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SYNTHESIS AND PHYSICOCHEMICAL STUDIES OF MIXED LIGAND COMPLEXES OF CO (II) WITH OXYGEN AND NITROGEN DONOR LIGANDS

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ABSTRACT

The mixed ligand complexes of the type $[ML_1L_2]Cl_2$. Where M=Co (II), AND L_1=Pyruvic acid semicarbazone L_2= Acetone semicarbazone, Acetophenone semicarbazone,Benz aldehyde semicarbazone, Cyclohexanone semicarbazone, O-hydroxy acetophenone 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, Benz aldehyde 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 coordination [1]. 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 drugresistance [2]. 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 America [3]. Metal complexes of pyruvic acid semicarbazone, benzaldehyde semicarbazone, and their derivatives as ligands with transition metals (ML_2) have been already reported in early days. Sulekha Chandra and Krishna K. Sharma.[4] have reported the synthesis and characterization of transition metal complexes of substituted Pyruvic acid semicarbazones and thiosemicarbazones. Mixed ligand complexes of Co(II) containing 5-bromosalicylaldehyde and β-diketones, hydroxylaryl aldehyds or ketones were reported by R.N.Prasad. etal. [5] Have reported synthesis and characterizationof Co(II), Ce(III) and Dioxouranium of 2,3-Dimethyl-1-phenyl-4-salicylidene-3-pyrazolin-5-one mixed ligand complexes, pyrolytic products and Biological activities.

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 metals. 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[L_1] and Benzaldehyde semicarbazone Acetone semicarbazone, Acetophenone semicarbazone, Benz aldehyde semicarbazone, Cyclohexanone semicarbazone, O-hydroxy acetophenone semicarbazone [L_2]. 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 cobalt (II) complexes of these semicarbazones, in the ratio 1:1:1 with metal: ligand L_1: ligand L_2. These complexes were characterized by various spectroscopic techniques, magnetic and conductivity studies, biological activities.

Synthesis of Ligand

Ligand L_1: To a mixture of aquous 25 mlsolution of pyruvic acid and 20ml (0.1M) sodium acetate solution 25ml (0.1M) aqueous solution of semicarbazide hydrochloride were slowly added with constant stirring. This mixture was ice cooled for 20-25minutes.On cooling white solid product was separated out. It was filtered, washed with cold ethanol, dried in air and recrystallized from hot water.

Ligand L_2: To a mixture of hot ethonalic 25ml (0.1M) solution of benzaldehyde and (20ml 0.1M) solution of sodium acetate 25ml (0.1M) aqueous solution of semicarbazide hydrochloride was added slowly with constant stirring. Then the reaction mixture was refluxed for 15-20 minutes on a waterbath. After cooling thoroughly, white solid product was precipitated out from the solution. This solid obtained was filtered, washed with cold ethanol and dried in air and recrystallized from ethanol. This is Benzaldehyde semicarbazone. Simillarly other Acetone semicarbazone, Acetophenone semicarbazone, Cyclohexanone semicarbazone, O-hydroxy acetophenone semicarbazone ligands are prepared.

Table I: Physical properties of Ligands.

Name of the ligand	Symbol	Colour and nature	Method purification.	M.P.^{0}c(observed) reported	Mol. wt	Molecular formula
Pyruvic acid semicarbazone	PASC	White shining crystals	Recrystallization from water	(214) 215	145	$C_4H_7N_3O_3$
Benzaldehyde semicarbazone	BZSC	White shining crystals	Recrystallization from Ethanol	224(225)	163	$C_8H_9N_3O$
Acetone Semicarbazone	ACSC	White shining crystals	Recrystallization from Ethanol	190(189)	115	$C_4H_9N_3O$
Acetophenone semicarbazone	ACPHSC	White Crystals	Crystallized from aq. Ethanol	199(198)	177	$C_9H_{11}N_3O$
Cyclohexanone semicarbazone	CYSC	White Crystals	Crystallized from aq. Ethanol	167(167)	155	$C_7H_{13}N_3O$
O-Hydroxy acetophenone semicarbazone	OH ACPHSC	White Crystals	Crystallized from aq. Ethanol	211(209)	193	$C_9H_{11}N_3O$

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, ACSC, ACPHSC, CYSC, OHACPHSC

To 20 ml ethanalic solution of 0.01M cobalt chloride a mixture of 20 ml ethanalic solution of0.01M benzaldehyde semicarbazone and 20 ml 0.01M pyruvic acid semicarbazone ligands were added with continuous stiring in a water bath .Then the reaction mixture is refluxed with water condenser for four to five hours. Then P^H of the reaction mixture was raised to 7.5 to 8.00 by adding 5% NaOH solution drop wise with constant stirring. The p^H was measured with the help of the p^H paper. Stirring was continued for another half an hour. The coloured precipitate of the complex seperates out from the solution .The complex is filtered and dried under IR lamp. By using similar procedure other complexes were prepared by mixing metal salt solutions with pyruvic semicarbazone and benzaldehyde semicarba zone in the ratio 1:1:1. In this way other complexes are prepared.

Experimental Analytical Technique

The compounds pyruvic acid, benzaldehyde, acetone, acetophenone, cyclohexanone, ortho hydroxyl acetophenone semicarbazide hydrochloride and cobalt chlorides used were of analytical grade The amount of metal present determined volumetrically by EDTA using double burette technique for optimum utilization of reagents. Indicator xylenol range is usedfor Co (II) 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 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 annexure B. Thermo gravimetric analysis was carried out on SHIMAdZU STA 6000.Antimicrobial activities are determined by using three microbial nutrients.

RESULT 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. Structures of these complexes are as shown on page no.7.

The resulting complexes were having different colors as given in the table II. They are insoluble in chloroform, carbon tetrachloride, methanol, and 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 show octahedral geometry.

The conductance's of the complexes are very low ($0.1\text{-}12\Omega^{-1}cm^{2}mol^{-1}$) indicating their non-electrolyte nature. In the IR spectra of the mixed ligand complexes the bands at 1544-1564cm^{-1}may be assigned to the symmetric and asymmetric v(C=N) vibrations. A strong band in the region 1604-1738$cm^{-1}$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) and (C=O) groups. A broad band appears in the region at 3200-3750cm^{-1} be attributed to the coordinated water molecule. The thermograms (TG) of the compounds have been recorded in flowing nitrogen atmosphere at the heating rate of 10°C/min on approximately 10 mg samples. Thermogravemetric analysis shows presence of one water molecule in the complexes of Co (II) with semicarbazones of benzaldehyde, acetone, acetophenone, cyclohexanone supports the octahedral nature of complexes. The physical properties of ligands and complexes are given in table I and II .While IR spectra and analytical properties are listed in table III and table IV respectively. The electronic spectra of Co(II) complexes shows absorption bands 10415-11862,18125-22319 and 24cm^{-1},corresponding to $^{4}T_{1}g\rightarrow{}^{4}A_{2}g$ (F), $^{4}T_{1}g(F)\rightarrow{}^{4}T_{1}g$ (P) and $^{4}T_{1}g(F)\rightarrow{}^{4}T_{2}g$ (F) transitions, respectively for octahedral geometry. Biological Activities the compound synthesized in the present investigation has 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, 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 II: Characterization Data of The Complexes Found (Calculated.) %

Ligand/Complex	**Colour**	**Mole. wt**	**%Yield of the comp.**	**%of metal (Calculated)**	**%of C**	**%of H**	**%of N**
Co[(PYACSC)$_1$ (BZSC)$_1$]	Faint green	455.69	68	12.93 (12.40)	(31.58) 32.06	(3.94) 3.87	(18.42) 18.03
Co [(PYACSC)$_1$(ACSC)$_1$]	Brown	407.69	74	(14.44) 13.67	(23.53) 22.89	(4.41) 4.02	(20.59) 18.95
Co[(PYACSC)$_1$(ACPHSC)$_1$]	pink	469.69	72	12.54	(33.19)	4.25	17.87
Co [(PYACSC)$_1$ (CYSC)$_1$]	Faint brown	447.69	78	(13.15) 14.12	(29.46) 31.08	(4.95) 4.04	(18.93) 18.65
Co[(PYACSC)$_1$(OHACPHSC)$_1$]	Light pink	485.93	67	12.59 (12.96)	(32.67) 33.33	(3.84) 4.04	(17.95) 18.35

Table III. Ir Spectra (Cm-1) Bands of The Parent And Mixed Ligand Transition Metal Complexes.

Ligand/Complex	**ν-(OH) from H_2O**	**ν--COOH**	**ν(C=O)**	**ν(C=N)**	**Monosubstituted benzene ring**
Co[(PYACSC)$_1$(BZSC)$_1$]	3750	2360	1604	1540	753
Co [(PYACSC)$_1$(ACSC)$_1$]	3697	2360	1699	1540	-
Co[(PYACSC)$_1$(ACPHSC)$_1$]	3697	2360	1633	1539	790
Co [(PYACSC)$_1$(CYSC)$_1$]	3750	2360	1738	1564	-
Co[(PYACSC)$_1$(OHACPHSC)$_1$]	-	2360	1738	1564	693

Table IV. Magnetic Moment and Molar Conductance Values of the Complexes

Ligand/Complex	**Magnetic moment**	**Molar cond.$\Omega^{1}cm^{2}mol^{1}$ at RT.($29^{0}C$)**	**Molar cond.$\Omega^{-1}cm^{2}mol^{1}$ at RT +$10^{0}C$($39^{0}C$)**
Co[$(PYACSC)_1(BZSC)_1$]	3.96	2.4	3.0
Co [$(PYACSC)_1(ACSC)_1$]	3.927	15.12	17.25
Co[$(PYACSC)_1(ACPHSC)_1$]	4.426	5.25	6.05
Co [$(PYACSC)_1(CYSC)_1$]	4.206	1.97	3.4
Co[$(PYACSC)_1(OHACPHSC)_1$]	4.375	3.4	4.1

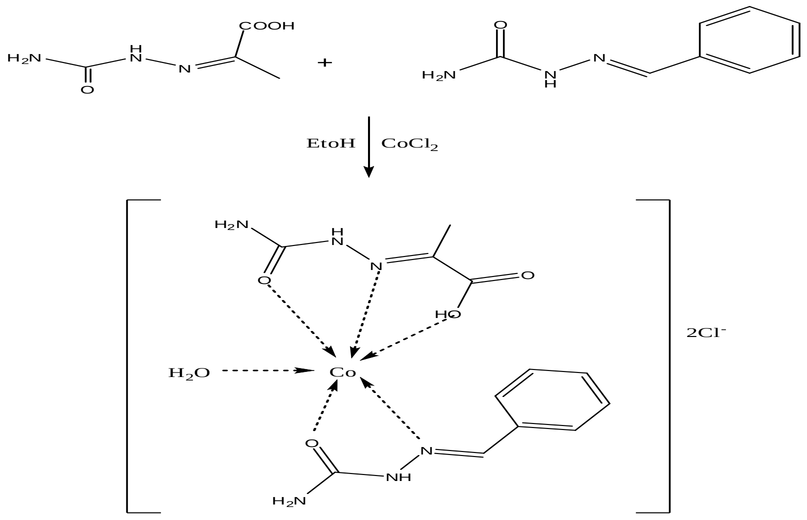
Table V: Electronic Spectra

Sr. No.	**Name of the Complex**	**ν1**	**ν2**	**ν3**	**B**	**β**	**ν2/ ν1**
1	Co[$(PYACSC)_1(BZSC)_1$]	11467	22319	28089	766.93	0.789	1.946
2	Co[$(PYACSC)_1(ACSC)_1$]	11405	25839	34129	990.627	0.961	2.265
3	Co[$(PYACSC)_1(ACPHSC)_1$]	11428	20986	24330	696.93	0.759	1.836
4	Co [$(PYACSC)_1(CYSC)_1$]	10415	19207	24603	818.89	0.843	1.8441
5	Co[$(PYACSC)_1(OHACPHSC)_1$]	11862	18125	28089	885.195	0.859	1.5278

Table VI: Thermodynamic Properties of Complexes

Ligand/Complex	**Temp.^{0}C**	**% Mass Loss Found**	**DSC peak in^{0}CEndo/Exo**	**ΔH in J g^{-1}**	**$\Delta S^{\#}$**	**ΔE**	**Δ G**
Co[$(PYACSC)_1$ $(BZSC)_1$]	50-200 200-350 250-436.73	4.84 34.82 3.698	209.71	-444.21	-1.160	514.93	-1004.15
Co [$(PYACSC)_1$ $(ACSC)_1$]	50-200 200-300 300-437.12	4.485 46.383 11.832	219.33	-423.47	-0.8598	554.78	-932.75
Co[$(PYACSC)_1$ $(ACPHSC)_1$]	50-150 150-250 250-393.29	4.206 48.589 8.504	384.39	-349.92	-0.5436	956.31	-707.28
Co [$(PYACSC)_1$ $(CYSC)_1$]	50-200 200-350 250-437.44	4.388 44.883 0.785	212.56	-110.62	-0.2278	474.66	-221.23
Co [$(PYACSC)_1$ $(OHACPHSC)_1$]	50-150 150-350 350-437.25	0.120 43.721 6.399	222.82	-1380.53	-2.784	395.34	-2760.89

Structure of the complexes



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