



Mixed ligand complexes of Benzaldehyde Thiosemicarbazone and Pyruvic acid semicarbazone with Co(II), Ni(II) and Cu(II)

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Abstract : The new Co(II), Ni(II) and Cu(II) complexes with benzaldehydethiosemicarbazone and pyruvic acid semicarbazone were prepared and characterized by various physico-chemical and spectroscopic methods. benzaldehydethiosemicarbazone is acting as bidentetneutral chelating ligand with S and N as the donor sites, while pyruvic acid semicarbazone acts as tridentate monobasic chelating ligand with O and N as the donor sites. The molecular structure of complexes were investigated by using elemental analysis, absorption spectroscopy, IR spectroscopy, conductivity measurement and magnetic measurement, thermal analysis and antimicrobial screening. All the complexes shows octahedral geometry.

Keywords : Mixed ligand, benzaldehydethiosemicarbazone, pyruvic acid semicarbazone, transition metals.

1. Introduction

Thiosemicarbazones kills several species of protozoan parasites through the inhibition of cysteine proteases as well as through action against other targets. Furthermore, semicarbazones, which can also be regarded as urea derivatives, have gained considerable importance [1] in recent years in the design of enzyme inhibitors [2], as replacement for the amide ($-\text{CO}-\text{NH}-$) bond in peptidomimetics [3] and as sources of self complementary bidirectional hydrogen bonding in supramolecular chemistry [4]. The metal complexes of thiosemicarbazones 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. Since peptides have poor metabolic stability and limited oral absorption, they are rarely useful drug candidates.

2. Experimental

2.1 Materials and measurements

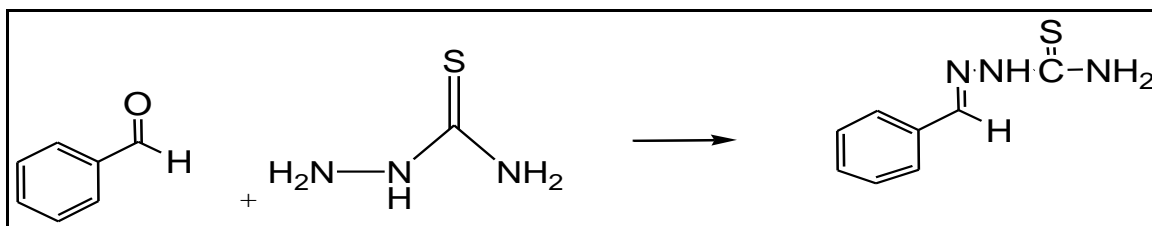
Chemicals were reagent grade Benzaldehyde, thiosemicarbazide, pyruvic acid, semicarbazide hydrochloride and chlorides of Co(II), Ni(II) and Cu(II) were purchased from E.Merk and S.D.fine chemicals. EDTA is used to determine amount of metals volumetrically using double burette technique for optimum utilization of reagents. Carbon, hydrogen, nitrogen and sulphur analysis were carried from Central Instrumentation Laboratory, Pratap College, Amalner. IR spectra and UV spectra of the complexes were recorded on JASCO instrument in the region $250-4000\text{ cm}^{-1}$ and $200-1400\text{ nm}$ respectively from Central Instrumentation Laboratory, Pratap College, Amalner. Thermo gravimetric analysis was carried out on Perkin

Elmer STA 6000 at the rate of 10°C per minute..Antimicrobial activities are determined by using three microbial nutrients.

2.2 Synthesis of ligands

2.2.1 Synthesis of Benzaldehydethiosemicarbazone

To a hot solution of 2 grams of thiosemicarbazide (10 mmole) in 50 ml methanol was added 2ml of benzaldehyde(10 mmole) in 50 ml methanol dropwise with constant stirring for about 30 minutes.The mixture was then refluxed for four hours, it is filtered and washed with cold ethanol and dried in vacuum.



Properties:

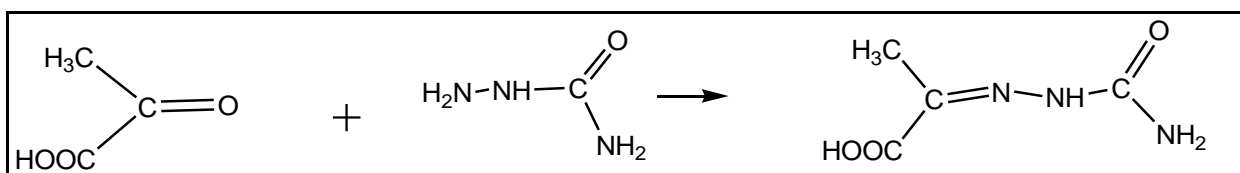
Colorless crystals,yield 79%,M.P. 169°C, Analytical calculations of C₈H₉N₃S (mol.wt.=179.2):

C, 53.6%; H, 5.1%; N, 23.4%; S, 17.9%. Found: C, 53.5%; H, 5.3%;5.1%; N, 23.4%; S, 17.9%. Found: C, 53.5%; H, 5.3%; N, 23.5%; S, 17.7%. IR (KBr,): ; ν_{NH} 3250; ν_{C=N} 1600; ν_{C=S} 885

2.2.2 Synthesis of Pyruvic acid semicarbazone

Dissolve 2 gm. of Semicarbazide hydrochloride and 3 gm. of sodium acetate in a 100 ml beaker then add 20-30ml distilled water & stir continuously to obtain a clear solution of mixture of semicarbazide hydrochloride & sodium acetate , filter the solution & place ice bath.Take 2ml of pyruvic acid in a test tube and cool it in ice bath.This ice cooled solution of pyruvic acid is very slowly drop wise added in a ice cooled solution of mixture of sodium acetate and semicarbazide hydrochloride with constant stirring.Stir the reaction mixture for another half an hour to separate out white precipitate of pyruvic acid semicarbazone.Recrystallize the crude product from hot water,dry and then melting point and yield is recorded .

Reaction:

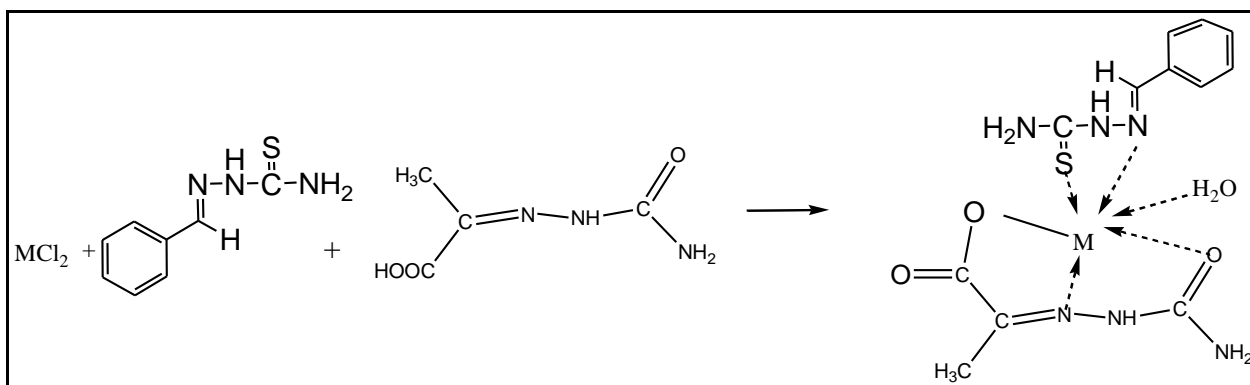


Properties:

Colorless shining crystals,yield 80%,M.P. 214°C, Analytical calculations of C₄H₇N₃O₃ (mol.wt.=145):C, 33.10%; H, 4.82%; N, 28.96%; O 33.10%. Found: C, 33.01%; H, 4.79%;4.78%; N, 28.85%; O, 33.12%. IR: ν_{NH}=3250; ν_{C=N} 1600; ν_{C=O}=1743.

2.3 Synthesis of Mixed ligand complexes ML₁L₂:

A1.0 mmol 30ml methanolic solution of metal chloride was added dropwise to a stirred solution of the mixture of a alcoholic solution of30 ml 1.0 mmol benzaldehyde thiosemicarbazone and 30ml 1.0 mmol Pyruvic acid semicarbazone. To this solution 10ml 2.0mmols of sodium acetate was then added.Then the solution was refluxed for four hours and stirred for 24 hours at room temperature.. 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.



2.3.1Co(II) complex of benzaldehyde thiosemicarbazone and pyruvic acid semicarbazone:

Brown solid, yield=64% Anal. Calc. (mol. Wt .471.93), mol. Formula $\text{CoC}_{12}\text{H}_{17}\text{O}_4\text{N}_6\text{SCl}$
:C=30.51%, H=3.60%, O=13.56, S=4.71, N=17.79 found C=30.31%, H=3.540%, O=13.46, S=4.67, N=17.59

Conductivity=121.0 Ω^{-1} , cm²mol⁻¹

IR spectra: $\nu_{\text{OH}}=3344$, $\nu_{\text{COOH}}=2360$, $\nu_{\text{C=O}}=1721$, $\nu_{\text{C=N}}=1581$ $\nu_{\text{C=S}}=860$, $\nu_{\text{M-S}}=802$ $\nu_{\text{M-N}}=692$

UV spectra: $\nu_1=8571\text{cm}^{-1}$, $\nu_2=17061\text{cm}^{-1}$, $\nu_3=29453\text{cm}^{-1}$, $\nu_2/\nu_1=1.990$,

2.3.2Ni(II) complex of benzaldehyde thiosemicarbazone and pyruvic acid semicarbazone:

Faint yellow solid yield 73%

Anal. Calc. (mol. Wt.471.69), mol. Formula $\text{NiC}_{12}\text{H}_{17}\text{O}_4\text{N}_6\text{SCl}$:C=30.52%, H=3.60%, O=13.56, S=4.71, N=17.70 Found C=30.42%, H=3.560%, O=13.49, S=4.73, N=17.65

IR spectra: $\nu_{\text{OH}}=3371$, $\nu_{\text{COOH}}=2360$, $\nu_{\text{C=O}}=1716$, $\nu_{\text{C=N}}=1585$ $\nu_{\text{C=S}}=855$, $\nu_{\text{M-S}}=799$ $\nu_{\text{M-N}}=693$

UV spectra: $\nu_1=9132\text{cm}^{-1}$, $\nu_2=15145\text{cm}^{-1}$, $\nu_3=31512\text{cm}^{-1}$, $\nu_2/\nu_1=1.658\text{cm}^{-1}$,

Conductivity=111.0 Ω^{-1} , cm²mol⁻¹ Ω^{-1} , cm²mol⁻¹

2.3.3 Cu(II) complex of benzaldehyde thiosemicarbazone and pyruvic acid semicarbazone:

Brown solid yield 65% Anal. Calc. (mol. Wt .476.54), mol. Formula $\text{CuC}_{12}\text{H}_{17}\text{O}_4\text{N}_6\text{SCl}$
:C=30.21%, H=3.77%, O=13.46, S=4.67, N=17.61 Found C=30.17%, H=3.69%, O=13.49, S=4.70, N=17.59

IR spectra: $\nu_{\text{OH}}=3397$, $\nu_{\text{COOH}}=2360$, $\nu_{\text{C=O}}=1734$, $\nu_{\text{C=N}}=1595$ $\nu_{\text{C=S}}=863$, $\nu_{\text{M-S}}=803$ $\nu_{\text{M-N}}=691$

UV spectra: $\nu_1=13992\text{cm}^{-1}$, $\nu_2=24178\text{cm}^{-1}$, $\nu_3=30103\text{cm}^{-1}$, $\nu_2/\nu_1=1.727\text{cm}^{-1}$,

Conductivity=100.5 Ω^{-1} , cm²mol⁻¹

Results and Discussion

The reactions of Co(II), Ni(II) and Cu(II) chloride with benzaldehyde thiosemicarbazone and pyruvic acid semicarbazone in 1:1:1 molar ratio results in the formation of mixed ligand complexes.

The resulting complexes are colored solids, insoluble in chloroform, carbon tetrachloride, ethanol, methanol, benzene etc but soluble in DMF. the conductance of the complexes are in the range 100-131 Ω^{-1} , cm²mol⁻¹ indicating their electrolytic nature.

The TLC of the mixed ligand complexes shows single spot 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 the two corresponding bis complexes.

In the IR spectra of the mixed ligand complexes bands at $1711-1734\text{ cm}^{-1}$ and $859-861\text{ cm}^{-1}$ may be assigned to $\nu_{\text{C=O}}$ and $\nu_{\text{C=S}}$. Thus, the lowering of $\nu_{\text{C=O}}$ and $\nu_{\text{C=S}}$ in the mixed ligand as compared to the free ligands supports the C=O groups to the metal atom [6]. In the mixed ligand complexes band at $1581-1595\text{ cm}^{-1}$ be due to $\nu_{\text{C=N}}$. Weak to medium intensity bands observed in the complexes in the region $799-803\text{ cm}^{-1}$ and $691-693\text{ cm}^{-1}$ maybe assigned for $\nu_{\text{M-N}}$ and $\nu_{\text{M-O}}$. A broad band appearing at $3344-3397\text{ cm}^{-1}$ maybe due to ν_{OH} of water associated with the complexes.

The electronic spectra of the Co(II) complex shows three bands at frequencies 8571 cm^{-1} , 17061 cm^{-1} and 29453 cm^{-1} which may be assigned to ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})$, ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{2g}(\text{F})$ and ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$ transitions respectively. The absorption band at 29453 cm^{-1} may be due to charge transfer. The ratio $\nu_2/\nu_1=1.990$ suggests octahedral geometry. The μ_{eff} value of this complex is 4.17 B.M. supplementing octahedral nature of the complex.

The electronic spectra of Ni(II) complex shows three bands at frequencies 9341 cm^{-1} , 15613 cm^{-1} and 30581 cm^{-1} with transitions ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}(\text{F})$, ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{F})$, and ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}(\text{P})$ respectively. The ratio $\nu_2/\nu_1=1.671$ suggests octahedral geometry of the complex supported by the value of magnetic susceptibility value $\mu_{\text{eff}}=3.21\text{ B.M.}$

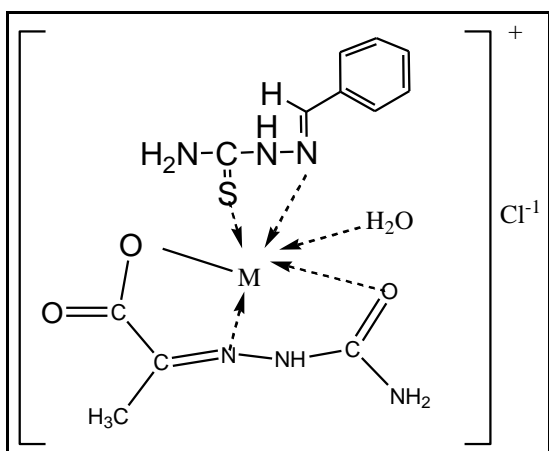
The electronic spectra of Cu(II) complex shows three bands at frequencies 8733 cm^{-1} , 13989 cm^{-1} and 30581 cm^{-1} with transitions ${}^2\text{B}_{1g} \rightarrow {}^2\text{A}_{1g}$, ${}^2\text{B}_{1g} \rightarrow {}^2\text{B}_{2g}$ and ${}^2\text{B}_{1g} \rightarrow {}^2\text{E}_{2g}$ respectively indicating octahedral geometry of the complex. The observed value of magnetic moment of the Cu(II) complex is 2.01 B.M. confirming the octahedral structure of the complex..

Thermogravimetric analysis shows presence of one water molecule in these three complex and confirming the octahedral nature.

Microbial activities were carried out with three different organisms E. Coli, Bacillus Sp and Staphylococcus Sp by dissolving the complex in DMF. Results shows that complexes of copper(II) are more active than Co(II) and Ni(II) complexes.

Conclusion:

The ligand benzaldehyde thiosemicarbazone is a bidentet ligand coordinating through 'N' and 'S' while Pyruvic acid semicarbazone is a bidentet ligand coordinating through 'N' and 'O'. Analytical data, electronic spectra, magnetic susceptibility, IR spectral data reveal octahedral geometry for all the complexes. The conductance values show electrolytic behavior of the complexes. The ligands and its all complexes were tested for antimicrobial activity. The complexes shows moderate to good antibacterial and antifungal activity compared to its ligand. On the basis of spectral evidence, the following probable structures have been assigned for synthesized compounds.



Acknowledgement

Author is very thankful to Principal ,Pratap college ,Amalner AND Head,Department of Chemistry ,Pratap college Amalner for providing necessary facilities.

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