

Synthesis and Physicochemical Studies of Mixed Ligand Complexes of Salicylaldehyde Anthranilic Acid and Salicylaldehyde Semicarbazone

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ABSTRACT: The mixed ligand complexes of the type $[ML_1L_2]Cl_2$ have been synthesized, by the reactions of metal chlorides with two different ligands in 1:1:1 molar ratios. [Where L_1 =Salicylaldehyde anthranilic acid(SAA) and L_2 =Salicylaldehyde semicarbazone. The resulting products have been characterized on the basis of elemental analysis, magnetic measurement, IR and Electronic spectra, conductivity measurement, thermal analysis, antimicrobial activities. The metal complexes shows octahedral nature bonding through oxygen and nitrogen donor atoms.

KEYWORDS:- Mixed ligand complexes, semicarbazone, salicylaldehyde and anthranilic acid.

I.INTRODUCTION

In the present study semicarbazone constitute one of the most important classes of Oxygen and nitrogen donor ligands. The formation of a variety of metal complexes from these ligands indicates the spectacular progress in co-ordination and bioinorganic chemistry to the real impetus towards developing.

Co-ordination chemistry of these ligands was probably provided by the remarkable antitumor, antiviral, anticancer, anti malaria, anti fungal and antibacterial activities. They were also found to be useful as potential drugs and the fungicidal agents. The antibacterial and fungicidal activities of transition metal complexes are due to their ability to form chelate with the essential metal ions bonding through nitrogen and oxygen donor as ligands.

In view of the above applications, synthesis and characterization and biochemical studies of series Co (II), Ni (II), Cu (II) complexes obtained from Salicylaldehyde anthranilic acid and salicylaldehyde semicarbazone is carried out. Salicylaldehyde anthranilic acid and Salicylaldehyde semicarbazone both are tridentate ligand with O and N as donor atoms. According to the IUPAC recommendations for the nomenclature of organic compounds, derivatives of semicarbazide of the types $R-CH-N-NH-CO-NH_2$ and $R_1R_2C-N-NH-CO-NH_2$ which are usually obtained by condensation of semicarbazide with suitable aldehydes and ketones, may be named by adding the class name 'semicarbazone'[1].

II.OBJECTIVES AND SCOPE OF THE PRESENT WORK

There has been considerable interest in the studies of semicarbazone due to their coordination modes when bound to metals .the wide applications and structural diversity of metal complexes of semicarbazone and anthranilic acid encouraged us to synthesize the tridentate ONO-donor salicylaldehyde semicarbazone and ONO -donor salicylaldehyde anthranilic acid ligands and their metal complexes. Metal complexes of salicylaldehyde semicarbazone and anthranilic acid, ligands with transition metal as (ML_2) complexes have been already reported in early days.

Due to good chelating ability, the present work is mainly concerned on the studies of mixed ligand complexes of Co(II),Ni(II) and Cu(II) with two novel ligands salicylaldehyde semicarbazone $[L_1]$ salicylaldehyde anthranilic acid, $[L_2]$ in the ratio 1:1:1.

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The synthesised complexes are characterised by elemental analysis, study of IR and electronic spectra, biological activities, magnetic properties, conductivity measurement.

The compositions of these complexes were determined by the CHN and S analyses. For the characterization of these compounds we have used IR and UV spectral studies. We have synthesized 3d transition metal complexes of Co (II), Ni (II) and Cu (II) with salicylaldehyde semicarbazone [L1] salicylaldehyde anthranilic acid, [L2] in the ratio 1:1:1.

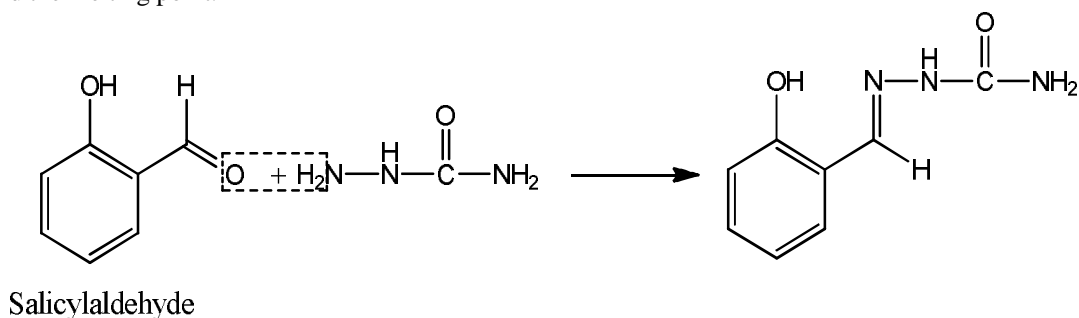
III. MATERIALS AND METHODS

The compounds salicylaldehyde, anthranilic acid and semicarbazide hydrochloride and metal chlorides of used were of analytical grade. The amount of metal is determined complex metrically by EDTA suitable indicator metal ions. Carbon, hydrogen and nitrogen analysis were carried from SAIF, Mumbai. Specific conductance were measured at room temperature in DMF by a Systronics direct reading 304 conductivity meter using a glass conductivity cell having a cell constant 1.0. IR spectra were taken on JASCO 6600 FTIR SPECTROPHOTOMETER and JASCO - 670 -UV SPECTROPHOTOMETER from Central Research Laboratory, Pratap College, Amalner. Thermo gravimetric analysis was performed on STA 6000 from Department of Physics, Pratap College, Amalner. Microbial activities were carried out from PG Department of Microbiology, Pratap College, and Amalner.

Synthesis of Ligands: Ligands L1 and L2 were prepared. The methods of their preparation are given below.

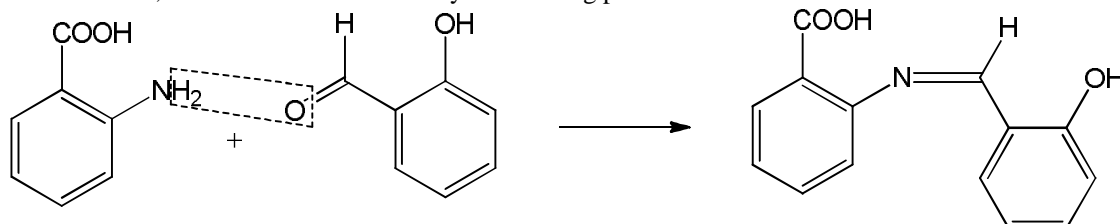
L₁. Salicylaldehyde Semicarbazone:

This ligand used in this study was prepared by well known following method. Dissolve one gram. Semicarbazide hydrochloride and 1.5 gram of crystallized sodium acetate in 8-10 ml distilled water, then add 0.5 gram of salicylaldehyde and shake well. Solution becomes turbid, add ethyl 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 in ice water. Filter the crystal on buchner funnel; wash the precipitate with cold water. The solid product was recrystallized from ethanol and record the melting point.



2. Salicylaldehyde Anthranilic Acid (SAA)

For preparation of this ligand 0.1molar solution of salicylaldehyde is prepared in 25ml ethyl alcohol and 0.1mol.anthranilic acid prepared in 25ml ethyl alcohol and were mixed together. The reaction mixture is acidified by 3-4 drops of glacial acetic acid. Then the reaction mixture was reflux on water bath for two hour.The precipitated compound was filtered, washed with cold water dry and melting point was recorded.



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The physical properties of ligands are listed in following Table.

Ligand	Mol. Formula	Mol. wt	Melting point	Method of purification
Salicylaldehyde Anthranilic Acid(SAA)(L ₁)	C ₁₄ N ₁ O ₃ H ₁₁	241	282	Recrystallization from ethanol
Salicylaldehyde Semicarbazone(SALSC)(L ₂)	C ₈ N ₃ O ₂ H ₉	179	228	Recrystallization from ethanol

Synthesis Of complexes

1) Preparation of M (L₁)₂ and M (L₂)₂ complexes:

Aqueous 25 ml(0.01M) solution of metal chloride were mixed slowly with hot alcoholic 25 ml(0.02M)solution of salicylaldehyde anthranilic acid (L₁)with constant stirring. The reaction mixture is heated in water bath for three hours. Then the reaction was stirred for further one hour after which colours .Solid product was obtained, which was then washed with ethanol and dried in air. Similarly, the complexes of metals were prepared by mixing solution of corresponding metal chlorides and semicarbazone ligand (L₂) in 1:2 molar ratio respectively.

2) Preparation of mixed ligand complexes the type ML₁L₂:

To a 20ml (0.02M) ethanolic solution of metal chloride, a mixture of 20ml (0.02M) methanol solution of salicylaldehyde anthranilic acid and Salicylaldehyde semicarbazone with constant stirring. This reaction mixture is refluxed in water bath for 3 to 4 hours on a heating mantle at about 60-70°C. The colored complex separates out from solution on cooling filter. Then product was filtered, wash with methanol dry and record the yield of the complex.

IV.RESULT AND DISCUSSION

The resulting complexes were having different colors as given in the table II. They are insoluble in chloroform, carbon tetrachloride, methanol, ethanol but soluble in DMF. The properties of complexes are indicated in table II. The TLC of the mixed ligand complexes exhibit single spots with 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. From the magnetic moments these complexes shows octahedral geometry. The conductance of the complexes are very low(33.31.124.92Ω⁻¹cm²mol⁻¹) indicating their non-electrolyte nature.

The resulting complexes were having different colors as given in the table II.

Table II: Characterization data of the complexes

Sr. No	Ligand/ Complex	Color	Mol. Wt	%Yield of complex	%of metal	%of C	%of H	%of N	%of O
1	Co(SAA) ₁ SALSC) ₁]Cl ₂	Brown	549.93	78.67	10.71 (10.74)	48.00 (47.67)	3.63 (3.66)	10.18 (10.28)	14.45 (14.41)
2	[Ni(SAA) ₁ SALSC) ₁]Cl ₂	Yellow	549.69	67.25	10.67 (10.63)	48.02 (48.17)	3.63 (3.59)	10.18 (10.11)	14.55 (14.53)
3	Cu[(SAA) ₁ SALSC) ₁] Cl ₂	Green	554.54	71.16	11.45 (11.57)	47.60 (47.69)	3.60 (3.67)	10.09 (10.01)	14.42 (14.38)

The amount of metals present in complexes was determined volumetrically by EDTA using double burette technique for optimum utilization of reagents. Indicator xylenol orange for Co(II) and mureoxide for Ni(II) and Cu(II). Carbon,

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hydrogen and nitrogen analysis were carried from SAIF, Mumbai AND Central Instrumentation Laboratory, Pratap College, Amalner. Specific conductance were measured at room temperature in DMF by a Systronics direct reading 304 conductivity meter using a glass conductivity cell having a cell constant L_1 and L_2 . IR spectra of the complexes were recorded on JASCO 6700 FTIR instrument using KBr pellets in the region $400-4000\text{ cm}^{-1}$ from Department of Physics, Pratap College, Amalner and Central Instrumentation Laboratory, Pratap College, Amalner. The spectral data of complexes is shown in table III. Electronic spectra of complexes were recorded on JASCO -670 UV-VISIBLE Spectrophotometer in the Department of Chemistry, Pratap College, Amalner. The spectral data of complexes is shown in tableIV. Thermo gravimetric analysis was carried out on Perkin Elmer STA 6000 from Department of Chemistry Pratap College, Amalner. Antimicrobial activities are determined in the PG department of Microbiology, Pratap College, and Amalner by using three microbial nutrients.

IR SPECTRA

Table: III

Sr.no	Name of the complex	$\nu\text{-OH}$	$\nu\text{-N-H}$	νNH_2	$\nu\text{C=O}$	$\nu\text{C=N}$	$\nu\text{C-O}$	$\nu\text{C-H}$	$\nu\text{M-N}$
1	SAA	3287	3191	2926	1668	1602	1361		
2	SALSC	3342	3156	3128	1686	1591	1434	1264	
6	$[\text{Co}(\text{SAA})_1(\text{SALSC})_1]\text{Cl}_2$	3291	3198	3055	1671	1613	1365	1190	549
7	$[\text{Ni}(\text{SAA})_1(\text{SALSC})_1]\text{Cl}_2$	3291	3187	3066	1671	1602	1361	1090	536
8	$[\text{Cu}(\text{SAA})_1(\text{SALSC})_1]\text{Cl}_2$	3283	3187	2933	1671	1598	1495	1184	549

In the IR spectra of the mixed ligand complexes the bands at $1591-1602\text{ cm}^{-1}$ may be assigned to the symmetric and asymmetric $\nu(\text{C=N})$ vibrations. A strong band in the region $1671-1686\text{ cm}^{-1}$ are due to $\nu(\text{C=O})$ 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) and (C=O) groups. Band appearing in the region at $3283-3342\text{ cm}^{-1}$ is due to presence of phenolic -OH group. The band at $3187-3198$ indicates presence of -NH group. The band in the region $536-549\text{ cm}^{-1}$ shows M-N band.

MAGNETIC PROPERTIES

Table IV. Magnetic moment and molar conductance values of the complexes

Sr. No	Name of the Complex	Magnetic moment	Molar cond. $\Omega\text{ cm}^2\text{ mol}^{-1}$ at
1	$[\text{Co}(\text{SAA})_1(\text{SALSC})_1]\text{Cl}_2$	4.192	33.31
2	$[\text{Ni}(\text{SAA})_1(\text{SALSC})_1]\text{Cl}_2$	3.592	61.02
3	$[\text{Cu}(\text{SAA})_1(\text{SALSC})_1]\text{Cl}_2$	2.121	124.02

The conductance of the complexes are very low (33.31 to $124.02\text{ }\Omega\text{-cm}^2\text{mol}^{-1}$) indicating their non-electrolyte nature. From the magnetic moments these complexes shows octahedral geometry.

THE ELECTRONIC SPECTRA

Table V: Electronic Spectra of complexes.

Sr.no	Name of the complex	ν_1	ν_2	ν_3	ν_2/ν_1
1	$[\text{Co}(\text{SAA})_1(\text{SALSC})_1]\text{Cl}_2$	8771	17035	28818	1.942
2	$[\text{Ni}(\text{SAA})_1(\text{SALSC})_1]\text{Cl}_2$	11273	20790	31948	1.844
3	$[\text{Cu}(\text{SAA})_1(\text{SALSC})_1]\text{Cl}_2$	8718	16286	26315	1.868

Electronic absorption spectra are often helping in the evaluation of result furnished by other methods of structural investigation. The electronic spectral measurement was used for assigning 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.

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Three bands are observed at 8771, 17035 and 28818 cm^{-1} in the electronic spectrum of Co (II) complex assigned to ${}^4\text{T}_{2g}(\text{F}) \leftarrow {}^4\text{T}_{1g}(\text{F})$, ${}^4\text{A}_{2g}(\text{F}) \leftarrow {}^4\text{T}_{1g}(\text{F})$, ${}^4\text{T}_{1g}(\text{P}) \leftarrow {}^4\text{T}_{1g}(\text{F})$ transition which is in conformity with octahedral geometry.

Nickel (II) complexes show absorption bands at 11273 cm^{-1} , 27790 cm^{-1} and 31948 cm^{-1} attributed to the transitions ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{2g}(\text{F})$, ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{F})$ and ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{P})$, respectively, are expected for d^8 system in octahedral field.

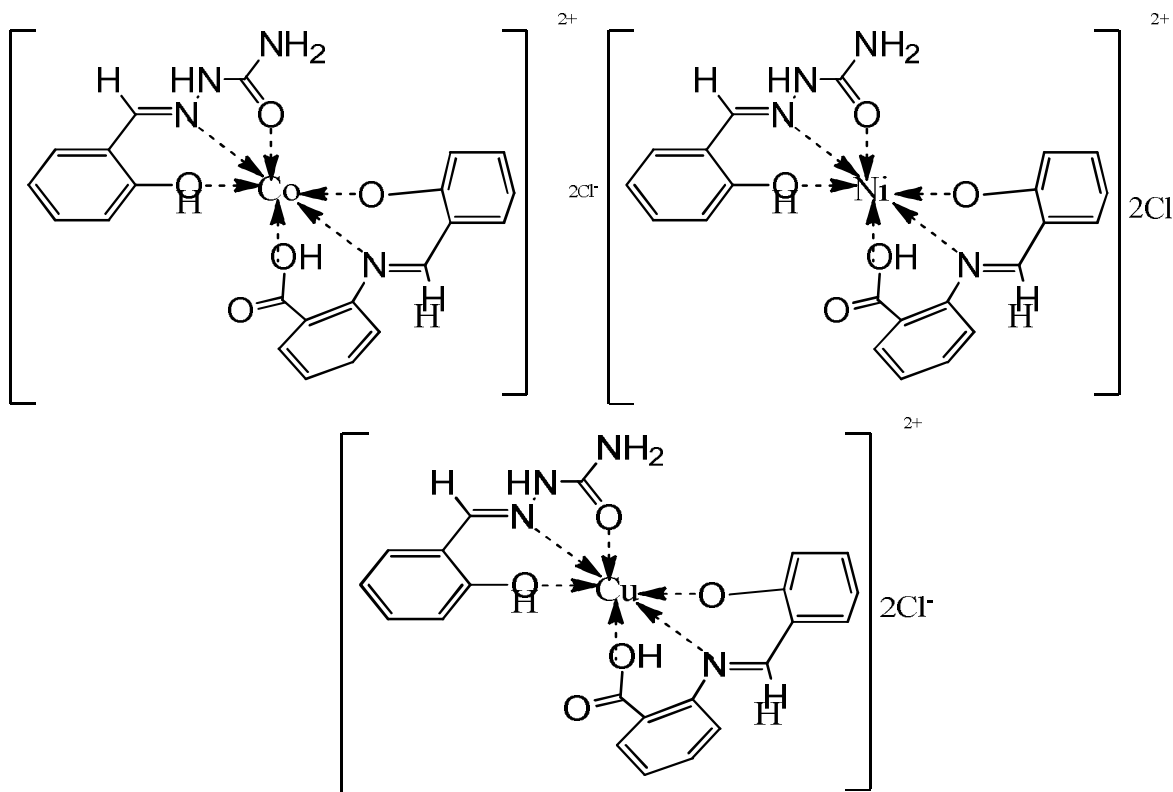
Copper complexes shows absorption bands at 8718, 16286 and 26315 cm^{-1} and ratio ν_2/ν_1 of 1.868 supports octahedral configuration.

BIOLOGICAL ACTIVITIES

Sr.no	Name of the complex	E-coli	Bacillus	Staphs
1	SAA	+ve	+ve	+ve
2	SALSC	+ve	+ve	+ve
3	[Co(SAA)1(SALSC)1Cl ₂	+ve	+ve	+ve
4	[Ni(SAA)1(SALSC)1Cl ₂	+ve	-ve	+ve
5	[Cu(SAA)1(SALSC)1Cl ₂	+ve	-ve	+ve

From the antimicrobial studies it inferred that, the Schiff bases was found to be potentially active against E. coli, P.aeruginosa and Aspergilla's Niger .Some of the complexes shown high antimicrobial activity against E.Coli, Pseudomonas and Aspergilla's Niger .This enhancement in the activity of the metal complexes can be explained on the basis of chelation theory .

STRUCTURE OF COMPLEXES



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