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## Physicochemical Characterization of Mixed Ligand Complexes of O and N Donor Ligands

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### ABSTRACT

The mixed ligand complexes of the type  $M(L_1L_2)Cl_2$ , where,  $M$ =Cobalt(II), nickel(II) and copper(II). While,  $L_1$ =O-hydroxy acetophenone oxime and  $L_2$ =Salicylaldehyde semicarbazone have been prepared by reacting equimolar quantities of transition metal(II) chloride with two ligands  $L_1$  and  $L_2$ . These synthesized complexes have been studied on the basis of elemental analysis, analysis of UV and IR, conductivity measurement, magnetic measurement, thermal analysis and antimicrobial activities. Analysis of results shows octahedral geometry of the complexes. The complexes show electrolytic nature and having more antimicrobial activity than the ligands. The central metal ion is bonded to ligands through oxygen and nitrogen.

**Keywords:**  $M(L_1L_2)Cl_2$ , Elemental analysis, Oxygen, Nitrogen

### INTRODUCTION

There has been growing interest in the preparation of mixed ligand chelates involving ligands containing different functional groups and transition metals of different oxidation states [1-4]. A transition metal complex of oxime and semicarbazone shows remarkable antitumor, antiviral, anticancer, antimalarial, antifungal, antibacterial and catalytic activities. In view of these applications, we have carried out synthesis and characterization and biochemical study of mixed ligand complexes of transition metal with ortho-hydroxyacetophenone oxime and salicylaldehyde semicarbazone. In this complexation reaction ortho-hydroxyacetophenone oxime is acting as a bidentate and salicylaldehyde semicarbazone is acting as a tridentate ligand with oxygen and nitrogen as the donor species [5-9].

### MATERIALS AND METHODS

The compounds semicarbazide hydrochloride, ortho-hydroxyacetophenone, salicylaldehyde and chlorides of Co(II), Ni(II) and Cu(II) used were of research grade. The amount of metals in the complexes was determined complexometrically using Ethylenediaminetetraacetic Acid (EDTA) by double burette technique for optimum utilization of reagents. Indicator xylenol orange was used for Co(II) and murexide for Ni(II) and Cu(II). Carbon, hydrogen and nitrogen analysis were carried from Central instrumentation laboratory, Pratap College, Amalner. Analytical properties are shown in Table 1.

### RESULTS AND DISCUSSION

IR spectra of the complexes were recorded on Perkin Elmer, FTIR instrument using KBr pellets in the region  $400-4000\text{ cm}^{-1}$  from Department of Physics, Pratap College, Amalner. The Electronic spectral data of complexes is shown in Table 2. Electronic spectra of complexes were recorded on Systronics UV-Visible spectrophotometer in the Department of Chemistry, Pratap College, and Amalner. The IR spectral data of complexes is shown in Table 3. Thermo gravimetric analysis was carried out on Shimadzu STA 6000. Antimicrobial activities are determined by using three microbial nutrients. Ligands  $L_1$  and  $L_2$  were prepared and the methods of their preparation are given below.

Table 1: Physical properties

Name of ligand	Molecular weight	Nature	Method of purification	Melting point °C (observed)
Salicylaldehyde semicarbazone	179	Yellowish shining crystals	Recrystallized from aq. Ethanol	228 (228)
O-hydroxy acetophenone oxime	151	White shining crystals	Recrystallized from methanol	114 (115)

Table 2: Electronic spectra

Name of the complex	$\nu_1$	$\nu_2$	$\nu_3$	$\nu_2/\nu_1$
Co[(OHACPHOX) <sub>1</sub> (SALSC) <sub>1</sub> (H <sub>2</sub> O) <sub>1</sub> ]	8695	15948	25974	1.83
Ni[(OHACPHOX) <sub>1</sub> (SALSC) <sub>1</sub> (H <sub>2</sub> O) <sub>1</sub> ]	1015	16000	25575	1.569
Cu[(OHACPHOX) <sub>1</sub> (SALSC) <sub>1</sub> (H <sub>2</sub> O) <sub>1</sub> ]	8764	15384	26315	1.755

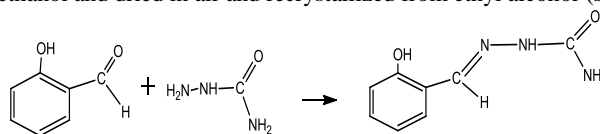
Table 3: IR spectra (cm<sup>-1</sup>) bands of the parent and mixed ligand transition metal complexes

Ligand/Complex	$\nu_{OH}$ (H <sub>2</sub> O)	$\nu_{N-OH}$ of oxime	$\nu_{C=O}$	$\nu_{C=N}$	$\nu_{N-H}$	$\nu_{C-N}$	$\nu_{M-N}$	$\nu_{M-O}$
OHACPHOX	3678	3136	1684	1592	1485	-	-	-
SALSC		3136	1685	1589	1485	1297	-	-
Co[(OHACPHOX) <sub>1</sub> (SALSC) <sub>1</sub> (H <sub>2</sub> O) <sub>1</sub> ]	3672	3148	1678	1591	1435	1287	681	544
Ni[(OHACPHOX) <sub>1</sub> (SALSC) <sub>1</sub> (H <sub>2</sub> O) <sub>1</sub> ]	3672	3148	1683	1594	1470	1284	668	554
Cu[(OHACPHOX) <sub>1</sub> (SALSC) <sub>1</sub> (H <sub>2</sub> O) <sub>1</sub> ]	3672	3149	1677	1591	1470	1288	647	544

## Synthesis of ligands

### Salicylaldehyde semicarbazone

A mixture of ethanolic solution of 25 ml (0.1 M) solution of salicylaldehyde and (20 ml 0.1 M) solution of sodium acetate is prepared and then 25 ml (0.1 M) aqueous solution of semicarbazide hydrochloride was added slowly with constant stirring. Then this reaction mixture was refluxed for 15-20 min on a water bath (Figures 1 and 2). After cooling thoroughly, white solid product was precipitated out from the solution. This solid obtained was filtered, washed with cold ethanol and dried in air and recrystallized from ethyl alcohol (Scheme 1).



Scheme 1: Synthesis of Salicylaldehyde semicarbazone

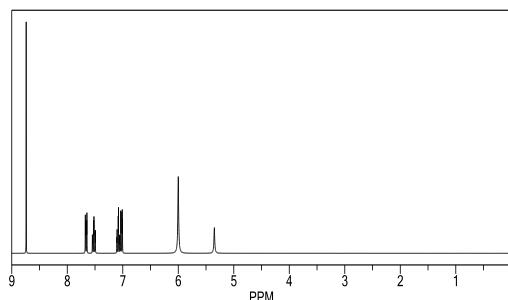
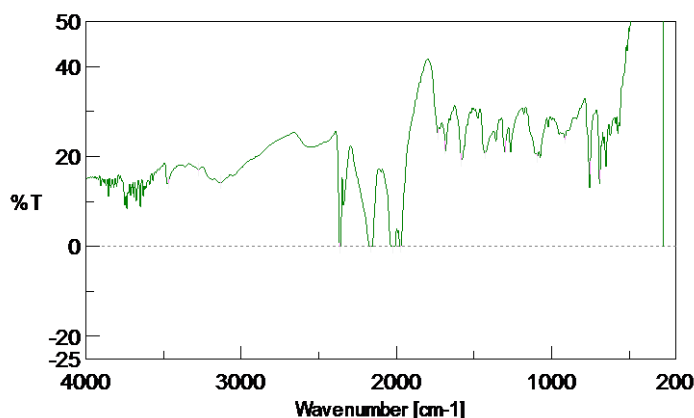
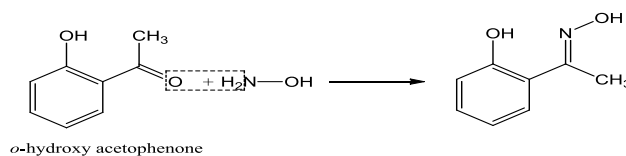
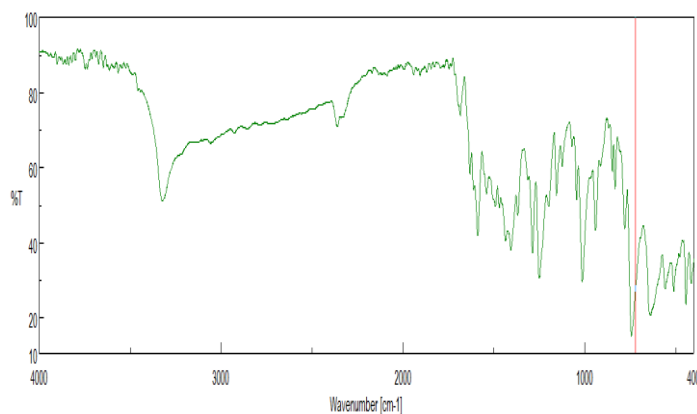
Figure 1: <sup>1</sup>H-NMR spectrum of salicylaldehyde semicarbazone

Figure 2: IR spectrum of salicylaldehyde semicarbazone

**O-hydroxy acetophenone oxime**

25 ml 0.1 M alcoholic solution of o-hydroxy acetophenone and 25 ml 0.1 M aqueous solution hydroxylamine hydrochloride were mixed together. The reaction mixture was acidified by 3-4 drops of glacial acetic acid and refluxed on water bath for 2 h (Figure 3). The precipitated compound was filtered, washed with cold water, dried and melting point was recorded (Scheme 2).

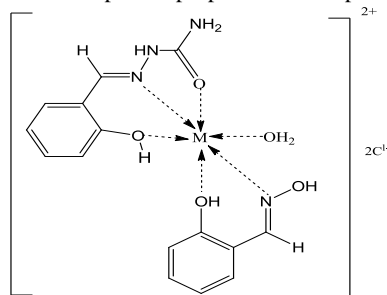
**Scheme 2: O-hydroxy acetophenone oxime****Figure 3: IR spectrum of O-hydroxy acetophenone****Synthesis of transition metal complexes ML<sub>2</sub>**

To methanolic solution of metal chloride, alcoholic solution of salicylaldehyde was added with continuous stirring at room temp, a clear solution was obtained. Then the solution was refluxed on a heating mental at about 60-70°C for 4 h. The colored solid complex separates out from solution. The solid product was filtered on cooling, washed with methanol, dried and weight of the complex obtained is taken to determine practical yield.

To methanolic solution of metal chloride, alcoholic solution of O-hydroxy acetophenone oxime was added with continuous stirring at room temp, a clear solution was obtained. Then the solution was refluxed on a heating mental at about 60-70°C for 4 h. The colored solid complex separates out from solution. The solid product is filtered on cooling, washed with methanol, dried.

**Synthesis of transition metal complexes ML<sub>1</sub>L<sub>2</sub>**

To methanolic solution of metal chloride a hot methanolic solution of mixture of salicylaldehyde semicarbazone and O-hydroxy acetophenone oxime was added with continuous stirring at room temperature, a clear solution was obtained. Then the solution was refluxed on a heating mental at about 60-70°C for 4 h. The colored solid complex separates out from solution. The solid product is filtered on cooling, washed with methanol, dried and weight of the complex obtained is taken to determine practical yield. The TLC technique was used to identify the formation of the mixed ligand complexes. These mixed ligand complexes exhibit single spots with Retardation Factor ( $R_f$ ) values being intermediate of the two corresponding symmetrical bis-complexes indicating that these are mixed ligand complexes rather than a mixture of two corresponding bis-complexes. The observed magnetic moments of these complexes shows octahedral structure. The conductance of the complexes are (99.03-108.26  $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ ) indicating their electrolytic nature. The spectral properties of complexes are shown in annexure BC (Figure 4).

**Figure 4: Structure of complexes****Spectral properties****Electronic spectra**

Absorption bands of Co(II) complexes were observed at 8695, 15948, 25974  $\text{cm}^{-1}$  with  $\nu_2/\nu_1$  ratio 1.83, corresponding to  ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ ,  ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$  and  ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$  transitions, respectively indicating octahedral geometry.

The electronic spectra of Ni(II) complexes shows presence of three bands in the range 10165, 16000 and 25575  $\text{cm}^{-1}$  with  $\nu_2/\nu_1$  ratio 1.645, corresponding to  ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ ,  ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$  and  ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$  transitions, respectively suggesting presence of octahedral geometry. While, the six coordinated copper complexes shows bands in the range 8764, 15384 and 26315  $\text{cm}^{-1}$  with  $\nu_2/\nu_1$  ratio 1.755 corresponding to  ${}^2B_{1g} \rightarrow {}^2A_{1g}$ ,  ${}^2B_{1g} \rightarrow {}^2B_{2g}$ ,  ${}^2B_{1g} \rightarrow {}^2E_{2g}$  transitions, respectively.

### IR spectra

The IR spectra of the mixed ligand complexes the bands observed at 1544-1604  $\text{cm}^{-1}$  shows presence of symmetric and asymmetric  $\nu_{(C=N)}$  vibrations. A strong band in the region 1748-1647  $\text{cm}^{-1}$  are observed due to  $\nu(C=O)$  groups. When complex is formed, the position of these bands is shifted toward lower side as compared to the metal free ligand. This clearly indicates that the coordination takes place through the nitrogen and oxygen atom of the (C=N) and (C=O) groups. A broad band appears in the region at 3200-3750  $\text{cm}^{-1}$  be assigned to the coordinated water molecule.

The thermo grams of the mixed ligand complexes have been recorded in flowing nitrogen atmosphere at the heating rate of 20°C/min by using approximately 10 mg sample. Thermogravimetric analysis shows presence of one water molecule in the complex supporting the octahedral nature of the complexes. While, IR spectra magnetic properties, electronic spectra respectively (Tables 2-4). While, physical properties of ligands and complexes are shown in Tables 1 and 5. Thermodynamic properties are shown in the Table 6.

Biological activities of the synthesized complexes in the present investigation have been subjected to various antimicrobial screening programs based on their structural features so as to observe their activity against different microorganisms. The solvent used was Dimethyl Sulfoxide (DMSO). The results of preliminary study on antimicrobial activity shows that few of the complexes were moderate and most were highly active against these organisms.

**Table 4: Magnetic moment and molar conductance values of the complexes**

Ligand/Complex	Magnetic moment B.M	Molar cond. $\Omega^1\text{cm}^2\text{mol}^{-1}$ at room temperature (29°C)
Co[(OHACPHOX) <sub>1</sub> (SALSC) <sub>1</sub> (H <sub>2</sub> O) <sub>1</sub> ]	3.603	99.93
Ni[(OHACPHOX) <sub>1</sub> (SALSC) <sub>1</sub> (H <sub>2</sub> O) <sub>1</sub> ]	3.390	108.26
Cu[(OHACPHOX) <sub>1</sub> (SALSC) <sub>1</sub> (H <sub>2</sub> O) <sub>1</sub> ]	2.134	99.03

**Table 5: Characterization data of the complexes found (Calculated) %**

Ligand/Complex	Colour	Molecular weight	% Yield of the compound	% of metal (Calculated)	% of C	% of H	% of N	% of O
Co[(OHACPHOX) <sub>1</sub> (SALSC) <sub>1</sub> (H <sub>2</sub> O) <sub>1</sub> ]	Brown	477.93	74.34	12.33 (12.09)	40.17 (40.29)	3.76 (3.72)	11.71 (11.44)	13.39 (13.54)
Ni[(OHACPHOX) <sub>1</sub> (SALSC) <sub>1</sub> (H <sub>2</sub> O) <sub>1</sub> ]	Brown	477.69	69.89	12.28 (12.13)	40.19 (40.01)	3.76 (3.78)	11.72 (11.34)	13.40 (13.63)
Cu[(OHACPHOX) <sub>1</sub> (SALSC) <sub>1</sub> (H <sub>2</sub> O) <sub>1</sub> ]	Green	482.54	71.45	13.16 (12.93)	39.78 (39.64)	3.73 (3.56)	11.60 (11.41)	13.26 (13.32)

**Table 6: Thermodynamic properties of complexes**

Ligand/Complex	Temperature (°C)	% Mass loss found	DSC peak in °C Endo/Exo	$\Delta H$ in $\text{J g}^{-1}$	$\Delta S^\# = -\Delta H/T$	$\Delta G = \Delta H - T\Delta S$
Co[(OHACPHOX) <sub>1</sub> (SALSC) <sub>1</sub> (H <sub>2</sub> O) <sub>1</sub> ]	50-200	4.485	219.33	-423.47	1.9307	847.46
	201-300	46.383				
	301-457.8	11.832				
Ni[(OHACPHOX) <sub>1</sub> (SALSC) <sub>1</sub> (H <sub>2</sub> O) <sub>1</sub> ]	70-200	3.064	298.62	-111.54	0.373	-222.92
	201-300	27.342				
	301-487	39.132				
Cu[(OHACPHOX) <sub>1</sub> (SALSC) <sub>1</sub> (H <sub>2</sub> O) <sub>1</sub> ]	50-150	3.685	266.95	-205.97	0.7715	-411.94
	151-275	10.243				
	276-400	32.542				

### CONCLUSION

The ligand salicylaldehyde semicarbazone is tridentate coordinating through 'N' and 'O' while ortho hydroxy acetophenone oxime is a bidentate ligand coordinating through 'N' and 'O'. Analytical data, electronic spectra, magnetic susceptibility, IR spectral data reveal octahedral geometry for all the complexes. The conductance values show electrolytic behavior of the complexes. The ligands and its all complexes were tested for antimicrobial activity. The complexes shows moderate to good antibacterial and antifungal activity compared to its ligand. On the basis of spectral evidence, the following probable structures have been assigned for synthesized compounds.

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