

Studies of some mixed ligand co-ordination compounds of some first series transition metal ions

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Abstract : Mixed ligand complexes of Ni (II) and Cu(II) with some tridentate (LH₂) and bidentate ligands (L'H) have been prepared and characterized having general formula (NH₄)₂ [M LL'X]

(Keywords : Semicarbazone, 2-hydroxy, 5 methoxy acetophenone (LH₂: HDMAAGH₂) and acetophenone Semicarbazone(L'H:ASCH).)

Introduction

In the present study, we report the preparation and characterization of metal complexes (Ni²⁺, Cu²⁺) with semicarbazone and amidoguanidine derived from 2 – hydroxy, 5 methoxy, acetophenone and 2 – hydroxy 4,6 dimethoxy acetophenone (LH₂: HDMAAGH₂, HMASCH₂) and acetophenone semicarbazone (L'H:ASCH)

Experimental

Preparation of Ligands

2-hydroxy ketones were completely dissolved in methanol (MeOH). Semicarbazide hydrochloride was completely dissolved in distilled water. Aminoguanidine was dissolved in dil HCl. The solution were heated for 2-hours on water bath¹ and was poured in water. The reaction mixture was cooled, crystals were filtered, washed and recrystallized from alcohol.

Preparation of complexes

A mixture of equimolar quantities (0.01m) of the hydrated metal Chlorides in distilled water and ligand solution in MeOH (M:L:L=1:1:1) was

heated on water bath for varying periods of time (20-45 minutes) depending upon the nature of the complex. The volume of the solution was reduced and the resulting solids were washed with methyl alcohol, (MeOH) dried and stored in a desiccator over CaCl₂.

The magnetic susceptibility data were obtained by Gouy method at room temperature IR. and electronic spectral data were obtained from CDRI, Lucknow.

Results and Discussion:

Studies of the ligands and their metal complexes was performed by elemental analysis, conductivity, magnetic moment measurements, I.R. and electronic spectral data (Table – 1,2)

Studies I.R. spectrum of semicarbazone complex shown the band at 1670-1660 cm⁻¹ due to (C = O) stretching². In the spectrum of the complex (C =O) stretching band is lowered by 10- 30 cm⁻¹ indicating the co-ordination through oxygen atom of keto form. A broad band observed around 3200 cm⁻¹ in the free ligand is assigned OH (H-bonded). This band disappears upon complexation indicating co-ordination through phenolic oxygen by deprotonation. The co-ordination through oxygen and nitrogen is further confirm by the occurrence of new band at 460-425 cm⁻¹ and 500-460 cm⁻¹. A band observed at 3500-3400cm⁻¹ in the I.R. Spectra of free ligand is assigned NH₂. This band remains unaffected upon

Table-1
Analytical, Physical and Infrared Spectral data cm^{-1} for metal complexes

Complex	State	Solubility	Colour	$\nu\text{C}=\text{N}$	$\nu\text{N}-\text{M}-\text{N}$	$\nu\text{C}=\text{O}$	$\nu\text{C}=\text{N}$	Metal %	
1. $(\text{NH}_4)_2[\text{Ni}(\text{ASC})(\text{HDMAAG})\text{Cl}]$	Solid Solid	DMF	Green	1635 1585	550	1370	1200	10.18	10.38
2. $(\text{NH}_4)_2[\text{Ni}(\text{ASC})(\text{HMAAG})\text{Cl}]$	Solid	DMF	Brick Red	1630 1610	565	1360	1190	10.7	20.94
3. $(\text{NH}_4)_2[\text{Cu}(\text{ASC})(\text{HDMAAG})\text{Cl}]$	Solid	DMF	Light Green	1630 1600	550	1370	1195	11.04	11.14
4. $(\text{NH}_4)_2[\text{Cu}(\text{ASC})(\text{HMAAG})\text{Cl}]$	Solid	DMF	Chocolate	1630 1610	550	1360	1200	11.5	11.73

(DMF = dimethyl formamide)

Table-2
Conductivity, magnetic susceptibility and electronic spectral data of metal complexes

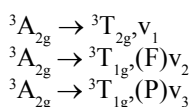
Sr. No.	Complex	Conductivity $\text{Ohm}^{-1}\text{cm}^2\text{mol}^{-1}$	μ_{eff} (B.M.)	${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}\nu_1$	${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g(\text{F})}\nu_2$	${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g(\text{P})}\nu_3$
1.	$(\text{NH}_4)_2[\text{Ni}(\text{ASC})(\text{HDMAAG})\text{Cl}]$	197	3.06	10040	16440	26500
2.	$(\text{NH}_4)_2[\text{Ni}(\text{ASC})(\text{HMAAG})\text{Cl}]$	173	3.06	10160	16550	26800
				${}^2\text{E}_g \rightarrow {}^2\text{T}_2^2g$		
3.	$(\text{NH}_4)_2[\text{Cu}(\text{ASC})(\text{HDMAAG})\text{Cl}]$	185	2.16	16110		
4.	$(\text{NH}_4)_2[\text{Cu}(\text{ASC})(\text{HMAAG})\text{Cl}]$	185	2.12	16570		

complexation indicating non-involvement of NH_2 nitrogen in coordination.

I.R. spectrum of aminoguanidine complexes showed the $\nu\text{C}=\text{N}$ stretching frequency at around $1650\text{--}1600\text{cm}^{-1}$. This band is shifted to a lower value by about $10\text{--}25\text{ cm}^{-1}$ in all the complexes indicating the co-ordination of the imine group of the Schiff Base to the metal ion. An interesting feature observed in the IR. Spectra of their complex is found in the region of 1700 cm^{-1} . A doublet band observed at about 1700 cm^{-1} in the free ligand changes its position one goes upto $1715\text{--}1725\text{ cm}^{-1}$ and is probably due to the bending mode of the NH_2 group which remains practically

unaffected in the complex and shows that the NH_2 moiety does not take part in the co-ordination. The other component which is due to the other NH_2 group or double band NH -group disappears in the complex. This indicates involvement of one of the $-\text{NH}_2$ groups in co-ordination by deprotonation. A broad band observed around 3200 cm^{-1} in the free ligand is assigned OH (H bonded). This band disappears upon completion indicating co-ordination. This fact is further extended by observing a positive shift in the frequency of νCO phenolic vibration by $10\text{--}15\text{ cm}^{-1}$. A strong and sharp band in the range $500\text{--}490\text{ cm}^{-1}$ Ni(II) complexes and $470\text{--}460\text{ cm}^{-1}$ were observed. No band was observed in the free ligand in this

range. This band is assigned to the N-N stretching through nitrogen is further confirmed by the occurrence of these new bands. The complexes of $(\text{NH}_4)_2 [\text{NiLL}'\text{X}]$ seems to be octahedral on the basis of their electronic spectra. The spectra show bands at $25100\text{--}25400\text{cm}^{-1}$ and the third $10300\text{--}10500\text{cm}^{-1}$ and these bands are quite similar to those observed in the spectrum of $\text{Ni}(\text{en})^{2+}$. 3 species and this is characteristic of octahedral $\text{Ni}(\text{II})$ complexes. These bands on symmetry may be assigned to the transition.



The ratio ν_2/ν_1 for these two complexes is around 1.65 as expected by the octahedral

stereochemistry. This is further supported by magnetic moment⁶⁻⁷ value 2.95 to 3.35 BM. Electronic spectra⁸ of all these complexes of $(\text{NH}_4)_2, \text{CuLL}'\text{X}$ type showed two absorption band maxima near $12300\text{--}12900\text{cm}^{-1}$ and $15200\text{--}15600\text{cm}^{-1}$ which is typical of pseudo octahedral $\text{Cu}(\text{II})$ Complexes. A broad shoulder band should be due to Jahn-Teller distortion, since the spectra showed similarities with $[\text{Cu}(\text{NH}_3)_6]^{2+}$ spectrum⁹ distorted octahedral structure¹⁰ is proposed for complexes.

The μ_{eff} values of $\text{Cu}(\text{II})$ complexes are in the range 1.90– 2.15 B.M. These results are in published complete agreement with the ligand field spectra present work of distorted octahedral complexes.

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