

Synthesis and Characterization of Mixed Ligand Complexes of Transition Metals with Schiff's Bases

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Abstract: The mixed ligand complexes of the type $[ML_1L_2]Cl_2$. Where M=Cr(III), Mn(II), Co(II), Ni(II) and Cu(II) and L_1 =Pyruvic acid semicarbazone L_2 = Benzaldehyde semicarbazone 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, Pyruvic acid semicarbazone, Benzaldehyde semicarbazone, Transition metals

Introduction

Semicarbazones shows a wide range of bioactivities and their chemistry and pharmacological applications have been extensively studied. The biological properties of semicarbazones are often related to metal ion coordination. Firstly, lipophilicity, which controls the rate of entry into the cell, is modified by coordination¹. 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. Moreover, coordination may lead to significant reduction of drug-resistance². A variety of 5-nitrofuryl semicarbazone derivatives have been developed for the therapy of Chagas disease, a major problem in the Central and the South America³. 4-Bromobenzaldehyde semicarbazone has been used as anticonvulsant. Recently, a review reported on the anticonvulsant activity of thiosemicarbazones, semicarbazones and hydrazones derived from aromatic and unsaturated carbonyl compounds as well as from other precursors⁴. In contrast to thiosemicarbazones, literature records fewer examples of semicarbazones presenting significant anticancer and cytotoxic activity but some nitro so, naphthopyran and fluorine derivatives showed anti-leukemia effect in mice⁵. Several *N*4- substituted semicarbazone

derivatives of *o*- and *p*- chlorobenzaldehyde and 2,6-dichlorobenzaldehyde exhibit potent anti-hypertensive effects⁶. The orally administered drug naftazone (1,2-naphthoquinone semicarbazone) protects the vascular system through an inhibitory effect on nitric oxide synthesis⁷. Many other bioactivities of semicarbazones have been reported, such as their antimicrobial⁸, pesticide⁹, herbicide¹⁰ and hypnotic¹¹ properties or the ability of some of their Cu(II) complexes to mimic superoxide dismutase activity¹². Semicarbazones are widely used as spectrophotometric agents for the analysis of metal ions¹³. Semicarbazones are frequently used in the qualitative organic analysis of carbonyl compounds¹⁴. Coordination compounds are widely used as potential drugs, in the field of catalysis and in biological fields. This includes a number of important biological materials such as vitamin B₁₂ and haemoglobin. The chemistry of transition metal complexes of semicarbazones and thiosemicarbazones has been receiving considerable attention primarily because of their bioinorganic relevance.

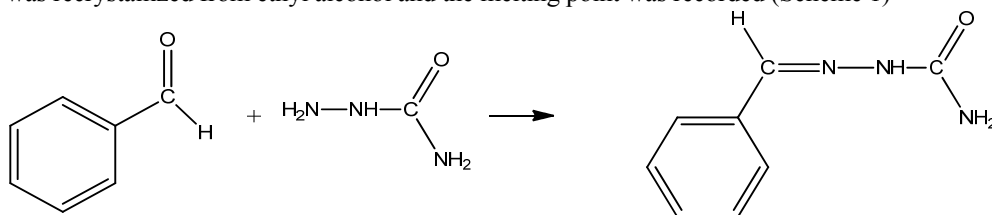
Objectives and scope of the present work

There has been considerable interest in the studies of semicarbazones due to their coordination modes when bound to metals¹⁵. The wide applications and structural diversity of metal complexes of semicarbazones encouraged us to synthesize the tridentate ONO-donor semicarbazones and their metal complexes. Due to good chelating ability, the present work is mainly concerned on the studies of two novel semicarbazones, pyruvic acid semicarbazone [L₁] and benzaldehyde semicarbazone [L₂]. The compositions of these semicarbazones were determined by the CHN analyses. For the characterization of these compounds we have used IR and UV spectral studies. We have synthesized manganese(II), cobalt(II), nickel(II) and copper(II) complexes of these semicarbazones, in the ratio 1:1:1 with metal:ligand L₁:ligand L₂. These complexes were characterized by various spectroscopic techniques, magnetic and conductivity studies, biological activities.

Synthesis of ligand

Benzaldehyde semicarbazone

2 g of semicarbazide hydrochloride and 3 g of crystallized sodium acetate was dissolved in about 25-30 mL distilled water in a hard glass test tube. To this solution 1.0 g/mL of benzaldehyde was added and shaken well. If the mixture is turbid then 1:1 ethyl alcohol was added until a clear solution is obtained. Then this reaction mixture was heated in water bath for 10 min. Then this solution was cooled and transferred into a beaker containing crushed ice. White crystals of the semicarbazone derivative were separated out from the solution. Then it was recrystallized from ethyl alcohol and the melting point was recorded (Scheme 1)

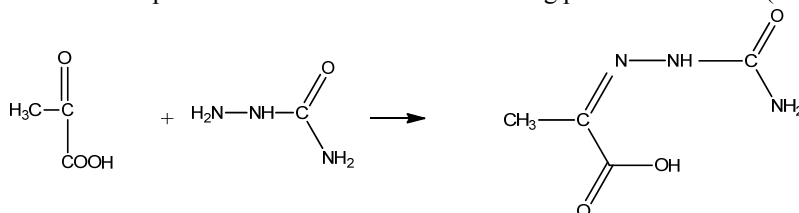


Scheme 1. Benzaldehyde semicarbazone synthesis

Pyruvic acid semicarbazone

2 g of Semicarbazide hydrochloride and 3 g of sodium acetate was dissolved 20-30 mL water in a 100 mL beaker then stirred continuously to obtain a clear solution of mixture

of semicarbazide hydrochloride and sodium acetate. The solution was filtered and placed in a ice bath. 2 mL of pyruvic acid was taken in a test tube and cooled it in ice bath. This ice cooled solution of pyruvic acid was added very slowly drop wise in an ice cooled solution of mixture of sodium acetate and semicarbazide hydrochloride with constant stirring. The reaction mixture stirred for another half an hour to separate out white precipitate of pyruvic acid semicarbazone. Recrystallized the crude product from hot water and the melting point was recorded (Scheme 2).



Scheme 2. Pyruvic acid semicarbazone synthesis

Synthesis of mixed ligand complexes of transition metals

$[M(L_1)_1(L_2)_1(H_2O)_1]Cl_2$ (Where L_1 = PASC and L_2 =BZSC)

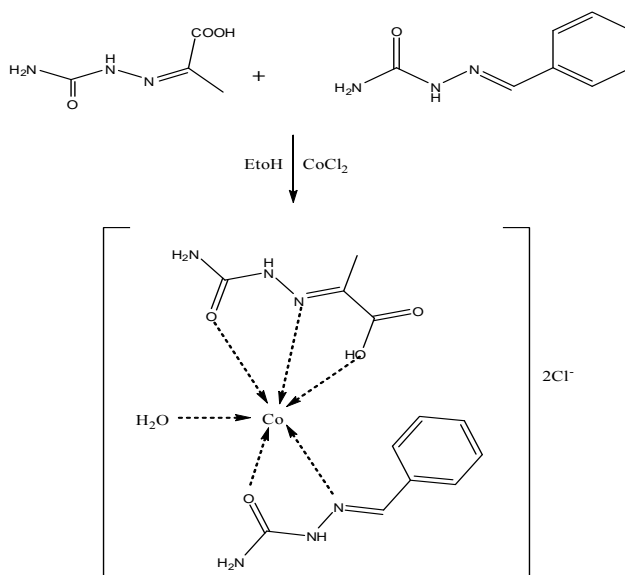
To 20 mL ethanolic solution of 0.01 M manganese chloride a mixture of 20 mL ethanolic solution of 0.01 M benzaldehyde semicarbazone and 20 mL 0.01 M pyruvic acid semicarbazone ligands were added with continuous stirring in a water bath. Then the reaction mixture was refluxed with water condenser for half an hour. Then pH of the reaction mixture was raised to 7.5 to 8.00 by adding 5% NaOH solution drop wise with constant stirring. The pH was measured with the help of the pH paper. Stirring was continued for another half an hour. The coloured precipitate of the complex separates out from the solution. The complex was filtered and dried under IR lamp. By using similar procedure other complexes were prepared by mixing metal salt solutions with pyruvic semicarbazone and benzaldehyde semicarbazone in the ratio 1:1:1.

Experimental analytical technique

The compounds pyruvic acid, benzaldehyde, semicarbazide hydrochloride and chlorides of Cr(III), Mn(II), Co(II), Ni(II) and Cu(II) used were of analytical grade. The amount of metals is determined volumetrically by EDTA using double burette technique for optimum utilization of reagents. Indicator Erich Rome Black T was used for Mn(II) and Mg, ammonium thiocyanate for Fe(III), xylenol orange for Co(II) and murexide for Ni(II) and Cu(II). Fast sulphone black F for calcium, 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 L_1 and L_2 . 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 spectral data of complexes is shown in annexure A. Electronic spectra of complexes were recorded on Systronics UV-Visible spectrophotometer in the Department of Chemistry, Pratap College, Amalner. The spectral data of complexes is shown in Tables 3-5. Thermogravimetric analysis was carried out on SHIMADZU STA 6000. Antimicrobial activities are determined by using three microbial nutrients.

Results and Discussion

The reactions of metal chlorides with pyruvic acid semicarbazone and benzaldehyde semicarbazones in the 1:1:1 molar ratio results in the formation mixed ligand complexes. Structure of these complexes is shown in Scheme 3.



Scheme 3. Structure of complex

The resulting complexes were having different colors as given in the Table 2. They are insoluble in chloroform, carbon tetrachloride, methanol, ethanol but soluble in DMF. The elemental analyses of the complexes are given in Table 2. The conductances of the complexes are very low ($0.1\text{-}12\Omega^{-1}\text{ cm}^2\text{ mol}^{-1}$) indicating their non-electrolyte nature.

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 conductances of the complexes are very low ($0.1\text{-}12\Omega^{-1}\text{ cm}^2\text{ mol}^{-1}$) indicating their non-electrolyte nature. In the IR spectra of the mixed ligand complexes (Table 3) the bands at $1544\text{-}1604\text{ cm}^{-1}$ may be assigned to the symmetric and asymmetric $\nu(\text{C}=\text{N})$ vibrations. A strong band in the region $1748\text{-}1647\text{ cm}^{-1}$ 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. A broad band appears in the region at $3200\text{-}3750\text{ cm}^{-1}$ be attributed to the coordinated water molecule.

The thermograms of the compounds have been recorded in flowing nitrogen atmosphere at the heating rate of $10\text{ }^\circ\text{C}/\text{min}$ on approximately 10 mg samples. Thermogravimetric analysis shows presence of one water molecules in the complexes supports the octahedral nature of complexes. Thermodynamic properties are shown in Table 6.

The electronic spectra of Cr(III) complexes (Table 5) exhibits bands in the range $11467, 22319$ and 28089 cm^{-1} with ν_2/ν_1 ratio 1.946 corresponding to ${}^6\text{A}_{1g}\rightarrow{}^4\text{T}_{1g}$ (${}^4\text{G}$), ${}^6\text{A}_{1g}\rightarrow{}^4\text{E}_{2g}$ (${}^4\text{G}$), ${}^4\text{A}_{1g}$ (${}^4\text{G}$) and ${}^6\text{A}_{1g}\rightarrow{}^4\text{E}_{2g}$ (${}^4\text{D}$), transitions, respectively suggesting octahedral environment around Cr(III) ion. Mn(II) complexes shows bands in the range $12529, 21296$ and 27032 cm^{-1} assignable to ${}^6\text{A}_{1g}\rightarrow{}^4\text{T}_{1g}$ (G), ${}^6\text{A}_{1g}\rightarrow{}^4\text{T}_{2g}$ (G) and ${}^6\text{A}_{1g}\rightarrow{}^4\text{A}_{1g}$ (G) transitions, respectively and magnetic moment indicates octahedral geometry. Co(II) complexes shows absorption bands $11428, 20986$ and 24330 cm^{-1} with ν_2/ν_1 ratio 1.836

corresponding to ${}^4T_{1g} \rightarrow {}^4A_{2g}$ (F), ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}$ (P) and ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}$ (F) transitions, respectively for octahedral geometry. The electronic spectra of Ni(II) complexes exhibits three bands in the range 10415, 19207 and 24603 cm^{-1} with ν_2/ν_1 ratio 1.844, 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 octahedral geometry. The six coordinated copper complexes shows bands in the range 11862, 18125 and 28089 cm^{-1} with ν_2/ν_1 ratio 1.5278 corresponding to ${}^2B_{1g} \rightarrow {}^2A_{1g}$, ${}^2B_{1g} \rightarrow {}^2B_{2g}$, ${}^2B_{1g} \rightarrow {}^2E_{2g}$ transitions, respectively.

The physical properties of ligands and complexes are given in Table 1 and 2. While IR spectra and analytical properties are listed in Table 3 and Table 4 respectively. Biological activities the compound synthesized in the present investigation have been subjected to various antimicrobial screening programs based on their structural features so as to ascertain their activity against different microorganisms. The solvent used was DMSO and the sample concentrations were 200, 100, 50, 25 and 12.5 ppm. The results of preliminary study on antimicrobial activity indicated that most of the compounds were highly and few were moderate active against these organisms.

Table 1. Physical properties of ligands

Name of the ligand	Symbol	Colour and nature	Method purification	M.P. $^{\circ}\text{C}$ (observed) reported	Mol. Wt.	Molecular formula
Pyruvic acid semicarbazone	PASC	White shining crystals	Recrystallization from water	(214) 215	145	$\text{C}_4\text{H}_7\text{N}_3\text{O}_3$
Benzaldehyde semicarbazone	BZSC	White shining crystals	Recrystallization from ethanol	(225) 224	163	$\text{C}_8\text{H}_9\text{N}_3\text{O}$

Table 2. Elemental analyses data of the complexes

Ligand/Complex	Colour	Mole. Wt.	%Yield of Compd.	% of metal % of C % of H % of N			
				(Calculated)		Found	
$\text{Cr}[(\text{PYACSC})_1(\text{BZSC})_1]$	Green	484.49	68	(10.73)10.89	(29.73)29.40	(3.71)3.87	(17.33)17.20
$\text{Mn}[(\text{PYACSC})_1(\text{BZSC})_1]$	Brown	451.99	74	(12.16)11.95	(31.85)31.30	(3.98)4.02	(18.58)18.95
$\text{Co}[(\text{PYACSC})_1(\text{BZSC})_1]$	Light pink	455.93	71	(12.93)13.60	(31.58)31.43	(3.94)4.12	(18.42)18.48
$\text{Ni}[(\text{PYACSC})_1(\text{BZSC})_1]$	Bluish green	455.69	78	(12.89)12.31	(31.60)31.38	(3.95)4.04	(18.43)18.25
$\text{Cu}[(\text{PYACSC})_1(\text{BZSC})_1]$	Green	460.54	63	(13.79)13.70	(31.26)31.45	(3.90)4.01	(18.23)18.44

Table 3. IR spectra (cm^{-1}) bands of the parent and mixed ligand transition metal complexes

Ligand/Complex	$\nu(\text{OH})$ from H_2O	ν COOH	$\nu(\text{C}=\text{O})$	$\nu(\text{C}=\text{N})$	Monosubstituted benzene ring
$\text{Cr}[(\text{PYACSC})_1(\text{BZSC})_1]$	3750	2360	1698	1582	693
$\text{Mn}[(\text{PYACSC})_1(\text{BZSC})_1]$	3697	2360	1647	1583	693
$\text{Co}[(\text{PYACSC})_1(\text{BZSC})_1]$	3697	2360	1680	1540	692
$\text{Ni}[(\text{PYACSC})_1(\text{BZSC})_1]$	3750	2360	1697	1547	693
$\text{Cu}[(\text{PYACSC})_1(\text{BZSC})_1]$	3750	2360	1697	1587	693

Table 4. Magnetic moment and molar conductance values of the complexes

Ligand/ Complex	Magnetic moment	Molar cond. $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ at 29 $^{\circ}\text{C}$	Molar cond. $\Omega^{-1} \text{cm}^2 \text{mol}$ at 39 $^{\circ}\text{C}$
Cr[(PYACSC) ₁ (BZSC) ₁]	4.879	2.4	3.0
Mn[(PYACSC) ₁ (BZSC) ₁]	4.402	2.86	3.25
Co[(PYACSC) ₁ (BZSC) ₁]	4.426	5.25	6.05
Ni[(PYACSC) ₁ (BZSC) ₁]	3.90	3.6	4.4
Cu[(PYACSC) ₁ (BZSC) ₁]	2.90	3.4	4.1

Table 5. Electronic spectra

S.No.	Name of the Complex	v1	v2	v3	B	β	v2/ v1
1	Cr[(PYACSC) ₁ (BZSC) ₁]	11467	22319	28089	766.93	0.789835	1.946
2	Mn[(PYACSC) ₁ (BZSC) ₁]	11405	25839	34129	990.627	0.961774	2.265
3	Co[(PYACSC) ₁ (BZSC) ₁]	11428	20986	24330	696.93	0.759183	1.836
4	Ni[(PYACSC) ₁ (BZSC) ₁]	10415	19207	24603	818.89	0.843347	1.8441
5	Cu[(PYACSC) ₁ (BZSC) ₁]	11862	18125	28089	885.195	0.859413	1.5278

Table 6. Thermodynamic properties of complexes

Ligand/ Complex	Temp. $^{\circ}\text{C}$	% Mass Loss Found	DSC peak in $^{\circ}\text{C}$ Endo/Exo	ΔH in J g^{-1}	$\Delta\text{S}^{\#}$	ΔE	ΔG
Cr[(PYACSC) ₁ (BZSC) ₁]	50-200	9.84	209.71	-444.21	-1.160	514.93	-1004.15
	200-350	34.82					
	250-436.73	3.698					
Mn[(PYACSC) ₁ (BZSC) ₁]	50-200	4.485	219.33	-423.47	-0.8598	554.78	-932.75
	200-300	46.383					
	300-437.12	11.832					
Co[(PYACSC) ₁ (BZSC) ₁]	50-150	2.206	384.39	-349.92	-0.5436	956.31	-707.28
	150-250	8.589					
	250-393.29	8.504					
Ni[(PYACSC) ₁ (BZSC) ₁]	50-200	0.988	212.56	-110.62	-0.2278	474.66	-221.23
	200-350	4.883					
	250-437.44	0.785					
Cu[(PYACSC) ₁ (BZSC) ₁]	50-150	2.945	222.82	-1380.53	-2.784	395.34	-2760.89
	150-350	43.721					
	350-437.25	6.399					

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