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SYNTHESIS AND CHARACTERIZATION STUDY OF MIXED LIGAND COMPLEXES OF O, N AND S DONAR LIGANDS

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ABSTRACT

A series of mixed ligand Salicylaldehyde phenyl hydrazine complexes with a general formula $[ML_1L_2]$, where M = Co(II), Ni(II), and Cu(II), L_1 = Salicylaldehyde phenyl hydrazine, and L_2 = salicylaldehyde thiosemicarbazone have been prepared and characterized by elemental analysis, FTIR and UV spectroscopy, magnetic moment, and conductance analysis. The infrared spectra showed that symmetrical tridentate coordination occurred with the oxygen, nitrogen and sulfur atoms. The electronic spectra, elemental analysis, and magnetic moment results proved that the complexes adopted octahedral geometry. The conductance measurement showed that the complexes are non electrolytes proving their nonionic nature. The complexes were subjected for anti-microbial and anti –fungal screening.

KEYWORDS:- Mixed ligand complexes, phenyl hydrazine, salicylaldehyde and thiosemicarbazone.

INTRODUCTION

Schiff bases are aldehyde- or ketone-like compounds in which the carbonyl group is replaced by an imine or azomethine group.[1] Schiff bases are versatile ligands synthesized from the condensation of an amino compound with carbonyl compounds[2,3,4] and were first reported by Hugo Schiff in 1864. Formation of Schiff base generally takes place under acid or base catalysis or with heat. The common Schiff bases are crystalline solids, which are feebly basic but at least some form insoluble salts with strong acids.[6] Today, Schiff bases are used as intermediates for the synthesis of amino acids or as ligands for preparation of metal complexes having a series of different structures.[7] In recent decades, hydrazone compounds

have attracted lots of attention not only because of their variety of structure, but also for their various biological and chemical applications[7,8,9] These properties of the hydrazones are attributed to the formation of stable chelated complexes with transition metals which catalyze physiological processes. Their metal complexes, have also found applications in various chemical processes like nonlinear optics, sensors, medicine.[10,11] Hydrazones and their metal complexes exhibit wide range of biological and pharmaceutical activities that includes antimicrobial, anti tuber culostatic, anticancer and antioxidant behavior. In addition, hydrazones also serve as an excellent poly dendate chelating agent capable of forming coordination complexes with variety of both transition and inner transition metal cations. Metal complexes derived from hydrazides of carboxylic acids have been extensively investigated due to the high physiological activities of the free ligands and the presence of a chelatophore group of donor atoms in the coordination sphere.[12-15] Nowadays, increasing cancer cases have been in a worrying trend and it has become one of the principal causes of death in most of the countries. It is the second most common disease after cardiovascular diseases, responsible for maximum numbers of deaths all over the world. The modernization of our society is a major factor contributing to the increasing incidence of cancer.[16-19] In this paper salicylaldehyde phenyl hydrazine and salicylaldehyde thiosemicarbazone ligands were synthesized by the reported methods, then mixed ligand complexes of transition metals Mn(II), Co(II), Ni(II), and Cu(II), were prepared by mixing 1:1:1 quantities of metal chloride, salicylaldehyde phenyl hydrazine and salicylaldehyde thiosemicarbazone. The synthesized complexes were characterized by elemental analysis, FTIR and UV spectroscopy, magnetic moment, and conductance analysis.

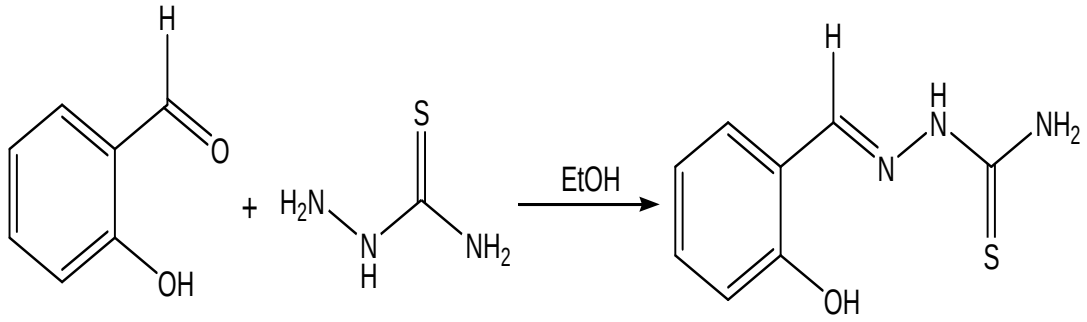
MATERIALS AND METHODS

The compounds metal chlorides, salicylaldehyde, phenyl hydrazine, thiosemicarbazide used were of analytical grade. The amount of metals are determined volumetrically by using EDTA complexometrically. IR spectra of the complexes were recorded on JASCO 6700 make FTIR spectrophotometer in the region 400-4000 cm^{-1}, electronic spectra were recorded on JASCO 670 UV-Visible spectrophotometer in the range 200-1400 nm from our DST funded Instrumentation Laboratory. Antimicrobial activities were determined by using three anti microbial nutrients from department of Microbiology Pratap College, Amalner.

Synthesis of Ligands

1. Salicylaldehyde thiosemicarbazone

Dissolve one gram. thiosemicarbazide hydrochloride and 1.5 gram of crystallized sodium acetate in 8-10 ml distilled water, Then add 0.5 gram of aldehyde or ketone and shake well. If the solution is turbid, add Alcohol or water until a clear solution is obtained. Heat the mixture on water bath for 10 to 15 minutes. Shake well and allow to stand for 10 minutes. The semicarbazone crystallizes from the cold solution on standing. Then cool the reaction mixture ice water. Filter the crystal on Buchner funnel; wash the precipitate with cold water. The solid product was recrystallized from hot ethanol and record the melting point.



2. Salicylaldehyde phenylhydrazone

Dissolve one ml. of phenyl hydrazine in 5ml ethyl alcohol. Take one gm. of sodium acetate dissolve it in 5ml distilled water and add it in to the above solution of phenyl hydrazine. Then take one ml of salicylaldehyde and dissolve it in 5ml of ethyl alcohol and transfer this solution in the above reaction mixture small quantity at a time with constant stirring, clear solution is obtained. Then reflux this reaction mixture on heating mental for 30 minutes. White crystals separates out form solution. Filter, wash with ethyl alcohol. Recrystallized from ethyl alcohol. dry and record the melting point.

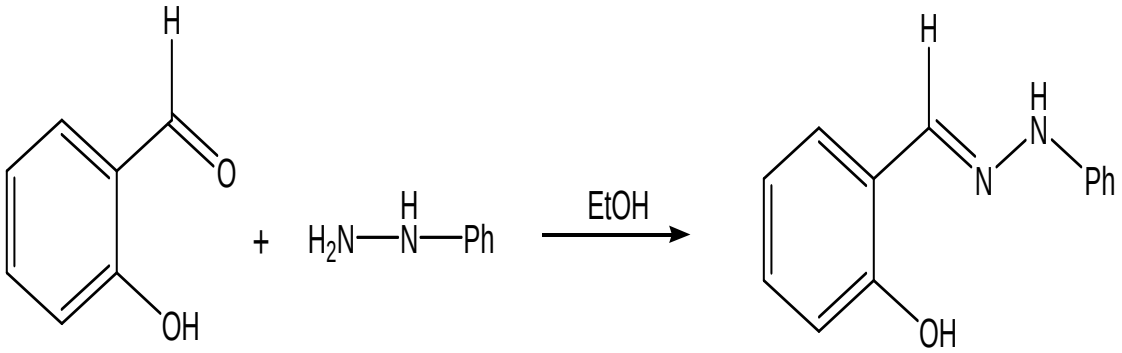


Table 1: The physical properties of ligands.

Ligand	Mol. Formula	Mol. wt	Melting point ^{0}C	Method of purification
Salicylaldehyde thiosemicarbazone (SALTSC)(L_1)	$C_8N_30SH_9$	195	210	Ethyl alcohol
Salicylaldehyde phenylhydrazone (SALPHH)(L_2)	$C_{13}N_20H_{12}$	212	145	Ethyl alcohol

Synthesis of metal complexes

1. Synthesis of metal complexes of type $M(L_1)_2$

In the synthesis of all the transition metal complexes, the following general procedure was used.

To 0.01M alcoholic solution of metal chloride a 0.02M alcoholic solution of salicylaldehyde semicarbazone 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^{0}C for four hours. 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.

2. Synthesis of metal complexes of type $M(L_2)_2$

In the synthesis of all the transition metal complexes, the following general procedure was used.

To 0.01M alcoholic solution of metal chloride a 0.02M alcoholic solution of salicylaldehyde phenyl hydrazone was added with continuous stirring at room temp, a clear solution was obtained. Then the reaction mixture was refluxed on a heating mental at about 60-70^{0}C for four hours. 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.

3. Synthesis of mixed ligand metal complexes of type ML_1L_2.

In the synthesis of all the transition metal complexes, the following general procedure was used.

To 0.01M alcoholic solution of metal chloride mixture of 0.01M alcoholic solution of salicylaldehyde thiosemicarbazone and alcoholic solution of 0.01M salicylaldehyde phenyl

hydrazone was added with continuous stirring at room temp. to get clear solution. Then the reaction mixture was refluxed on a heating mental at about 60-70^{0}C for four hours. 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.

RESULTS AND DISCUSSION

Analytical properties

The mixed ligand complexes obtained having different colors, their physical properties are listed in table 2. These complexes were insoluble in chloroform, carbon tetrachloride, methanol, ethanol but soluble in DMF and DMSO. For the conformation of the formation of the mixed ligand complexes $ML_1 L_2$, the TLC of the mixed ligand complexes with $M(L_1)_2$ and $M(L_2)_2$ was taken. It shows that the R_f value of mixed ligand complexes is being intermediate of the two corresponding symmetrical bis-complexes.

Table 2: Physical properties of complexes.

Sr. No.	Complex	Colour	Mole. Wt	% Yield Of the comp.	% of metal (Calculated)	% of C	% of H	% of N	% of S
1	[Co(SALTSC) (SALPHH)(H_2O)] Cl_2	Brown	553.93	71	10.69 (10.63)	45.41 (45.49)	4.13 (4.15)	12.58 (12.63)	5.81 (5.77)
2	Ni(SALTSC) (SALPHH)(H_2O)] Cl_2	Faint Green	553.69	73	10.70 (10.59)	45.55 (45.61)	4.19 (4.15)	12.55 (12.63)	5.69 (5.77)
3	[Cu(SALTSC) (SALPHH)(H_2O)] Cl_2	Green	558.54	78	11.41 (11.37)	45.02 (45.11)	4.07 (4.11)	12.47 (12.53)	5.65 (5.72)

Spectral properties

1. Electronic spectra

Electronic absorption spectra are generally supporting the results obtained for the structural investigation by other methods. The electronic spectral measurement was used for determining the stereochemistry of metal ions in the complex based on the positions and number of d-d transitions peaks. The electron absorption spectra of the Schiff bases and its Co (II), Ni (II) and Cu (II) complexes were recorded at room temperature.

Table 3: The electronic spectra of mixed ligand complexes in cm^{-1}.

Sr.no	Name of the complex	ν_1	ν_2	ν_3
1	[Co(SALTSC)(SALPHH)(H_2O)]Cl_2	1147	644	309
2	Ni(SALTSC)(SALPHH)(H_2O)] Cl_2	1119	853	384
3	[Cu(SALTSC)(SALPHH)(H_2O)] Cl_2	1000	578	307

Three bands are observed at 1147, 644 and 309 in the electronic spectrum of Co (II) complex assigned to $^4T_{2g}$ (F) $\leftarrow$ $^4T_{1g}$ (F), $^4A_{2g}$ (F) $\leftarrow$ $^4T_{1g}$ (F), $^4T_{1\ g}$(P) $\leftarrow$ $^4T_{1g}$(F) transition which is in conformity with octahedral geometry. Nickel (II) complexes show absorption bands at 1119, 853 and 384 attributed to the transitions $^3A_{2g}$ (F) $\rightarrow$ $^3T_{2g}$ (F), $^3A_{2g}$ (F)$\rightarrow$ $^3T_{1g}$ (F) and $^3A_{2g}$(F)$\rightarrow$ $^3T_{1g}$ (P), respectively, are expected for d^8 system in octahedral field . Copper complexes shows absorption bands at 1000, 578 and 307 and ratio v2/v1 of 1.868 supports octahedral configuration.

IR spectra

In the IR spectra of the mixed ligand complexes the bands at 1344-1385cm^{-1} may be assigned to the symmetric and asymmetric $v_{(N-H)}$ vibrations. A strong band in the region 1661-1697cm^{-1} are due to v(C=O) groups. On complex formation, the position of these bands is shifted toward lower side as compared to the metal free ligand. This indicates that the coordination takes place through the nitrogen and oxygen atom of the(C=N) (C=S) and (C=O) groups. A broad band appears in the region at 3698-3710cm^{-1} be attributed to the coordinated water molecule The presence of metal oxygen bond is observed in the range 448-471 cm^{-1}, while metal nitrogen bonding is observed in the range 592-594 cm^{-1}.

Table 4: IR spectra of Ligand and Complexes.

Sr. no	Name of the complex	v_{-OH}	v_{N-H}	v_{NH2}	$v_{C=O}$	$v_{C=N}$	$v_{C=S}$	V_{M-O}	V_{M-N}
1	SALTSC		1344	3286	1691	1598	1154	-	-
2	SALPHH		1385	3350	-	1536		-	-
3	[Co(SALTSC)(SALPHH)(H_2O)]Cl_2	3698	1354	3303	1667		1152	469	592
4	Ni(SALTSC)(SALPHH)(H_2O)] Cl_2	3710	1327	3373	1662	1589	1149	471	594
5	[Cu(SALTSC)(SALPHH)(H_2O)]Cl_2	3708		3373	1661	1569	1150	448	592

Molar Conductivity and Magnetic susceptibility

On measurement of magnetic susceptibility, structure of complexes has been assigned. In which the complexes of Co(II), Ni (II) and Cu(II), shows paramagnetic nature and have octahedral structural arrangement. While conductometric measurement shows electrolytic behaviour of complexes as shown in the following table.

Table 5: Molar Conductivity and magnetic susceptibility of complexes.

Complex	Molar Conductance(ohm^{1}cm^{2}mol^{-1})	μeff (B.M.)
[Co(SALTSC)(SALPHH)(H_2O)]Cl_2	69.12	3.421
Ni(SALTSC)(SALPHH)(H_2O)] Cl_2	51.83	3.912
[Cu(SALTSC)(SALPHH)(H_2O)]Cl_2	60.48	2.030

Microbiological activities

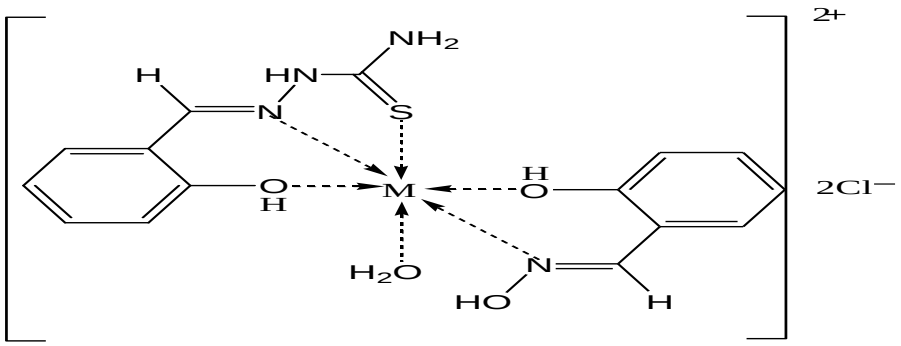
The compound synthesized in the present investigation has been subjected to antimicrobial screening programs based on their structural features so as to ascertain their activity against five different microorganisms *E.coli., Baciullus Sp Staphylococcus sp.,*

The solvent used was DMSO, and the sample concentrations were, 100ppm. The results of preliminary study on antimicrobial activity indicated that most of the complexes show moderate activity against these organisms.

Table 6: Microbiological activities (zone inhibition in mm).

Ligand/Complex	*E.coli.*	*Baciullus Sp.*	*Staphyloc-occus sp.*
SALTSC	10	08	09
SALPHH	10	12	13
[Co(SALTSC)(SALPHH)(H_2O)]Cl_2	14	13	16
Ni(SALTSC)(SALPHH)(H_2O)] Cl_2	13	16	-ve
[Cu(SALTSC)(SALPHH)(H_2O)]Cl_2	12	14	17

By considering all the above properties of the mixed ligand complexes the structure of the metal complexes should be as given below



Where M=Co,Ni and Cu

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