



Synthesis, Thermal and Spectroscopic Studies of P-Methoxy Isonitroso Acetophenone with Transition Metal Co (II) And Cu (II)

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Abstract:

Metal complexes of transition metal such as Cobalt & Copper with p-methoxy isonitroso acetophenone (PMINAP) have been synthesized and characterized on the basis of elemental analysis, Magnetic Susceptibility, Infrared spectroscopy and thermal studies. The spectra along with magnetic data suggest Octahedral geometry of Co(II) Complex and distorted tetrahedral geometry for Cu(II) Complex.

Keywords:

PMINAP, Co(II), Cu(II), Magnetic Susceptibility, Octahedral, distorted tetrahedral geometry

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 cancer¹⁻³. The ligand p-methoxy isonitrosoacetophenone (p-MINAP) have been used for few analytical applications⁴⁻⁵. The ligand p-bromoisonitrosoacetophenone (p-BrINAP) & p-chloroisonitrosoacetophenone (P-ClINAP) have also been studied for few transition metals⁶⁻⁷. The structural studies of ligand p-methoxy isonitroso acetophenone (P-MINAP) have already been studied with transition metals for possible complex formation⁴. However, structural studies of the complexes of Transition metals with p-methoxy isonitroso acetophenone have not been reported so far. The present paper describes the isolation and characterization of complexes of Transition metals such as Co (II) and Cu (II) with p-methoxy isonitroso acetophenone on the basis of elemental analysis & spectroscopic study.

Material and Methods:

All the chemicals used were of A.R. grade. The ligand p-Methoxy isonitroso acetophenone (P-MINAP) is commercially available in the market. The basic principle underlying this preparation is that of Claisen rearrangement⁵. It was synthesized by dissolving 11.5 g of sodium in 230 ml of absolute alcohol and to these solution small portions of 58 ml amyl nitrate and 65 ml of p-Methoxy acetophenone was added with constant stirring and cooling in the freezing mixture containing ice and sodium chloride at about zero degree Celsius. The mixture was kept for three days in a well Stoppard bottle in a refrigerator. At the end of this time, the yellowish green color mixture of sodium salt was obtained. It was filtered and dried in air. The dried sodium salt was dissolved in minimum quantity of ice cooled water and treated with equal volume of water-ethanol mixture. Precipitated p-methoxy isonitroso acetophenone was then filtered through suction and dried in





vacuum. The crude product was recrystallized from benzene. Its melting point was found to be 299 °C.

Preparation of complexes

The 100 mL of 0.1M solution of sodium salt of p-ethoxyisonitrosoacetophenone 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.

Result 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. 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.

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 shown 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 complexes show absorption bands in the region 3674 cm^{-1} indicating the presence of coordinated water molecules⁸ which is also supported by TGA and DTA. The spectra of copper complex do not show a peak corresponding to coordinated water molecule.

The sharp and strong absorption band at 1617 cm^{-1} is assigned to $\nu_{\text{C=O}}$, which is shifted to lower frequency and observed below at 1611 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 619-638 cm^{-1} . The band at 1581 cm^{-1} in the spectra of ligand is assigned to $\nu_{\text{C=N}}$ stretching vibrations. This is shifted to lower frequency and observed between 1540-1560 cm^{-1} in case of the complexes⁹. This indicates that the complexation leads to the bonding through the nitrogen. This is further confirmed by the presence of a new peak between 695-699 cm^{-1} due to stretching frequency of $\nu_{\text{M-N}}$. A strong band at 1037 cm^{-1} in the reagent is attributed to $\nu_{\text{N-O}}$ stretching frequency. This band is missing in the spectra of metal complexes and a new band in the range 1181- 1185 cm^{-1} in the metal complexes may be assigned to $\nu_{\text{N-O}}$. This shift to the higher wavelength in metal complexes indicates increase in double bond character of the N-O linkage on complexation¹⁰. The aromatic ketone band appears at 1241 cm^{-1} in the ligand. This band is also shifted to higher frequency and observed at around 1419-1420 cm^{-1} .





The observed magnetic moment 4.33 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 observed magnetic moment 1.83 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 complexes⁸.

Thermal study of reagent indicates a continuous decomposition above 300°C. This indicates that reagent is quite stable at room temperature¹². The TG - DTA thermogram of cobalt complex shows loss in weight corresponding to decomposition of coordinated H₂O molecules in the temperature range 98 to 210°C 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 Cu - complex shows a single step thermogram. The small loss in weight around 110°C may be due to the loss of lattice water molecule. The complex is stable up to 225°C 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. 1: Analytical and physical data of the reagent and metal complex.

Sr. No.	Compound	Colour	Decom. Temp. (°C)	Element Analysis			
				M	C	H	N
1	Na-PMINAP	Yellowish brown	> 299	11.91 (12.01)	53.98 (53.73)	4.12 (4.08)	7.03 (6.96)
2	[Co(PMINAP) ₂ . 2H ₂ O]	Reddish brown	> 280	15.18 (15.38)	51.99 (52.05)	3.70 (3.85)	6.58 (6.74)
3	[Cu(PMINAP) ₂]	Greenish Brown	224	17.13 (17.28)	51.42 (51.49)	3.79 (3.84)	6.59 (6.67)

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

Sr. No.	Compound	vM-OH cm ⁻¹	vC=O cm ⁻¹	vC=N cm ⁻¹	vC-O cm ⁻¹	vN-o cm ⁻¹	vM-N cm ⁻¹	vM-O cm ⁻¹
1	Na-PMINAP		1617	1581	1241	1037		
2	Co(PMINAP) ₂ . 2H ₂ O	3674	1606	1560	1419	1181	699	619
3	Cu (PMINAP) ₂		1610	1540	1420	1185	695	638

Table. 3: Thermal decomposition data of the reagent and complexes

Sr. No.	Compound	Decomp. Temp	Loss of weight (cal)	Species decomposed	DTA sign
1	Na-PMINAP	> 300	81.1 (80.6)	PMINAP	Endothermic
2	[Co(PMINAP) ₂ . 2H ₂ O]	98 - 210	8.1 (7.9)	2H ₂ O	Endothermic
		210 - 510	77.10 (75.40)	2PMINAP	Endothermic
3	[Cu(PMINAP) ₂]	225 - 625	83.24 (85.55)	2 PMINAP	Endothermic





Conclusion:

On the basis of analytical, TGA and DTA, Magnetic Susceptibility, IR and spectral data, the metal ligand composition was found to be 1 : 2 and octahedral geometry has been assigned to Co (II) complexes and distorted tetrahedral geometry for Cu (II) complex.

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