

The Synthesis, Spectral and Antimicrobial Study of Heterobinuclear Complexes of Copper (II) Schiff Base with Alkali Metals Salts

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ABSTRACT

The condensation reaction of a primary amine with carbonyl compounds results in a Schiff base, which is effectively incorporated in the preparation of metal complexes. Herein, a series of hetero binuclear complexes have been synthesized of the general formula CuPS.ML, where PS = Schiff base prepared by condensation of salicylaldehyde and propylene diamine; ML = Li, Na or K salts of 2-nitrophenol; 2,4-dinitrophenol; 2,4,6-trinitrophenol & 1-nitroso-2-naphthol. The compounds are generally soluble in most of the organic solvents but insoluble in water. These complexes have been characterized by elemental analysis, IR spectra, UV-VIS spectra, magnetic measurement and molar conductance results. The low value of molar conductance of the complexes suggested the non-electrolyte nature of the complexes. The spectral analysis suggested that the bonding between copper (II) metal chelate and alkali metal, appeared through the dative bond through the phenolic oxygen atoms. The study also revealed the square planar structure of the complexes. Some of these complexes showed the antimicrobial activity on *E. coli*, *S. aureus* and *C. albicans* and so, these complexes may be considered as good antimicrobial agents.

Keywords: *Heterobinuclear Complexes; Alkali Metal; Schiff Base; Spectra; Antimicrobial Studies*

Introduction

Schiff bases have capability in the formation of metal complexes (Singh & Chaudhary, 2019) and they also deserve great attention because of their biological properties (Mishra *et al.*, 1991). Transition metal complexes of the Schiff base are established to be of great attentiveness in inorganic chemistry and it also, has been considered significantly in the complexes (Ahmed, Dalia & Fatmaa, 2015; Patel *et al.*, 2005). The heterobinuclear alkali metal complexes of Cu (II) Schiff base are also biologically active (Zhong *et al.*, 1994) and they exhibit enhanced activities as compared to their parent ligand. They have previously reported the preparation and characterization of number of heterobinuclear complexes derived with Schiff base (Kumar, 2017; Prakash, Kumar & Singh, 2008). In continuation of their earlier works, they have reported here, the study of some novel heterobinuclear alkali metal complexes. The bonding between the metal complex as ligand and the alkali metal is

probably with the two phenolic oxygen atoms of the ligand, this has been assisted by the Infrared, UV-Visible spectra and magnetic properties. The prepared complexes show the antimicrobial effectiveness.

Methodology

The chemicals used were of AR grade. Sigma Aldrich chemicals were used in the synthesis without purification. All the compound synthesis was carried out in the solvent which was purified and dried before use by using standard literature methods. IR spectra were recorded in KBr phase through the FTIR spectrophotometer, Shimadzu model 8201PC. The UV-visible spectra of the complexes were recorded through a Perkin Elmer Lambda 15 UVB VIS spectrophotometer and magnetic measurements were taken from Gouys balance. Systronics digital conductivity meter was used to measure molar conductance. Elemental analysis was carried out by Thermo Fisher Scientific-Flash Smart V. An electrical melting point apparatus was used for melting point measurements.

Synthetic Procedure

The Schiff base was prepared by refluxing salicylaldehyde and 1,2-propylenediamine in ethanol in 2:1 molar proportion. The solution was stirred for 15 minutes at 70°C. The yellow Schiff base; N,N'-1,2-propylene-bis(salicylaldimine); PS was precipitated after cooling in ice bath. This solid yield was separated from solution, recrystallized with absolute ethanol and then dried in oven. Then a ethanolic solution of copper (II) acetate (2.0g) was added gradually with continuous stirring to a hot alcoholic solution of the Schiff base (2.82g). The solution for cooling the purple copper (II) complex obtained. It was filtered, washed two times with ethanol and dried.

Synthesis of Heterobinuclear Complexes of Cu(II) Metal and Alkali Metal.

In the alcoholic solution of N,N'-1,2-propylene-bis(salicylideneiminato)copper (II); CuPS, the different alkali metal salts of organic acids o-nitrophenol, dinitrophenol, trinitrophenol or 1-nitroso-2-naphthol were separately added with a 1:1 molar ratio. The mixture was refluxed with stirring at 75–80 °C for 1-1½ hours. The characteristic color complexes were precipitated, and then it was filtered, washed two times with absolute alcohol and dried.

Results and Discussion

The copper (II) metal chelate and also their alkali metal adducts are colored solid (Table. 1.), non-hygroscopic and stable at room temperature. The complexes are soluble in acetone, methanol, benzene, and DMF but insoluble in water. Most of the complexes were decomposed after melting. The elemental analysis results of the compounds revealed a good consensus with their calculated values. The molar conductivities of complexes were measured in DMF at 30(±0.5) °C at 10⁻³M. The compounds show molar conductivity in the range 0.5-8.9 Ω⁻¹cm²mol⁻¹ shows the non-electrolytic nature (Geary, 1971) of the complexes.

Infrared Spectra:

The IR spectra of the copper metal chelate and its adducts are shown in Table 2. The band at range 1538-1570 suggests that these bands are due to the C-O stretching of the phenolic group (Sonbati *et al.*, 2004). Comparing the C-O infrared bands for both the transition metal complex ligand and their alkali metal binuclear complexes, they arrive at the conclusion that the infrared bands for both are nearly the same. The metal complex as ligand copper exhibits the ν_{C-O} (phenolic) at 1538 cm^{-1} , that shifts to the direction of higher energy side on the complex formation, these shifts indicate the coordination with the phenolic oxygen (Sonbati *et al.*, 2012). This shift may be due to the maintenance of a ring current emerging from the electron delocalization in the ring. The ν_{C-O} (phenolic) shifts to higher energy with 12 to 42 cm^{-1} in heterobinuclear complexes of copper is certainly indicating the presence of phenoxo-bridge. It is, therefore, suggesting the phenol C-O link attained a significant amount of partial double bond character in these complexes. In the complexes, the bands are found in the far IR region at ranging to $505\text{-}548\text{ cm}^{-1}$ and $461\text{-}470\text{ cm}^{-1}$ may be assigned to ν_{M-O} and ν_{M-N} modes respectively (Nakamoto, 2009). It is also observed that there is a positive shift in adducts compared to the metal complex as ligand, suggesting that the formation of adducts is the by the phenolic oxygen. These results are explained on the assumption that the nitrogen atom is less electronegative than the oxygen atom and the M-N band tends to be less ionic than the M-O bond. The above considerations coordinate the coordination of the oxygen atom of the phenolic group and the nitrogen atom of $-\text{NO}$, $-\text{NO}_2$ etc. to the alkali metal in all the heterobinuclear complexes.

Table 1: Physical Characteristics, Analytical Results of The Complexes

Complexes (CuPS.ML)	Colour	m.p. (°C)	Mol. Cond. $\Omega^{-1}\text{ cm}^2$ mol^{-1}	Elemental analysis (%) Found (Calculated)					Yield (%)
				C	H	N	Cu	M	
CuPS	Purple	255	-	58.91 (59.39)	4.42 (4.66)	7.68 (8.15)	18.21 (18.49)	-	74.62
CuPS.LiONP	Golden brown	228	1.4	56.46 (56.50)	4.01 (4.09)	8.52 (8.60)	12.88 (13.00)	1.37 (1.43)	77.79
CuPS.NaONP	Purple	247	0.5	54.62 (54.71)	3.87 (3.96)	8.22 (8.33)	12.53 (12.59)	4.41 (4.56)	72.84
CuPS.KONP	Purple	245	0.6	52.82 (53.03)	3.72 (3.84)	7.88 (8.07)	12.12 (12.20)	7.41 (7.49)	66.76
CuPS.LiDNP	Brownish red	242	3.2	51.55 (51.73)	3.47 (3.56)	10.45 (10.51)	11.83 (11.92)	1.21 (1.29)	73.1
CuPS.NaDNP	Brownish yellow	202	3.3	50.18 (50.23)	3.35 (3.46)	10.13 (10.19)	11.49 (11.56)	4.14 (4.19)	75.07
CuPS.KDNP	Teak brown	241	6.1	48.77 (48.81)	3.22 (3.36)	9.81 (9.90)	11.14 (11.23)	6.78 (6.90)	76.04

CuPS.Li1N1P	Brownish yellow	218	6.5	47.52 (47.11)	3.02 (3.11)	12.02 (12.11)	10.79 (10.98)	1.11 (1.21)	6.92
CuPS.Na1N1P	Brownish yellow	266	7.2	46.31 (46.43)	2.88 (3.03)	11.62 (11.77)	10.55 (10.68)	3.73 (3.87)	0.65
CuPS.K1N1P	Brownish yellow	278	8.9	45.05 (45.21)	2.82 (2.95)	11.41 (11.47)	10.28 (10.40)	6.31 (6.39)	6.75
CuPS.Li1N2N	Brown	228	0.7	61.83 (62.01)	4.03 (4.21)	7.95 (8.04)	12.05 (12.15)	1.3 (1.34)	8.95
CuPS.Na1N2N	Light Brown	226	2	60.1 (60.17)	3.91 (4.09)	7.67 (7.80)	11.68 (11.79)	4.18 (4.27)	0.57
CuPS.K1N2N	Brown	225	2.4	58.38 (58.43)	3.82 (3.97)	7.48 (7.57)	11.31 (11.45)	6.88 (7.03)	4.39

Table 2: IR and UV-Vis Data of Complexes

Compound	IR spectra (cm ⁻¹) phenolic/ u(C-O) u(M-O)/u(M-N)	UV-Vis spectra Diffuse reflectance (in nm)	Magnetic moment (in BM)
CuPS	1538, 505, 466	219, 242, 352, 652	1.95
CuPS.Li1N1P	1570, 520, 465	226, 267, 351, 652	1.84
CuMPS.Li1DNP	1550, 548, 469	224, 266, 352, 653	1.74
CuPS.Na1N1P	1568, 541, 461	224, 266, 351, 652	1.73
CuPS.K1N2N	1565, 516, 470	225, 267, 353, 652	1.94

UV-Vis Spectra and Magnetic Moment:

The UV-visible absorption spectra of the heterobinuclear complexes are shown in Table 2. The absorption bands are found in the range 219–267 nm, suggesting the formation of $\pi\text{-}\pi^*$ transition. The bands observed between 351–653 nm in the complexes show the d-d transition and charge transfer (Condrate & Nakamoto, 1965; Jaffé & Orchin, 1962 & Thirumavalavan *et al.*, 2006). These absorption band of binuclear alkali metal complexes also suggesting the same square planar geometry with coordination number four (Jaffé & Orchin, 1962). The spectra of transition metal complexes as ligands and their oxygen bridge complexes show similar types of bands, these results suggest that there is no change in their stereochemistry of them. The magnetic moment of transition metal complex CuPS has been observed at 1.95 BM and its binuclear complexes varied between 1.73 to 1.94 BM (table 2), strongly indicating the presence of one unpaired electron. These results suggested that the transition metal complex as ligand and its heterobinuclear complexes are in square planar geometry with coordination number four.

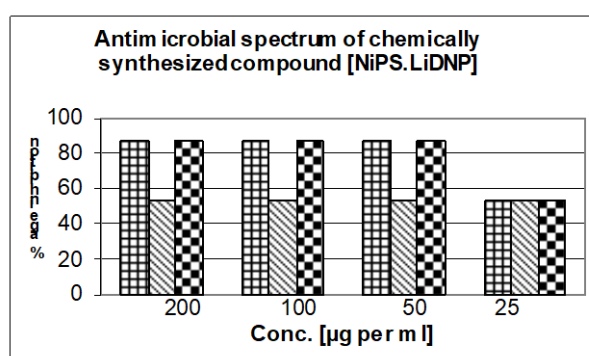
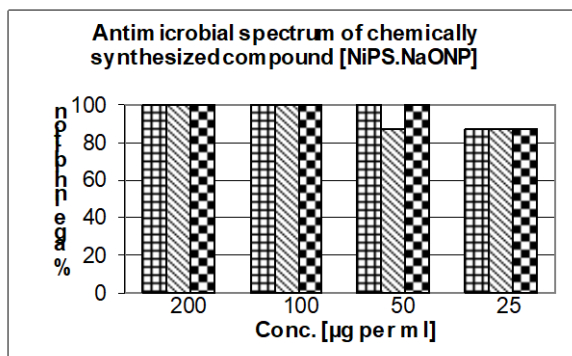
Antimicrobial Activity:

The antimicrobial activity of the some of the heterobinuclear complexes was tested on bacteria viz. *Escherichia coli*, *Staphylococcus aureus* and fungus viz. *Candida albicans* by the serial dilution method in DMF in the concentration range 25–200 $\mu\text{g ml}^{-1}$. From results

(table 3 and figure 1) they found that the complexes show better antimicrobial activity at higher concentrations against the test organism and antimicrobial activity increases gradually as the concentration of these compounds increases (Singh *et al.*, 2006). Better activities of the complexes can be explained with chelation theory (Ghosh *et al.*, 2012), The decrease in polarizability of the metal cloud increases the lipophilicity of the compound which results to the breakdown of the permeability of the cells. Chelation also reduces the polarity of the metal ion because its positive charge is considerably shared by the donor groups and the p electron delocalizes over the chelate ring. Therefore the chelation could increase the lipophilic character of the metal atoms, which afterwards favors their permeation by the lipid layer of the cell-membranes (Panchal & Patel, 2006).

Table 3: Antimicrobial Result of Compounds

Compound	Conc. (μgml^{-1})	Percentage inhibition		
		<i>E.coli</i>	<i>S.aureus</i>	<i>C.albicans</i>
CuPS.NaONP	200	100	100	100
	100	100	100	100
	50	100	85-90	100
	25	85-90	85-90	85-90
CuPS.LiDNP	200	85-90	50-55	85-90
	100	85-90	50-55	85-90
	50	85-90	50-55	85-90
	25	50-55	50-55	50-55
CuPS.KTNP	200	100	85-90	85-90
	100	85-90	85-90	85-90
	50	85-90	50-55	50-55
	25	50-55	50-55	50-55
CuPS.K1N2N	200	100	100	100
	100	100	100	100
	50	85-90	85-90	100
	25	85-90	85-90	85-90



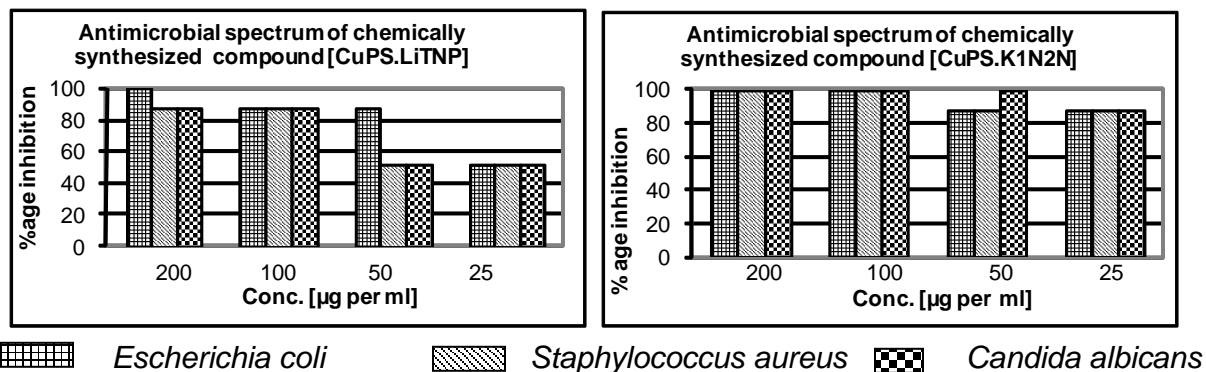


Figure 1: Antimicrobial Data of Binuclear Complexes

Conclusion

The bonding of N,N'-1,2-propylene-bis(salicylideneiminato)copper(II) complex (CuPS) and the alkali metal is probably by the dative bonding through the two phenolic oxygen atoms, which is supported by the infrared spectra UV-visible spectra and magnetic results. The stoichiometry and the physico-chemical studies as discussed above suggested the square planar geometry of the complexes with coordination number 4. The proposed structure of the prepared compounds of general formula [CuPSML]; Where, M = Li, Na or K; L = alkali metal salts of 2-nitrophenol; 2,4-ditrophenol, 2,4,6-trinitrophenol or 1-nitroso-2-naphthol may be shown as in [Fig.2]. The compound also show the good results of antimicrobial activity against the bacteria viz. *Escherichia coli*, *Staphylococcus aureus* and fungus viz. *Candida albicans*

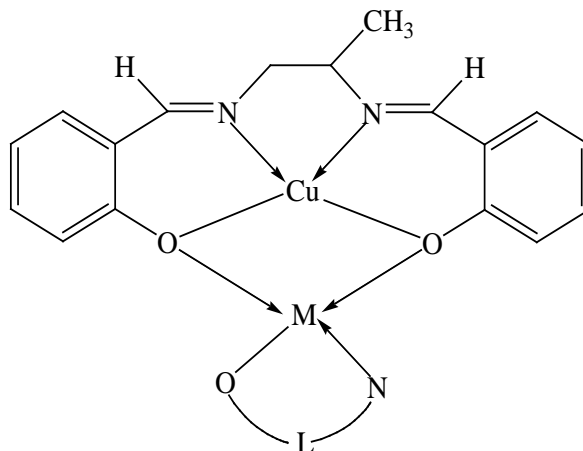


Figure 2: Probable Structure and Bonding of Complex

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