

Complexes Derived from Copper and Nickel Schiff Base and Alkali Metal Salts: Preparation and Antimicrobial Study

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Abstract

Complexes derived from Schiff bases received prominent attention because of their specific structure and antimicrobial properties. The preparation and characterization of heterobinuclear alkali metal complexes of copper(II) and nickel(II) Schiff bases are investigated in this study. The Schiff's base has been obtained by condensation of 2-hydroxyacetophenone with ethylenediamine, which is used to prepare binuclear complexes with transition and alkali metals. These complexes are characterized by analytical, spectral and magnetic measurement results. The bondings in the complexes are explained on the basis of spectral studies. The lower conductivity measurement values suggested the non-electrolytic property of the compounds. It is found that the $\nu_{C-O(phenolic)}$ in infrared spectra shifted to the higher side on complexation, which revealed the dative bond of C-O(phenolic). Ultraviolet spectra specify the d-d transition as well as charge transfer of ligand to metal. The square planar geometry of the complex is explained with the magnetic measurement results. These complexes show considerable positive antimicrobial properties with fungi *S. aureus* and also with bacteria *E. coli* and *C. albicans*.

Keywords: 2-hydroxyacetophenone; Alkali Metal; Antimicrobial Studies; Binuclear Complexes; Ethylenediamine; Schiff Base; Spectra

Introduction

Schiff bases have a strong ability to generate a large number of metal complexes (Meena *et al.*, 2023) and it deserve commendable attention because of their biological activity (Zoubi, 2013 & Thakur *et al.*, 2024). Several Schiff base complexes have been synthesized, characterized, and studied for antimicrobial activities; they have been found to have antibacterial and antifungal activities (More *et al.*, 2001). The heterobinuclear complexes show antimicrobial properties and they exhibit appreciably more activities in comparison to their parent ligands. In continuation of our earlier works (Prakash *et al.*, 2009; Kumar, 2024), the study of heterobinuclear complexes prepared with copper and nickel Schiff bases is reported here. The Schiff's base was obtained by refluxing ethylenediamine and o-hydroxyacetophenone, which form the binuclear complex with transition and alkali metals. The spectral study supported that there is a dative bond between the transition metal and alkali metal complex through the oxygen atom of the phenolic group. These antimicrobial compounds show significant antibacterial and antifungal properties.

Methodology

The chemicals and reagents were of AR grade. Infrared spectra were recorded through the Shimadzu-FTIR spectrophotometer and Perkin Elmer Lambda-UV-visible spectra (Refat *et al.* 2013). Molar conductance was measured through a Systronics conductivity meter. The results of elemental analysis were recorded with the Thermo Fisher Scientific Flash instrument. An electrical melting point apparatus was used to measure the melting point of the compounds.

Methods of Preparation

Schiff base and metal complex as ligand: The Schiff base N,N'-bis(2-hydroxyacetophenone) ethylenediamine (HAPEN) was prepared from 2-hydroxyacetophenone and ethylenediamine through

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refluxing them in alcohol in 2:1 molar ratio for 30-60 min. The obtained Schiff base was yellow in color, which was filtered and dried. The Cu(II) complex (CuHAPEN) was prepared by adding copper(II) acetate (2.0g) gradually in a hot alcoholic solution of Schiff base. A deep red copper complex was deposited after cooling, which was filtered and dried. Similarly, brownish orange Ni(II) complex (NiHAPEN) was obtained by mixing nickel(II) acetate tetrahydrate (2.5g) and Schiff base.

Heterobinuclear complexes containing Cu(II) metal and alkali metal: The alcoholic solution of (CuHAPEN) and alkali metal salts of *o*-nitrophenol was added in 1:1 molar proportion. This mixture was refluxed and stirred for 30-60 min at 75-80°C. The adducts of characteristic colour were precipitated, which was cooled, filtered and dried.

Heterobinuclear complexes containing Ni(II) metal and alkali metal: The alcoholic solution of [NiHAPEN] and alkali metal salts of *o*-nitrophenol were added in 1:1 molar proportion. This mixture was refluxed and stirred for 30-60 min at 75-80°C. The adducts of characteristic colour were precipitated, which was cooled, filtered and dried.

Results and Discussion

The heterobinuclear alkali metal complexes with formula $M_aHAPEN.M_bL$, where $M_a = \text{Cu(II) or Ni(II)}$, HAPEN = Schiff base of *o*-hydroxyacetophenone and ethylenediamine, $M_bL = \text{Li, Na or K}$ salts of 2-nitrophenol, were synthesized. The Schiff base metal chelates of Cu(II) and Ni(II) and their alkali metal binuclear complexes are powder and stable compounds. All the compounds are generally soluble in acetone, benzene, methanol and DMF, while in water they are insoluble. The elemental analysis results indicated well with the planned formula for the binuclear complexes. Molar conductivities ($\Omega^{-1}\text{cm}^2\text{mol}^{-1}$) are measured at 30(± 0.5)°C at the concentration of 10^{-3}M in DMF. The compounds show lower value of molar conductivity, suggesting their covalent nature (Geary, 1971) (Table 1).

Table 1: Analytical Results of the Complexes

Compounds [$M_a\text{EDHAP. } M_bL$]	Colour	M.P (°C)	Molar cond.	Elemental analysis (%) Found(cal)					Yield (%)
				C	H	N	M_a	M_b	
CuHAPEN	Deep rose	280	2.7	60.13 (60.42)	4.92 (5.03)	7.61 (7.83)	17.59 (17.76)	- -	71.00
CuHAPEN.LiL	Pale rose	282	2.1	57.25 (57.31)	4.31 (4.38)	8.32 (8.36)	12.55 (12.64)	1.37 (1.39)	77.11
CuHAPEN.NaL	Pale rose	285	3.1	55.45 (55.54)	4.21 (4.24)	8.01 (8.10)	12.15 (12.25)	4.41 (4.44)	71.36
CuHAPEN.KL	Pale rose	292	2.6	53.75 (53.88)	4.10 (4.12)	7.83 (7.86)	11.80 (11.88)	7.23 (7.30)	79.51
NiHAPEN	Brownish orange	280	4.8	61.05 (61.24)	5.02 (5.10)	7.76 (7.94)	16.56 (16.64)	- -	75.50
NiHAPEN.LiL	Yellowish orange	265	2.4	57.78 (57.87)	4.38 (4.42)	8.36 (8.44)	11.76 (11.79)	1.38 (1.41)	74.34
NiHAPEN.NaL	Yellowish orange	>300	2.0	56.00 (56.06)	4.21 (4.28)	8.11 (8.18)	11.39 (11.43)	4.41 (4.48)	74.95
NiHAPEN.KL	Yellowish orange	>300	1.8	54.32 (54.37)	4.11 (4.15)	7.88 (7.93)	11.01 (11.08)	7.33 (7.36)	73.15

Spectra and Magnetic Results:

The IR spectra of heterobinuclear complexes display certain deviations from that of the transition metal complex, as the ligand furnishes information about the nature of bond and structure. The disappearance of sharp absorption peak (3500 cm^{-1} , ν_{OH}) in the complexes indicates the loss of phenolic proton.

Table 2: Spectral and Magnetic Results of Complexes

Compound	Infrared spectra (cm^{-1})			UV-Vis spectra $\lambda(\text{nm})$	μ_{eff}
	$\nu(\text{C-O})$	$\nu(\text{M-N})$	$\nu(\text{M-O})$		
CuHAPEN	1531	521	490	227, 270, 400, 653	1.50
CuHAPEN.LiL	1537	560	470	228, 266, 347, 653	1.70
CuHAPEN.NaL	1532	562	440	230, 232, 350, 652	1.74
CuHAPEN.KL	1535	550	465	227, 260, 345, 653	1.73
NiHAPEN	1530	518	495	212, 246, 390, 653	Dia.
NiHAPEN.LiL	1590	565	460	207, 261, 384, 653	Dia.
NiHAPEN.NaL	1568	562	465	207, 261, 384, 653	Dia.
NiHAPEN.KL	1565	555	462	214, 280, 389, 653	Dia.

The metal complexes' ligand of transition metal and their binuclear alkali metal complexes show bands in region $1530\text{--}1590\text{ cm}^{-1}$ (Table 2). This may be due to stretching frequency of phenolic C-O in complexes rather than that of C=N (El-Sonbati *et al.*, 2012).

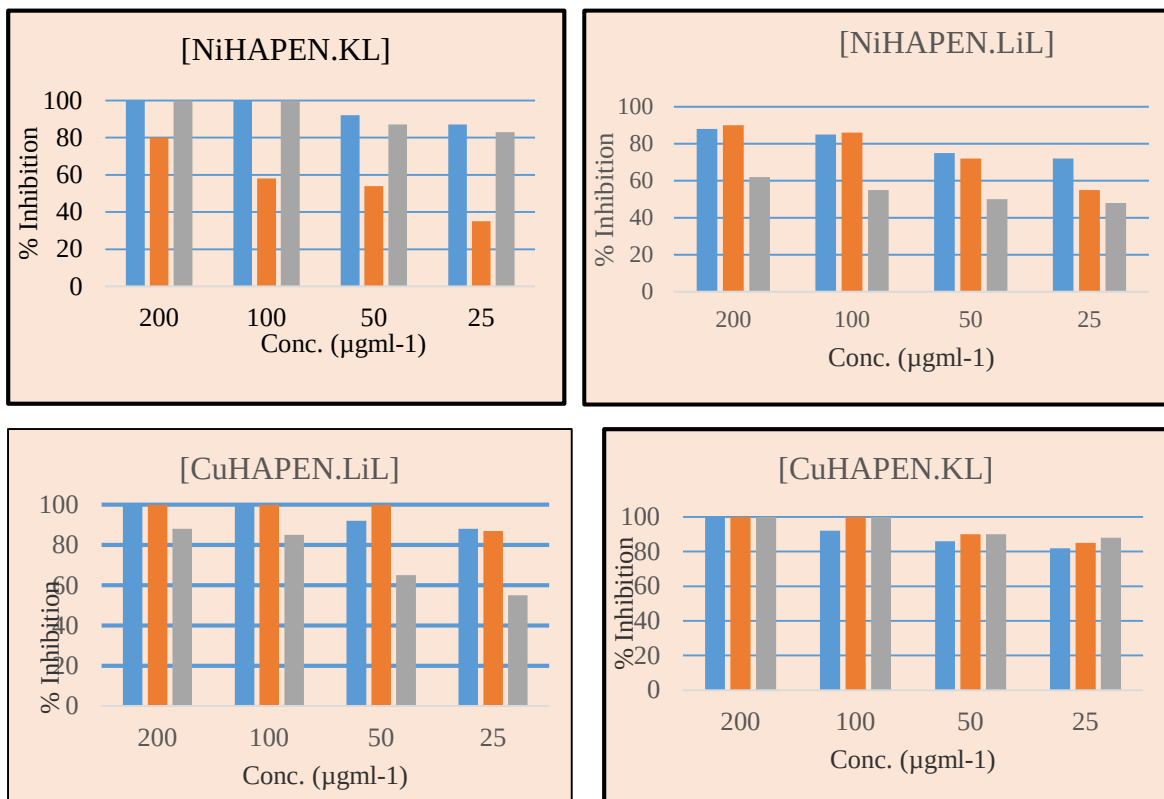


Figure 1: Antimicrobial Activity of Complexes

Comparing the C-O infrared bands of binuclear alkali metal complexes with the metal complex as a ligand, it is found they remain almost near to each other. However, the considerable shifting of C-O frequency of binuclear complex to higher side as compared to the metal complex as a ligand is observed. This is because the ring current arises from delocalized electrons. The shift of around 69 cm^{-1} is found, revealing

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the presence of a phenoxy bridge in the compound. The IR bands in the range 440-470 cm^{-1} and 550-565 cm^{-1} of medium intensity in binuclear complexes may be expected due to $\nu_{\text{M-O}}$ and $\nu_{\text{M-N}}$ respectively (Nakamoto, 2009 & Kumar *et al.*, 2025). These bands are not found in the transition of metal chelates, while these show at regions 490-495 cm^{-1} and 518-521 cm^{-1} . This result indicated the coordination of phenolic oxygen and nitrogen atoms of $-\text{NO}_2$ with alkali metals (Barreras-Contreras *et al.*, 2025).

The electronic spectra absorption at 207-280 nm of compounds indicates a $\pi-\pi^*$ transition in aromatic ring as well as due to C=N chromophore. The band of medium intensity at 350-400 nm is due to transfer transition from ligand to metal (Table 2). The bands appearing between ~653 nm in all the complexes indicated a d-d transition (Thirumavalavan *et al.*, 2006; Popov *et al.*, 2023). These results propose that the complexes have square planar geometry with four coordination numbers. The copper complexes show the magnetic moment value (μ_{eff}) 1.5 BM, indicating the presence of one unpaired electron. However, the magnetic moment values of its adducts lie in the range of 1.70 to 1.74 BM. These results revealed the compound has square planar geometry with four coordination numbers. The magnetic moment values of NiHAPEN and its binuclear complex show much less value, suggesting the diamagnetic nature and square planar geometry. On the basis of results, the proposed structure of prepared compounds having general formula ($\text{M}_a\text{HAPEN.M}_b\text{L}$) [where $\text{M}_a = \text{Cu(II)}$ or Ni(II) ; $\text{M}_b\text{L} = \text{Li, Na or K salt of 2-nitrophenol}$] is shown with Fig.1. The complexes have shown significant antimicrobial activity.

Antimicrobial Activity

Antimicrobial activity of some binuclear complexes was examined against bacteria viz. *E. coli*, *S. aureus* and fungi viz. *C. albicans*. The serial dilution method was used at the concentration from 25 to 200 $\mu\text{g ml}^{-1}$ for this test. The results are demonstrated with Table 3 and Fig.2, which indicate that complexes show great degree of activity. It is observed that with concentration the antimicrobial activity of the adduct increases simultaneously. The activities of some of the complexes explained by chelation theory (Panchal & Patel, 2006).

Table 3: Antimicrobial Results of Complexes

Compound	Conc. (μgml^{-1})	Percentage Inhibition		
		<i>E.coli</i>	<i>S.aureus</i>	<i>C. albicans</i>
NiHAPEN.KL	200	100	80	100
	100	100	58	100
	50	92	54	87
	25	87	35	83
NiHAPEN.LiL	200	88	90	62
	100	85	86	55
	50	75	72	50
	25	72	55	48
CuHAPEN.LiL	200	100	100	88
	100	100	100	85
	50	92	100	65
	25	88	87	55
CuHAPEN.KL	200	100	100	100
	100	92	100	100
	50	86	90	90
	25	82	85	88

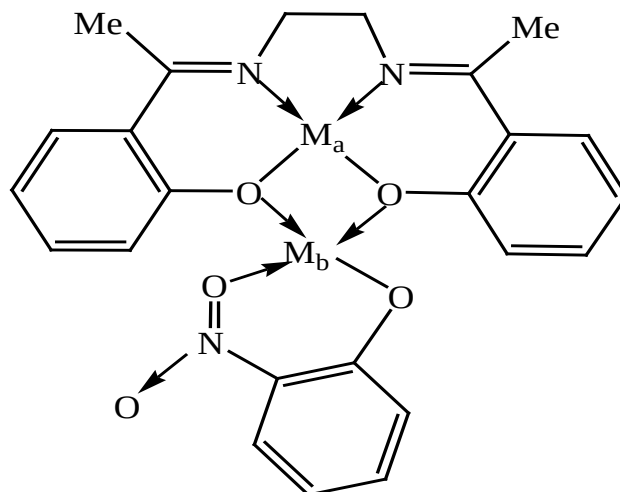


Figure 2: Proposed Structure of Complex

Conclusion

The copper and nickel metal complexes as ligands and their alkali metals were prepared. The characteristics and structure of the compounds are supported by analytical, spectral and magnetic results. They are bonded through a dative bond through two oxygen atoms of the phenolic group. The results are discussed, which indicate that the metal complex as a ligand and its adducts have square planar geometry.

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