of above applications it is highly desirable to synthesize and characterize transition metal complexes with such ligands (Figure 1). In the present paper we report the synthesis, and spectroscopic characterization of Cu(II) complexes with ligand Salicyldehyde Thiosemicarbazone(L₁) and 4-hydroxy acetophenonethiosemicarbazone(L₂) of the type[Cu(L₁)X(H₂O)₂]and [Cu(L₂)₂X₂], [(where X = Cl⁻, NO₃⁻ and CH₃COO⁻].

2. EXPERIMENTAL

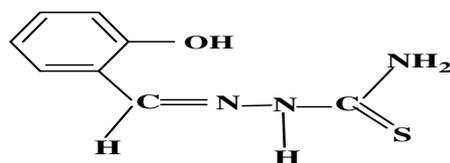
2.1. Materials

The entire chemical used were of analytical reagent and procured from sigma

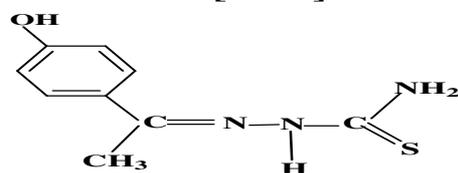
Aldrich and used without further purification. Metal salts were purchased from E.Merck and were used as received

2.2. Physicochemical measurements

The C, H, and N were analyzed on Carlo-Erba 1106 elemental analyzer. Molar conductance was measured at 25°C on the ELICO (CM82T) conductivity bridge. Magnetic susceptibilities were measured at room temperature on a Gouy balance using $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ as calibrant. Electronic impact mass spectrum was recorded on JEOL, JMS - DX-303 mass spectrophotometer. Proton (^1H) NMR spectra were recorded on JEOL -DELTA 2 NMR model ECX 400P spectrometer using DMSO as a solvent. Chemical shifts are given in ppm relative to tetramethylesilane(TMS). The electronic spectra were recorded in DMSO on Shimadzu UV mini-1240 spectrophotometer. IR Spectra (KBr) were recorded on a FTIR spectrum BX-II spectrophotometer.



[Str.1]



[Str. 2]

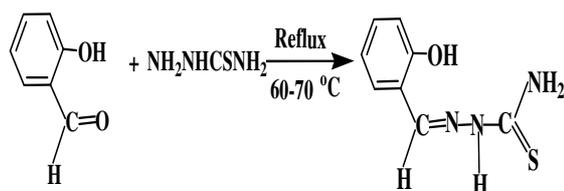
Figure - 1: Structure of L_1 and L_2

2.3. Synthesis of ligands and Cu(II) complexes

2.3.1. Synthesis of ligands

2.3.1.1. Synthesis of ligand (L_1)

Hot ethanolic solution of thiosemicarbazide (1.82g,0.02mol) and salicyldehyde (2.10mL, 0.02 mol) were mixed slowly in the presence of acetic acid with constant stirring. This mixture was refluxed at 60-70°C for 5-6 hrs on a water bath. On cooling, cream coloured crystals of compound were precipitated out. They was filtered washed with cold EtOH and dried under vacuum over P_4O_{10} . (yield 65%, m.p 240°C) The structure of ligand and method of synthesis is shown below in the scheme 1.

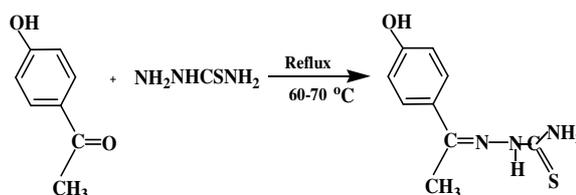


Salicyldehyde Thiosemicarbazide L_1

Scheme -1: Synthesis of salicyldehyde thiosemicarbazone (L_1)

2.3.1.2. Synthesis of ligand L_2

Hot ethanolic solution of thiosemicarbazide (1.82g,0.02mol) and 4-hydroxy acetophenone (2.44mL, 0.02 mol) were mixed slowly in the presence of acetic acid with constant stirring. This mixture was refluxed at 60-70°C for 5 -6 hrs on a water bath. On cooling, cream coloured crystals of compound were precipitated out . They were filtered washed with cold EtOH and dried under vacuum over P_4O_{10} . The structure of ligand and method of synthesis is shown below in the scheme 2.



4- hydroxy acetophenone L_2

Scheme - 2: Synthesis of 4-hydroxy acetophenone thiosemicarbazone(L_2)

2.3.1.3. Preparation of the Cu(II)complexes with ligands L_1 , and L_2

The complexes with ligand L_1 , and L_2 , were prepared by mixing the hot ethanolic solution (15mL) of the respective copper(II) salt (0.001 mol) and an ethanolic solution (15mL) of corresponding ligand (0.001 mol) in 1:1 molar ratio in case of L_1 and 1:2 molar ratio in case of L_2 , were mixed together with constant stirring. This mixture was refluxed for 5- 6 hrs at 85-90 °C. On cooling colored precipitate was formed. It was filtered, washed with cold EtOH and dried under vacuum over P_4O_{10} . The preparation of complexes can be represented by the following general equations.

Schiff base Ligand (L) + copper salt \rightarrow colored complex

3. Results and Discussion

3.1. Characterization of the Copper(II) complexes

The analytical and physical properties of prepared complexes are given in (Table 1). The

reported copper(II) complexes provide satisfactory C, H, N, and Cu analyses and confirmed the general composition of $[\text{Cu}(\text{L}_1)\text{X}(\text{H}_2\text{O})_2]$ and $[\text{Cu}(\text{L}_2)_2\text{X}_2]$ with ligand L_1 and L_2 respectively (where $\text{X} = \text{Cl}^-$, NO_3^- and CH_3COO^-). The isolated solid complexes are stable in air.

Table - 1: Physical properties, elemental analysis, magnetic moment and molar conductance data of Cu(II) complexes with ligand L1 and L2

Complexes	Molar conductance $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$	Color	m.p (°C)	Yield (%)	Elemental Analysis data found / (calculated)%				μ_{eff} (B.M)
					Cu	C	H	N	
L_1 ($\text{C}_8\text{H}_9\text{N}_3\text{OS}$)	-	Cream	240	65	-	49.25 (49.23)	4.66 (4.62)	21.55 (21.54)	-
$[\text{Cu}(\text{L}_1)(\text{Cl})(\text{H}_2\text{O})_2]$ $\text{CuC}_8\text{H}_{13}\text{N}_3\text{O}_3\text{SCl}$	20	Dark Green	260	55	19.15 (19.12)	29.18 (29.14)	3.97 (3.94)	12.71 (12.74)	1.93
$[\text{Cu}(\text{L}_1)(\text{CH}_3\text{COO})(\text{H}_2\text{O})_2]$ $\text{CuC}_{10}\text{H}_{16}\text{N}_3\text{O}_5\text{S}$	23	Brown	265	75	17.81 (17.85)	33.94 (33.99)	4.58 (4.53)	11.87 (11.89)	1.94
$[\text{Cu}(\text{L}_1)(\text{NO}_3)(\text{H}_2\text{O})_2]$ $\text{CuC}_8\text{H}_{13}\text{N}_4\text{O}_6\text{S}$	17	Brown	258	62	17.66 (17.69)	26.99 (26.97)	3.61 (3.65)	15.78 (15.73)	2.02
L_2 $\text{C}_9\text{H}_{11}\text{N}_3\text{OS}$	-	Cream	220	68	-	51.65 (51.67)	5.29 (5.26)	20.14 (20.10)	-
$[\text{Cu}(\text{L}_2)_2\text{Cl}_2]$ $\text{CuC}_{18}\text{H}_{22}\text{N}_6\text{O}_2\text{S}_2\text{Cl}_2$	24	Dull Green	285	65	11.39 (11.41)	39.11 (39.13)	3.97 (3.98)	15.20 (15.22)	1.96
$[\text{Cu}(\text{L}_2)_2(\text{CH}_3\text{COO})_2]$ $\text{CuC}_{22}\text{H}_{28}\text{N}_6\text{O}_6\text{S}_2$	25	Brown	268	77	10.51 (10.52)	44.05 (44.07)	4.65 (4.67)	14.00 (14.02)	1.97
$[\text{Cu}(\text{L}_2)_2(\text{NO}_3)_2]$ $\text{CuC}_{18}\text{H}_{22}\text{N}_8\text{O}_8\text{S}_2$	17	Brown	269	58	10.39 (10.41)	35.71 (35.70)	3.63 (3.64)	18.50 (18.51)	2.00

Table - 2: Important IR spectral bands (cm^{-1}) of ligands and Cu(II) complexes

Complexes	$\nu(\text{-OH}) + \nu(\text{-NH})$	$\nu(\text{C=N})$	$\nu(\text{C=S})$	$\nu(\text{M-N})$	$\nu(\text{M-S})$	$\nu(\text{M-X}), \text{X}=\text{Cl}^-, \text{NO}_3^-, \text{CH}_3\text{COO}^-$
Ligand (L_1)	3444,3320	1614	829	-	-	-
$[\text{Cu}(\text{L}_1)(\text{Cl})(\text{H}_2\text{O})_2]$	3377,3299	1603	815	438	370	345
$[\text{Cu}(\text{L}_1)(\text{CH}_3\text{COO})(\text{H}_2\text{O})_2]$	3468,3353	1602	810	474	384	1546,1306
$[\text{Cu}(\text{L}_1)(\text{NO}_3)(\text{H}_2\text{O})_2]$	3294	1605	816	474	392	1426,1328,1034
Ligand (L_2)	3444,3320	1604	829	-	-	-
$[\text{Cu}(\text{L}_2)_2\text{Cl}_2]$	3397	1560	815	493	385	320
$[\text{Cu}(\text{L}_2)_2(\text{CH}_3\text{COO})_2]$	3327	1599	794	460	380	1525,1301
$[\text{Cu}(\text{L}_2)_2(\text{NO}_3)_2]$	3169	1526	753	469	382	1438,1322,1014

Table - 3: EPR spectral data of Cu(II) complexes at RT (as polycrystalline)

Complexes	g_{\parallel}	g_{\perp}	g_{iso}	G
$[\text{Cu}(\text{L}_1)(\text{Cl})(\text{H}_2\text{O})_2]$	2.2576	2.0641	2.1286	4.0187
$[\text{Cu}(\text{L}_1)(\text{CH}_3\text{COO})(\text{H}_2\text{O})_2]$	2.1892	2.0318	2.0842	5.9496
$[\text{Cu}(\text{L}_1)(\text{NO}_3)(\text{H}_2\text{O})_2]$	2.2266	2.0318	2.0967	7.125
$[\text{Cu}(\text{L}_2)_2\text{Cl}_2]$	2.1929	2.0382	2.0897	5.0497
$[\text{Cu}(\text{L}_2)_2(\text{CH}_3\text{COO})_2]$	2.2894	2.0641	2.1392	4.5148
$[\text{Cu}(\text{L}_2)_2(\text{NO}_3)_2]$	2.2343	2.0446	2.1078	5.2533

3.2. Conductivity studies

All the complexes have shown good solubility in DMSO. The molar conductance of the complexes in fresh solution of DMSO lies in the range of 17– 25 Ω^{-1} cm² mol⁻¹ indicating their non-electrolytic behavior. Thus, the complexes may be formulated as [Cu(L₁)(X)(H₂O)₂] and [Cu(L₂)₂X₂] (Table 1).

3.3. Magnetic susceptibility measurements

Magnetic susceptibility measurements of the complexes show that the Cu(II) complexes are paramagnetic which correspond to +2 state of Copper in these complexes the room temperature value for μ_{eff} (1.93-2.02 B.M.) (where μ_{eff} is the effective magnetic moment) is higher than that expected for the spin only value (1.73B.M.) due to mixing of angular momentum from excited state via spin-orbit coupling [23]. (Table - 1)

3.4. Spectroscopic characterization

3.4.1. Infrared spectra

The assignments of the significant IR spectral bands (4000-400cm⁻¹) of ligand and its metal complexes are presented in (Table 2). The position of bands provides significant indications regarding the bonding sites of the ligand molecule when complexed with Cu(II). In principle, the ligand can exhibit thione-thiol tautomerism since it contains a thioamide -NH-C=S functional group. The ν (S-H) band at 2565 cm⁻¹ is absent in the IR spectrum of ligand but ν (-NH) band at 3320 cm⁻¹ is present, indicating that in the solid state, the ligand remains as the thione tautomer. The position of ν (C=N) band of the ligand(L₁) appeared at 1614 cm⁻¹ is shifted towards lower wave number in the complexes indicating coordination via the azomethine nitrogen [24-25]. This is also confirmed by the appearance of bands in the range of 438-493cm⁻¹, this has been assigned to the ν (M-N) [26]. The position of this band is shifted towards higher wave number in the spectra of complexes. It is due to the increase in the bond strength, which again confirms the coordination via the azomethine nitrogen. The position of ν (-OH) band of the (L₁) appeared at 3444cm⁻¹ is shifted towards lower wave number in the complexes indicating coordination via oxygen of phenolic group. The band appearing at 829 cm⁻¹ corresponding to ν (C=S) in the IR spectrum of ligand is shifted towards lower wave number (Figure - 2). It indicates that thione sulphur coordinates to the metal ion [27-28]. Thus, it may be concluded that the ligand behaves as tridentate chelating agent coordinating through phenolic oxygen, azomethine nitrogen and thiolate sulphur. But with ligand L₃ the (-OH) band remained intact at their position, which indicated that it is not

coordinating on complexation with metal ion. So ligand L₂ behave as bidentate.

3.4.2. Bands due to anions

The coordination modes of nitrate anion in nitrate complexes show three vibrational bands at 1466-1438,1322-1306 and 1034-1014 cm⁻¹. The separation of the two highest frequency is more than 90 cm⁻¹ indicating the unidentate coordination [29-30]. In the IR spectra of Cu(II) chloride complexes, bands corresponding to ν (Cu-Cl) observed at 345-320 cm⁻¹ indicating the presence of M-Cl bond and the coordination modes of acetate anion in acetate complexes show two vibrational bands at 1546-1525 and 1306-1301 cm⁻¹. The separation of the two frequency is more than 217 cm⁻¹ indicating the unidentate coordination. In the IR spectra of Cu(II) complexes with ligand L₁, also show a clear band of water molecule at 673-640 cm⁻¹ indicating that water molecule is also coordinating [31].

3.4.3. Electronic spectra

Electronic spectra of copper(II) complexes of L₁ and L₂ were recorded in DMSO in the range 400-1100nm. The electronic spectrum of Cu(II) complex displayed three bands in the range of 9900-11223,13850-16949 and 18621-27424cm⁻¹. These bands correspond to the transitions ²B_{1g}→²A_{1g} (dx²-y²→dz²)(ν_1) and ²B_{1g}→²B_{2g} (dx²-y²→dzy)(ν_2) and ²B_{1g}→²E_g (dx²-y²→d_{xy,yz}) respectively. The band at 31152-35842 cm⁻¹ may be due to charge transfer. Therefore, the complexes may be considered to possess a tetragonal geometry [32-33]. The energy level sequence will depend on the amount of tetragonal distortion due to ligand field and Jahn Teller effects [34-35].

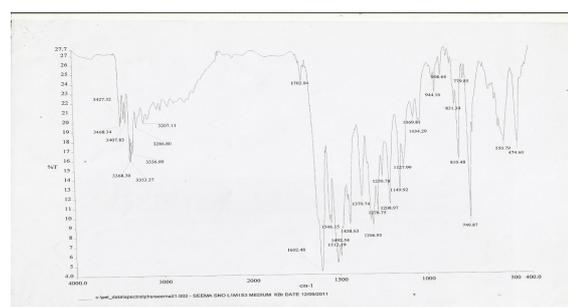


Figure - 2a : [Cu(L₁)(CH₃COO)(H₂O)₂]

3.4.4. Electronic ¹H NMR spectra of ligand

¹H NMR spectrum of Ligands in DMSO show the signals [36] as follows (chemical shift in ppm): ¹H NMR spectrum of Ligand L₁ (salicyldehyde thiosemicarbazone) : δ :3.4 ppm (s)(2H, H₂N-C=S), δ :7.9ppm(s)(1H,HN-C=S), δ :6.8ppm(m)(4H,-Ph-), ppm(s)(1H,CH=N), δ :11.37 ppm(s)(Ph-OH)., and ¹H NMR spectrum of Ligand L₂ (4-hydroxy acetophenone

thiosemicarbazone) δ : 3.3ppm (s) (2H, H₂N-C=S), δ :7.9 ppm (s) (1H, HN-C=S), δ :6.9 ppm(m)(4H, Ph-), δ :9.86 ppm(s)(3H, H₃C-C=N), δ : 11.37 ppm(s)(-Ph-OH) and δ : 2.5 ppm(-C-CH₃).

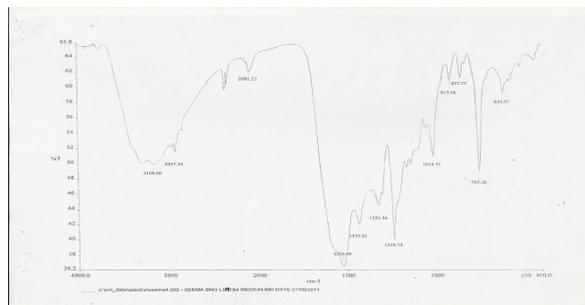


Figure - 2b: [Cu(L₂)₂(NO₃)₂]

Figure - 2: IR spectra of ligand L₁ and L₂ with Cu(II) complexes

3.4.5. EPR spectra

EPR spectra of Cu(II) complexes were recorded at room temperature as polycrystalline sample, on X band at frequency of 9.1GHz under the magnetic-field strength of 3000G exhibit well resolved anisotropic signals with the g values, $g_{||} = 2.189-2.289$, $g_{\perp} = 2.012-2.064$ and $G = 4.018-8.588$ (Figure 3)[Table 3]. The observed $g_{||}$ values for the complex are less than 2.3 in agreement with the covalent character of the metal ligand bond. The trend $g_{||} > g_{\perp} > 2.0023$ observed for the complex indicates that unpaired electron is localized in dx²-y² orbital of the Cu(II) ion and the spectral features are a characteristic of axial symmetry. Thus, a tetragonal geometry is confirmed for the aforesaid complex [37-38].

Kivelson and Neiman [39] have shown that $g_{||}$ is an important function for indicating covalent character of M-L bond. For ionic character of the metal ligand bond $g_{||} > 2.3$ and for covalent character $g_{||} < 2.3$. In addition, exchange coupling interaction between two copper centre explained by Hathaway [40], expression $G = (g_{||} - 2) / (g_{\perp} - 2)$, which measures the exchange interaction between the metal centers in a polycrystalline solid, has been calculated. If the value of $G > 4$, the exchange interaction is negligible, whereas when $G < 4$ indicates considerable exchange interaction in the solid complex between copper centers. The "G" value for Cu (II) complex reported in this paper, is > 4 indicating the exchange interaction is negligible in complexes.

3.4.6. Mass spectra

The electronic impact mass spectrum of the ligand L₁ (Figure 4) shows a molecular ion (M⁺) peak at m/z = 195 amu corresponding to species [C₈H₉N₃OS]⁺, which confirms the proposed formula. It also shows a series of peaks corresponding to species [C₈H₉N₃S]⁺ i.e at 179

amu and various fragments at ,135, 120 ,91amu. The electronic impact mass spectrum of the ligand L₂, a molecular ion (M⁺) peak at m/z = 209 amu corresponding to species [C₉H₁₁N₃OS]⁺, which confirms the proposed) shows formula. It also shows a series of peaks corresponding to various fragments. Intensity of these peaks give an idea of the stability of the fragments (Figure4).

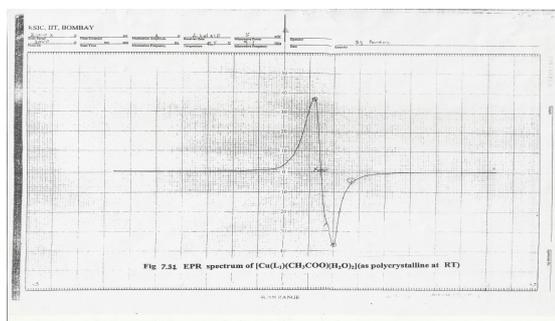


Figure - 3a: [Cu(L₁)(CH₃COO)(H₂O)₂]

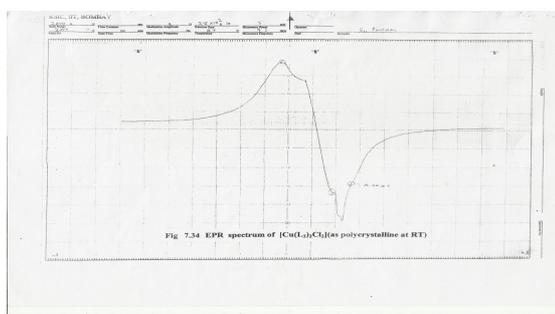


Figure - 3b: [Cu(L₂)₂Cl₂]

Figure - 3: EPR spectra of of Cu(II) complexes with ligand L₁ and L₂

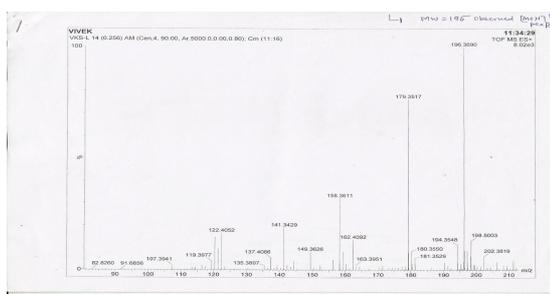
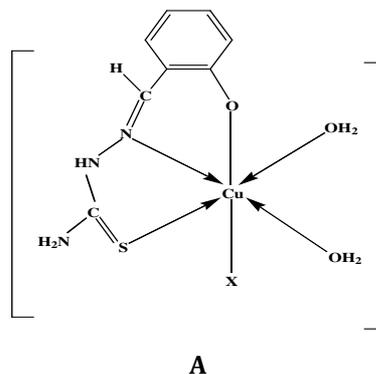


Figure - 4: Mass spectrum of ligand L₁



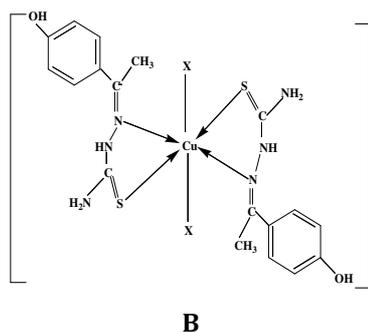


Figure - 5: [A] proposed Structure of the Cu(II) complexes with ligand L₁, Salicyldehyde thiosemicarbazone, (where X= Cl⁻, NO₃⁻ and CH₃COO⁻), [B] proposed Structure of the Cu(II) complexes with ligand L₂, 4-hydroxyacetophenone thiosemicarbazone) (where X= Cl⁻, NO₃⁻ and CH₃COO⁻).

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