

Synthesis and Structural Investigation of Mixed Ligand Metal Complexes of Isonitroso-*p*-methyl Acetophenone and Dienes

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Studies of the complexes of metal ions with *p*-methyl acetophenone and dienes have been carried out on the basis of elemental analysis, molar conductance, electronic spectra etc. The complexes have been assigned the formula $M_2(APPD)_2$ ($M = Co, Ni$ or Cu).

Key Words: Spectral, Co(II), Ni(II), Cu(II) complexes, *p*-Methyl isonitroso acetophenone, Dienes.

INTRODUCTION

The ligand, *p*-methyl isonitroso acetophenone and dienes has been used for a few analytical applications¹⁻³. However, structural studies of the complexes of metal ions with *p*-methyl isonitrosoacetophenone and dienes have not been reported so far. The present paper describes the isolation and characterization of the complexes of Co(II), Ni(II), Cu(II) on the basis of elemental analysis, magnetic measurement and spectral analysis. The infrared spectra of complexes indicate bonding through imino and oximino nitrogen and also shows involvement of the terminal $-NH_2$ group in coordination to the metal.

EXPERIMENTAL

Conductance values were measured in nitrobenzene (10^{-3} M solution). The infrared spectra were recorded in KBr disc on an FTIR spectrophotometer. The magnetic susceptibility measurements were carried out by Gouy method.

All the chemicals used were of AR grade. 1,4-diammine benzene was recrystallized before use, while the solvents were purified and double distilled before use. Isonitroso acetophenone was prepared as per the procedure reported by Welcher⁴. The *p*-substituted isonitroso acetophenone derivatives were prepared in a similar manner using appropriately substituted acetophenones and *n*-butyl nitrite. The metal complexes were prepared *in situ* by refluxing isonitroso acetophenone and 1,4-phenylenediamine in ethanol (1 : 1 molar ratio for 6 h). After cooling, the reaction mixture, metal chloride (1 : 1 molar proportion) in ethanol was added dropwise with stirring, when metal chelates precipitated out. The products were filtered, washed with ethanol and Et_2O and finally dried in vacuum.

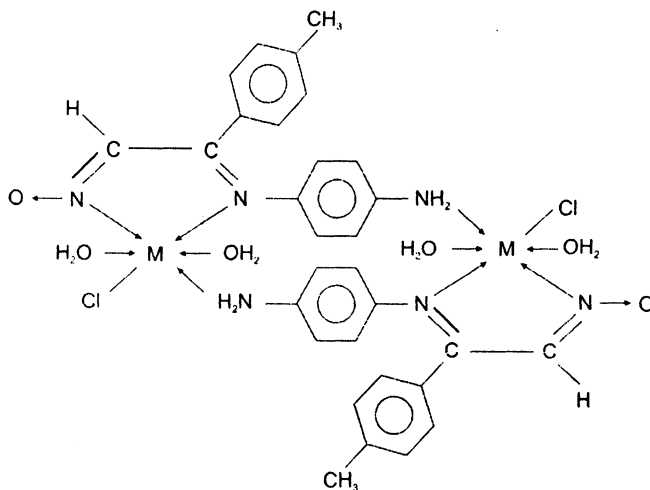
RESULTS AND DISCUSSION

The complexes are coloured and thermally stable (at least 300°C) solids. but are somewhat soluble in DMF and nitrobenzene at room temperature. The analytical data of the metal complexes (Table-1) indicate that the complexes have 1 : 1 metal-ligand stoichiometry and can be formulated as $M_2L_2Cl_2 \cdot 4H_2O$ where $M = Co(II), Ni(II), Cu(II)$; $L = p$ -methyl isonitrosoacetophenone.

TABLE-1
ANALYTICAL DATA, MOLAR CONDUCTANCE OF
SYNTHESIZED COMPLEXES $M_2L_2Cl_2 \cdot 4H_2O$

Complex (Colour)	% Analysis: Found (Calcd.)					μ_{eff} (B.M.)
	M	C	N	H	Cl	
$Co_2(APPD)_2$ (Black)	14.06 (14.09)	47.26 (47.84)	10.02 (11.01)	3.86 (4.66)	8.48 (9.16)	0.01
$Ni_2(APPD)_2$ (Yellow)	15.03 (15.01)	47.96 (47.99)	12.02 (11.09)	4.48 (4.46)	9.01 (9.13)	0.02
$Cu_2(APPD)_2$ (Brown)	16.03 (16.01)	46.06 (46.84)	12.48 (10.99)	3.43 (4.40)	8.49 (9.01)	0.03

The molar conductance values for the complexes in nitrobenzene at 10^{-3} M dilution are in the range of $3.2-6.8 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ suggesting non-electrolytic nature of these complexes⁵. The ligands have three coordination sites but involvement of all the three donor atoms in bonding to the same metal ion in the complexes is sterically not favourable. However, linear dimmers^{6,7} are possible. The probable structures of the complexes may be represented as shown in Fig. 1.



$M = Co(II), Ni(II), Cu(II)$

Fig. 1.

Since none of the ligands could be isolated in the free state, the task of interpreting the infrared spectra without ambiguity is rendered somewhat difficult. However, several structurally significant vibrational bands have been evaluated on the basis of the infrared spectra of related compounds like imino complexes of some carbonyl oximes^{8,9}, isonitroso acetophenone¹⁰ and 1,4-phenylenediamine¹¹.

The strong band due to $\nu(\text{C}=\text{O})$ stretching vibrations $1679\text{--}1663\text{ cm}^{-1}$ in isonitroso acetophenone¹⁰ is absent in all the metal complexes; this confirms the successful replacement of the carbonyl oxygen by imino nitrogen during Schiff base formation. Since two types of $\text{C}=\text{N}$ groups (azomethine and oximino) are present in the complexes, the spectra are expected to show $\nu(\text{C}=\text{N})$ modes. These are observed between 1495 and 1610 cm^{-1} . The bands around $1610\text{--}1569\text{ cm}^{-1}$ are assigned to azomethine group, whereas those around $1594\text{--}1496\text{ cm}^{-1}$ are attributed to oximino $\text{C}=\text{N}$ vibrations. The infrared spectra also indicate that $\nu(\text{C}=\text{N})$ (azomethine) is affected by substitution in phenyl moiety of the parent ligand. The electron releasing substituents like methyl tend to increase the electron density on the nitrogen of $\text{C}=\text{N}$, thereby facilitating strong σ and poor π interaction.

All the complexes show two sharp bands in the region around 3600 and 3300 cm^{-1} which are attributed to symmetric and asymmetric $\nu(\text{N}\text{--}\text{H})$ stretching vibrations of the NH_2 group. A new medium to strong intensity band observed in the $1274\text{--}1196\text{ cm}^{-1}$ region in the spectra of all complexes is ascribed to $\nu(\text{N}\text{--}\text{O})$ appearing due to the formation of $\text{N} \rightarrow \text{O}$ linkage in the complexes¹². This is indicative of bonding through oximino nitrogen, leading to a five-membered chelate ring formation. Bonding through oximino oxygen donor, leading to formation of six-membered chelate ring in a symmetrical or asymmetrical structure is ruled out as $\nu(\text{N}\text{--}\text{O})$ due to *o*-coordinated oximino group¹³, expected to occur around 1000 cm^{-1} , is not observed in the present cases.

All the metal complexes also show a broad band around $3539\text{--}3330\text{ cm}^{-1}$, which has significantly different characteristics from the band due to hydrogen bonded $\nu(\text{NOH})$ vibrations observed for isonitroso acetophenone¹⁴. This band is, therefore, attributed to stretching modes of water molecules. Their centre of gravity near 3396 cm^{-1} implies coordination of water molecules to the metal ion¹⁵. This view is further supported by the appearance of band corresponding to $\nu(\text{M}\text{--}\text{O})$ $500\text{--}440\text{ cm}^{-1}$ in the complexes. In addition, medium to weak intensity bands are observed around $619\text{--}516$ and $400\text{--}390\text{ cm}^{-1}$ which may be assigned as $\nu(\text{M}\text{--}\text{N})$ and $\nu(\text{M}\text{--}\text{Cl})$ respectively in the complexes.

The magnetic moments of Co(II), Ni(II) and Cu(II) complexes are very low, *i.e.*, diamagnetic probable octahedral configuration.

The electronic spectrum Co(II) complex (Table-2) show very broad band in the 43.36 kK region and two bands in the $25\text{--}33\text{ kK}$ range. This region screened by the intense charge transfer band exhibited a broad maxima at 25.77 kK . The electronic spectrum resembles with those of Co(II) complexes in octahedral environment¹⁶.

TABLE-2
ELECTRONIC SPECTRAL DATA OF THE METAL COMPLEXES

Complex	Absorption spectra	Wave No. (kk)
Co ₂ (APPD) ₂ Cl ₂ ·2H ₂ O	225	43.36
	290	33.38
	388	25.76
Ni ₂ (APPD) ₂ Cl ₂ ·4H ₂ O	211	46.36
	228	29.30
	335	49.83
Cu ₂ (APPD) ₂ Cl ₂ ·2H ₂ O	206	37.99
	232	36.66
	233	42.80

All the complexes show groups of three or more bands in the 46.43 kk range which can be assigned as π - π^* or ligand-metal transitions¹⁷⁻¹⁹.

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