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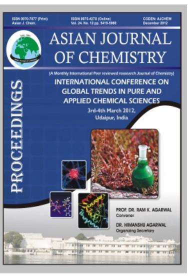

Synthesis and Physico-chemical Studies of Mixed Ligand Complexes of Mn(II), Fe(III), Co(II), Ni(II) and Cu(II) with Acetophenone Semicarbazone and Cyclohexanone Semicarbazone†

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The mixed ligand complexes of the type $[M(L_1)(L_2)]Cl_2$ (where M= Mn(II), Fe(III), Co(II), Ni(II) and Cu(II) and L_1 = acetophenone semicarbazone, L_2 = cyclohexanone semicarbazone) have been synthesized by the reactions of metal chlorides with two different semicarbazone compounds in 1:1:1 molar ratios. The resulting complexes have been characterized on the basis of elemental analysis, magnetic measurement, IR and electronic spectra, conductivity measurement. The metal complexes shows ratio 1:1:1 with metal, ligand L_1 and ligand L_2. The ligands acts as bidentate ligands and are bonded through oxygen and nitrogen to metal ion. The two co-ordination positions are occupied by two water molecules. The complexes have octahedral structure.

Key Words: Synthesis, Metal(II) complexes, Acetophenone semicarbazone, Cyclohexanone semicarbazone.

INTRODUCTION

Mixed ligand complexes play an important role in biological processes like activation of enzymes by metals[1,2]. Such complexes are useful in the storage and transport of active substances through membranes[3]. Semicarbazones constitute one of the most important class of oxygen and nitrogen donor ligands[4-7]. The formation of a variety of metal complexes from these ligands indicates the spectacular progress in coordination and bioinorganic chemistry. The real efforts used for developing the coordination chemistry of these ligands was probably due to antitumor, antimalarial, antifungal and antibacterial activities. They were also found to be useful as potential drugs fungicidal agents. The antibacterial and fungicidal activities of transition metal complexes are due to their ability to form chelates with the essential metal ions bonding through nitrogen as donor atom of the ligand.

The present course of study was initiated to understand the characteristic nature and applications and applications of the biologically active metal complexes of nitrogen and oxygen donor ligands. By considering all these applications, in this paper we are reporting the synthesis and characterization of series of Mn(II), Fe(III), C(II), Ni(II) and Cu(II) complexes obtained from acetophenone semicarbazone and cyclohexanone semicarbazone as ligands.

EXPERIMENTAL

All the chemicals used were of analytical reagent grade and metal salts are also of standard quality. All solvents are or of standard spectroscopic grade.

All the transition metals were determined volumetrically by using EDTA using double burette technique for optimium utilization of reagents[8]. Indicator Erichrome black T is used for Mn(II), ammonium thiocynate for Fe(III), Xylenol orange for Co(II) and Mureoxide for Ni(II) and Cu(II). Carbon, hydrogen and nitrogen analysis were carried out from SAIF, Mumbai. Specific conductance were measured at room temperature and at 10 ºC higher than room temperature in DMF by a systronics direct reading 304 conductivity meter using glass conductivity cell having cell constant 1.0 cm^{-1}. Magnetic measurements were carried out at room temperature on a Gouy balance using $Hg[CO(NCS)_4]$ as a calibrant. IR spectra of the complexes (KBr) were recorded in the region 400-4000 cm^{-1} on Perkin elmer FTIR spectrometer and electronic spectra were recorded n a Shimadzu 2450 UV-Visible spectrophotometer in the department of physics, pratap college, Amalner.

Synthesis of ligands: Ligands L_1 and L_2 were prepared and the methods of their preparation are given below.

Ligand L_1 (acetophenone semicarbazone): To a mixture of hot ethanolic 25 mL (0.1 M) solution of acetophenone and

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TABLE-1
PHYSICAL PROPERTIES OF LIGANDS

Name of the ligand	Colour and nature	Method of purification	m.p. ºC (observed) reported	m. w.	m. f.
Acetophenonesemicarbazone	White shining crystals	Recrystallization from ethanol	(200) 199	177	$C_9H_{12}N_3O$
Cyclohexanone semicarbazone	White shining crystals	Recrystallization from ethanol	167	163	$C_7H_{13}N_3O$

TABLE-2
CHARACTERIZATIONDATA OF THE COMPLEXES FOUND (CALCD.) %

Ligand/complex	Colour	Mole wt.	Yield of the comp. (%)	Elemental analysis (%): Found (calcd.)			
				M	C	H	N
$Mn[(APS)_1(CS)1\ (H_2O)_2]Cl_2$	Faint brown	487.71	63	10.89 (11.79)	44.30 (44.28)	4.90 (4.92)	17.20 (17.22)
$Fe[(APS)_1(CS)_1\ (H_2O)_2]Cl_3$	Light green	518.36	69	10.52 (10.77)	41.63 (41.65)	4.64 (4.63)	16.18 (16.20)
$Co[(APS)_1(CS)_1\ (H_2O)_2]Cl_2$	Light pink	485.93	71	11.60 (12.07)	44.43 (44.45)	4.32 (4.32)	17.28 (17.28)
$Ni[(APS)_1(CS)_1\ (H_2O)_2]Cl_2$	Bluish green	485.71	78	12.31 (12.33)	44.38 (44.43)	4.30 (4.31)	17.25 (17.27)
$Cu[(APS)_1(CS)_1\ (H_2O)_2]Cl_2$	Green	454.84	63	12.70 (13.22)	47.45 (47.49)	4.57 (4.61)	18.44 (18.47)

20 mL (0.1 M) sodium acetate solution, 25 mL (0.1 M) aqueous solution of semicarbazide hydrochloride were slowly added with constant stirring. This mixture was refluxed in water bath at 70-80 ºC for 20-25 min. On cooling white solid product separated out. It is filtered, washed with cold ethanol, dried in air and recrystallized from ethanol.

Ligand L_2 (cyclohexanone semicarbazone): To a mixture of hot ethanolic 25 mL (0.1 M) solution of (cyclohexanone and (20 mL 0.1 M) solution of sodium acetate 25 mL (0.1 M) aqueous solution of semicarbazide hydrochloride was added slowly with constant stirring. Then the reaction mixture was refluxed for 15-20 min 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.

Synthesis of complexes

Preparation of M $(L_1)_2$ and $M(L_2)_2$ complexes: Hot ethanolic 25 mL (0.01 M) solution of manganese chloride were mixed slowly with hot ethanolic 25 mL (0.02 M) solution of the acetophenone semicarbazone with constant stirring. The reaction mixture is heated in water bath for 1 h. Then the reaction was stirred for further one hour after, which colour solid product was obtained, which was then washed with ethanol and dried in air. Similarly, the complexes of other metals Fe(III), Co(II), Ni(II) and Cu(II) with acetophenone semicarbazone and cyclohexanonesemicarbazone were prepared by mixing solution of corresponding metal chlorides and semicarbazone ligand in 1:2 molar ratio respectively.

Preparation of mixed ligand complexes the type ML_1L_2: To a 20 mL (0.02 M) ethanolic solution of manganese chloride, a mixture of 20 mL (0.02 M) ethanolic solution of acetophenone semicarbazone and 20 mL (0.02 M) ethanolic solution of cyclohexanone semicarbazone were added slowly with constant stirring. This reaction mixture is heated in water bath for 1 to 1.5 h. And then 10 % sodium hydroxide is added to adjust the pH to about 7 to 7.5.The pH of the solution is tested by pH paper. In case of complexes of cobalt and copper the pH of the reaction mixture must not exceed 7.5 unless the colour of the complexes darken more and more to give a black colour. The solution is stirred further for one hour, cooled to separate the solid coloured complex. It is filtered, washed with ethanol and dried in air. In this way the complexes. Similarly, the complexes of other metals Fe(III), Co(II), Ni(II) and Cu(II) with acetophenone semicarbazone and cyclohexanone semicarbazone were prepared by mixing solution of corresponding metal chlorides and semicarbazone ligand in 1:1:1 molar ratio respectively.

RESULTS AND DISCUSSION

The reactions of metal chlorides with acetophenone semicarbazone and cyclohexanone semicarbazone in 1:1:1 molar ratio results in the formation mixed ligand complexes. The resulting complexes were having different colours. They are insoluble in chloroform, carbantetrachloride, methanol, ethanol but soluble in DMF. The physical properties of ligands are indicated in Table-1 and of metal complexes in Table-2. The conductance of the complexes are very low (1-42 Ω^{-1} cm^2 mol^{-1}) indicating their non-electrolyte nature (Table-3).

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. In the IR spectra of the mixed ligand complexes the bands at 1596-1590 cm^{-1} may be assigned to the symmetric and asymmetric ν(C=N) vibrations. A strong band in the region 1710-1690 cm^{-1} are due to ν(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 band in the region 1740-1733 cm^{-1} indicates presence of cyclohexane ring in the cyclohexanonesemicarbazone complex. A broad band appears in the region at 3750-3200 cm^{-1} be attributed to the coordinated water molecule (Table-3). Thermogravemetric analysis shows presence of two water molecules in the complexes supports the octahedral nature of complexes. The electronic spectra of Mn(II) complexes exhibits bands in the range 17534-17568, 23224-23255 and 28542-28592 cm^{-1} corresponding to ${}^6A_{1g} \rightarrow {}^4T_{1g}$ (4G), ${}^6A_{1g} \rightarrow {}^4E_{2g}$ (4G), ${}^4A_{1g}$ (4G) and ${}^6A_{1g} \rightarrow {}^4E_{2g}$ (4D), transitions, respectively suggesting octahedral environment around Mn(II) ion. Fe(III) complexes shows bands in the range 12500-12529, 21270-21296 and 26978-27032 cm^{-1} assignable to ${}^6A_{1g} \rightarrow {}^4T_{1g}$ (G), ${}^6A_{1g} \rightarrow {}^4T_{2g}$ (G) and ${}^6A_{1g} \rightarrow {}^4A_{1g}$ (G) transitions, respectively and magnetic moment indicates octahedral geometry. Co(II) complexes shows absorption bands in the range 13657-13699, 16947-16978 and 27744-27781 cm^{-1}, 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 10749-11212, 18524-18595 and 22457-22667 cm^{-1} 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 11151-11521,16216-1667 and 22914-23024 cm^{-1} corresponding to $^2B_{1g} \rightarrow {}^2A_{1g}$, $^2B_{1g} \rightarrow {}^2B_{2g}$.

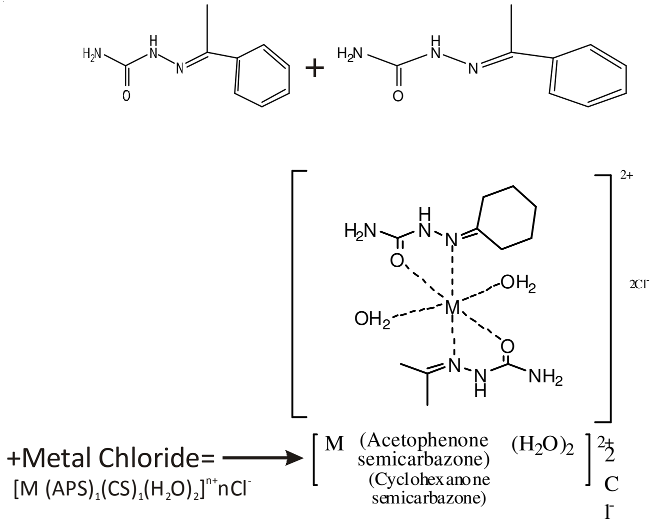
TABLE-3
IR SPECTRA (cm^{-1}) BANDS OF THE PARENT AND MIXED LIGAND TRANSITION METAL COMPLEXES

Ligand/complex	ν (OH) from H_2O	ν (C=O)	ν (C=N)	Monosubstituted benzene ring
Mn[$(APS)_1(CS)_1(H_2O)_2]Cl_2$	3735	1670	1540	692
Fe[$(APS)_1(CS)_1(H_2O)_2]Cl_3$	3529	1651	1539	688
Co[$(APS)_1(CS)_1(H_2O)_2]Cl_2$	3226	1669	1543	692
Ni[$(APS)_1(CS)_1(H_2O)_2]Cl_2$	3229	1659	1548	690
Cu[$(APS)_1(CS)_1(H_2O)_2]Cl_2$	3611	1689	1568	688

TABLE-4
MAGNETIC MOMENT, MOLAR CONDUCTANCE AND ELECTRONIC SPECTRA OF THE COMPLEXES

Ligand/ Complex	Magnetic moment	Molar cond. Ω^{-1} cm^2 mol^1 at room temp.
Mn[$(APS)_1(CS)_1(H_2O)_2]Cl_2$	5.02	17
Fe[$(APS)_1(CS)_1(H_2O)_2]Cl_3$	5.27	16
Co[$(APS)_1(CS)_1(H_2O)_2]Cl_2$	4.74	10
Ni[$(APS)_1(CS)_1(H_2O)_2]Cl_2$	3.45	09
Cu[$(APS)_1(CS)_1(H_2O)_2]Cl_2$	2.27	21

Structure of the ligands:



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