SYNTHESIS AND CHARACTERISATION OF Co (II), Ni (II) AND Cu (II) COMPLEXES WITH SODIUM SALT OF p-METHOXYISONITROSOACETOPHENONE

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ABSTRACT

In the present studies, the complexes of Co (II), Ni (II) and Cu (II) were prepared with sodium salt of p-methoxyisonitrosoacetophenone and characterized by elemental analysis, electrical conductance, magnetic susceptibility, spectral techniques like UV-Visible, IR, NMR and thermal studies. Analytical data support 1 : 2 stoichiometry for metal : ligand. The molar conductivity data indicate that the complexes are non electrolytic in nature. The electronic spectra along with magnetic data suggest octahedral geometry for Co (II) and Ni (II) complexes and distorted tetrahedral geometry for Cu (II) complex.

Key words: p-Methoxyisonitrosoacetophenone, Cobalt, Nickel, Copper.

INTRODUCTION

The literature survey of the past few years reveals the fact that a significant development in the field of biological activity of metal chelates plays a vital role in the cause and treatment of cancer[1-3]. The complexes of transition metals like Co (II), Ni (II) and Cu (II) are influenced by various physiochemical parameters. The clear understanding of electronic structure and spectral properties for their applications is the aim of present work. The present work deals with the synthesis and characterization of Co (II), Ni (II) and Cu (II) complexes with sodium salt of p-methoxyisonitrosoacetophenone.

EXPERIMENTAL

Synthesis of the reagent

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Preparation of isoamyl nitrite[4]

A solution of 95 g of sodium nitrite in 375 mL of doubled distilled water was taken in a three necked flask, which was equipped with a powerful mechanical stirrer. The solution was cooled below 0ºC by keeping in mixture of ice and common salt.

A solution of mixture of 25 mL of water, 34 mL of conc. H_2SO_4 and 125 mL of n-amyl alcohol, which was cooled to 0ºC was added slowly, with constant stirring. The rate of addition of mixture was controlled so that the temperature was maintained 0ºC to ±1ºC. The mixture was allowed to stand at 0ºC for 90 minutes and transferred into a separating funnel. The upper yellow layer containing isoamyl nitrite was removed and washed with twice portion of solution containing 1 g of sodium carbonate and 12.5 g of pure NaCl and dried over $MgSO_4$.

Preparation of sodium salt of p-methoxyisonitrosoacetophenone

The sodium salt of p-methoxyisonitrosoacetophenone (Na-PMINAP) was synthesized by the following procedure. 11.5 g of sodium was dissolved in 230 mL of absolute alcohol. To this solution, 58 mL of isoamyl nitrite was added in small portion with cooling. Then 67 mL of p-methoxyacetophenone was added similarly. This was kept at 5ºC in a refrigerator for two days in a well stoppered bottle. The brown Na-salt precipitated was filtered, washed and dried.

Preparation of complexes

The 100 mL of 0.1 M solution of sodium salt of p-methoxyisonitrosoacetophenone was taken in a round bottom flask. To this solution, 50 mL of 0.1 M solutions of metal salts were added dropwise. This mixture was stirred using magnetic stirrer for 15 minutes and then refluxed on a water bath for three hours. The product was then filtered and washed with distilled water and dried.

RESULTS AND DISCUSSION

The metal complexes were prepared by the reaction of sodium salt of p-methoxyisonitrosoacetophenone with respective metal salt solution in water. The ease of synthesis and high yield in single step reaction from commercially inexpensive reagents make these extremely attractive in coordination compounds. These metal complexes are insoluble in water and show varying degree of solubility in different polar and non-polar solvents like chloroform, benzene, acetone, carbon tetrachloride, DMSO, DMF etc. The metal complexes decompose only at high temperatures suggesting that these are thermally

very stable. The elemental analysis is in agreement with the molecular formula of the metal complexes. The analytical data (Table 1) indicate that the metal : ligand stoichiometry is 1 : 2 in all metal complexes. The resultant metal complexes are coloured. Molar conductance values of the metal complexes in DMF (0.001M) at 27^0C are in the range 0.020-0.083 mhos cm^2mol^{-1} suggest their non- electrolytic nature.

Table 1: **Analytical and physical data of the reagent and metal complexes**

Compound	Colour	Decom. temp. (^oC)	Elemental analysis found(Calculated)			
			M	**C**	**H**	**N**
Na-PMINAP	Yellowish brown	>310	11.92 (12.01)	53.99 (53.73)	4.13 (4.08)	7.04 (6.96)
[Co(PMINAP)$_2$.2H$_2$O]	Reddish brown	>284	15.20 (15.38)	51.96 (52.05)	3.68 (3.85)	6.59 (6.74)
[Ni (PMINAP)$_2$.2H$_2$O]	Brown	310	15.14 (15.24)	51.94 (52.09)	3.79 (3.88)	6.68 (6.75)
[Cu (PMINAP)$_2$]	Greenish brown	225	17.13 (17.28)	51.38 (51.49)	3.74 (3.84)	6.52 (6.67)

FTIR spectra of the reagent and metal complexes have been examined in KBr disc in the region 4000-400 cm^{-1}. The infrared spectral data are summarized in Table 2. The IR spectra are very complex and it is difficult to assign the bands without any ambiguity. However, an attempt has been made to assign some important bands on the basis of their positions reported in the compounds of known structures.

The spectra of cobalt and nickel complexes show absorption bands in the range 3614-3676 cm^{-1} indicating the presence of coordinated water molecules[5] which is also supported by TGA and DTA. The spectra of copper complex does not show a peak compounding to coordinated water molecule.

The sharp and strong absorption band at 1618 cm^{-1} is assigned to $\nu_{C=O}$, which is shifted to lower frequency and observed below at 1610 cm^{-1} in case of the complexes. This shows that there is a formation of bond between M-O, which is further confirmed by the presence of a new peak between 620-641 cm^{-1}. The band at 1580 cm^{-1} in the spectra of ligand is assigned to $\nu_{C=N}$ stretching vibrations. This is shifted to lower frequency and

observed between 1538-1559 cm^{-1} in case of the complexes[6]. This implies that the complexation leads to the bonding through the nitrogen. This is further confirmed by the presence of a new peak between 691-698 cm^{-1} due to stretching frequency of ν_{M-N}.

A strong band at 1035 cm^{-1} in the reagent is attributed to ν_{N-O} stretching frequency. This band is missing in the spectra of metal complexes and a new band in the range 1173-1177 cm^{-1} in the metal complexes may be assigned to ν_{N-O}. This shift to the higher wavelength in metal complexes implies increase in double bond character of the N-O linkage on complexation[7]. The aromatic ketone band appears at 1240 cm^{-1} in the ligand. This band is also shifted to higher frequency and observed at around 1417-1423 cm^{-1}.

Table 2: Characteristics of IR frequencies of the reagent and metal complexes

Compound	ν_{M-OH} cm^{-1}	$\nu_{C=O}$ cm^{-1}	$\nu_{C=N}$ cm^{-1}	ν_{C-O} cm^{-1}	ν_{N-O} cm^{-1}	ν_{M-N} cm^{-1}	ν_{M-O} cm^{-1}
Na-PMINAP	-	1618	1580	1240	1035	-	-
[Co(PMINAP)$_2$.2H$_2$O]	3676	1607	1559	1418	1173	698	620
[Ni (PMINAP)$_2$.2H$_2$O]	3614	1609	1538	1417	1174	699	622
[Cu (PMINAP)$_2$]	-	1608	1541	1423	1177	691	641

The PMR spectra of the reagent and its metal complexes were recorded in DMSO-d$_6$ solvent. The spectra of reagent show signals at 3.44 due to –CH$_3$ and at 3.73 for =C-H. The aromatic multiplet is observed between 6.79 to 7.82. PMR spectral studies for the complexes failed due to limited solubility of these complexes in DMSO as well as their paramagnetic nature led to noisy base line and broadening of signals, which, therefore, did not yield NMR spectra of desired quality.

The observed magnetic moment 4.35 B.M. of Co (II) complex is in consistence with reported magnetic moment (4.40-4.25 B.M.), which indicates the paramagnetic nature of the complex. The experimentally measured magnetic moment for Ni (II) complex is 3.30 B.M. falling in the range (3.18-3.53 B.M.), which also shows paramagnetic nature of this complex. The observed magnetic moment (1.85 B.M.) of Cu (II) complex at room temperature lies in between (1.75-1.85 B.M.). The magnetic moment values are normal at room temperature indicating negligible or non-observable magnetic interaction in the complexes[8].

The electronic absorption spectra of reagent and metal complexes could not give the

peaks in the spectra, which may be due to their poor solubilities in the suitable solvents. However, the diffused reflectance spectra of complexes in the solid state show some of the expected d-d transitions. The diffused reflectance spectra of the solid complexes were recorded by using pure $BaSO_4$ as a diluent.

The cobalt complex shows two bands, a broad and weak band (hump) at 16,000 cm^{-1} assigned to ${}^4T_{1g} \rightarrow {}^4T_{2g}$ and a weak shoulder at 11,425 cm^{-1} for ${}^4T_{1g} \rightarrow {}^4T_{2g}$ (P). These peaks belongs to d-d transitions in Co (II) complex. Thus, on the basis of reflectance spectra and magnetic data, an octahedral coordination may be suggested to the Co (II) complex[9].

The nickel complex shows three bands; a broad band at 16,125 cm^{-1} assigned to ${}^3A_{2g} \rightarrow {}^3T_{2g}$ (υ_1), a weak shoulder at 12,660 cm^{-1} due to ${}^3A_{2g} \rightarrow {}^3T_{2g}$ (υ_2) and a weak band at 10,800 cm^{-1} for ${}^3A_{2g} \rightarrow {}^3T_{2g}$ (υ_3). The magnetic value indicates paramagnetic nature along with the spectral data and an octahedral geometry has been assigned[10] to Ni (II) complex.

The divalent copper with $3d^9$ electronic configuration is subject to Jahn-Teller distortion and hence, regular octahedral complexes can not be expected. The correlation diagram suggests that extreme cases of distortion of the octahedron terminate into a square planar or a tetrahedral configuration. However, tetrahedral Cu (II) complexes are rare because of Jahn-Teller effect, which causes a flattening of tetrahedron due to lifting of the degeneracy ${}^2T_{2g}$ ground state. Thus, the Cu (II) complex under study appears to have distorted tetrahedral geometry. The diffuse reflectance spectra of Cu (II) complex show two bands. The low energy less intense at around 14,000 cm^{-1} and a relatively more energetic intense and broad band around 10,250 cm^{-1}. The low intensity band due to $d_{x^2-y^2} \rightarrow d_{yz}$ transition has been reported for certain Cu (II) pseudo tetrahedral geometry[11].

Thermal study of reagent indicates a continuous decomposition above 300^0C. This indicates thatreagent is quite stable at room temperature[12]. The TG - DTA thermogram of cobalt complex shows loss in weight corresponding to decomposition of coordinated H_2O molecules in the temperature range 96 to 210^0C accompanied with an endothermic peak in the first step of decomposition. In second step, there is a continuous loss of the complex supported by an endotherm and the final product is metal oxide i.e. CoO.

The TG-DTA analysis of nickel complex shows loss in weight corresponding to decomposition of water molecules in the temperature range 162 to 250^0C accompanied with the two endothermic peaks in first step decomposition. In that second step, there is continuous loss of the complex supported by an endotherm and the final product is metal oxide i.e. NiO. The TG - DTA analysis of Cu - complex shows a single step thermogram.

The small loss in weight around 110^0C may be due to the loss of lattice water molecule. The complex is stable up to 225^0C and there is a continuous loss in weight, which is also supported by two endothermic peaks and the ultimate product of heating is CuO.

Table 3: Thermal decomposition data of the reagent and complexes

Complexes	Decomp. temp. ^{0}C	Loss in weight Obs. (Cal)	Species decomposed	DTA Sign
Na-PMINAP	> 300	81.1 (80.6)	PMINAP	Endothermic
[Co(PMINAP)$_2$.2H$_2$O]	96 -210	8.1 (7.9)	2H$_2$0	Endothermic
	210 - 550	77.10 (75.40)	2PMINAP	Endothermic
[Ni(PMINAP)$_2$.2H$_2$O]	162 – 250	7.8 (7.99)	2H$_2$0	Endothermic
	250 - 600	81.9 (83.51)	2PMINAP	Endothermic
[Cu(PMINAP)$_2$]	225 - 625	83.24 (85.55)	2 PMINAP	Endothermic
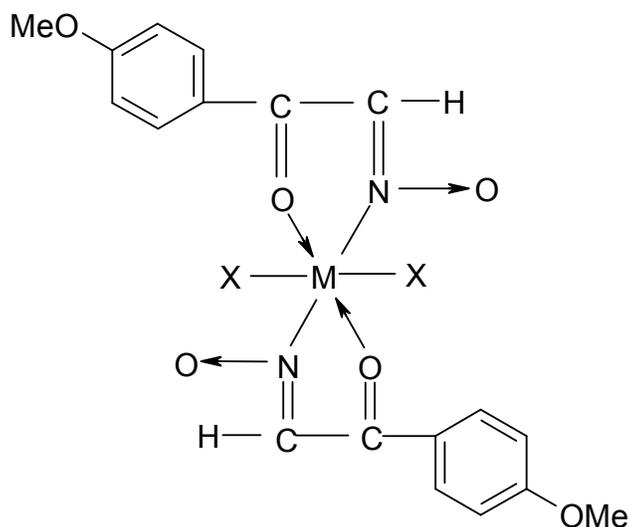
Fig. 1: Proposed structures of the complexes
M = Co (II), Ni (II) and Cu (II)
X = H$_2$O for Co (II) & Ni (II) complxes and X = Nil for Cu (II) complex

CONCLUSION

On the basis of analytical, conductivity, magnetic susceptibility, TGA and DTA, IR and reflectance spectral data, the metal ligand composition was found to be 1 : 2 and

octahedral geometry has been assigned to Co (II) and Ni (II) complexes and distorted tetrahedral geometry for Cu (II) complex.

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