

**INTERNATIONAL JOURNAL OF CURRENT RESEARCH IN
CHEMISTRY AND PHARMACEUTICAL SCIENCES**

(p-ISSN: 2348-5213; e-ISSN: 2348-5221)

www.ijcrops.com

DOI:10.22192/ijcrops

Coden: IJCROO(USA)

Volume 4, Issue 2 - 2017

Research Article



DOI: <http://dx.doi.org/10.22192/ijcrops.2017.04.02.002>

**Synthesis of mixed ligand complexes of pyruvic acid
thiosemicarbazone and acetone semicarbazone with
transition metals**

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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 $Cu(II)$ with $L_1=$ Pyruvic acid thiosemicarbazone $L_2=$ Acetone 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 and sulphur to metal ion.

Keywords: Mixed ligand, Pyruvic acid thiosemicarbazone, acetone semicarbazone, transition metals.

Introduction

The Schiff bases are among the most widely used ligands due to their facile synthesis, remarkable versatility and good solubility in common solvents. They have played an important role in the development of coordination chemistry as they readily form stable complexes with most of the metals [1-2]. Metal chelates of Schiff bases have been a subject of extensive investigations during last few decades due to their biochemical, pharmacological [3] and catalytic applications. On the basis of nature of the metal as well as the type of ligand, these metal complexes have wide applications in different fields of human curiosity [4,5].

In this context, thiosemicarbazones are a class of compounds obtained by condensation of thiosemicarbazide with suitable aldehydes or ketones. In most complexes thiosemicarbazones behave as bidentate ligands because they can bond to metals through sulphur and the hydrazine nitrogen atoms, although pyruvic acid derivative acts as tri dentate ligand

and bonding through sulphur, nitrogen and oxygen. Thiosemicarbazone derivatives are of special importance because of their versatile biological and pharmacological activities. Thiosemicarbazone derivatives have found application in drug development for the treatment of central nervous system disorders, of bacterial infection, as well as analgesic and anti allergic agent. Thiosemicarbazones are potent intermediates for the synthesis of pharmaceutical and bioactive materials and thus, they are used extensively in the field of medicinal chemistry. Moreover, thiosemicarbazones have found their way into almost every branch of chemistry; commercially they are used as dyes, photographic films, plastic and in textile industry. Over the years, thiosemicarbazone derivatives have demonstrated wide range of biological activity viz. Antimicrobial [5-10], antitumor [11-12], sodium channel blocker [13], anticancer [14-15], antitubercular [16], antiviral [17]. Keeping in mind various biomedical

application of these class of compounds, we report the synthesis and characterization of mixed ligand complexes of acetone semicarbazone and pyruvic acid thiosemicarbazone with Cr(III), Mn(II), Fe(III), Co(II), Ni(II) and Cu(II).

B1.2. Synthesis

The compounds pyruvic acid thiosemicarbazone and acetone semicarbazone prepared and characterized in the laboratory for the synthesis of mixed ligand complexes with transition metal complexes. transition metal chlorides. The metal chlorides of Cr(III), Mn(II), Co(II), Ni(II) and Cu(II) used were of E MEARK, BDH, S D fine analytical grade.

The following general procedure was used to prepare the mixed ligand complexes of pyruvic acid thiosemicarbazone (PYSC) and acetone semicarbazone (ACSC) with Cr(III), Fe(III), Mn(II), Co(II), Ni(II) and Cu(II). To 20 ml ethanolic solution of 0.01M metal chloride a mixture of ethanolic solution of 20 ml 0.01M acetone semicarbazone and 20 ml 0.01M pyruvic acid thio semicarbazone ligands were added with continuous stirring in a water bath. Then the reaction mixture is refluxed with water condenser for two 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. (for Co complex P^H of the reaction mixture should be 8.5-9.0) 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 separates out from the solution. The contents were cooled and the solid product of mixed ligand complex was filtered, washed thoroughly first with hot water and finally with ethanol and air dried, Yield is about 60-78%.

B1.3: Analytical Properties

The resulting complexes were having different colors as given in the table 1., They are insoluble in chloroform, carbon tetrachloride, methanol, ethanol but soluble in DMF. The properties of complexes are indicated in table 1. 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 amount of metals present in complexes were determined volumetrically by EDTA using double burette technique for optimum utilization of reagents. Indicator Erichrome Black T was used for Mn(II), ammonium thiocyanate for Fe(III), xylene orange for Co(II) and Cr(III), murexide for Ni(II) and Cu(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 JASCO 6700 FTIR instrument using KBr pellets in the region $400-4000\text{ cm}^{-1}$ from Department of Physics, Pratap College, Amalner and Central Instrumentation Laboratory, Pratap College, Amalner. Electronic spectra of complexes were recorded on JASCO -670 UV-VISIBLE Spectrophotometer in the Department of Chemistry, Pratap College, Amalner. Thermo gravimetric analysis was carried out on SHIMADZU STA 6000 from Department of Physics, Pratap College, Amalner. Antimicrobial activities are determined in the PG department of Microbiology, Pratap College, Amalner by using three microbial nutrients.

B1.4: Spectral Properties

B1.4.1. Electronic Spectra

The electronic spectra of mixed ligand complexes of transition metals with pyruvic acid thiosemicarbazone and acetone semicarbazone discussed below.

Cr(III) Complex:

The electronic spectra of the Cr(III) complex exhibits band at 8733 cm^{-1} , 14492 cm^{-1} and 36487 cm^{-1} which may be assigned to ${}^4A_{2g}(F)$, ${}^4T_{2g}(F)$, ${}^4A_{2g}(F)$, ${}^4T_{1g}(F)$, and ${}^4A_{2g}(F)$, ${}^4T_{1g}(P)$ transitions. The ground state in octahedral field is ${}^4A_{2g}$. On octahedral model three spin-allowed transitions, (3) are expected in d^3 system such as Cr(III): but 3 is generally submerged under charge-transfer and inter ligand transitions in a near UV spectra. The first spin-allowed transitions (1) whose energy is assumed to be equal to $10Dq$ is observed at 11417 cm^{-1} in Cr(III) complex. The second spin-allowed transition (2) has been assigned to the transition peak observed at 14492 cm^{-1} . Both 1 and 2 bands are some what but do not show any sign of splitting. The broadening of these bands may be due to a small distortion from octahedral structure. Assignment of these transition s makes it possible to extract only two ligand field parameters, $10Dq$ and B_{35} . Racha's parameter of interelectronic repulsion.

The assignment of the of the third spin allowed (3) transition is usually observed in Cr(III) complexes which involves weak ligand field; with medium and strong ligand fields this transition is generally masked by intense ligand/or charge-transfer absorption. Using the computed values of Dq and B_{35} , 3 occurs at 36487 cm^{-1} indicating octahedral geometry of the complex. $B_{35} = B_{35}/B_{\text{free ion}}$ and it comes out to be 0.9575 which is less than unity indicating ${}^-$ -type of interactions between the metal. LFSE for Cr(III) in octahedral field is equal to $12Dq$. It comes out to be 10.47 Kcal/mole .

Mn(II) complex:

Manganese (II), showed very weak absorption bands, which may not help in assigning geometry. The bands at

(11723) cm^{-1} , (21739) cm^{-1} , and (31746) cm^{-1} . The electronic ground state of Mn (II) is ${}^6A_{1g}$ and as in the isoelectronic Fe(III), all the transitions are spin-forbidden. Spectral assignments based on the earlier calculations of Tanabe and Sugano and Orgel for several Mn(II) complexes are investigated.

The reflectance spectrum of Mn(II) complex shows bands in the normally expected regions for octahedral stereochemistry. The observed transitions may be assigned as ${}^6A_{1g} \rightarrow {}^4T_{1g}$ (G) for 11723 cm^{-1} , ${}^6A_{1g} \rightarrow {}^4A_{1g}$ (G) for 21739 cm^{-1} and ${}^6A_{1g} \rightarrow {}^4E_g$ (D) for 31746 cm^{-1} .

Fe(III) complex:

Fe(III) forms large number of complexes, mostly octahedral ones, and the octahedron may be considered as its characteristic coordination shell. The spectrum of octahedral Fe (III) has not been adequately characterized. The ground term is ${}^6A_{1g}$ in high spin complexes. The absence of any other spin sextet terms implies that all crystal field transitions from ${}^6A_{1g}$ will be spin-forbidden, as well as Laporte-forbidden. The intensities of these transitions are very weak.

The spectrum of our Fe(III) complex consists of three bands. The first two bands observed at 10604 and 17636 are assigned to ${}^6A_{1g} \rightarrow {}^4T_{1g}$ and ${}^6A_{1g} \rightarrow {}^4T_{2g}$ transitions. The third band observed at has been assigned to the pair of transitions to ${}^6A_{1g} \rightarrow {}^4A_{1g}$ (G) and ${}^6A_{1g} \rightarrow {}^4E_g$ (G) which are degenerate in octahedral symmetry.

Co(II) Complex:

The reflectance spectrum of Co(II) complex is characteristic of Co(II) in octahedral environment, exhibiting three bands at 8032, 11723 and 31948 cm^{-1} assigned as ${}^4T_{1g} \rightarrow {}^4A_{2g}$ (F), ${}^4T_{1g}$ (F) $\rightarrow {}^4T_{1g}$ (P) and ${}^4T_{1g}$ (F) $\rightarrow {}^4T_{2g}$ (F) respectively. Further support for the octahedral geometry is provided by the ratio $\lambda_{2/1}$ which is 1.459 indicating octahedral stereochemistry. The ligand field parameters are calculated using the following equations:

LFSE is calculated as LFSE for Co(II) in octahedral Stereochemistry is equal to $6Dq$. It comes out to be 6.65 kcal/mole.

Ni(II) complex:

The reflectance spectrum of Ni(II) complex is characteristic of Ni(II) in octahedral environment, exhibiting three bands at 8347, 14227 and 29673 cm^{-1} assigned as shown in table 2. Ni(II) complexes with regular octahedral structure, the ratio $\lambda_{2/1}$ is expected to be in the range 1.5-1.7. The ratio is 1.704, which is near the expected range.

Cu(II) complex:

The electronic spectra of Cu(II) complex shows bands at 13351, 25839 and 31347 cm^{-1} . Distorted octahedral structure of complexes show bands at these positions. The $\lambda_{2/1}$ ratio 2.928 corresponding to ${}^2B_{1g} \rightarrow {}^2A_{1g}$, ${}^2B_{1g} \rightarrow {}^2B_{2g}$, ${}^2B_{1g} \rightarrow {}^2E_g$ transitions, respectively.

B1.4.2. IR Spectra

The infrared spectra technique was used to identify the prepared coordination complexes, specially on comparing with the free ligand spectra so as to locate the position of the donor atoms. Besides identifying the ligands (L_1 and L_2) the infrared spectra were also to determine the position of absorption bands for the different active groups such as (NH_2), (OH of carboxylic gr) ($\text{C}=\text{O}$), ($\text{C}=\text{N}$), (NH), ($\text{C}-\text{N}$), ($\text{C}-\text{N}$), ($\text{M}-\text{S}$), ($\text{M}-\text{N}$), ($\text{M}-\text{O}$). Ligand (L_1), shows five bands at (3498) cm^{-1} , (2356) cm^{-1} , (1678) cm^{-1} , (1546) cm^{-1} and (1256) cm^{-1} , (1140) cm^{-1} which are attributed to (NH_2), (OH of carboxylic gr), ($\text{C}=\text{N}$), (NH), ($\text{C}-\text{N}$) and ($\text{C}=\text{S}$) groups, respectively. Ligand (L_2), shows six bands at (3370) cm^{-1} , (1731) cm^{-1} , (1685) cm^{-1} , (1544) cm^{-1} , (1263) cm^{-1} and (1123) cm^{-1} , which are assigned for (NH_2), ($\text{C}=\text{O}$), ($\text{C}=\text{N}$), (NH), ($\text{C}-\text{N}$) and ($\text{C}=\text{S}$) groups, respectively.

For metal complexes of ligand (L_1 and L_2) the stretching frequencies for the ($\text{C}=\text{N}$), ($\text{C}=\text{O}$), (NH) and ($\text{C}=\text{S}$) are weakened and shifted to lower frequencies to about (5-25) cm^{-1} , while those for the ($\text{C}-\text{N}$), ($\text{N}-\text{N}$) and (NH_2) become weaker too but with no shift because these groups no coordination with metals ions. New bands are observed indicating coordination as ($\text{M}-\text{N}$), ($\text{M}-\text{S}$) and ($\text{M}-\text{O}$). In addition one band is observed in the region (3514-3629) cm^{-1} indicating presence of co-ordinated water molecule.

B1.5: Magnetic Properties

The magnetic moments, μ_{eff} of the complexes. The $3d^3$ Cr (III) ion has three unpaired electrons and its complex have magnetic moment close to the spin-only value of 3.87 B.M. The magnetic moment (4.07 B.M.) observed for our Cr (III) complex is slightly less than the spin-only value. Indicating octahedral geometry.

Mn(II) complex:

The observed magnetic moment (5.623 B.M.) of Mn(II) complex is very close to observed for spin-free d^5 system. It shows octahedral nature of the complex.

Fe(III) complex:

Generally Fe(III) is high-spin in nearly all of the complexes. In high-spin complexes, the magnetic moments are always very close to the spin-only value of 5.92 and are independent of temperature. The observed magnetic moment (5.67 B.M.) of Fe(III) complex is lower

than the expected value but much higher than the low-spin complexes (~ 2.3 B.M.). So Fe (III) must be high-spin in the complexes. The low magnetic moment might be due to the metal-metal interaction.

Co(II) Complex :

The Co(II) complex shows a magnetic moment of 4.497 B.M. This value is in the range of octahedral geometry.

Ni(II) complex:

For six coordinate Ni(II) complexes in a regular octahedral geometry consideration of spin-orbit coupling and contributions from $^3A_{2g}$ and next higher $^3T_{2g}$ state predicts the maximum value somewhat above the spin-only moment of 4.61 B.M. The magnetic moment of the complex is 3.972 B.M. suggesting octahedral structure for this complex.

Cu(II) complex:

The Cu(II) complex has a magnetic moment value of 2.01 B.M. Which supports octahedral character of the complex.

Conductometric measurement of the complexes shows conductivity in the range of 31.40-100.1 moh., supporting non-electronic nature of the complexes.

B1.6: Thermogravimetric Analysis

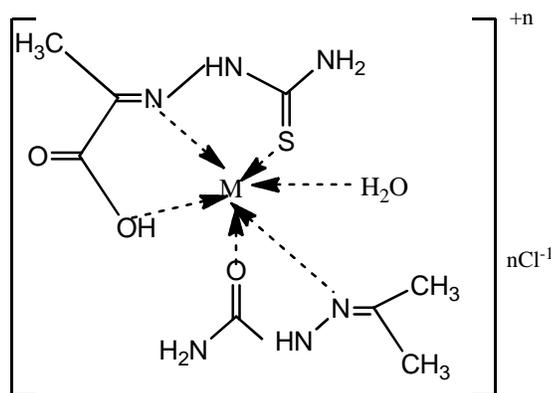
The thermo grams (TG) of the compounds have been recorded in flowing nitrogen atmosphere at the heating rate of 10°C/min on approximately 10 mg samples.

In thermogravimetric analysis of Cr(III), Mn(II), Fe(III), Co(II), Ni(II) and Cu(II) complexes shows weight loss % of 4.150, 4.157, 4.358, 3.892, 4.145 and 4.578 in the temperature range of 100-350°C indicating loss of one co-ordinated water molecule (=3.987, 4.276, 3.944, 4.245, 4.248 and 4.200 respectively). Also these complexes shows further weight loss of about 15-50% in the temperature range 250-700°C. due to decomposition of the complexes. Thermodynamic properties are shown in table B1.5. TGA and DSC curves are shown 3.1 to 1.3.6

B1.7: Biological Activities.

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 100 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.

Structure of complexes.



Acknowledgments

The authors are thankful to Principal, Pratap college, Amalner ; Head, Department of Chemistry and, Physics Pratap college, Amalner ; Principal, R.L.College, Parola for providing necessary facility and Director, SAIF, Mumbai for providing elemental facilities.

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Quick Response Code	
DOI: 10.22192/ijcrops.2017.04.02.002	

How to cite this article:

P.R. Shirode, P.M. Yeole. (2017). Synthesis of mixed ligand complexes of pyruvic acid thiosemicarbazone and acetone semicarbazone with transition metals. Int. J. Curr. Res. Chem. Pharm. Sci. 4(2): 5-9.
DOI: <http://dx.doi.org/10.22192/ijcrops.2017.04.02.002>