

SYNTHESIS AND PHYSICOCHEMICAL CHARACTERIZATION OF MIXED LIGAND COMPLEXES OF TRANSITION METALS WITH PYRUVIC ACID THIOSEMICARBAZONE

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ABSTRACT: The mixed ligand complexes of the type $[ML_1L_2]Cl_2$. Where L_1 =Pyruvic acid thiosemicarbazone L_2 = Benzaldehyde semicarbazone. These complexes have been synthesized, by the reactions of metal chlorides with two different semicarbazones in 1:1:1 molar ratios. 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 show ratio 1:1:1 with metal, ligand L_1 and ligand L_2 . The ligands are bonded through oxygen and nitrogen to metal ion.

KEYWORDS-: Mixed ligand complexes, semicarbazone, thiosemicarbazone, pyruvic acid, benzaldehyde, thermal analysis, antimicrobial analysis.

I. INTRODUCTION

The coordination compounds have been widely used in catalysis and as potential drugs in biological fields [1,2]. Thiosemicarbazones are highly reactive compounds which form chelate complexes with metal ions. There are many complexes with Sulphur and nitrogen as donor atoms [3]. Thiosemicarbazones possess beneficial biological activities. The biological activities of thiosemicarbazones are due to their ability to coordinate to metal centers in enzymes. Some pharmaceutically promising thiosemicarbazone derivatives have additional functional groups which are not coordinated to their "primary" metal ion. Thus biological activity is also dependent on the non-coordinating groups. Thiosemicarbazones have variable biological activities and prospective use as drugs [4] and therefore, thiosemicarbazones and their metal complexes have been explored for 50 years [5,6]. Thiosemicarbazones and their metal complexes have been studied widely for their variety of biological properties such as anticancer, antitumor, antifungal, antibacterial, antimalarial, antiviral and anti-HIV activities [7-14].

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 thiosemicarbazone encouraged us to synthesize the tridentate ONO-donor semicarbazone and ONS-donor thiosemicarbazone ligands and their metal complexes. Metal complexes of pyruvic acid semicarbazone, semicarbazone of acetone, acetophenone, Benzaldehyde, cyclohexane, O-hydroxyacetophenone and their derivatives as ligands with transition metal as (ML_2) complexes have been already reported in early days.

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Due to good chelating ability, the present work is mainly concerned on the studies of two novel semicarbazone, pyruvic acid thiosemicarbazone [L₁] and Benz aldehyde semicarbazone,[L₂]. The compositions of these semicarbazones 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 Cr (III),Mn (II),Fe(III),Co(II),Ni(II) and Cu(II) with pyruvic acid thiosemicarbazone[L₁] and Benz aldehyde semicarbazone,[L₂] in the ratio 1:1:1.

III.MATERIALS AND METHODS

The compounds pyruvic acid, benzaldehyde and semicarbazide hydrochloride and chlorides of Fe(III)used were of E MEARK ,BDH analytical grade. The amount of metal is determined

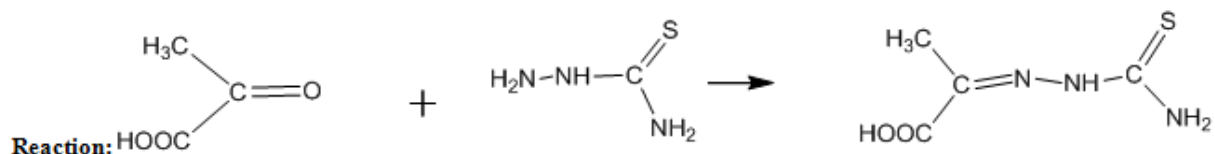
Complex metrically by EDTA suitable indicator metal ions. Carbon, hydrogen and nitrogen analysis were carried from SAIF, Mumbai. Specific conductance were measured at room temperature in DMF by a Systronics direct reading 304 conductivity meter using a glass conductivity cell having a cell constant.IR spectra were taken on JASCO 6600 FTIR SPECTROPHOTOMETER and JASCO - 670 -UV SPECTROPHOTOMETER from Central Research Laboratory, Pratap College, Amalner. . Thermo gravimetric analysis were performed on STA 6000 from Department of Physics, Pratap College, Amalner. Microbial activities were carried out from PG Department of Microbiology, Pratap College, Amalner.

Synthesis of Ligands : Ligands L₁ and L₂were prepared. The methods of their preparation are given below.

Ligand: L₁

PYRUVIC ACID THIOSEMICARBAZONE (PYTSC):

One mmole of pyruvic acid was added drop wise to the 20ml. methanolic solution of thiosemicarbazide (1mmole) with constant stirring. The reaction mixture was heated with reflux condenser for four hours. Then the reaction mixture is cooled to ambient temperature in a crushed ice. A light brown crystalline solid was formed. The product is filtered, washed and recrystallized from methanol, dried and melting point was recorded.



Ligand:L₂

3. BENZALDEHYDE SEMICARBAZONE (BZSC):

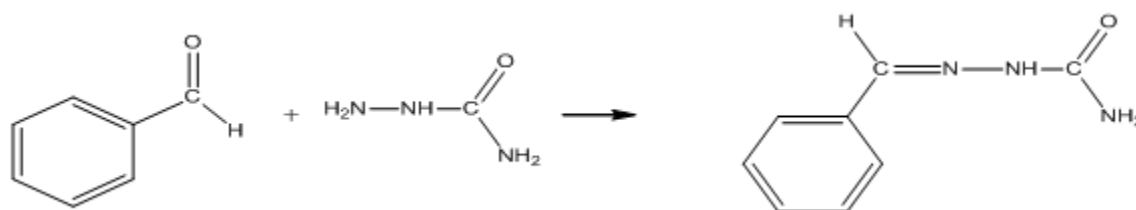
Dissolved 2 gm. of semicarbazide of hydrochloride &3 gm. of crystallized sodium acetate in about in about 25-30ml distilled water hard glass test tube to this solution add 1ml of Benz aldehyde and shake well .If the mixture is turbid then add 1:1 ethyl alcohol until a clear solution is obtained. Than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

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Reaction:



The physical properties of ligands

Table I

Name of the ligand	Color and nature	Method purification.	M.P. °c (observed)reported	Mol. wt	Molecular formula
Pyruvic acid semicarbazone	White shining crystals	Recrystallization from water	186 (186)	161	C ₄ H ₇ N ₃ O ₂ S
Benzaldehyde semicarbazone	White shining crystals	Recrystallization from ethanol	222 (221)	163	C ₈ H ₉ N ₃ O

Both the ligands synthesized are white crystalline solids

Synthesis Of complexes

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

Aqueous 25ml(0.01M) solution of metal chloride were mixed slowly with hot aqueous 25 ml(0.02M) solution of the Pyruvic thiosemicarbazone (L₁) with constant stirring. The reaction mixture is heated in water bath for three hour. Then the reaction was stirred for further one hour after which colored

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) methanolic solution of chromium chloride, a mixture of 20ml (0.02M) methanolic solution of Pyruvic thiosemicarbazone and 20ml (0.02M) methanolic solution of benz aldehyde semicarbazone were added slowly 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.

By using similar procedure other complexes were prepared by mixing aqueous solution of metal chloride with pyruvic thiosemicarbazone and Benz aldehyde semicarbazone in the ratio 1:1:1.

IV.RESULT AND DISCUSSION

The reactions of metal chlorides with pyruvic acid thiosemicarbazone and benzaldehyde semicarbazone in the 1:1:1 molar ratio results in the formation mixed ligand complexes. 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

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complexes rather than a mixture of two corresponding bis-complexes. From the magnetic moments these complexes shows octahedral geometry. 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	Mole. Wt.	%Yield of the comp.	%of metal (Calculated)	%of C	% of H	% of N	% of S
1	Cr[(PATSC) ₁ (BZSC) ₁ (H ₂ O) ₁]Cl ₃	Green	500.49	61	10.27 (10.38)	28.77	3.59	16.78	6.39
2	Mn[(PASC) ₁ (BZSC) ₁ (H ₂ O) ₁]Cl ₂	Yellow	502.35	67	11.59 (11.75)	30.77	3.84	17.95	6.83
3	Fe[(PATSC) ₁ (BZSC) ₁ (H ₂ O) ₁]Cl ₃	Gray	488.35	62	11.24 (11.07)	28.55	3.56	16.65	6.52
4	Co[(PATSC) ₁ (BZSC) ₁ (H ₂ O) ₁]Cl ₂	brown	480.35	74	11.98 (12.46)	30.52	3.87	17.80	6.78
5	Ni[(PATSC) ₁ (ZSC) ₁]Cl ₂	Blue	486.35	70	12.12 (12.40)	30.51	3.86	17.79	6.78
6	Cu[(PATSC) ₁ (BBZSC) ₁]Cl ₂	Green	500.35	63	8.64 (8.81)	30.25	3.74	17.62	6.71

All the complexes are insoluble in chloroform, carbon tetrachloride, methanol, ethanol but soluble in DMF.

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.

IR spectra

Table III IR spectra of the mixed ligand transition metal complexes

Sr.No.	Name of the Complex	v- (OH) from H ₂ O	v- COOH	v(C=O)	v(C=N)	v(C-O)	v(N-N)	v(C=S)
1	Cr[(PATSC) ₁ (BZSC) ₁ (H ₂ O) ₁]Cl ₃	3166	2356	1649	1557	1241	1136	756
2	Mn[(PASC) ₁ (BZSC) ₁ (H ₂ O) ₁]Cl ₂	3257	2358	1699	1506	1221	1112	689
3	Fe[(PATSC) ₁ (BZSC) ₁ (H ₂ O) ₁]Cl ₃	2924	2362	1740	1539	1233	1156	817
4	Co[(PATSC) ₁ (BZSC) ₁ (H ₂ O) ₁]Cl ₂	3146	2358	1604	1540	1240	1151	689
5	Ni[(PATSC) ₁ (BZSC) ₁ (H ₂ O) ₁]Cl ₂	3180	2358	1612	1506	1259	1134	811
6	Cu[(PATSC) ₁ (BZSC) ₁ (H ₂ O) ₁]Cl ₂	2994	2356	1654	1514	1219	1182	689

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the bands at $1557-1506\text{cm}^{-1}$ may be assigned to the symmetric and asymmetric $\nu(\text{C}=\text{N})$ vibrations. A strong band in the region $1740-1604\text{cm}^{-1}$ are due to $\nu(\text{C}=\text{O})$ 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 $(\text{C}=\text{N})$ and $(\text{C}=\text{O})$ groups. The bands observed in the region $689-811\text{cm}^{-1}$ indicates presence of $(\text{C}=\text{S})$ group. A band in the region $2356-2362\text{cm}^{-1}$ shows presence of carboxylic group and $-\text{OH}$ group taking in the bond formation shifting the bands towards lower side. A broad band appears in the region at $2954-3750\text{cm}^{-1}$ for complexes is attributed to the coordinated water molecule. Thermogravimetric analysis shows presence of one water molecules in the all complexes supporting the octahedral nature of complexes.

Magnetic properties of complexes

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

Sr.No.	Name of the Complex	Magnetic moment	Molar cond. $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$ at room temp. (29°C)	Molar cond. $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$ at roomtemp+ 10°C (39°C)
1	$\text{Cr}[(\text{PATSC})_1(\text{BZSC})_1(\text{H}_2\text{O})_1]\text{Cl}_3$	3.798	12.72	12.72
2	$\text{Mn}[(\text{PASC})_1(\text{BZSC})_1(\text{H}_2\text{O})_1]\text{Cl}_2$	5.768	36.36	36.36
3	$\text{Fe}[(\text{PATSC})_1(\text{BZSC})_1(\text{H}_2\text{O})_1]\text{Cl}_3$	5.459	72.70	74.52
4	$\text{Co}[(\text{PATSC})_1(\text{BZSC})_1(\text{H}_2\text{O})_1]\text{Cl}_2$	4.182	32.72	34.52
5	$\text{Ni}[(\text{PATSC})_1(\text{ZSC})_1]\text{Cl}_2$	3.610	10.90	10.90
6	$\text{Cu}[(\text{PATSC})_1(\text{BBZSC})_1]\text{Cl}_2$	2.161	50.89	50.90

The conductance of the complexes are very low (12.72 to $74.52\Omega^{-1}\text{cm}^2\text{mol}^{-1}$) indicating their non-electrolyte nature. From the magnetic moments these complexes shows octahedral geometry.

The electronic spectra of complexes

Table V: Electronic Spectra

Sr.No.	Name of the Complex	Absorbance wavelength in nm	Electronic transition	Geometry of the complex	Magnetic moment
1	$\text{Cr}[(\text{PATSC})_1(\text{BZSC})_1(\text{H}_2\text{O})_1]\text{Cl}_3$	11961	${}^4\text{A}_{2g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})$	octahedral	3.798
		24154	${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{1g}(\text{F})$		
		31746	${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{1g}(\text{P})$		
2	$\text{Mn}[(\text{PASC})_1(\text{BZSC})_1(\text{H}_2\text{O})_1]\text{Cl}_2$	11595	${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{1g}({}^4\text{G})$	octahedral	3768
		28571	${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{2g}({}^4\text{G})$		
		33422	${}^6\text{A}_{1g} \rightarrow {}^4\text{E}_g, {}^4\text{A}_{1g}({}^4\text{G})$		
3	$\text{Fe}[(\text{PATSC})_1(\text{BZSC})_1(\text{H}_2\text{O})_1]\text{Cl}_3$	11428	${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{1g}$		4.459
		26385	${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{2g}$		

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		32051	${}^6A_{1g} \rightarrow {}^4T_{1g}(P)$		
4	Co[(PATSC) ₁ (BZSC) ₁ (H ₂ O) ₁]Cl ₂	11560	${}^4T_{1g} \rightarrow {}^4T_{2g}$	octahedral	4.182
		19841	${}^4T_{1g} \rightarrow {}^4A_{2g}$		
		27100	${}^4T_{1g} \rightarrow {}^4T_{1g}(P)$		
5	Ni[(PATSC) ₁ (BZSC) ₁ (H ₂ O) ₁]Cl ₂	11547	${}^3A_{2g} \rightarrow {}^3T_{2g}(F)$	octahedral	3.610
		28801	${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$		
		31446	${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$		
6	Cu[(PATSC) ₁ (BZSC) ₁ (H ₂ O) ₁]Cl ₂	11467	${}^2B_{1g} \rightarrow {}^2A_{1g}$	octahedral	2.261
		25773	${}^2B_{1g} \rightarrow {}^2E_g$		
		33068	Charge transfer band		

Cr(III) complex shows bands corresponding to ${}^6A_{1g} \rightarrow {}^4T_{1g}$ (4G), ${}^6A_{1g} \rightarrow {}^4E_{2g}$ (4G), and ${}^6A_{1g} \rightarrow {}^4E_{2g}$ (4D), transitions respectively with magnetic moment 3.798BM, suggesting octahedral environment around Cr(III) ion. Mn(II) complex shows bands corresponding to ${}^6A_{1g} \rightarrow {}^4T_{1g}$ (4G), ${}^6A_{1g} \rightarrow {}^4T_{2g}$ (4G) and ${}^6A_{1g} \rightarrow {}^4E_g$, ${}^4A_{1g}$ (4G) transitions respectively with magnetic moment 5.768BM, suggesting octahedral environment around Mn(II) ion. Fe (III) complex shows bands corresponding to ${}^6A_{1g} \rightarrow {}^4T_{1g}$, ${}^6A_{1g} \rightarrow {}^4T_{2g}$ and ${}^6A_{1g} \rightarrow {}^4T_{1g}(P)$ transitions respectively with magnetic moment 5.459BM, suggesting octahedral environment around Fe(III) ion. Co(II) complex exhibit bands corresponding to ${}^4T_{1g} \rightarrow {}^4T_{2g}$, ${}^4T_{1g} \rightarrow {}^4A_{2g}$ and ${}^4T_{1g} \rightarrow {}^4T_{1g}(P)$ transitions respectively with magnetic moment 4.182BM, suggesting octahedral environment around Co(II) ion. Ni (II) complex exhibit bands corresponding to ${}^3A_{2g} \rightarrow {}^3T_{2g}(F)$, ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$ and ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$ transitions respectively with magnetic moment 3.610BM, suggesting octahedral environment around Ni(II) ion. Cu (II) complex exhibit bands corresponding to ${}^2B_{1g} \rightarrow {}^2A_{1g}$, ${}^2B_{1g} \rightarrow {}^2E_g$ and charge transfer transitions respectively with magnetic moment 2.160BM, suggesting octahedral environment around Cu(II) ion.

Antimicrobial assay:

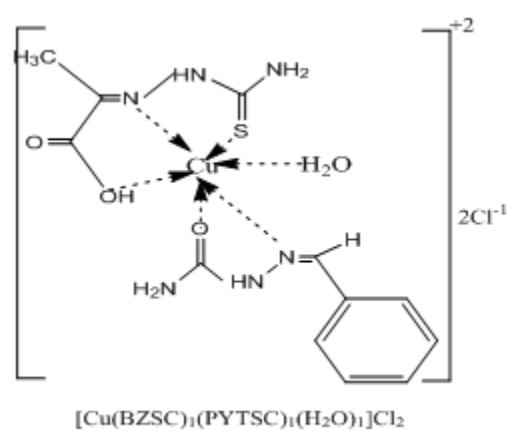
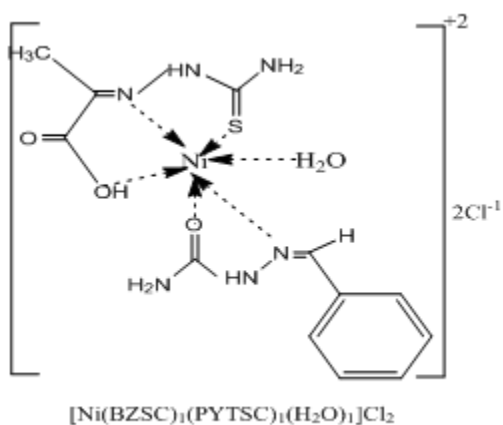
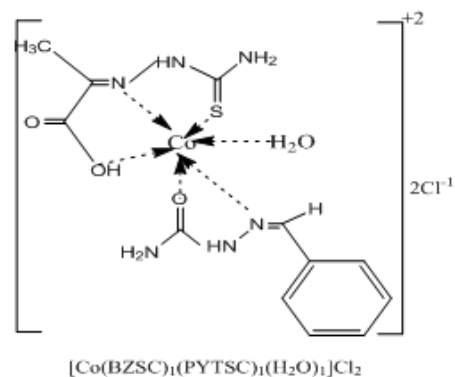
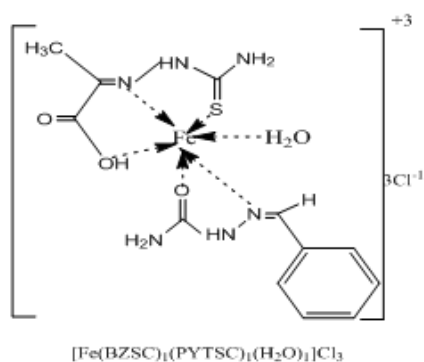
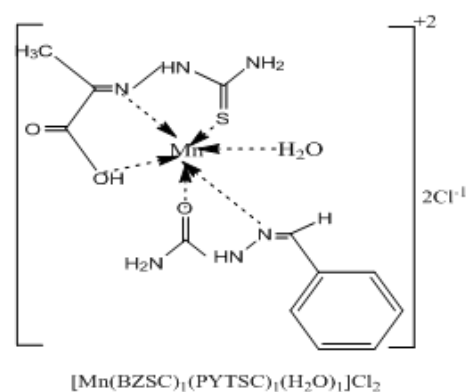
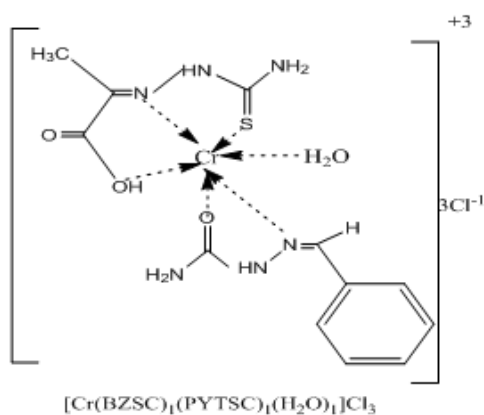
From the antimicrobial studies it inferred that, the Schiff bases was found to be potentially active against E. coli, P. aeruginosa and Aspergilla's Niger. Some of the complexes shown high antimicrobial activity against E. Coli, Pseudomonas and Aspergilla's Niger. This enhancement in the activity of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

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Structure of the Complexes



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