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A STUDY OF MIXED LIGAND COMPLEXES OF ANTHRANILIC ACIDSEMICARBAZONE AND BENZALDEHYDE WITH Co(II), Ni(II) AND Cu(II)

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ABSTRACT

Anthranilic acid and benzaldehyde semicarbazone have the ability to form complexes with the metal ions, which were found to be important for various applications. In the present study, the attempts were carried to form complexes of anthranilic acid and benzaldehyde semicarbazone as ligands with Cobalt chloride ($CoCl_2$. $6H_2O$), Nickel chloride $NiCl_2$. $6H_2O$ and Copper chloride ($CuCl_2$. $5H_2O$), in the molar ratio 1:1:1. The resulting complexes have been characterized on the basis of elemental analysis, magnetic measurement, IR and UV spectral analysis, conductivity measurement, thermal analysis, antimicrobial activities. Analysis of results reviles that the complexes shows octahedral geometry, electrolytic nature and having more antimicrobial activity than the ligands. The ligands are bonded through oxygen and nitrogen.

KEYWORDS: Anthranilic acid, benzaldehyde, semicarbazone oxygen and nitrogen.

INTRODUCTION

Anthranilic acid is one of important compound that have wide biological activity, as an important precursor of tryptophen. Anthranilic acid is used with some mono oxidation metals to studies the demeanor of potassium in the biological systems.[1] Complexes that anthranilic acid contain ligand have extensive biological activity, anti-inflammatory activities[2], Antibacterial activity[3] The metal complexes of semicarbazones play an essential role in agriculture, pharmaceutical and industrial chemistry and they are used as catalysts, in various biological systems, polymers and dyes, besides some uses antifertility and enzymatic agents. The biological properties of semicarbazones are often related to metal ion coordination.

Firstly, lipophilicity, which controls the rate of entry in to the cell, is modified by coordination.[4] Also, the metal complex can be more active than 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. Recently it has been shown that semicarbazones of aromatic and unsaturated carbonyl compounds have anticonvulsant properties.[5] Moreover, coordination may lead to significant reduction of drug-resistance.[6] They are also used as spectrophotometric agents as well for the analysis of metalions[7] and are frequently used in the qualitative organic analysis of carbonyl compounds[8] The characterization and quantitative investigation of the binding properties of amino acids towards transition metal ions plays an important role in our understanding of metal~protein interactions.[9] There are many reports on the metal-anthranilate complexes along with the structure of many of these compounds. Some transition metal anthranilates have capability for aren't hydrogenation.[10,11]

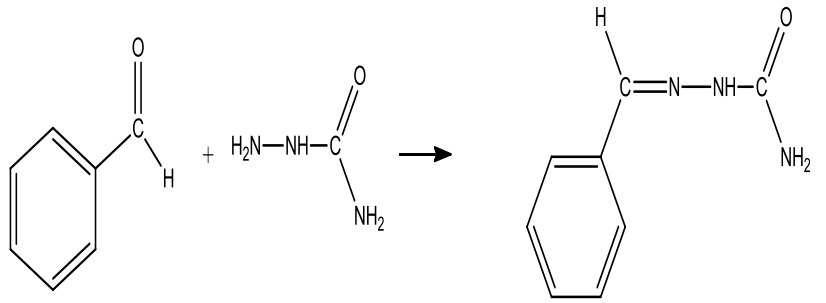
MATERIALS AND METHODS

The compounds, benzaldehyde, anthranilic acid, semicarbazide hydrochloride, Cobalt chloride ($CoCl_2$. $6H_2O$), Nickel chloride $NiCl_2$. $6H_2O$ and Copper chloride ($CuCl_2$. $5H_2O$) used were of analytical grade. The amount of metals are determined volumetrically by EDTA as a Complexometric titration. Carbon, hydrogen and nitrogen analysis were carried On Perkin Elmr CHNS analyser, IR spectra of the complexes were recorded on Jasco FTIR analyser and electronic spectra on Jasco uv-visible spectrophotometer from Central Instrumentation laboratory, Pratap College, Amalner. Antimicrobial activities are determined by using three microbial nutrients. Preparation of benzaldehyde semicarbazone ligand is as given below.

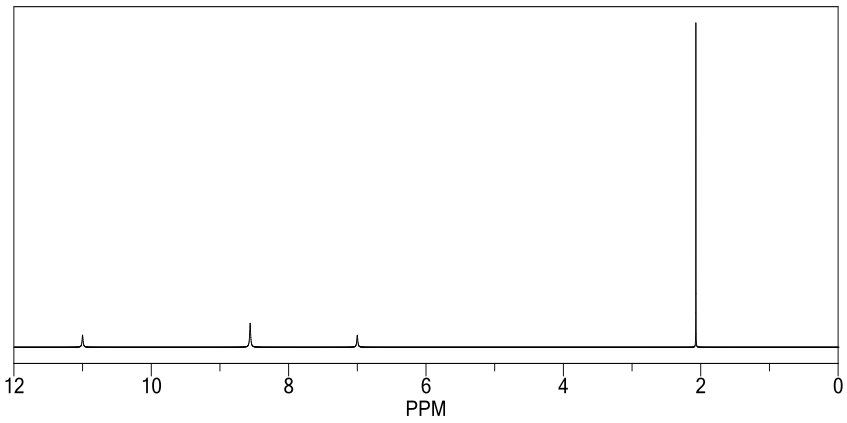
Synthesis of benzaldehyde semicarbazone(ligand L_1)

Dissolved 2 gm. of semicarbazide of hydrochloride & 3 gm. of crystallized sodium acetate In about 25-30ml distilled Water in hard glass test tube, to this solution add 1ml of benzaldehyde & shake well. If the mixture is turbid then add 1:1 ethyl alcohol until a clear solution is obtained. Than heat this reaction mixture in water bath for 10 mints. Than cool this solution & transfer into a beaker containing crashed ice. White crystals of the semicarbazone derivative Separates out from the solution. Filter the crystals & recrystallized from ethyl alcohol, dry and then melting point and yield is recorded.

Reaction

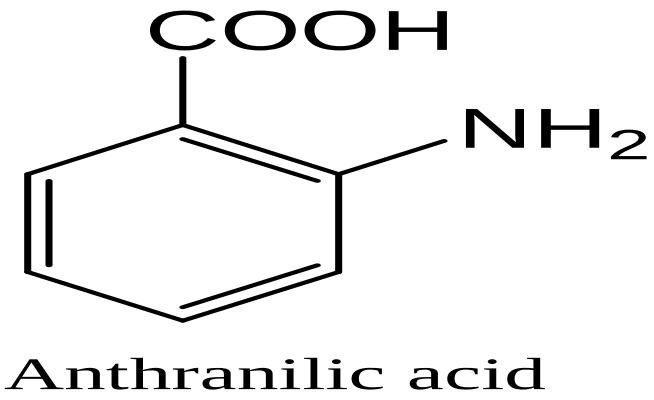


NMR Spectrum of Benzaldehyde semicarbazone



Sythesis of anthranilic acid (ligand L_2)

As anthranilic acid is easily available in market**,** SDfine make of analytical reagent grade anthranilic acid is used by recrystallizing it from aquous ethanol.



Anthranilic acid

NMR Spectrum of Anthranilic acid

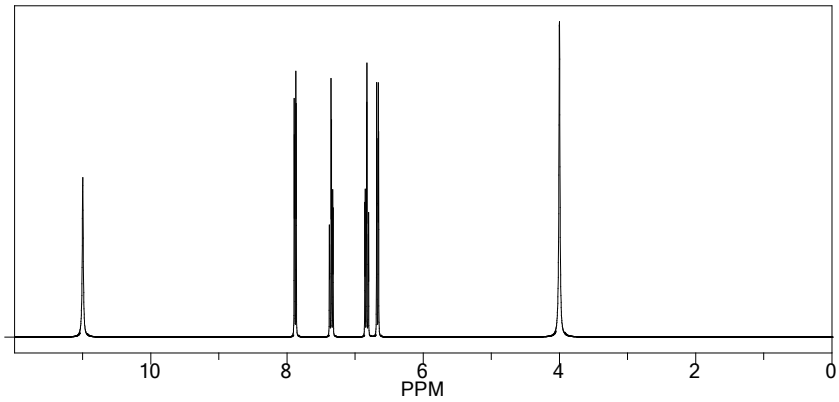


Table 1: The physical properties of ligands.

Name of ligand	Nature	Method of purification	Meltingpoint	
			°C(observed)	°C(reported)
Benzaldehyde semicarbazone	Yellowish Shining Crystals	Recrystallized from aq. Ethanol	225	225
Anthranilic acid	White Shining Crystals	Recrystallized from aq. Ethanol	60	60

Synthesis of transition metal complexes of the type $M(L_1)_2$

Ethanolic solutions of benzaldehyde semicarbazone and metal chloride are mixed together in in 1:2 molar praporation with continuous stirring at room temp, till 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 product was filtered on cooling, washed with methanol, dried under inert atmosphere and practical yield of complex is measured.

Synthesis of transition metal complexes of the type $M(L_2)_2$

For preparation of this complex ethanolic solution of anthranilic acid and ethanolic solution of metal chloride was mixed together in 1:2 molar proportions in a round bottom flaske with continuous stirring at room temperature. The clear shown was refluxed in a water bath for three hours. The colored solid complex separates out from solution. The solid product is filtered on cooling, washed with methanol, dried in inert atmosphere.

Synthesis of transition metal complexes of the type ML_1L_2

To methanolic solution of metal chloride a mixture of benzaldehyde semicarbazone and anthranilic acid ligands dissolved in hot methanol were added in molar ratio 1:1:1 with continuous stirring at room temp to get clear solution. Then the solution was refluxed on a on

water bath 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 physical properties the mixed ligand complexes are shown in the table 2. These complexes were insoluble in chloroform, carbon tetrachloride, methanol, ethanol but soluble in DMF. The TLC of the mixed ligand complexes with $M(L_1)_2$ and $M(L_2)_2$ with Mixed ligand complexes $ML_1\ L_2$ 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 Mixed ligand complexes.

Complex	Colour	Mole. wt	% Yield Of the comp.	% of metal (Calculated)	% of C	% of H	% of N
[Co(BZSC)(ANT)$(H_2O)_2$]Cl	Brown	430.19	64.38	(12.64) 12.09	21.83 (21.61)	(3.63) 3.60	(13.58) 13.24
[Ni(BZSC)(ANT)$(H_2O)_2$]Cl	Green	430.49	68.00	(12.65) 12.43	(21.81) 21.40	(3.63) 3.47	(13.56) 13.40
[Cu(BZSC)(ANT)$(H_2O)_2$]Cl	Gray	435.0	75.45	(13.50) 13.29	(21.58) 21.41	(3.59) 3.43	(13.42) 13.29

SPECTRAL PROPERTIES

Electronic Spectra

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.

Table 3: The electronic spectra of mixed ligand complexes.

Sr.no	Name of the complex	ν_1	ν_2	ν_3
1	BZSC	1196	678	316
2	ANT	1140	481	380
3	[Co(BZSC)(ANT)$(H_2O)_2$]Cl	1147	644	309
4	[Ni(BZSC)(ANT)$(H_2O)_2$]Cl	1119	853	384
5	[Cu(BZSC)(ANT)$(H_2O)_2$]Cl	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) ←$^4T_{1g}$ (F), $^4A_{2g}$ (F) ←$^4T_{1g}$ (F), $^4T_{1\ g}$(P) ←$^4T_{1g}$(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)→$_3T_{2g}$ (F), $_3A_{2g}$ (F)→ $_3T_{1g}$ (F) and $_3A_{2g}$(F)→$_3T_{1g}$ (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.

The electronic spectra of Cu(II) complexes exhibits bands in the range 1000,578 and 367cm^{-1} with $\nu_2/\ \nu_1$ ratio 1.417 corresponding to ^6A_1g→^4T_1g (^4G), ^6A_1g→^4E_2g (^4G), ^4A_1g (^4G) and ^6A_1g→^4E_2g(^4D) transitions, respectively suggesting octahedral environment around Cr(III) ion.

IR spectra

In the IR spectra of the mixed ligand complexes the bands at 1537- 1539cm^{-1}may be assigned to the symmetric and asymmetric ν(C=N) vibrations. A strong band in the region 1657-1686cm-1 are due to ν(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 3544--3652cm^{-1} is due to presence of -OH from water molecule. The band at 874-877 cm^{-1} indicates presence of metal mitrogen bonding while bands in the region 731-734 cm^{-1} shows presence of metal oxygen bonding.

Table 4: IR spectra of mixed ligand complexes.

Ligand/ Complex	$\nu_{OH\ (H2O)}$	$\nu_{C=O}$	$\nu_{C=N}$	ν_{N-H}	ν_{C-O}	ν_{M-N}	ν_{M-O}
BZSC		1645	1580				
ANT		1713	1571	1570	1379		
[Co(BZSC)(ANT)$(H_2O)_2$]Cl	3544	1657	1546	1079	1347	874	731
[Ni(BZSC)(ANT)$(H_2O)_2$]Cl	3592	1644	1539	1134	1358	879	734
[Cu(BZSC)(ANT)$(H_2O)_2$]Cl	3652	1651	1557	1114	1361	877	733

Electrical comductivity, Magnetic Properties and thermogravimetric analysis

Molar conductivity of the complexes is ranging from 51-69 $ohm^1cm^2mol^{-1}$, indicating electrolytic nature of the complexes. Thermo gravimetric analysis shows loss in wt in the

range 8.230-8.412 within the temp. Range 50-250^{0}C, indicating loss of two water molecules. Magnetic susceptibility values of the complexes shows octahedral geometry of the complexes.

Complex	TGA		Molar Conductance(ohm^{1}cm^{2}mol^{-1})	μeff (B.M.)
	Decomposition temp(± 5°C)	% loss		
[Co(BZSC)(ANT)(H_2O)$_2$]Cl	50-200	8.412.	69.12	3.432
[Ni(BZSC)(ANT)(H_2O)$_2$]Cl	50-200	8.390	51.83	3.812
[Cu(BZSC)(ANT)(H_2O)$_2$]Cl	100-250	8.230	60.48	2.130

Microbiological Activities

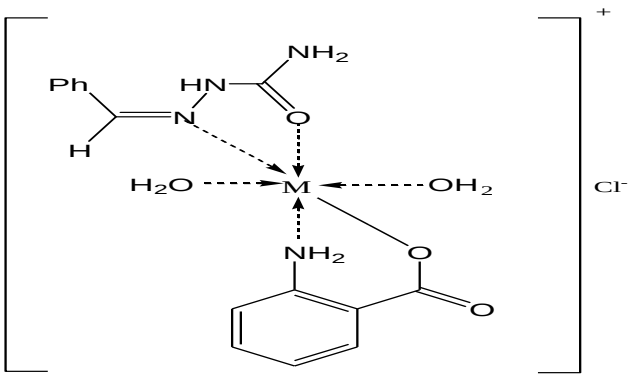
The compound synthesized in the present investigation has been subjected to antimicrobial screening programs based on their structural features so as to ascertain their activity against five different microorganisms *E.col., Baciullus Sp Staphylococcus sp., Pseudomonas Sp.and Proteus Sp.*

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 5: Microbiological activities (zone inhibition in mm).

Ligand/Complex	*E.coli.*	*Baciullus Sp.*	*Staphyloc-occus sp.*
BZSC	11	10	11
ANT	10	11	10
[Co(BZSC)(ANT)(H_2O)$_2$]Cl	10	10	10
[Ni(BZSC)(ANT)(H_2O)$_2$]Cl	12	12	10
[Cu(BZSC)(ANT)(H_2O)$_2$]Cl	10	10	10
[Co(BZSC)(ANT)(H_2O)$_2$]Cl	12	12	14

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(II),Ni(II) or Cu(II)

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