

Synthesis and Physicochemical Studies of Mixed Ligand Complexes of Mn(II), Fe(III), Co(II), Ni(II) and Cu(II) with Acetophenone Semicarbazone and Acetone Semicarbazone

P. R. SHIRODE

Department of Chemistry, Pratap College, Amalner -425401, India
prshirodepca@gmail.com

Received 12 May 2012 / Accepted 30 May 2012

Abstract: 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 =Acetone 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.

Keywords: Synthesis, Physicochemical studies, Semicarbazone, Ligands

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 membranes³⁻⁵. Mixed ligand complexes have been used in the analysis of semiconductor material. Semicarbazones constitute one of the most important class of oxygen and nitrogen donor ligands⁶⁻¹¹. 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 remarkable 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 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), Co(II), Ni(II) and Cu(II) complexes obtained from acetophenone semicarbazone and acetone 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 optimum utilization of reagents. Indicator Erichrome Black T is used for Mn(II), ammonium thiocyanate 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 temp and at 10 °C higher than room temp. 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 temp. 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 on a Shimadzu 2450 UV-Visible spectrophotometer in the Department of Physics, Pratap College, Amalner.

Synthesis of ligands

Ligands L₁ and L₂ were prepared and the methods of their preparation are given below.

Ligand L₁

Acetophenone Semicarbazone: To a mixture of hot ethanolic 25 mL (0.1 M) solution of acetophenone and 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 °C for 20-25 minutes. On cooling white solid product separated out. It is filtered, washed with cold ethanol, dried in air and recrystallized from ethanol.

Ligand L₂

Acetone Semicarbazone: To a mixture of hot ethanolic 25 mL (0.1 M) solution of (Acetone 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 5-10 minutes on a water bath. 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 CCl₄.

Synthesis of complexes

Preparation of M(L₁)₂ and M(L₂)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 one hour. Then the reaction was stirred for further one hour after which color 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, acetone semicarbazone 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 ML₁L₂

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

acetone semicarbazone were added slowly with constant stirring. This reaction mixture is heated in water bath for 1 to 1.5 hour 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 color of the complexes darkened more and more to give a black color. The solution is stirred further for one hour, cooled to separate the solid colored complex. It is filtered, washed with ethanol and dried in air. In this way the complexes of other metals Fe(III), Co(II), Ni(II) and Cu(II) with acetophenone semicarbazone and acetone 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 acetone semicarbazone in 1:1:1 molar ratio results in the formation mixed ligand complexes. The resulting complexes were having different colors. They are insoluble in chloroform, carbon tetrachloride, 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 ($1-42\Omega^{-1}\text{cm}^2\text{mol}^{-1}$) indicating their non-electrolyte nature.

Table 1. Physical properties of ligands

Name of the ligand	Colour and nature	Method of purification.	M.P. $^{\circ}\text{C}$ (observed) reported	Mol. wt	Molecular formula
Acetophenone semicarbazone	White shining crystals	Recrystallization from Ethanol	(200) 199	177	$\text{C}_9\text{H}_{12}\text{N}_3\text{O}$
Acetone semicarbazone	White shining crystals	Recrystallization from Ethanol	167	115	$\text{C}_7\text{H}_{13}\text{N}_3\text{O}$

Table 2. Characterization data of the complexes found (Calcd.) %

Ligand/ Complex	Colour	Mol. wt	% Yield of the comp.	% of metal (Calculated)	% of C	% of H	% of N
$\text{Mn}[(\text{APS})_1(\text{AS})_1(\text{H}_2\text{O})_2]\text{Cl}_2$	Faint brown	487.71	63	(11.70) 10.89	(44.8) 41.63	(4.92) 4.90	(17.22) 17.20
$\text{Fe}[(\text{APS})_1(\text{AS})_1(\text{H}_2\text{O})_2]\text{Cl}_3$	Light green	518.36	69	(10.77) 10.52	(41.5) 41.63	(4.63) 4.64	(16.20) 16.18
$\text{Co}[(\text{APS})_1(\text{AS})_1(\text{H}_2\text{O})_2]\text{Cl}_2$	Light pink	485.93	71	(12.07) 11.60	(44.5) 44.43	(4.32) 4.32	(17.28) 17.28
$\text{Ni}[(\text{APS})_1(\text{AS})_1(\text{H}_2\text{O})_2]\text{Cl}_2$	Bluish green	485.71	78	(12.33) 12.31	(44.3) 44.38	(4.57) 4.54	(17.27) 17.25
$\text{Cu}[(\text{APS})_1(\text{AS})_1(\text{H}_2\text{O})_2]\text{Cl}_2$	Green	429.74	63	(13.22) 12.70	(47.49) 47.45	(4.61) 4.57	(18.47) 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	$\nu(\text{C=O})$	$\nu(\text{C=N})$	Monosubstituted benzene ring
$\text{Mn}[(\text{APS})_1(\text{AS})_1(\text{H}_2\text{O})_2]\text{Cl}_2$	3735	1670	1540	692
$\text{Fe}[(\text{APS})_1(\text{AS})_1(\text{H}_2\text{O})_2]\text{Cl}_3$	3529	1668	1539	688
$\text{Co}[(\text{APS})_1(\text{AS})_1(\text{H}_2\text{O})_2]\text{Cl}_2$	3211	1670	1541	692
$\text{Ni}[(\text{APS})_1(\text{AS})_1(\text{H}_2\text{O})_2]\text{Cl}_2$	3229	1659	1548	690
$\text{Cu}[(\text{APS})_1(\text{AS})_1(\text{H}_2\text{O})_2]\text{Cl}_2$	3611	1689	1568	688

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

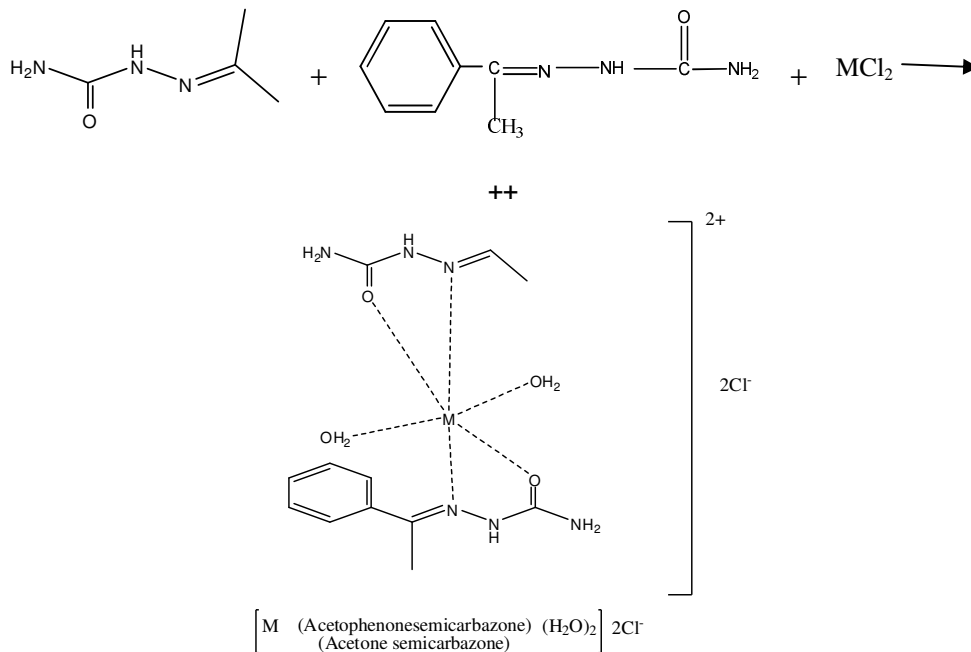
Ligand/ Complex	Magnetic moment	Molar cond. $\Omega^{-1}\text{cm}^2$ mol^{-1} at room temp.	Molar cond. $\Omega^{-1}\text{cm}^2$ mol^{-1} at room temp.
$\text{Mn}[(\text{APS})_1(\text{AS})_1(\text{H}_2\text{O})_2]\text{Cl}_2$	5.026	17	31
$\text{Fe}[(\text{APS})_1(\text{AS})_1(\text{H}_2\text{O})_2]\text{Cl}_3$	5.184	16	33
$\text{Co}[(\text{APS})_1(\text{AS})_1(\text{H}_2\text{O})_2]\text{Cl}_2$	4.7062	10	31
$\text{Ni}[(\text{APS})_1(\text{AS})_1(\text{H}_2\text{O})_2]\text{Cl}_2$	3.560	09	39
$\text{Cu}[(\text{APS})_1(\text{AS})_1(\text{H}_2\text{O})_2]\text{Cl}_2$	2.075	21	20

Table 3 shows IR spectral data of the complexes and Table 4 shows values of magnetic moments and molar conductivities of the complexes. 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 ligands the bands at $1596\text{-}1590\text{cm}^{-1}$ may be assigned to the symmetric and asymmetric $\nu(\text{C=N})$ vibrations and a strong band in the region $1710\text{-}1690\text{cm}^{-1}$ are due to $\nu(\text{C=O})$ groups present in the ligands. On complex formation, the position of these bands is shifted towards lower side ($1568\text{-}1539$) and ($1689\text{-}1659$) as compared to the metal free ligands. 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 $3200\text{-}3750\text{cm}^{-1}$ for $-\text{OH}$ group be attributed to the coordinated water molecule. Thermogravimetric analysis shows presence of two water molecules in the complexes supports the octahedral nature of complexes. The electronic spectra obtained for Mn(II) complexes exhibits bands in the range $17534\text{-}17568$, $23224\text{-}23255$ and $28542\text{-}28592\text{cm}^{-1}$ corresponding to $6\text{A}_{1g}\text{-}4\text{T}_{1g}$ (4G), $6\text{A}_{1g}\text{-}4\text{E}_{2g}$ (4G), 4A_{1g} (4G) and $6\text{A}_{1g}\text{-}4\text{E}_{2g}$ (4D), transitions, respectively suggesting octahedral environment around Mn(II) ion. Fe(III) complexes shows bands in the range $12500\text{-}12529$, $21270\text{-}21296$ and $26978\text{-}27032\text{cm}^{-1}$ assignable to $6\text{A}_{1g}\text{-}4\text{T}_{1g}$ (G), $6\text{A}_{1g}\text{-}4\text{T}_{2g}$ (G) and $6\text{A}_{1g}\text{-}4\text{A}_{1g}$ (G) transitions, respectively and magnetic moment indicates octahedral geometry. Co(II) complexes shows absorption bands in the range $13657\text{-}13699$, $16947\text{-}16978$ and $7\text{744}\text{-}27781\text{cm}^{-1}$, corresponding to $4\text{T}_{1g}\text{-}4\text{A}_{2g}$ (F), $4\text{T}_{1g}(\text{F})\text{-}4\text{T}_{1g}$ (P) and $4\text{T}_{1g}(\text{F})\text{-}4\text{T}_{2g}$ (F) transitions, respectively for octahedral geometry. The electronic spectra of Ni(II) complexes exhibits three bands in the range $10749\text{-}11212$, $18524\text{-}18595$ and $22457\text{-}22667\text{cm}^{-1}$ corresponding to $3\text{A}_{2g}(\text{F})\text{-}3\text{T}_{2g}(\text{F})$, $3\text{A}_{2g}(\text{F})\text{-}3\text{T}_{1g}(\text{F})$ and $3\text{A}_{2g}(\text{F})\text{-}3\text{T}_{1g}(\text{P})$ transitions, respectively

suggesting octahedral geometry. The six coordinated copper complexes shows bands in the range 11151-11521, 16216-16671 and 22914-23024 cm^{-1} corresponding to ${}^2B_{1g} \rightarrow {}^2A_{1g}$, ${}^2B_{1g} \rightarrow {}^2B_{2g}$, ${}^2B_{1g} \rightarrow {}^2E_{2g}$ transitions, respectively.

Structure of the ligands



Acknowledgement

I am grateful to Principal, Pratap College, Amalner and the Head Chemistry Department Pratap College, Amalner for laboratory facilities. I am also thankful to the Head Physics Department Pratap College, Amalner for Electronic spectra and IR spectra and Head, SAIF, IIT Mumbai for elemental analysis.

References

1. Anliazuk E, *Racznikiz Chmii.*, 1977, **51**, 627.
2. Panda P K and Mohaptra B K, *J Indian Chem Soc.*, 1984, **61**, 365.
3. Sulekh Chandra and Monika Tyagi J, *Indian Chem Soc.*, 2008, **85**, 42-47
4. Prasad R N, Kirti Mohan Sharma and Anjali Agrawal, *Indian J Chem.*, 2007, **46A**, 600-604.
5. Prasad R N, Kirti Mohan Sharma and Anjali Agrawal, *J Indian Chem Soc.*, 2007, **84**, 742-745.
6. Vogel A I, *A Text Book of Quantitative Inorganic Analysis*, 3rd Edn., ELBS-Longmans, Green & Co. Ltd., London, 1964.
7. Prasad R N and Jindal M, *J Indian Chem Soc.*, 1989, **66**, 188.
8. Prasad R N, Jindal M, Jain M, Varshney A and Chand P, *J Indian Chem Soc.*, 1990, **67**, 91
9. Prasad R N, Jindal M and Jain M, *J Indian Chem Soc.*, 1990, **67**, 874.
10. Sulekha Chandra, Krishna Sharma K, *Transition Met Chem.*, 1984, **9**, 1-3.
11. Chandra S, Pandeya K B and Singh R B, *J Inorg Nucl Chem.*, 1977, **39**, 2079.