



Synthesis And Spectral Characterization Of Binuclear Compound Of Cu(II) And Ni(II) Schiff Base Of 2-Hydroxy-5-Methylacetophenone And 1,2-Propylenediamine With Alkali Metal Salts Of Dinitrophenol

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Abstract: A series of novel binuclear complexes of general formula $M_aMAPD.M_bL$ were synthesized by interaction of stable Cu(II) and Ni(II) metal chelate of Schiff base derived from propylenediamine and 2-hydroxy-5-methylacetophenone with alkali metal salts of organic acids such as 2,4-dinitrophenol. The structure of heterobinuclear alkali metal complexes were discussed on the basis of elemental analysis, IR spectra, UV-Vis spectra and magnetic measurement. The low value of conductivity measurement of the complexes shows that non-electrolytic nature. The spectral studies were suggested that the Cu(II) and Ni(II) metal chelate act as ligand and coordination towards alkali metal salts takes place through phenolic oxygen atom. All the binuclear complexes of Schiff base have square planar geometry. There are no change in the stereochemistry of the Ni^{2+} and Cu^{2+} in adducts with their metal chelate.

Keywords: 2-hydroxy-5-methylacetophenone, Schiff base, propylenediamine, alkali metal complexes, IR, UV-Visible

I. INTRODUCTION

Schiff base possess strong ability to form metal complexes [1] and they deserve a proper attention because of their biological properties [2,3]. The heterobinuclear complexes of Cu(II) and Ni(II) Schiff base are also biologically active [4] and they exhibit enhanced activities as compared to their parent ligands. Schiff bases and their transition metal complexes are still found to be of great interest in inorganic chemistry and has been studied extensively [5,6]. We have already reported the synthesis, characterization and also biological studies of number of heterobinuclear Schiff base alkali metal complexes [7,8]. In view of the scanty information available on the binuclear alkali metal complexes, we are therefore reported the synthesis and spectral characterization of such complexes of Cu(II) and Ni(II) Schiff base. The Schiff base obtained by refluxing propylenediamine and 2-hydroxy-5-methylacetophenone, which was used to prepare transition metal complex as ligand and finally prepared the heterobinuclear alkali metal complexes with alkali metal salts of dinitrophenol. The bonding between the N,N' -propylenebis(5-methylacetopheniminato)metal(II) complex and the alkali metal is most likely to occur by the dative bond via the two phenolic oxygen atoms of the ligand which has been supported by the Infrared, electronic absorption spectra and magnetic studies of the adducts.

II. MATERIAL AND METHODS

Chemicals used were of analytical reagent grade and purchased from commercial sources. Sigma Aldrich chemicals were used in the synthesis without purification. All the synthesis of the compounds was carried out in the solvent that was purified and dried before use, using standard literature methods. 1H NMR was carried out on Bruker Avance/400 Avil HD-300 (FT NMR). Infrared spectra measurements were recorded between $4000-450\text{ cm}^{-1}$ with the help of FTIR spectrophotometer-Agilent Cary 630 FTIR. The UV-Vis absorption spectra studied by spectrophotometer using Agilent technologies Cary Series (model-5000). Electrical conductance were used to measure molar conductance was Systronics digital conductivity meter. Faraday method was adopted for magnetic measurement of the complexes. Elemental analyses were carried out by Thermo Fisher Scientific-Flash Smart V. Electrical melting point apparatus named Zenix was used for melting point measurements.

Synthesis of the Schiff base [MAPPD] and its spectral characterization

2-hydroxy-5-methylacetophenone (20 mmol, 3 g) was refluxed with 1,2-propylenediamine (10 mmol, 0.82 ml) in ethanolic medium. The solution was stirred for half an hour at 70°C. The crystalline compound N,N'-propylenebis(2-hydroxy-5-methylacetophenimine) was precipitate after cooling in the ice bath. The solid yield was separated from solution and recrystallized with ethanol. Yield: 75.4% (1.27 g); M.P. 128 °C; Molecular formula: C₂₁H₂₆N₂O₂; Mol Wt. 338.44; Elemental analysis (%): Calculated: C-74.56, H-7.69, N-8.28. Found: C-73.23, H-7.45 and N-8.06.

¹H NMR spectra: The ¹H NMR spectra of the Schiff base was carried out on instrument Bruker Avance 400 in CDCl₃ at room temperature using TMS as an internal standard. δ ppm: 1.38 (s, -N=C-CH₃), 1.40 (s, -CH₃), 3.7 (s, CH), 3.76 (s, CH₂), 6.79 (s, OH), 7.07-7.28 (m, 3H of aromatic ring)

Infrared Spectra: IR (KBr) ν_{max} (cm⁻¹): 3389 (O-H stretching of phenol), 2923 (C-H stretching of aromatic ring), 1618 (C=N stretching), 1500 (C=C stretching of aromatic ring), 1292 (C-O stretching of phenol).

Synthesis of Cu (II) and Ni (II) complexes, [MaMAPPD]

An ethanolic solution of 1.99 g copper acetate (10mmol) was added slowly to a hot ethanolic solution of 3.38 g (10 mmol) MAPPD and the mixture was refluxed for two hours at 80 °C to yield coloured solid. The resulting coloured solid complex of Cu(II) was isolated by filtration, washed with ethanol and dried in an electric oven. Similarly, Ni(II) complex was prepared with nickel acetate and Schiff base by refluxing these in 1:1 molar ratio.

Synthesis of Heterobinuclear complexes, (MaMAPPD.MbL)

The ethanolic solution of N,N'-propylenebis(methylacetopheniminato)metal(II) complex (MaMAPPD) was taken in a conical flask and salt (Na and K) of 2-dinitrophenol (MbL) was added to it in 1:1 molar ratio. Then the mixture was refluxed for 60-90 minutes at 80°C and then concentrated to obtain coloured complex, which was separated out by filtration. These prepared heterobinuclear complexes were washed with absolute alcohol and dried in oven.

III. RESULTS AND DISCUSSION

Both the Copper(II) and Nickel(II) metal chelate and their alkali metal adducts are coloured solid, non-hygroscopic and stable at room temperature. The complexes are generally soluble in acetone, benzene, methanol and DMF while insoluble in water. These complexes were decomposed after melting. The change of melting/decomposition temperature of these adducts than that of MaMAPPD are due to the weak bonding through phenolic oxygen atoms to the alkali metals. The elemental analysis data of the complexes revealed the good agreement with their calculated results. The molar conductivities of complexes were measured at 30(±0.5) °C at the concentration of 10⁻³M. The molar conductivities of complexes have been found in the range 2.3-4.2 Ω⁻¹cm²mol⁻¹ (Table 1), indicates the non-electrolytic in nature [9] of the complexes.

IR Spectra

The Infrared spectra of the Cu(II) and Ni(II) metal chelate and their adducts are shown in Table 2. The IR spectra band of complexes exhibit at the 1529-1618 cm⁻¹ suggesting that this band may be due to the C-O stretching of phenolic group [10].

Table 1. Physical characterization, molar conductance and Analytical data of the complexes

Complexes (MaMAPED.MbL)	Colour	m.p. (°C)	Mol. Cond. Ω ⁻¹ cm ² mol ⁻¹	Elemental analysis (%)					Yield (%)
				C	H	N	M _a	M _b	
CuMAPPD	Dark brown	266	3.5	62.56 (63.08)	5.65 (6.01)	6.57 (7.01)	15.31 (15.89)		69.8
CuMAPPD.NaDNP	Dark brown	230	2.3	52.76 (53.51)	4.32 (4.46)	9.13 (9.25)	10.31 (10.49)	3.75 (3.80)	73.4
CuMAPPD.KDNP	Brownish orange	244	2.7	51.82 (52.13)	4.21 (4.34)	8.91 (9.01)	10.12 (10.22)	6.08 (6.28)	74.2
NiMAPPD	Orange	144	3.9	62.08 (63.85)	6.05 (6.08)	6.88 (7.09)	14.56 (14.87)		78.2
NiMAPPD,NaDNP	Brownish orange	260	2.9	53.75 (53.94)	4.37 (4.49)	9.21 (9.32)	9.71 (9.77)	3.78 (3.83)	74.3
NiMAPPD.KDNP	Brownish orange	256	4.2	52.45 (52.54)	4.31 (4.38)	9.03 (9.08)	9.41 (9.52)	6.27 (6.32)	70.5

Comparing C-O infrared bands for both the transition metal complex ligand and their alkali metal binuclear complexes, we arrive at conclusion that the infrared bands for both are remain almost same. The metal complex as ligand copper exhibit the ν_{C-O} (phenolic) at 1529 cm⁻¹ and that of nickel at 1584 cm⁻¹ which shifts towards higher energy side on complex formation, indicating the coordination through the phenolic oxygen [11]. This shift is expected due to maintenance of a ring current arising from electron delocalization in the chelating ring. The major shift of ν_{C-O} (phenolic) to higher energy by 2 and 32 cm⁻¹ in heterobinuclear complexes of copper and

nickel respectively, certainly indicating the presence of phenoxo-bridge. It is, therefore, suggestive that the phenol C-O link attained a considerable amount of partial double bond character in these complexes. This is what to be expected from the desier readiness with which these binuclear complexes were formed.

In all the present complexes, the bands with medium to strong absorption the far IR region $499\text{-}540\text{ cm}^{-1}$ and $450\text{-}490\text{ cm}^{-1}$ tentatively assigned to $\nu_{\text{M-O}}$ and $\nu_{\text{M-N}}$ modes respectively [12,13]. It is observed that there are positive shift in adducts than the metal complex as ligand, suggesting that the formation of adducts with the coordination of the phenolic oxygen. These assignments are based on the assumption that since oxygen atom is more electronegative than nitrogen atom, the M-O band tends to be more ionic than the M-N bond. Consequently, M-O vibrations are expected to appear at lower frequency.

Table.2. Spectral data and magnetic moment of metal chelate and their metal complexes

Compound	Infrared spectra (cm^{-1}) $\nu(\text{C-O})_{\text{phenolic}}/\nu(\text{M-O})/\nu(\text{M-N})$	UV-Vis spectra Diffuse reflectance(in nm)	Magnetic moment (in BM)
CuMAPPD	1529, 499, 450	221, 254, 350, 554, 570	1.97
CuMAPPD.NaDNP	1545, 520, 465	230, 261, 380, 562, 612	2.03
CuMAPPD.KDNP	1531, 529, 465	202, 258, 362, 532, 580	1.92
NiMAPPD	1584, 525, 480	230, 265, 348, 560, 620	Diamagnetic
NiMAPPD.NaDNP	1591, 523, 485	206, 269, 323, 485, 629	Diamagnetic
NiMAPPD.KDNP	1618, 540, 490	227, 261, 318, 532, 605	Diamagnetic

UV-Vis Spectra and Magnetic moment

The UV-Visible absorption spectra for the heterobinuclear complexes of transition metal complexes as ligand and alkali metal salt of organic acids shown in table 2. The absorption bands are observed between 202-265 nm indicating the formation of $\pi\text{-}\pi^*$ transition. The bands appearing between 323-629 nm in Cu(II) and Ni(II) complexes shows that there is d-d transition and charge transfer [14-16]. These absorption band of binuclear alkali metal complexes also suggesting the same square planar geometry with coordination number four [14]. The spectra of all oxygen bridge complexes also shows similar type of bands to those of the Cu(II) and Ni(II) complexes of Schiff base, suggested there is no change in stereochemistry of complexes after the formation of heterobinuclear complexes.

The magnetic moment of transition metal complex CuMAPPD has been found 1.97 BM; and its binuclear complexes CuMAPPD.NaDNP and CuMAPPD.KDNP show that 2.03 and 1.92 BM (table 2), strongly indicate the presence of one unpaired electron. These result suggested that transition metal complex as ligand and its adducts are in square planar geometry with coordination number four. The magnetic moment of NiMAPPD and its adducts are found to very low (approximately zero), which indicate the diamagnetic nature and square planar geometry with coordination number four.

IV. CONCLUSION

From the above results and discussion, it may be summarized that transition metal complex of Schiff base and further heterobinuclear complexes with alkali metal salts of 2,4-dinitrophenol were synthesized. They were characterized by analytical results, IR spectra, UV-Visible spectra and magnetic studies. The spectral studies were suggested that Cu(II) and Ni(II) metal

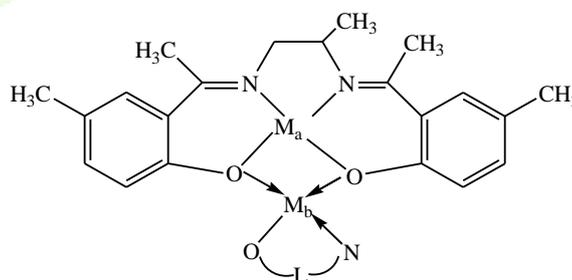


Fig.1. Heterobinuclear Schiff base complex $[\text{M}_a\text{MAPED.M}_b\text{L}]$

chelate act as ligand and coordination towards alkali metal salts takes place through phenolic oxygen atom. The structure and bonding of the newly prepared compounds by us of the general formula $[\text{M}_a\text{MAPED.M}_b\text{L}]$ may have the structure shown in Fig.1. [Where, $\text{M}_a = \text{Cu, Ni}$; MAPED = Schiff base derived from 2-hydroxy-5-methylacetophenone and propylenediamine; $\text{M}_b\text{L} =$ alkali metal (Na, K) salt of 2,4-dinitrophenol. Spectral characterization of these heterobinuclear complexes revealed square planar geometry of copper (II) and nickel (II) with coordination number four.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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