

Synthesis, Characterization and Biological activity of Schiff Base Metal (II) Binuclear Complexes with Alkali metal salt of o-Nitrophenol

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Abstract

A series of binuclear complexes with copper(II) and nickel(II) and alkali metals derived from Schiff bases were studied. Schiff base was prepared by the condensation of 1,2-phenylenediamine and 2-hydroxy-1-naphthaldehyde. The FT-IR and UV-Vis spectra have been used to explain the structures of the synthesized complexes. The bonding of Schiff base's complexes of copper(II) and nickel(II) with alkali metals are occurred by oxygen atoms. The outcome of spectral and magnetic results showed that the binuclear Schiff base complexes of transition metal(II) and alkali metal have coordination number four with square planar geometry. The ligands are found to be bonded to the transition metal atom through the nitrogen atoms of imine and oxygen atoms of the hydroxyl groups. The molar conductance values are low, indicating that the complexes are non-electrolytic. These complexes show significant results against the bacteria *E. coli* and *S. aureus* and also against the fungus viz. *C. albicans*.

Keywords: *Alkali Metal; Antimicrobial Studies; Binuclear Complexes; Infrared Spectra; Schiff Base; UV-Vis*

Introduction

Appreciable attention has been devoted in recent years to the field of preparation and characterization of heterobinuclear complexes due to their significant approach in biological inorganic chemistry as well as in material science (Rao & Zacharias, 1997; Zanello *et al.*, 1987). The synthesis of transition metal complexes with Schiff bases is regarded as a great passion in inorganic chemistry and has been studied significantly (Patel, Parekh, & Patel, 2005). Several binuclear Cu(II) complexes with Schiff bases derived from 1,2-diamino-2-propanol and 2-hydroxy-1-naphthaldehyde have been synthesized and considerably interpreted (Cheng *et al.*, 1996). The Schiff base complexes of many transitions metal possess the great antimicrobial activity (Panchal & Patel, 2006). A series of biologically active bimetallic complexes of Copper Schiff base are synthesized and significantly characterized (Zhong *et al.*, 1994), with the antimicrobial effect of the transition metal complexes being higher as compared to the ligand. The synthesis of a large number of heterobinuclear complexes with Schiff base

and their characterization are reported (Kumar, 2017; Kumar, 2023). This work reported herein has concentrated on developing a series of new binuclear complexes of transition metals and alkali metals.

Methodology

Chemicals of AR grade was used for synthesizing the Schiff bases and complexes. IR spectra and electronic spectra have been recorded through FTIR spectrophotometers, Shimadzu-8201PC in KBr phase and Perkin Elmer Lambda 15 UVB-VIS spectrophotometers, respectively. The magnetic results were recorded through the Gouy balance method. Molar conductance and melting point were measured using a Systronics digital conductivity meter and electrical melting point apparatus, respectively. The Elemental analysis results were taken out through Thermo Fisher Scientific Flash Smart instrument.

Synthesis

The Schiff base was synthesized by condensation of 1,2-phenylenediamine with alcoholic solution of 2-hydroxy-1-naphthaldehyde in 1:2 molar ratios. This mixture was continuously stirred at 70-75°C for 25 minutes. The solid yellow Schiff base, N,N'-1,2-phenylene-bis(naphthaldimine), PHDND, was filtered and then recrystallized with alcohol.

Synthesis of Cu (II) and Ni (II) complexes: A solution of copper(II) acetate hydrate (2.0 g) in ethanol was slowly added to the hot solution of the Schiff base (PHDND, 4.16 g). This mixture was stirred up to 20 minutes at 70-75 °C. The solution on cooling, golden brown Cu(II) complex was separated out. Similarly, the Ni(II) complexes were prepared by adding nickel(II) acetate tetrahydrate (2.5g) in solution of the Schiff base (PHDND, 4.16g). The mixture on cooling, the deep orange Ni(II) complex was separated. These transition metal complexes were filtered, washed with ethanol, and then dried.

Synthesis of binuclear complexes containing Cu(II) metal and alkali metal: The N,N'-1,2-phenylene-bis(naphthaldiniminato)copper(II) [CuPHDND] was taken in absolute alcohol and the prepared alkali metal salts of *o*-nitrophenol were added in 1:1 molar proportion. This mixture was stirred and refluxed for 1 hour at 75-80°C. The specific coloured complexes were deposited in hot conditions and then cooled, filtered, washed with alcohol and dried.

Synthesis of binuclear complexes containing Ni(II) metal and alkali metal: The N,N'-1,2-phenylene-bis(naphthaldiniminato)nickel(II) [NiPHDND] was taken in absolute alcohol and the prepared alkali metal salts of *o*-nitrophenol were added to it in 1:1 ratio. This mixture was stirred and refluxed for 1 hour at 75-80°C. The specific-

coloured complexes were separated in hot conditions, then cooled, filtered, washed with alcohol and then dried.

Results and Discussion

Both the copper(II) and nickel(II) transition metal complexes and their alkali metal adducts are stable and have characteristic coloured solids. The colour, melting point, conductivity, elemental analysis data and yields are presented in Table 1. These adducts are mostly soluble in organic solvents such as acetone and DMF, but in water they are insoluble. The molar conductivities of complexes at temperature 30(\pm 0.5) $^{\circ}$ C in DMF at 10^{-3} M (Table 1) range from 0.6-1.5 $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$. These values are low, which suggests their covalent (Geary, 1971) nature.

Table 1: Physical characteristics of the complexes

Complexes (CuPHDND. ML)	Colour	m.p. ($^{\circ}$ C)	Mol. Cond. Ω^{-1} cm^2 mol^{-1}	Elemental analysis (%) Found (Calculated)					Yield (%)
				C	H	N	Cu	M	
CuPHDND	Golden brown	>300	1.3	69.89 (70.37)	3.62 (3.77)	5.73 (5.86)	13.15 (13.30)	-	70.6
CuPHDND.L iONP	Yellowish brown	248	1.5	65.48 (65.54)	3.49 (3.53)	6.65 (6.75)	10.16 (10.20)	1.05 (1.12)	77.11
CuPHDND.N aONP	Golden brown	296	0.9	63.83 (63.90)	3.40 (3.45)	6.51 (6.58)	9.87 (9.95)	3.58 (3.60)	71.26
CuPHDND.K ONP	Golden brown	290	0.8	62.27 (62.34)	3.28 (3.36)	6.35 (6.42)	9.65 (9.70)	5.92 (5.96)	68.37
NiPHDND	Deep orange	>300	1,1	70.48 (71.08)	3.72 (3.81)	5.78 (5.92)	12.28 (12.42)	-	67.5
NiPHDND.Li ONP	Reddish brown	>300	0.6	65.97 (66.12)	3.51 (3.56)	6.69 (6.80)	9.43 (9.50)	1.07 (1.13)	81.75
NiPHDND.N aONP	Reddish brown	>300	0.8	65.32 (64.38)	3.39 (3.47)	6.61 (6.63)	9.22 (9.26)	3.55 (3.63)	75.75
NiPHDND.K ONP	Reddish brown	>300	0.6	62.74 (62,80)	3.35 (3.39)	6.42 (6.46)	8.96 (9.03)	5.91 (6.00)	72.73

IR Spectra: The Infrared spectral bands of the transition metal complexes and their binuclear complexes with alkali metals show bands in the range 1535-1610 cm^{-1} , this may be due to the phenolic C-O stretching (El-Sonbati, Al-Shihri & El-Binary, 2004). The C-O bands for both Cu (II) and Ni(II) transition metal complexes as ligands are a little higher as compared to those of their binuclear complexes. The copper and nickel metal complex as ligands show absorption at 1535 cm^{-1} and 1597 cm^{-1} respectively, due to $\nu_{\text{C-O}}$ (phenolic). This band shifts towards the higher energy side of the complex formation by up to 55 cm^{-1} and 13 cm^{-1} in copper and nickel, respectively, in binuclear complexes. This is due to the coordination of metals by phenolic oxygen (El-Sonbati, Diab & El-Binary, 2012) and suggests the existence of a phenoxo-bridge.

Table 2: Spectral results of complexes

Compound	IR spectra (cm ⁻¹) u(C-O)phenolic/ O)u(M-N)	u(C-u(M-	UV-Vis spectra (in nm)	Magnetic moment (in BM)
CuPHDND	1535, 556, 470		225, 237, 324, 651	1.97
CuPHDND.LiONP	1570, 565, 490		228, 240, 330, 651	1.85
CuPHDND.NaONP	1539, 563, 470		224, 262, 328, 652	1.75
CuPHDND.KONP	1590, 561, 485		225, 238, 338, 652	1.92
NiPHDND	1597, 550, 460		205, 238, 340, 653	Dia
NiPHDND.LiONP	1610, 555, 485		206, 239, 328, 652	Dia
NiPHDND.NaONP	1598, 571, 490		207, 242, 324, 653	Dia
NiPHDND.KONP	1598, 561, 480		206, 240, 359, 652	Dia

These are expected because of a ring current arising from the delocalization of electrons in the chelating ring and also because of the phenolic C-O link. The far IR bands from medium to strong range at 550-571 cm⁻¹ and 460-490 cm⁻¹ correspond to ν_{M-O} and ν_{M-N} bonds, respectively (Nakamoto, 2009; Jasim, Kadhum & Badr, 2024; Golcu *et al.*, 2005). These positive shifts in the absorption band in the binuclear complex compared to those of the transition metal complex assigned to the synthesis complex contribute to their coordination through oxygen atom of the Schiff base. These are suggested on the basis of electronegativity. The electronegativity of oxygen is higher as compared to the nitrogen atom, which is why M-O bond is considerably more ionic than that of M-N. The infrared spectral results suggest the coordination of oxygen in the phenolic group of the transition metal complex with nitrogen in the alkali metal salt of o-nitrophenol in binuclear complexes.

UV-Vis Spectra and Magnetic moment. Both copper (II) and nickel (II) metal chelate of Schiff base and their binuclear complexes show UV-Vis absorption between 224-262 and 205-242 nm, respectively (Table 2). These absorptions are due to the p-p* transition (aromatic ring) and C=N (chromophore) (Jabbar, Kadhum & Hassan, 2023). The band ranges at 324-653 nm are due to the d-d transition as well as charge transfer (Condrate & Nakamoto, 1965; Jaffer & Orclin, 1962; Thirumavalavan, Akilan & Kandaswamy, 2006). These results suggested coordination number four with square planar geometry (Jaffer & Orclin, 1962) in metal chelate and its adducts. The absorption of both metal complexes and their binuclear complexes is almost the same, which indicates that the stereochemistry of complexes does not change after heterobinuclear complex formation.

The magnetic moment of binuclear alkali complexes ranges from 1.75 to 1.92 BM (Table 2), and copper(II) Schiff base complex shows it at 1.97 BM. These results indicate the presence of one unpaired electron and also their square planar geometry with coordination number four. Nickel(II) metal complex and its alkali metal complex show very low values (about to zero), these suggest the diamagnetic nature and four coordination numbers with square planar geometry.

Antimicrobial activity: This activity of some of the binuclear complexes was carried out against bacteria, viz. *Escherichia coli* and *Staphylococcus aureus* and also with the fungus viz. *Candida albicans* in DMF at a concentration between 25-200 $\mu\text{g ml}^{-1}$ by the serial dilution method. The results are shown in Table 3 and Figure 1, the antimicrobial activity (Sharma *et al.*, 2022) of the compounds gradually increases as its concentration increases and compounds show significantly better results at high concentrations.

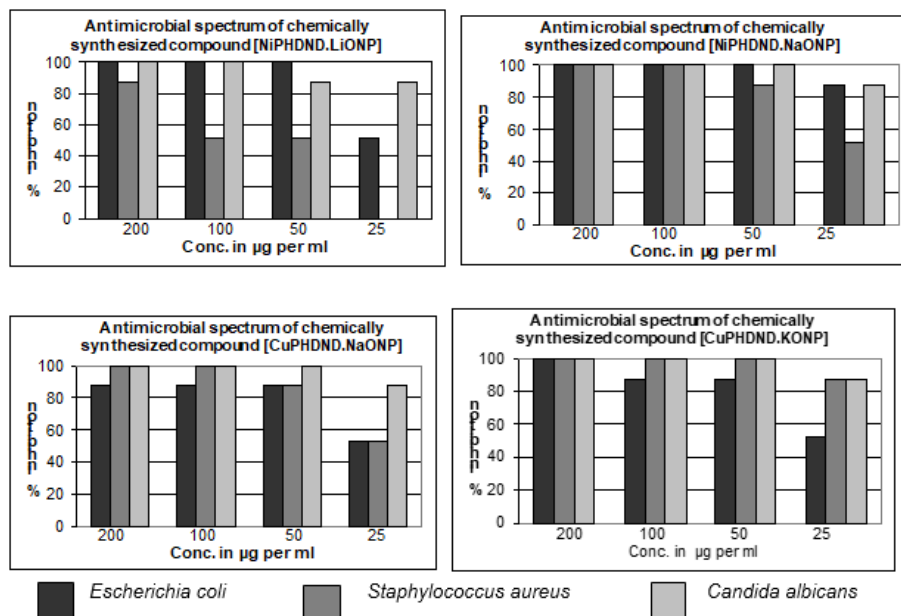


Figure 1: Antimicrobial data of binuclear complexes

Table 3: Antimicrobial result of compounds

Compound	Conc. (μgml^{-1})	Percentage inhibition		
		<i>E.coli</i>	<i>S.aureus</i>	<i>C.albicans</i>
NiPHDND.LiONP	200	100	85-90	100
	100	100	50-55	100
	50	100	50-55	85-90
	25	50-55	0	85-90
NiPHDND.NaONP	200	100	100	100
	100	100	100	100
	50	100	85-90	100
	25	85-90	50-55	85-90
CuPHDND.NaONP	200	85-90	100	100
	100	85-90	100	100
	50	85-90	85-90	100
	25	50-55	50-55	85-90
CuPHDND.KONP	200	100	100	100
	100	85-90	100	100
	50	85-90	100	100
	25	50-55	85-90	85-90

These results have explained, based on the chelation theory, that the lipophilicity of the compound increases as the polarizability of the metal cloud decreases, which leads to the breakdown of the permeability of the cells (Ghosh *et al.*, 2012). The chelation reduced the polarity of metal- ions due to its positive charge and share by p electron delocalization and donor groups (Panchal & Patel, 2006).

Structure and bonding: The proposed general formula of binuclear complexes of copper(II) and nickel(II) with alkali metal is considered $M_aPHDND.M_bL$ on the basis of quantitative results, where $M_a = Cu(II)/Ni(II)$; $M_b = Li/Na/K$; PHDND = N,N'-1,2-phenylene-bis(naphthaldimine) and L = *o*-nitrophenol (deprotonated). The analytical results and spectral analysis suggested the square planar geometry (Figure. 2). The bonding between the metal(II) complexes and the alkali metals is caused by two oxygen atoms (phenolic) in the Schiff base.

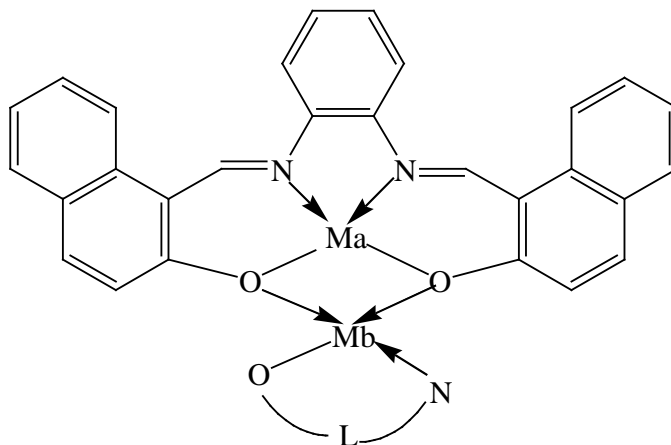


Figure 2: Structure of the complex

Conclusion

The synthesis and coordination chemistry of some novel binuclear complexes derived from the multi-dentate Schiff-base ligand PHDND are explored in this paper. The results are supported by analytical, IR spectral, UV-visible spectral and magnetic results. The structure and bonding of the complexes are established; the geometry of the complexes is square-planar. The compounds give significant antimicrobial results against *E. coli*, *S. aureus* and *C. albicans*.

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