



Synthesis, Spectral study of Ni (II) and CU (II) metal ions with Heterocyclic Ligands

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Abstract:

Four Complexes of Cu (II) and Ni (II) Schiff bases have been prepared. The Schiff bases are derived by the reaction of Salicylaldehyde primary ligand with heterocyclic compounds such as 2-aminopyridine (S-L₂), 2-2'-bipyridine (S-L₄) to form the secondary ligand, which then react with the metal halides to form corresponding complexes. The elemental analysis data shows that the metal to ligand ratio in all Ni(II) and Cu(II) simple complexes are 1:2 while for mixed ligand complexes having ratio 1:2:2 for S-L₂ while it is 1:2:1 for S-L₄. The structural features have been determined from IR, UV-Vis, and ESR data. All the complexes exhibit a distorted octahedral geometry to mononuclear Ni(II), Cu(II) complexes of mixed ligands, while square planar geometry to mononuclear Ni(II), Cu(II) complexes of oximes. All the synthesised ligands and their metal complexes were screened for antimicrobial activity.

Keywords: Cu (II), Ni (II) Salicylaldehyde, mixed heterocyclic ligands of 2-aminopyridine, 2-2'-bipyridine, Metal Complexes, Spectral analysis, Antimicrobial study.

Introduction

Schiff bases are condensation products of amines with active carbonyl compounds. The Schiff bases are also called as imines⁽¹⁾, anils and azomethines. They contain azomethine (>C=N) group and hence can act as effective ligand. The Schiff bases and their metal complexes play an important role in modern coordination chemistry. These compounds are regarded as model system of biochemical interest⁽²⁾. Various studies have shown that, the azomethine group (>C=N-) in Schiff base metal complexes has considerable biological significance⁽³⁾ and found to be responsible for biological activity such as fungicidal and insecticidal⁽⁴⁾. Schiff bases of nitroguanidine with various aldehyde and ketones were studied for their antineoplastic and tuberculostatic activities⁽⁵⁾. Many other metal

chelates were studied for antitumour and antineoplastic activities⁽⁶⁾. 2-Pyridine carbaldehyde (2-pyca) and its hydrazones are used to collect semen antipode for cyanide poisoning⁽⁷⁾. The complexes of Schiff bases derived from bezaldehyde and p-amino phenyl thiazol have significant role in anticancer activity⁽⁸⁾. The Schiff base transition metal complexes are used as inorganic polymers in polymer industry⁽⁹⁾.

Because of their excellent chelating properties, and diverse structural features, the mixed ligand complexes of following types contributed to a greater extent for the development of coordination chemistry.

Material and Method:

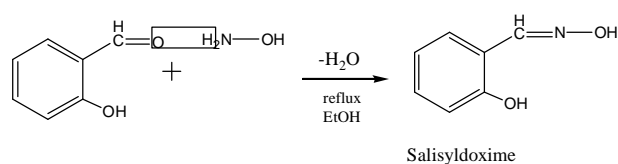
All the chemicals used for experimental work were of AR-grade. The purity of chemicals was checked

by routine test like melting point, boiling point, thin layer chromatography etc. The purification of liquid chemicals and solvents were done by distillation as suggested in literature⁽¹⁰⁾.

Synthesis of primary ligand-Salisylaldoxime

Salisylaldoxime were prepared by the standard method⁽¹¹⁾. in which 20 gm (0.164 mol) of salisylaldehyde in 30 ml alcohol (Rectified spirit) and 15 gm (0.216 mol) of hydroxyl amine hydrochloride in 10 ml water were mixed with each other. Then 10 % solutions of sodium carbonate were added to it so that mixture became alkaline. It was kept for overnight. Then it was acidified with acetic acid and then distilled off the alcohol under reduced pressure later on it was diluted with twice the volume of water and extracted with 50 ml portion of ether. The ethereal extract were dried with sodium sulphate and allowed the residue to crystallize. Then it was recrystallised from chloroform or light petroleum ether (B.P. 40°C -60°C) . The purity of the product was checked by T.L.C. and by taking M.P. of product . The melting point of Salisylaldoxime is 57°C.

Scheme



Preparation of simple complexes of Ni (II) and Cu (II) Salisylaldoxime

Mixing of metal chloride (Ni(II), Cu(II)) (0.025M) with salisylaldoxime (0.05 mole). In 1:2 proportion in ethyl alcohol which gets precipitate by maintaining the pH with addition of alcoholic ammonia or sodium acetate solution. The corresponding coloured precipitate formed was filtered and washed with hot water and cold

methanol. Finally all these metal oxime complexes were dried at 110°C.

Preparation of mixed ligand complexes of Ni(II) and Cu(II) Salisylaldoxime with S-L₂ and S-L₄

It involves discussion with respect to synthesis of mixed ligand complexes from primary ligand complexes and secondary ligands. Such as

1. 2-aminopyridine (S-L₂)

2. 2-2'-bipyridine (S-L₄)

Ni(II) Salisylaldoxime and Cu(II) Salisylaldoxime complex solution (0.01 mol) in ethanol and solution of S-L₂ and S-L₄ were dissolved in 25 ml ethanol or 25 ml CH₂Cl₂ were mixed separately in 250 ml round bottom flask. The reaction mixture was refluxed on a water bath for 2-4 hrs on cooling the coloured precipitate separate that was filtered, washed with cold hexane solvent and dried under vacuum over night⁽¹²⁾.

Result and Discussion

Magnetic Moment

The Ni (II) complexes of salisylaloximes i.e. simple complexes are diamagnetic in nature which indicates the square planar structure. The magnetic moment values are in the range of 2.74 to 3.25 B.M. of mixed ligand complexes indicates octahedral geometry⁽¹³⁾.

The observed magnetic moment values of the Cu (II) complexes in the present investigation were found to be in the range 1.79–1.83 B.M. for simple complexes while 1.80 to 2.70 B.M. for mixed ligand complexes at room temperature corresponding to one unpaired electron. The magnetic moment values of Cu(II) complexes are slightly higher than spin only value (1.73 B.M.) for one unpaired electron can be attributed to spin-orbit coupling indicative of distorted or pseudo-octahedral geometry⁽¹⁴⁾.

Similarly the electronic absorption bands are found in the range of 9880-10820 cm^{-1} (D₁) 16120-17840 cm^{-1} (D₂) and 25640-29235 cm^{-1} (D₃)

from lower energy to higher energy, which indicate the octahedral geometry of complexes.

Table II: Analytical data of Ni (II), Cu (II) complexes

Complex of ligand	Mol. formula	Colour	M.P °C	% element Found (Calculated)						Mol. Wt
				C	H	O	N	S	M	
SAO Ni (II)	(C ₁₄ H ₁₂ O ₄ N ₂ (Ni))	Dark green	246	50.29 (50.22)	3.59 (3.50)	18.99 (18.90)	8.38 (8.25)	--	17.96	334
SAO Cu(II)	(C ₁₄ H ₁₂ O ₄ N ₂ (Cu))	Green	212	50.07 (50.03)	3.57 (3.51)	19.09 (19.00)	8.34 (8.20)	--	18.90	335.5
Ni (II) SAO +2-amino pyridine	(C ₂₄ H ₂₄ O ₄ N ₆ Ni)	Green	252	55.38 (55.36)	4.61 (4.65)	12.30 (12.37)	16.15 (16.18)	--	11.53 (11.55)	520
Ni (II) SAO +2,2'-bipyridine	(C ₂₄ H ₂₀ O ₄ N ₄ Ni)	Terracota	215	59.16 (59.18)	4.10 (4.15)	13.14 (13.17)	11.49 (11.51)	--	12.11 (12.12)	487
Cu (II) SAO + 2-amino pyridine	(C ₂₄ H ₂₄ O ₄ N ₆ Cu)	Faint green	214	55.01 (55.06)	4.58 (4.61)	12.22 (12.25)	16.04 (16.05)	---	12.12 (12.15)	523.5
Cu (II) SAO + 2,2'- bipyridine	(C ₂₄ H ₂₀ O ₄ N ₄ Cu)	Green gold	198	58.59 (58.60)	4.06 (4.09)	13.02 (13.08)	11.39 (11.38)	---	12.91 (12.90)	491.5

Elemental Analysis

The newly synthesized Ni (II) complexes are green and bluish in colour. They are stable to air and moisture. The complexes decompose at a high temperature. The elemental analysis shows that the metal to ligand ratio in all Ni(II) and Cu(II) simple complexes are 1:2 while for mixed ligand complexes having ratio 1:2:2 for S-L₂ while it is 1:2:1 for S-L₄.

The ligand field parameter values i.e. LFSE observed in the range 25.447 to 26.938 Kcal/mole for mixed ligand complexes and 43.912 to 45.309 kcal/mole. LFSE values shows a distorted octahedral geometry to mononuclear Ni (II) complexes of mixed ligands, while square

planer geometry to mononuclear Ni (II) complexes of oximes. Whereas Most of the Cu (II) complexes are blue or green in colour because of single broad absorption band in the region 10000-16000 cm^{-1} and a distorted octahedral geometry to mononuclear Cu (II) complexes of mixed ligands, while square planer geometry to mononuclear Cu (II) complexes of oximes is found. The ligand field parameter values i.e. LFSE observed in the range 38.671 to 48.800 Kcal/mole are in good agreement with octahedral Cu (II) complexes.

Table II Ligand field parameters of Ni(II), Cu(II) Complexes

Complexes	Dq (cm^{-1})	B' (cm^{-1}) ¹¹¹¹¹¹¹¹¹¹¹¹	$\beta = B/B'$	v^1/v^2	LFSE (Kcal mol ⁻¹)
Ni-PL ₁	1926	---	---	1.468	43.912
Ni- PL ₁ + SL ₂	1172.625	1444.93	0.7128373	1.741	26.735
Ni- PL ₁ + SL ₄	1171.50	1327.66	0.7758010	1.729	26.710
Cu-PL ₁	3180.625	---	---	1.0318	48.800
Cu-PL ₁ + SL ₂	1696.125	---	---	1.169	38.671
Cu-PL ₁ + SL ₄	1705.375	---	---	1.235	38.882

IR Spectroscopy

The azomethine C=N stretching is found at 1630 cm^{-1} in primary ligand i.e. salicylaloxime. It is shifted to lower frequencies in complexes of primary ligand and observed at 1617 cm^{-1} for Ni (II) SAO which is again shifted up to 30 cm^{-1} and at 1610 cm^{-1} for Cu(II) complexes. which is again shifted up to 60 cm^{-1} lower frequency in case of the mixed ligand complexes i.e. adducts of Ni(II) complexes and a band appear at 1587-1597 cm^{-1} and that of Cu(II) a band appear at 1550-1565 cm^{-1} .

A strong band at 1250 cm^{-1} is appear it is due to phenolic C-O stretching in the ligand salicylaloxime which is appreciably shifted to the lower frequency side and appear at 1218 cm^{-1} for simple complexes and 1206 to 1210 cm^{-1} in mixed complexes of Ni (II) ¹⁵ and at 1209 to 1212 cm^{-1} for Cu(II) complexes.

A very broad band in the IR spectra of free ligand observed in the 3400 -3200 cm^{-1} region it assigned to phenolic -OH. This band is absent in the spectra of the Ni (II) SAO, Cu(II) SAO complexes and Ni(II)(SAO), Cu(II)(SAO) + heterocyclic ligand complexes suggesting the coordination of phenolic oxygen atom to Ni and Cu. A broad and nearly flat band present in the region 3200-2900 cm^{-1} is assigned to OH group of the >C=N-OH chromophore involved in strong H-bonding. This band is not affected in the IR spectra of Ni (II) complexes indicating no involvement of oxime -OH in chelation⁽¹⁵⁾.

The ligand band at 1403 is due to the O-H deformation mode of the oximino hydroxyl group identified at 1640-1645 cm^{-1} for Cu adducts (mixed ligand complexes) indicating that the oximino hydroxyl group remains intact⁽¹⁶⁾. in the complex of Cu(II) with all heterocyclic ligands used in present work. However the O-H deformation

band of the phenolic oxygen appears at the 1315 cm^{-1} in the ligands disappears in the complexes showing co-ordination through phenolic oxygen.

In simple complexes of Ni(II) and Cu(II) with salox a band appear at 475 cm^{-1} and 466 due to metal-nitrogen stretching and at 596 cm^{-1} , 526 cm^{-1} due to metal-oxygen stretching.

The metal oxygen bond shifted to higher value in case of mixed ligand complex of Ni(II) with Salox and appears in the range 562 to 566 cm^{-1} and in Cu(II) it is at 534-539 cm^{-1} . A metal nitrogen weak band appears for all mixed ligand complexes in the range 482-488 cm^{-1} and at 473-478 cm^{-1} this is due to formation of a bond between nitrogen atom of primary ligand and central metal Ni(II) ion and Cu(II) ion. In case of mixed ligand complex of Ni(II), Cu(II) salox with 8-hydroxyquinoline one more band is observed at 608 cm^{-1} and at 484 cm^{-1} . This clearly indicates that the phenolic oxygen bonded to Ni(II) and Cu(II).

In case of mixed ligand complexes 2-aminopyridine the band appears at 3493 cm^{-1} . This is due to free N-H stretch proves that the -NH₂ group do not participate in complex formation.

ESR Spectroscopy

The ESR spectrum of Cu (II) complexes of salicylaloxime as well as their mixed ligand complexes was recorded at room temperature using tetracyanomethylene radical as 'g' marker. The H_{||} and H_⊥ values were measured from the spectrum and used to calculate the g_{||} and g_⊥ values. ESR spectrum of Cu (II) complexes exhibit typical monomeric spectra with four (Cu⁶³, I=3/2) hyperfine lines, impressed on g_{||} and g_⊥ signals

In case of these Cu (II) complexes order of $g_{\parallel} > g_{\perp}$ is an indication presence of an unpaired electron in the dx^2-y^2 orbital of the copper ion. The appreciable difference between g_{\parallel} and g_{\perp} is indicative of a

pronounced John Teller distortion of the tetrahedral geometry⁽¹⁷⁾. The g_{av} value leads further support to appreciable distortion from octahedral stereochemistry⁽¹⁷⁾.

Selected IR bands (cm⁻¹) of Ni(II), Cu(II) SAO with, SL₂ and SL₄ (mixed ligand) complexes

Complex	C=N	C=C	Aromatic	Oximino	M-N	M-O	M-O / M-N	-NH
			C-O	O-H	Prim. Lig.	Prim. Lig.	Sec. Lig.	Sec. Lig.
Ni(SAO) + SL ₂	1589	1442-1600	1208	3208	483	564	/ 423	3428
Ni(SAO) + SL ₄	1587	1444-1605	1210	3212	482	562	/ 421	- -
Cu(SAO) + SL ₂	1563	1436-1600	1219	3396	475	539	/ 426	3493
Cu(SAO) + SL ₄	1550	1445-1600	1216	3388	478	537	/ 423	- -

X-ray Diffraction study of Ni (II) Complexes-

The complexes of (Ni(II) (PL₁+(SL₄))) were used to study. The indexing in the powder diffraction was done independently by trial and error method. The standard deviation observed is within the permissible limit. The observed density for (Ni(II)(PL₁+(SL₄))) is 1.342 gcm⁻³ while calculated density from Z value and unit cell volume for complexes is 1.3041 gcm⁻³. The porosity percentage calculated from the observed and calculated densities was found to be 5.725. The crystal system was found to be monoclinic with four molecules per unit cell having probable space group p2/m.

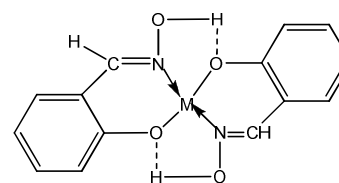
Conclusively, the X-ray powder diffractogram suggest that Ni (II) complexes under investigation crystallize with monoclinic crystal system with probable space group P²/m.

X-ray Diffraction Study of Cu (II) Complexes-

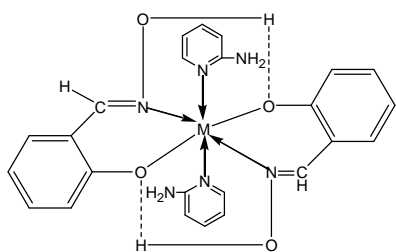
The Cu (II) complexes of ligand PL₁ +SL₂ was subjected to X-ray powder diffraction studies. X-ray powder data of all the main peaks have been indexed independently by trial and error method. The standard deviation observed for Cu (II) complexes is within permissible limit of 2%. The

crystal volume is obtained from indexing of the diffraction pattern. The Z value was calculated and rounded up to the nearest whole number. The porosity percentage was calculated from the observed and calculated densities. The density calculated from diffraction data and the observed density was found to be very close to each other indicating perfection in indexing. The observed density Cu (II) (PL₁)₂ + (SL₂)₂ is 1.875 gcm⁻³ and calculated density is, 1.863 gcm⁻³ respectively. The porosity percentage is 1.496 % respectively and complex crystallises in the monoclinic crystal system with 2 molecules per unit cell. The probable space group is P²/m.

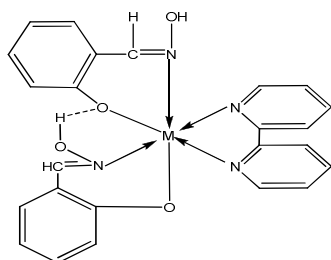
Conclusively the X-ray powder diffractograms suggest that the Cu (II) complexes under investigation crystallize with monoclinic crystal system and space group P²/m.



M(II)PL₁ M= Cu(II), Ni(II)



M(II)PL₁+ SL₂ M= Cu(II),Ni(II)



M(II)PL₁+ SL₄ M= Cu(II),Ni(II)

Antimicrobial activity

The *in vitro* antimicrobial activity was carried out by Ditch-plate method⁽¹⁸⁻¹⁹⁾.

a) Antibacterial activity by Ditch-Plate method

Nutrient agar of 20ml. was placed in a flat bottomed Petri dish. When solidified, 4 ml of second nutrient sol., Seed with test bacteria was poured evenly onto the first layer (at 48°C). As soon as the second layer was solidified, in six sterile stainless steel cylinders were added an equal amount of a standard penicillin solution of concentrations 2.0,1.5,1.0,0.5 and 0.25 mg/ml. Sample of the test solutions were deposited analogously on the other Petri dishes. The dishes were incubated at 37°C for 16-18 hours. During this time the penicillin diffuses out of the cylinder into the surrounding agar and suppresses the growth of the test organism. Thus the cylinder was surrounded by clear zone, free of bacteria. The diameter of each zone provides an index of activity of the penicillin preparation. The mean values obtained from 10-20 standard plates are used to draw a curve and the biological activity

of the test solution in international unit is determined using conversion table.

b) Antifungal activity by paper Disc Diffusion method

Whatman No. 1 filter paper disc of 5mm diameter were sterilized by autoclaving for 15 min. at 121°C. The sterile disks were impregnated with different compounds. Agar plates were surface inoculated uniformly from the both culture of the tested microorganisms. The impregnated disks were placed on the medium suitably spaced apart and plates were incubated at 28°C for 72 hours. The inhibition zones caused by various compounds on the microorganisms were examined.

Table III: Antimicrobial activity of the synthesised compound

Sr. No.	Ligand / Complex	Bacterial Strain		Fungal Strain	
		E.Coli	S.Aureus	A.niger	A.flavus
1	PL ₁	7	8	9	10
2	SL ₂	6	0	0	7
3	SL ₄	4	0	0	5
4	Ni(II) PL ₁	0	0	0	7
5	Cu(II) PL ₁	0	6	0	9
6	Ni(II) PL ₁ + SL ₂	12	14	0	8
7	Ni(II) PL ₁ + SL ₄	11	13	0	10
8	Cu(II) PL ₁ + SL ₂	14	14	6	15
9	Cu(II) PL ₁ + SL ₄	13	17	0	12

Conclusion:

All these complexes are insoluble in water but moderately soluble in DMSO, DMF, dioxane and chloroform. From the above discussion and on the basis of results of elemental analysis, Magnetic susceptibility, electronic spectral data, IR, X-ray diffraction and ESR study, it may be concluded that, the simple complexes of all metal ions have square planer structure while

mixed ligand complexes of all metal ions have octahedral structure.

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