

Metal complexes of salicylaldoxime: Preparation characterisation and biological activity

Sachin R.Joshi¹, S.P.Pachling¹, Seema I.Habib^{2*}

¹Department of Chemistry, N.S.B College, Nanded (INDIA)

²Department of Chemistry, Shankarrao Chavan Mahavidyalaya, Ardhapur, Nanded (M.S.), (INDIA)

Email: seemahabib12@gmail.com

ABSTRACT

Eight neutral complexes of Cu(II), Ni(II), Co(II) and Zn(II) have been prepared with a new heterocyclic Schiff base (PL) derived from salicylaldehyde and hydroxyl amine hydrochloride. The analytical data shows that the metal to ligand ratio is 1:2:1 for metal complex with oxime as a primary ligand and 1:2:2 for mixed heterocyclic ligand. The structural features have been determined from IR, UV-Vis, ¹H-NMR, and ESR spectral data. All the complexes exhibit octahedral geometry around the central metal ion. The molar conductance values of metal complexes suggest their non electrolytic nature. The free Schiff bases and their complexes have been tested for their antibacterial and antifungal activities against several human pathogenic bacteria and fungi, the obtained result showed enhancement in activity on coordination of metals with ligands. © 2014 Trade Science Inc. - INDIA

KEYWORDS

Salicylaldoxime;
Mixed heterocyclic ligands;
Metal complexes;
Spectral study;
Antimicrobial study.

INTRODUCTION

Transition metal complexes of Schiff bases have drawn considerable attention due to their remarkable antifungal, antibacterial, antitumour and other activities^[1-6]. Some drugs were known to show increased activity when administered as metal chelates rather than as organic compounds^[7,8]. They are found useful in catalysis, in medicine as antibiotics and anti-inflammatory agents and in the industry as anticorrosion^[9-15]. Literature is abundant on physico-chemical properties of various Schiff bases and chelates with their pyridine, 2,2'-bipyridine adducts^[16-20], while comparatively little is known on heterocyclic mixed Schiff-base ligands and their transition metal complexes. Consequently, my findings on the heterocyclic mixed ligand complexes of

Ni(II), Cu(II), Co(II), Zn(II) metals derived from Salicylaldoxime and 2-amino thiazole, 2-amino pyridine, 8-hydroxy quinoline, 2,22 -bipyridine as secondary ligand and metal halides. All these compounds with the ligand are new, being reported for the first time.

Experimental

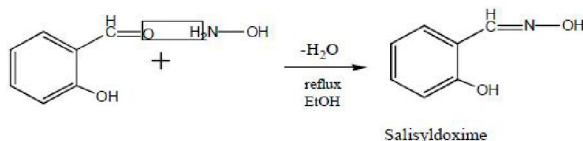
All the chemicals used for experimental work were of AR-grade. The purity of chemicals was checked by routine test like melting point, boiling point, thin layer chromatography etc. The purification of liquid chemicals and solvents were done by distillation as suggested in literature^[21].

Synthesis of primary ligand: Salicylaldoxime

Salicylaldoxime were prepared by the standard method^[22], in which 20 gm (0.164 mol) of

salicylaldehyde 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 take 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 (M.P. = 57°C).

Scheme



Preparation of simple complexes of Salicyldoxime

(a) The complexes of Ni-Salicyldoxime, Cu-Salicyldoxime, CO-Salicyldoxime and Zn-Salicyldoxime has been synthesized as follows

Mixing of metal chloride [Ni(II), Cu(II), Co(II) and Zn(II)] (0.025M) with salicyldoxime (0.05 mole) in 1:2 proportions in ethyl alcohol this gets precipitate by maintaining the pH with addition of alcoholic ammonia or sodium acetate solution. The corresponding coloured precipitate (except Zn) formed was filtered and washed with hot water and cold methanol. Finally all these metal oxime complexes were dried at 110°C.

(b) Preparation of mixed ligand complexes of Ni-Salicyldoxime, Cu-Salicyldoxime, CO-Salicyldoxime and Zn-Salicyldoxime with S-L₁, S-L₂, S-L₃ and S-L₄

Ni-Salicyldoxime, Cu-Salicyldoxime, CO-Salicyldoxime and Zn-Salicyldoxime complex solution (0.01 mol) in ethanol and solution of S-L₁, S-L₂, S-L₃ 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^[23].

RESULT AND DISCUSSION

Magnetic susceptibility and absorption spectral studies

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 indicative of distorted or pseudo-octahedral geometry^[24]. 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. The elemental analysis shows that the metal to ligand ratio in all Cu(II) simple complexes is 1:2 while for mixed ligand complexes having ratio 1:2:2 for S-L₁ and S-L₂ 1:2:1 for S-L₃ and S-L₄.

The Ni(II) complexes of salicyldoximes are diamagnetic in nature in present work, which indicates the square planer structure. The magnetic moment values are in the range of 2.74 to 3.25 B.M. of mixed ligand complexes in present work indicates octahedral geometry^[25]. 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 for simple complexes are in good agreement with octahedral Ni(II) complexes and square planer complexes respectively. The elemental analysis shows that the metal to ligand ratio in all Ni(II) simple complexes are 1:2 while for mixed ligand complexes having ratio 1:2:2 for S-L₁ and S-L₂ while it is 1:2:1 for S-L₃ and S-L₄.

For the Co(II) complexes the magnetic moment values are in the range of 2.74 to 3.25 B.M. of mixed ligand complexes in present work indicates octahedral geometry^[25]. The ligand field parameter values i.e. LFSE observed in the range 30.383 to 30.979 Kcal/mole for mixed ligand complexes and 42.986 to 43.445 kcal/mole for simple complexes are in good agreement with octahedral Co(II) complexes and square planer complexes respectively. 1:2 metal to ligand ratio for simple complexes and 1:2:2 for metal complex with oxime as a primary ligand and SL₁ and SL₂ as a secondary ligand

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TABLE 1 : Analytical data of Ni(II), Cu(II), Co(II) and Zn(II) complexes with SAO

Complex of ligand	Molecular formula	Colour	M.P °C	% element Found (Calculated)						Mol. Wt
				C	H	O	N	S	M	
1 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
2 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
3 SAO Co(II)	[C ₁₄ H ₁₂ O ₄ N ₂ (Co)]	Reddish Brown	332	50.90 (50.80)	3.63 (3.50)	19.39 (19.35)	8.48 (8.42)	---	17.57	330
4 SAO Zn(II)	[C ₁₄ H ₁₂ O ₄ N ₂ (Zn)]	Faint yellow	292	49.85 (49.90)	3.56 (3.52)	19.16 (19.11)	8.30 (8.22)	---	19.28	337
5 Ni (II) SAO + 2-amino thiazole	[C ₂₀ H ₂₀ O ₄ N ₆ S ₂ Ni]	Brick red	250	45.19 (45.21)	3.76 (3.80)	12.05 (12.07)	15.81 (15.85)	12.05 (12.08)	11.11 (11.15)	531
6 Ni (II) SAO + 8-hydroxy quinoline	[C ₂₃ H ₁₈ O ₅ N ₃ Ni]	Green	254	58.10 (58.11)	3.78 (3.80)	16.84 (16.85)	8.84 (8.86)	---	12.42 (12.43)	475
7 Cu (II) SAO + 2-amino thiazole	[C ₂₀ H ₂₀ O ₄ N ₆ S ₂ Cu]	Blue	215	44.81 (44.82)	3.73 (3.75)	11.95 (11.97)	15.68 (15.70)	11.95 (11.96)	11.85 (11.87)	535.5
8 Cu (II) SAO + 8-hydroxy quinoline	[C ₂₃ H ₁₈ O ₅ N ₃ Cu]	Dark green	217	57.55 (57.58)	3.75 (3.78)	16.68 (16.72)	8.75 (8.74)	---	13.24 (13.25)	479.5
9 Co(II) SAO + 2-amino pyridine	[C ₂₄ H ₂₄ O ₄ N ₆ Co]	Reddish brown	340	55.59 (55.57)	4.63 (4.65)	12.35 (12.40)	16.21 (16.22)	---	11.19 (11.20)	518
10 Co(II) SAO + 2,2'-bipyridine	[C ₂₄ H ₂₀ O ₄ N ₄ Co]	Yellow gold	325	59.13 (59.16)	4.10 (4.13)	13.14 (13.17)	11.49 (11.47)	---	12.11 (12.15)	487
11 Zn (II) ASO + 2-amino pyridine	[C ₂₄ H ₂₄ O ₄ N ₆ Zn]	Yellow	297	54.85 (54.81)	4.57 (4.56)	12.19 (12.18)	16.00 (16.05)	---	12.38 (12.42)	525
12 Zn (II) ASO + 2,2'-bipyridine	[C ₂₄ H ₂₀ O ₄ N ₄ Zn]	Lemon yellow	287	56.79 (56.83)	4.05 (4.04)	12.98 (13.01)	11.35 (11.38)	---	13.18 (13.21)	493

while it is 1:2:1 for metal complex with oxime as a primary ligand and SL₃ and SL₄ as a secondary ligand.

Due to completely filled 'd' shell as expected for Zn(II) ion it exhibits diamagnetic nature. The present complexes are found to be diamagnetic in nature for the square planar^[26] geometry. In present work the electronic absorption spectrum of Zn (II) complexes shows only one absorption band in UV-visible spectrum in the range 357 nm (2800 cm⁻¹) to 372 nm (26882 cm⁻¹). This is due to absence of d-d transition. This observed peak is because of metal to ligand charge transfer spectra. The values are in agreement with octahedral geometry of these complexes^[27-29]. The elemental analysis indicates that Zn(II) complexes of mixed ligand exhibit the stoichiometry 1:2:2. The Zn (II) complexes undergo decomposition at high temperature.

IR spectroscopy

The azomethine C=N stretching is found at 1640 cm⁻¹ in primary ligand i.e. salicylaldoxime. It is shifted to lower frequencies in complexes of primary ligand and observed at 1615 cm⁻¹ for Co (II) SAO and at 1652 cm⁻¹ for Zn (II) SAO which is again shifted by 50 cm⁻¹ lower frequency in case of the mixed ligand com-

plexes i.e. adducts of Co (II), Zn (II) complexes and a band appear at 1567-1575 cm⁻¹ and at 1579-1589 cm⁻¹.

The Ligand SAO exhibit four peaks in the range of 1420 cm⁻¹ to 1600 cm⁻¹ attributed to aromatic C=C stretch and its Co(II), Zn(II) complexes shows same C=C stretch at 1445-1600 cm⁻¹. While their mixed ligand complex exhibit in the range of 1444-1605 cm⁻¹.

In present work a strong band at 1250 cm⁻¹ is appear, it is due to phenolic C-O stretching in the ligand salicylaldoxime which is appreciably shifted to the lower frequency side and appear at 1222 cm⁻¹ for simple complexes and 1212 -1218 cm⁻¹ in mixed complexes of Co(II)^[30] and at 1203-1212 cm⁻¹ for Zn(II) complexes.

The IR spectrum of the ligand SAO shows a sharp band at 3450 cm⁻¹ and a broad band at 3300 cm⁻¹. These bands are ascribed to frequency of OH of the intermolecular hydrogen bonded oximino hydroxyl group and intermolecular hydrogen bonded phenolic OH group^[31,32].

The later band is absent on complexation with Co (II) and Zn (II) suggest breakdown of intermolecular

TABLE 2 : Ligand field parameter of Cu(II), Co(II) and Ni(II) complexes

Complexes	Dq (cm ⁻¹)	B' (cm-1)	β =B/B'	ν ² /ν ¹	LFSE (Kcal mol-1)
Ni-PL ₁	1926	--	--	1.468	43.912
Ni- PL ₁ + SL ₁	1177	1457.33	0.7067720	1.743	26.835
Ni- PL ₁ + SL ₃	1181.50	1444.40	0.7130989	1.743	26.938
Cu-PL ₁	3180.625	--	--	1.0318	48.800
Cu-PL ₁ + SL ₁	1698.375	--	--	1.221	38.722
Cu-PL ₁ + SL ₃	1710	--	--	1.212	38.988
Co-PL ₁	1885.375	--	--	1.103	42.986
Co- PL ₁ + SL ₂	1352.875	1009.06	0.9622817	1.574	30.845
Co- PL ₁ + SL ₄	1342.50	999.86	0.971136	1.564	30.677

hydrogen bonding. It revealed by the presence of a broad band in the range 3261-2980 cm⁻¹³³ and 3318-3000 cm⁻¹³³, but in the case of mixed ligand complex of 2-aminothiazole and 8-hydroxyquinoline frequency of OH is shifted to 3389-3398 cm⁻¹ showing weakening of intramolecular hydrogen bonding.

The ligand band at 1403 cm⁻¹ is due to the O-H deformation mode of the oximino hydroxyl group it identified at 1640-1645 cm⁻¹ for Co(II) adducts (mixed ligand complexes) indicating that the oximino hydroxyl group remains intact³³ in the complex of Co(II), Zn(II) with all heterocyclic ligands used. 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 Co(II) with SAO a band appears at 437 cm⁻¹ due to metal-nitrogen stretching and at 539 cm⁻¹ due to metal-oxygen stretching. The metal oxygen bond shifted to higher value in case of mixed ligand complex of Co(II) with SAO and appears in the range 544 to 548 cm⁻¹ and at 566-613 cm⁻¹ in case of Zn(II) complex. A metal nitrogen weak band appears for all mixed ligand complexes in the range 442-448 cm⁻¹ and at 485-492 cm⁻¹ this is due to formation of a bond between nitrogen atom of primary ligand and central metal copper ion and Zn ion. In case of mixed ligand complex of Co(II) salox with 8-hydroxyquinoline one more band is observed at 426 cm⁻¹ and at 428 cm⁻¹ for Zn(II) complex. This clearly indicates that the phenolic oxygen bonded to Co(II). In case of mixed ligand complexes of 2-aminothiazole and 2-aminopyridine the bands appears at 3430 cm⁻¹ and 3443 cm⁻¹. This is due to free N-H- stretch proves that the –NH₂ group do not participate in complex formation.

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)³⁴ and at 1209 to 1212 cm⁻¹ for Cu(II) complexes.

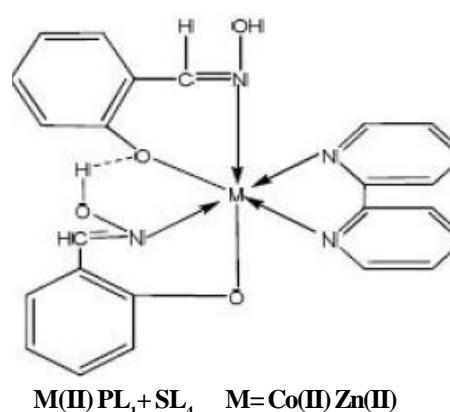
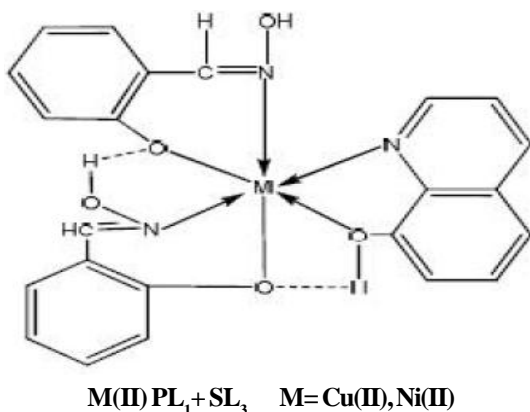
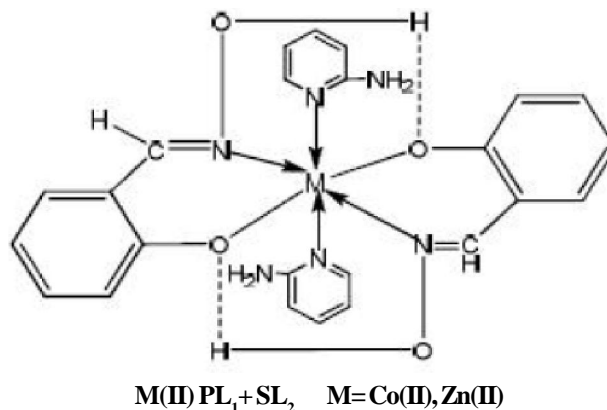
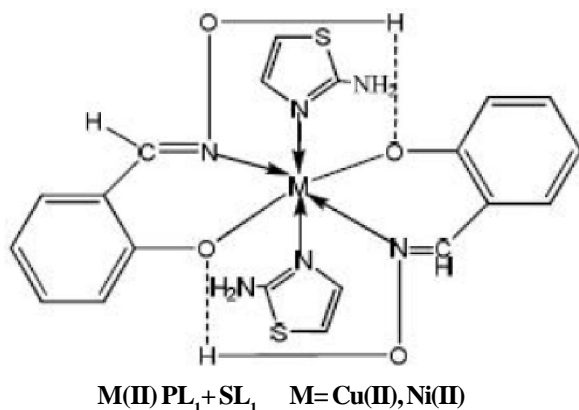
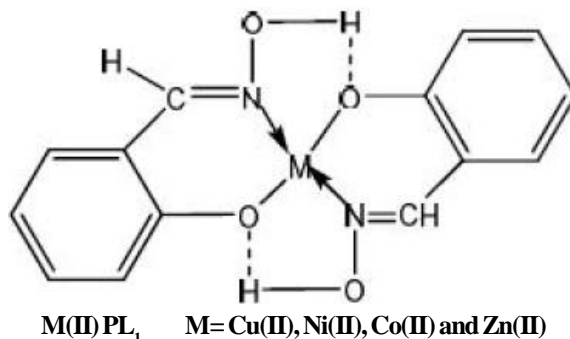
A very broad band in the IR spectra of free ligand observed in the 3400 -3200 cm⁻¹ region it assigned to phenolic -OH. This band is absent in the spectra of the Ni(II) SAO, Cu(II) SAO complexes and Ni(II)(SAO), Cu(II)(SAO) + heterocyclic ligand complexes suggesting the coordination of phenolic oxygen 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 in not affected in the IR spectra of Ni (II) complexes indicating no Involvement of oxime -OH in chelation^[15,34].

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, in the complex of Cu(II) with all heterocyclic ligands used in present work. However the O-H de-

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ESR spectral data with g values of Cu(II) complexes

Sr.No.	Complex	g_{\parallel}	g_{\perp}	g_{av}	G axial symmetry $g_{\parallel} + g_{\perp}$
1	Cu (II) PL ₁ + SL ₁	2.25721	2.05780	2.12427	4.31501
3	Cu (II) PL ₁ + SL ₃	2.22804	2.05909	2.1154067	4.28713



formation 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 oxy-

gen 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 $-\text{NH}_2$ group do not participate in complex formation.

ESR spectroscopy

The ESR spectrum of Cu(II) complexes of salicylaldehyde as well as their mixed ligand complexes was recorded at room temperature using tetracyanomethylene radical as 'g' marker. The H_{\parallel} and H_{\perp} values were measured from the spectrum and used to calculate the g_{\parallel} and g_{\perp} values. ESR spectrum of Cu(II) complexes exhibit typical monomeric spectra with four (Cu^{63} , $I=3/2$) hyperfine lines, impressed on g_{\parallel} and g_{\perp} signals

In case of these Cu(II) complexes order of g values is $g_{\parallel} > g_{\perp}$ 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^[35]The g_{av} value leads further support to appreciable distortion from octahedral stereochemistry^[35].

ANTIMIROBIALACTIVITY

The in vitro antimicrobial activity was carried out by Ditch-plate method^[36-37].

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

TABLE 3 : 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 ₁	5	0	0	6
3	SL ₂	6	0	0	7
4	SL ₃	0	12	0	0
5	SL ₄	4	0	0	5
6	Cu(II) PL ₁	0	6	0	9
7	Ni(II) PL ₁	0	0	0	7
8	Co(II) PL ₁	0	0	0	0
9	Zn(II) PL ₁	0	0	2	7
10	Cu(II) PL ₁ + SL ₁	12	12	2	9
11	Cu(II) PL ₁ + SL ₃	11	12	2	2
12	Ni(II) PL ₁ + SL ₁	10	10	0	7
13	Ni(II) PL ₁ + SL ₃	7	15	0	0
14	Co(II) PL ₁ + SL ₂	14	16	4	12
15	Co(II) PL ₁ + SL ₄	12	15	0	8
16	Zn(II) PL ₁ + SL ₂	13	15	3	11
17	Zn(II) PL ₁ + SL ₄	11	14	0	6

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.

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.

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 octahe-

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dral structure.

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