



Synthesis and spectral characterization of binuclear compounds of Cu(II) and Ni(II) Schiff base of 2-Hydroxy-5-methylacetophenone and 1,2-Propylenediamine with alkali metal salts of trinitrophenol

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ABSTRACT

A series of new binuclear complexes of general formula $M_2MAPD.M_bL$ were synthesized by the interaction of stable Cu(II) and Ni(II) metal chelate of Schiff base derived from propylene diamine and 2-hydroxy-5-methylacetophenone with alkali metal salts of organic acids such as 2,4,6-trinitrophenol. The structure of these hetero-binuclear alkali metal complexes was discussed based on the elemental analysis, IR spectra, UV-Vis spectra, and magnetic measurement. The low value of conductivity measurement shows the non-electrolytic nature. The IR spectral studies suggested that copper(II) and nickel(II) metal chelate act as ligands and coordination towards alkali metal salts takes place through a phenolic oxygen atom. The binuclear nickel(II) or copper(II) complex of the Schiff base has square planar geometry. There is no change in the stereochemistry of the Ni(II) and Cu(II) in adducts with their metal chelate.

1. Introduction

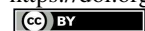
Schiff base possess a strong ability to form metal complexes[1] and they deserve proper attention because of their biological properties[2,3]. The heterobinuclear complexes of Cu(II) and Ni(II) Schiff base are also biologically active[4] and they exhibit enhanced activities as compared to their parent ligands. Schiff bases and their transition metal complexes are still found to be of great interest in inorganic chemistry and have been studied extensively[5,6]. We have already pointed out the synthesis, characterization, and biological studies of a number of heterobinuclear Schiff base alkali metal complexes[7,8]. Because of the scanty information available on the binuclear alkali metal complexes, we reported the synthesis and spectral characterization of such complexes of Cu(II) and Ni(II) Schiff base. The Schiff base was obtained by refluxing propylenediamine and 2-hydroxy-5-methylacetophenone, which was used to prepare the transition metal complex as ligand and finally prepared the heterobinuclear alkali metal complexes with alkali metal salts of trinitrophenol. 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.

2. Material And Methods

The chemicals used were of A.R. grade and purchased from commercial sources. Sigma Aldrich chemicals were used in the synthesis without purification. All the compounds synthesized were carried out in the solvents that were 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 cm⁻¹ with the help of FTIR spectrophotometer-Agilent Cary 630 FTIR. The UV-Vis absorption spectra were studied by spectrophotometer using Agilent technologies Cary Series (model-5000). Electrical conductance was used to measure molar conductance was Systronics digital conductivity meter. Faraday method was adopted for

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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.

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

2-hydroxy-5-methylacetophenone (20 mmol, 3g) was refluxed with 1,2-propylene-diamine (10 mmol, 0.82 ml) in an ethanolic medium. The solution were 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 were separated from the 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 were 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) (Fig. 1).

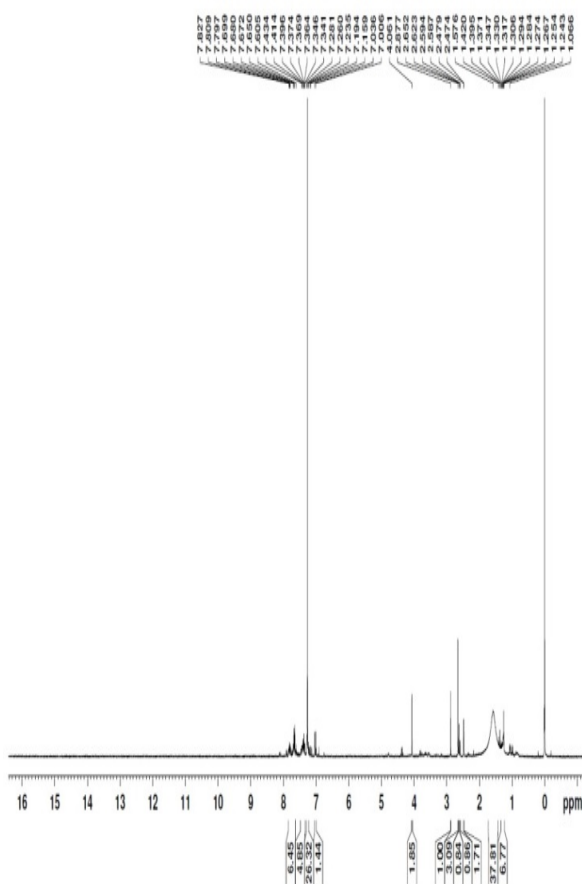


Fig.1. ¹H NMR spectra of Schiff base MAPPD

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) shown in Fig.2.

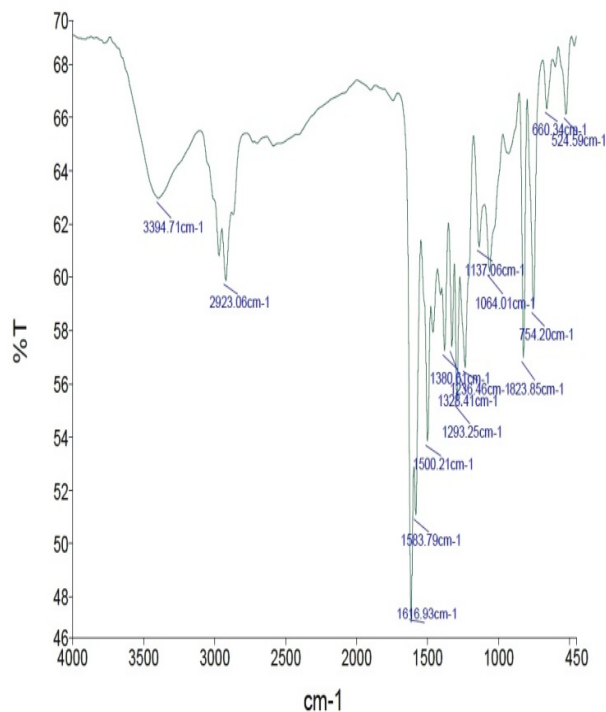


Fig.2. IR spectra of Schiff base MAPPD

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

An ethanolic solution of 1.99 g copper acetate (10 mmol) 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 a coloured solid. The resulting coloured solid complexes of Cu (II) were 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 a 1:1 molar ratio.

Synthesis of Heterobinuclear complexes, (M_aMAPPD.M_bL)

The ethanolic solution of N,N'-propylenebis(methylacetopheniminato)metal(II) complex (M_aMAPPD) was taken in a conical flask and salt (Na and K) of 2,4,6-trinitrophenol (M_bL) 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 a coloured complex, which was separated out by filtration. These prepared heterobinuclear complexes were washed with absolute alcohol and dried in the oven.

3. 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 M_n MAPPD

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^{-3} M. The molar conductivities of complexes have been found in the range 1.9-4.8 $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ (Table 1) indicate the non-electrolytic in nature[9] of the complexes.

Table 1. Spectral data and magnetic moment of metal chelate and their metal complexes

Complexes (MaMAPED.MbL)	Colour	m.p. (°C)	Mol. Cond. $\Omega^{-1} \text{cm}^2$ mol^{-1}	Elemental analysis (%)					Yield (%)
				C	H	N	M _a	M _b	
CuMAPPD	Dark brown	266	4.8	62.56 (63.08)	5.65 (6.01)	6.57 (7.01)	15.31 (15.89)		69.8
CuMAPPD.NaTNP	Maroon	248	3.6	49.69 (49.81)	3.93 (4.00)	10.63 (10.76)	9.67 (9.76)	3.47 (3.54)	71.7
CuMAPPD.KTNP	Deep orange	266	4.2	48.55 (48.61)	3.79 (3.90)	10.43 (10.50)	9.51 (9.53)	5.80 (5.85)	74.2
NiMAPPD	Orange	144	4.1	62.08 (63.85)	6.05 (6.08)	6.88 (7.09)	14.56 (14.87)		78.2
NiMAPPD.NaTNP	Reddish orange	275	1.9	50.03 (50.18)	3.97 (4.03)	10.75 (10.84)	9.02 (9.09)	3.53 (3.56)	74.5
NiMAPPD.KTNP	Light orange	271	3.8	48.79 (48.96)	3.84 (3.93)	10.52 (10.58)	8.81 (8.87)	5.81 (5.89)	76.3

3.1. 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 1529-1620 cm^{-1} suggesting that this band may be due to the C-O stretching of phenolic group[10]. 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 the higher energy side on complex formation, indicating the coordination through the phenolic oxygen[11]. This shift is expected due to the 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 6 and 36 cm^{-1} in heterobinuclear complexes of copper and nickel respectively, certainly indicates the presence of phenoxobridge. It is, therefore, suggestive that the phenol C-O link attained a considerable amount of partial double bond character in these complexes. This might be expected from the alacrity with which these diatomic complexes were formed. In all the present complexes, the bands with medium to strong absorption in the far IR region 499-545 cm^{-1} and 450-485 cm^{-1} tentatively assigned to ν M-O and ν M-N modes

respectively[12,13]. It is observed that there is a positive shift in adducts than the metal complex as ligand, suggesting the formation of adducts with the coordination of the phenolic oxygen. These assignments are based on the assumption that since the oxygen atom is more electronegative than the 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 frequencies.

3.2. 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 202-273 nm indicating the formation of π - π^* transition. The bands appearing between 350-636 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].

Table 2. Spectral data 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	Magnetic moment (in BM)
		Diffuse reflectance(in nm)	
CuMAPPD	1529, 499, 450	221, 254, 350, 554, 570	1.97
CuMAPPD.NaTNP	1535, 520, 460	204, 319, 361, 533, 620	2.01
CuMAPPD.KTNP	1535, 520, 460	217, 273, 370, 470, 636	2.05
NiMAPPD	1584, 525, 480	230, 265, 348, 560, 620	Diamagnetic
NiMAPPD.NaTNP	1614, 519, 455	207, 256, 355, 523, 624	Diamagnetic
NiMAPPD.KTNP	1620, 545, 485	202, 256, 362, 503, 626	Diamagnetic

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.NaTNP and CuMAPPD.KTNP show that 2.01 and 2.05 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.

4. Conclusion

From the above results and discussion, it may be summarized that the transition metal complex of Schiff base and further heterobinuclear complexes with alkali metal salts of 2,4,6-trinitrophenol 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 chelate act as ligands and coordination towards alkali metal salts takes place through a phenolic oxygen atom. The structure and bonding of the newly prepared compounds by us of the general formula $[M_a\text{MAPED}.M_b\text{L}]$, may have the structure shown in Fig.3. [Where, $M_a = \text{Cu or Ni}$; MAPED = Schiff base

References

derived from 2-hydroxy-5-methylaceophenone and propylenediamine; $M_b\text{L} =$ alkali metal (Na, K) salt of 2,4,6-trinitrophenol].

Spectral characterization of these heterobinuclear complexes revealed square planar geometry of copper(II) and nickel(II) with coordination number four.

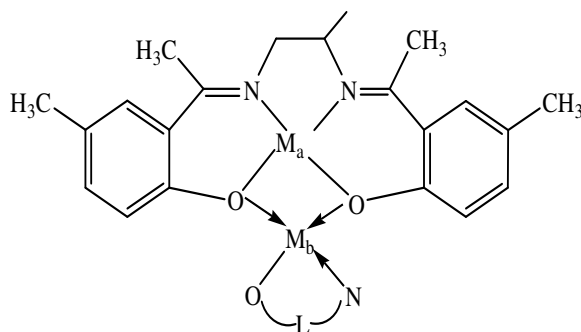


Fig.3. Heterobinuclear Schiff base complex $[M_a\text{MAPED}.M_b\text{L}]$

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Conflict of Interest

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

- [1] D. R. Smith, Copper 1996, *Coordination Chemistry Reviews*, 172-1(1998)457-573, ISSN 0010-8545 [https://doi.org/10.1016/S0010-8545\(98\)00098-8](https://doi.org/10.1016/S0010-8545(98)00098-8).
- [2] P. Mishra, P. N. Gupta, & A. K. Shakya, Synthesis of some Schiff Bases of 3-Amino-2methylquinazolin-4(3H)-ones and their Antimicrobial Activities. *Journal of Indian Chemical Society*, 68 (1991) 618–619 <https://doi.org/10.5281/zenodo.6138515>
- [3] W. Zishen, L. Zhiping, Y. Zhenhuan, Synthesis, characterization and antifungal activity of glycyglycine Schiff base complexes of 3d transition metal ions. *Transition Met. Chem.*, 18 (1993) 291-294 <https://doi.org/10.1007/BF00207949>
- [4] W. Zhong, W. Zishen., Y. Zhenhuan et al. Synthesis, characterization and antifungal activities of copper(II), zinc(II), cobalt(II) and nickel(II) complexes with the Schiff base derived from 3-chlorobenzaldehyde and glycine. *Transition Met. Chem.*, 19 (1994) 235–236. <https://doi.org/10.1007/BF00161897>
- [5] N.H. Patel, H.M. Parekh & M.N. Patel, Synthesis, characterization and biological evaluation of manganese(II), cobalt(II), nickel(II), copper(II), and cadmium(II) complexes with monobasic (NO) and neutral (NN) Schiff bases. *Transition Met. Chem.*, 30 (2005) 13–17. <https://doi.org/10.1007/s11243-004-3226-5>
- [6] J. S. Kumaran, S. Priya, J. Muthukumaran, N. Jayachandramani, S. Mahalakshmi, *J. Chem. Pharm. Res.*, 5(7) (2013) 56.
- [7] D. Prakash, C. Kumar, S. Prakash, A. K. Gupta, K. R. R. P. Singh, Synthesis, spectral characterization and antimicrobial studies of some new binuclear complexes of Cu^{II} and Ni^{II} Schiff base, *J.Indian Chem. Soc.*, 86 (2009) 1257-1261. <https://doi.org/10.5281/zenodo.5823781>
- [8] Chandan Kumar, Synthesis, characterization and biological evaluations of heterobinuclear complexes of Cu^{II} and Ni^{II} Schiff base of ethylenediamine and o-hydroxyacetophenone with alkali metal salts of o-nitrophenol, *J.Indian Chem. Soc.*, 94 (2017) 857-861 <https://doi.org/10.5281/zenodo.5595126>
- [9] W.J. Geary, The use of conductivity measurements in organic solvents for the characterisation of coordination compounds, *Coordination Chemistry Reviews*, 7/1 (1971) 81-122, ISSN 0010-8545. [https://doi.org/10.1016/S0010-8545\(00\)80009-0](https://doi.org/10.1016/S0010-8545(00)80009-0).
- [10] A.Z. El-Sonbati, A.S. Al-Shihri, A.A. El-Bindary, Stereochemistry of new nitrogen containing heterocyclic aldehyde: Part XI. Novel ligational behaviour of quinoline as chelate ligand toward transition metal ions, *Spectrochimica Acta*, Part A: Molecular and Biomolecular Spectroscopy, 60/8–9 (2004) 1763-1768, ISSN 1386-1425 <https://doi.org/10.1016/j.saa.2003.08.026>.
- [11] A.Z. El-Sonbati, M.A. Hefni, Polymer complexes, part XXI. Stereochemical changes of metal chelates of poly(5-vinylsalicylidene-2benzothiazoline). *Monatsh Chem.*, 124 (1993) 419–424. <https://doi.org/10.1007/BF00814137>
- [12] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, Third ed. John Wiley and Sons (1978).
- [13] Aysegul Golcu, Mehmet Tumer, Havva Demirelli, R. Alan Wheatley, Cd(II) and Cu(II) complexes of polydentate Schiff base ligands: synthesis, characterization, properties and biological activity, *Inorganica Chimica Acta*, 358/6 (2005) 1785-1797, ISSN 0020-1693. <https://doi.org/10.1016/j.ica.2004.11.026>
- [14] H. H. Jaffer and M. Orclin.: Theory and application of U.V spectroscopy, Wiley, New York, (1962) 347.
- [15] P. Cheng, D Liao., S. Yan, et. al., Paramagnetic and diamagnetic binuclear copper(II) complexes with different bidentate exogenous bridges: synthesis, spectroscopy and magnetic properties. *Transition Met. Chem.*, 21 (1996) 515–518. <https://doi.org/10.1007/BF00229703>
- [16] M. Thirumavalavan, P. Akilan, M. Kandaswamy, Synthesis of heterobinuclear Cu(II)Zn(II) complexes derived from lateral macrobicyclic tricompartamental ligands: Spectral, electrochemical and kinetic studies, *Polyhedron*, 25/13 (2006) 2623-2628, ISSN 0277-5387. <https://doi.org/10.1016/j.poly.2006.03.018>.