CHAPTER: 5 Ternary binuclear complexes with planar bridged.

5.1 Introduction

5.2 Experimental

5.3 Results and Discussion

5.4 References

5.1 Introduction

The study of magnetic exchange interaction propagated by multi-atom bridges has received a lot of attention in the last two decades [1-3]. The interest in this area stems from attempts to mimic the structural and functional properties of biological system and to design molecular based magnets [4-6].

The extent of magnetic exchange is affected by several structural parameters such as bridging identity, the metal-metal separation, the bond angles subtended at the bridging atoms, the dihedral angles between the plane containing the metal ions, the metal-bridge ligand bond lengths and the streochemistry around the metal ion [7-10]. Magneto-structural correlations in symmetrical binary and ternary binuclear complexes has been discussed earlier in chapter 2 – 4 and the extent of magnetic exchange was shown to depend of the torsional angle between metal coordination planes. It was thought of interest to synthesize binuclear complexes with completely conjugated planar bridging groups to assure coplanarity of the copper ion coordination and electron delocalization in the molecule. Such compounds can be expected to have interesting catalytic or biological activity because of modification of redox.

Mixed ligand complexes play an important role in biological processes as exemplified by many instances in which enzymes are known to be activated by metal ions [11-13]. Copper is an important trace element for plants and animals [14, 15] and is involved in mixed ligand complex formation in a number of biological processes [16-19]. Copper (II) complexes have great variety of biological properties ranging from anticancer [20-22], antibacterial [23] and antiviral [24]. Copper (II) complexes containing polypyridine ligand like 2,2'-bipyridine and 1,10-phenanthroline have been shown to be useful as photophysical and chemical probes of DNA in view of their relevance to various biochemical and biomedical application [25-28].

Complexation of a drug molecule with a metal ion is always expected to alter its activity. It is specially so with copper (II) due to the redox properties associated with it. The antibiotic activity of the simplest drug molecule aspirin is known to be

enhanced on coordination with copper (II). Another well known antibiotic ciprofloxacin has been shown to have enhanced activity when coordinated to copper (II) ion in a binary complex or a ternary complex with another polypyridine or amine ligand [29]. A variety of copper complexes including those with salicylaldoxime [30], 8-hydroxyquinoline [31], penicillamine [31] and oxindole derivatives [32] are shown to possess anticancer activity. The anticancer / antitumer activity of known anticancer drugs like netropsin, daunamycin and combilexin have copper dependent activity [33]. The copper complex of isonicotinic acid hydrazide has been shown to possess antiviral activity [34].

Apparently the functional groups like phenolic –OH, amides, amines, hydrazides, imines have important role to play in combination with the redox associated with copper (II). The binuclear complexes designed for study in this chapter have more than one such functional group, namely, hydrazides and phenolate. They also have planar aromatic bridging groups to ensure electron delocalization and facile redox. Hence, it was thought of interest to screen these complexes for biological activity.

In the present chapter we have synthesized new binuclear complexes of copper (II) with general formula $[Cu_2(AA)L(CH_3CO_2)_n].xH_2O$ where L = N-benzoyl-N'-[1-(5-acetyl-2,4-dihydroxy-phenyl)-ethylidene]-hydrazine or L = N-phenylacetyl-N'-[1-(5-acetyl-2,4-dihydroxy-phenyl)-ethylidene]-hydrazine or L = N-nicotinoyl-N'-[1-(5-acetyl-2,4-dihydroxy-phenyl)-ethylidene]-hydrazine or L = N-isonicotinoyl-N'-[1-(5-acetyl-2,4-dihydroxy-phenyl)-ethylidene]-hydrazine and the secondary ligand AA = 2,2'-bipyridine (**5-I, 5-V, 5-VIII, 5**-X), 1,10-phenanthroline (**5-II, 5-VI, 5-IX 5-XI**), 2-hydroxybenzoic acid (**5-III, 5-VII**) or 5-bromo-2-hydroxybenzoic acid (**5-IV**). The complexes have been characterized by means of elemental analysis, thermal analysis and spectroscopic properties. The binucleating ligands have both neutral as well as anionic donor chelating sites, one site involving an amide and phenolate and the other involving carbonyl and phenolate functionalities which can provide dissimilar environment to the metal ions. Further variation in the nucleophilicty of the

coordinating atom or π- bonding ability can be brought about by changing the substituents over the aromatic ring as well as on the secondary ligand. Thus, the combination of ligands are expected to provide geometrically similar but electronically distinct coordination environment to the metal ions. Antibacterial activity of these ligands and complexes has been examined against *S. aureus, B. megaterium* (gram positive) and *S. typhi, S. marsescens, P. vulgaris* (gram negative) strains.

5.2 Experimental

5.2.1 Chemicals:

Benzoyl hydrazine, phenylacetyl hydrazine, nicotinoyl hydrazine and isonicotinoyl hydrazine were prepared from their ethyl esters by condensation with hydrazine [35]. Luria agar (Himedia), acetic anhydride (Allied), hydrazine hydrate (Qualigens), resorcinol, anhydrous zinc chloride, ethyl benzoate, ethyl-phenyl acetate, ethyl-3-pyridine carboxylate, ethyl-4-pyridine carboxylate, DMSO and DMF procured from Marck were of A. R. grade and were used as received without further purification.

All other chemicals were used, as described in the previous chapters.

5-bromo-2-hydroxybenzoic acid was prepared by low temperature (5 °C, ice – salt bath) bromination of 2-hydroxybenzoic acid. Yield 60.00% and mp 164-166 °C (Lit.: 164–166 °C) [36].

5.2.2 Physical measurements:

The elemental analysis, thermal analysis and conductivity measurements were done as described in chapter 3.

UV-VIS, IR, ESR and FAB-Mass spectral analysis were done using the instruments described in chapter 3.

^{1}H NMR and ^{13}C NMR of the ligand were recorded on the same instrument as used earlier in chapter 2.

The thermogravimetric analysis of the complexes **5-II, 5-III** and **5-VIII**, in air atmosphere and complexes **5-I, 5-IV, 5-V, 5-VI, 5-VII, 5-IX, 5-X** and **5-XI** in nitrogen atmosphere were carried out by using thermal analyser, Perkin Elmer (Pyris Diamond) instrument with a heating rate of 10 °C/minutes.

Room temperature magnetic measurements were made by using Faraday set up as described in chapter 2. Magnetic moments per atom were calculated using the formula,

$$\mu_{eff} = 2.303 (\chi_M T \times 10^{-6} / 2)^{1/2}$$

where, χ_M = molar magnetic susceptibility per copper atom and other terms have their usual meanings. Pascal corrections for ligands and counter ions have been incorporated.

5.2.3 Synthesis of ligands:

5.2.3.1: 1-(5-Acetyl-2,4-dihydroxy-phenyl)-ethanone (DAR):

20 g (0.18 mol) of resorcinol was placed in a dry 500 ml round bottom flask. 75.63 g (0.694 mol) of acetic anhydride was added slowly to resorcinol. The later dissolved quickly. The reaction mixture was treated with 3 drops conc. H_2SO_4 where upon exothermic reaction was set in. The reaction mixture was allowed stand for 30 minutes to allow the formation of 1,3-diacetoxy benzene. Without isolation of the product, the reaction mixture was treated with 60 g (1.18 mol) anhydrous $ZnCl_2$ and was heated under CO_2 environment for 3 hrs, maintaining the temperature between 140 - 150 °C. The resulting suspension was added slowly to ice cold water acidified with HCl (pH ~ 4). A dark brown sticky compound separated. It was filter, washed with 200 ml (10×20 ml) water and dried. The product was treated with 14 g activated charcoal in 300 ml ethanol and allowed to reflux for ~ 30 min. The solution was

filtered hot. The brownish microcrystalline product separated on cooling was filtered, dried and recrystallised from hot toluene (**Fig. 5.1**).

Yield: 15% (5.20 g). mp 178–181°C.

Elemental analysis : (obsd.) %C 63.08, %H 5.15.

(calc. for the formula $C_{10}H_{10}O_4$) %C, 61.86, %H 5.15,

IR (KBr, $\bar{\nu}$ cm^{-1}) 3335, 2891, 1622, 1347, 1240, (**Fig. 5.2**).

^1H NMR ($CDCl_3$), (δ): 2.63 (s, 6H (CH_3)); 6.40 (s, 1H (ArH)); 8.19 (s, 1H (ArH); 12.92 (s, 2H (OH)) (**Fig. 5.3**)

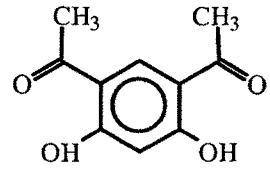


Fig. 5.1 Structure of 1-(5-Acetyl-2,4-dihydroxy-phenyl)-ethanone (DAR).

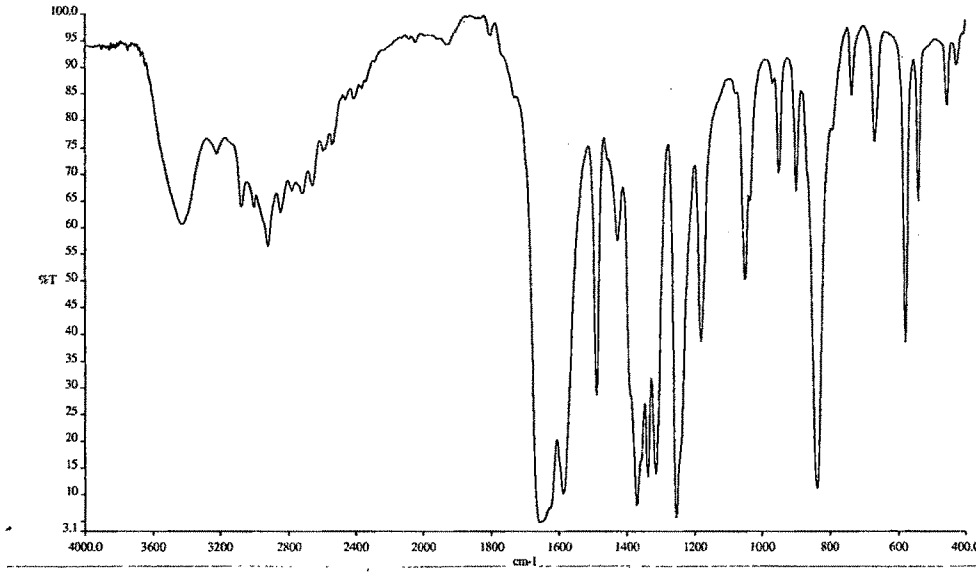


Fig. 5.2 FTIR of 1-(5-Acetyl-2,4-dihydroxy-phenyl)-ethanone.

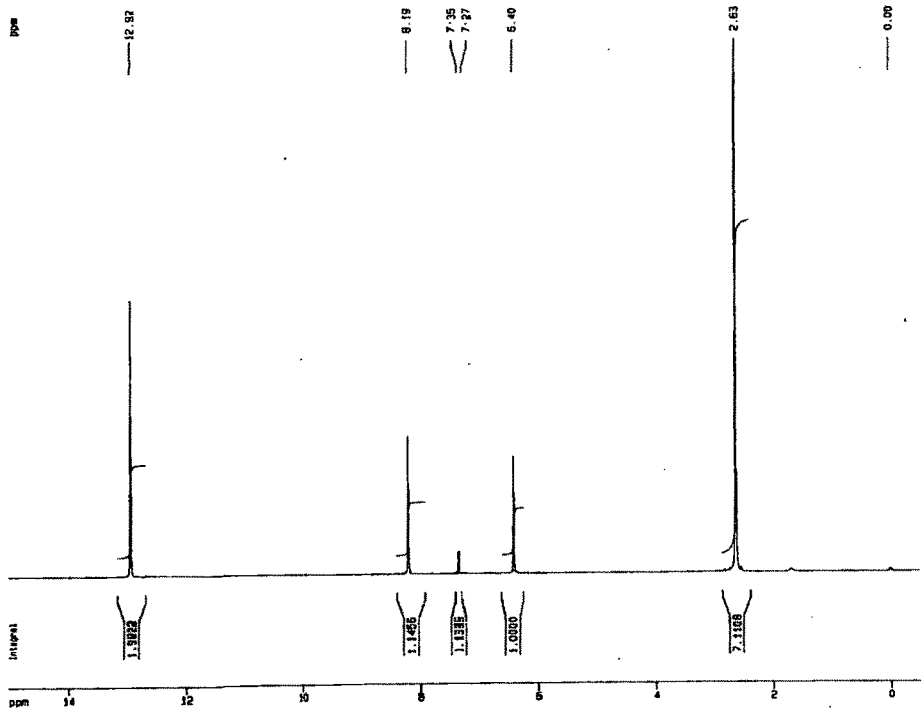
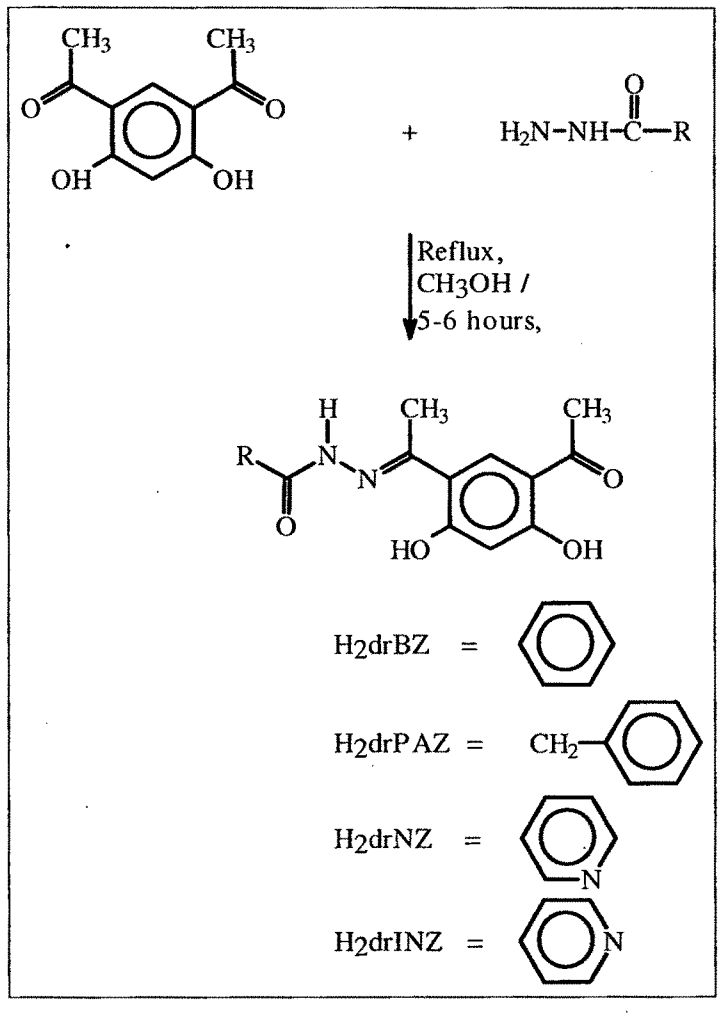


Fig. 5.3 ^{1}H NMR of 1-(5-Acetyl-2,4-dihydroxy-phenyl)-ethanone.

5.2.3.2 N-Benzoyl-N'-[1-(5-acetyl-2,4-dihydroxy-phenyl)-ethylidene]-hydrazine, (H_2drBZ):

To a solution of 0.485 g (2.5 mmol) of 1-(5-Acetyl-2,4-dihydroxy-phenyl)-ethanone (DAR) dissolved in 30 ml methanol, 20 ml methanolic solution of 0.34 g (2.5 mmol) benzoyl hydrazine was added. The reaction mixture was allowed to reflux for 5 hours with constant stirring. At the end of 5 hours creamy white solid separated on cooling. It was filtered, washed thoroughly with 30 ml methanol and dried at 50 – 60 °C.

Ligands, H_2drPAZ, H_2drNZ and H_2drINZ were prepared by similar method using appropriate quantities of phenylacetyl hydrazine, nicotinoyl hydrazine or isonicotinoyl hydrazine and 1-(5-Acetyl-2,4-dihydroxy-phenyl)-ethanone (DAR). **(Scheme 5.1)**. Yields, analytical and spectral data the above binucleating ligands are given in **Table 5.1**.


CH3
CH3
O
O
OH
OH
+
H2N-NH-C-R
O
Reflux,
CH3OH /
5-6 hours,
H
CH3
CH3
R
N
N
O
O
HO
OH
H2drBZ =
H2drPAZ =
CH2
H2drNZ =
N
H2drINZ =
N

(Scheme 5.1)

Table 5.1 Yields, elemental analysis and IR spectral data of binucleating ligands.

Comp.	Yields (%)	Mp (°C)	Elemental analysis Found (Calc)* C	H	N	IR (KBr) ($\bar{\nu}$ in cm^{-1})
H_2drBZ	73	225–	65.57	4.98	9.75	3650, 3404, 3058,
$C_{17}H_{16}N_2O_4$		228	(65.38)	(5.12)	(8.97	1676, 1639
H_2drPAZ	68	257–	66.57	5.92	8.75	3650, 3475, 3030,
$C_{18}H_{18}N_2O_4$		260	(66.26)	(5.52)	(8.59)	1690, 1638
H_2drNZ	92	257–	61.94	4.56	13.50	3649, 3447, 3120,
$C_{16}H_{15}N_3O_4$		260	(61.34)	(4.79)	(13.42)	1664, 1636
H_2drINZ	92	~300	61.88	4.65	13.01	3650, 3448, 3125,
$C_{16}H_{15}N_3O_4$			(61.34)	(4.79)	(13.42)	1678, 1643.

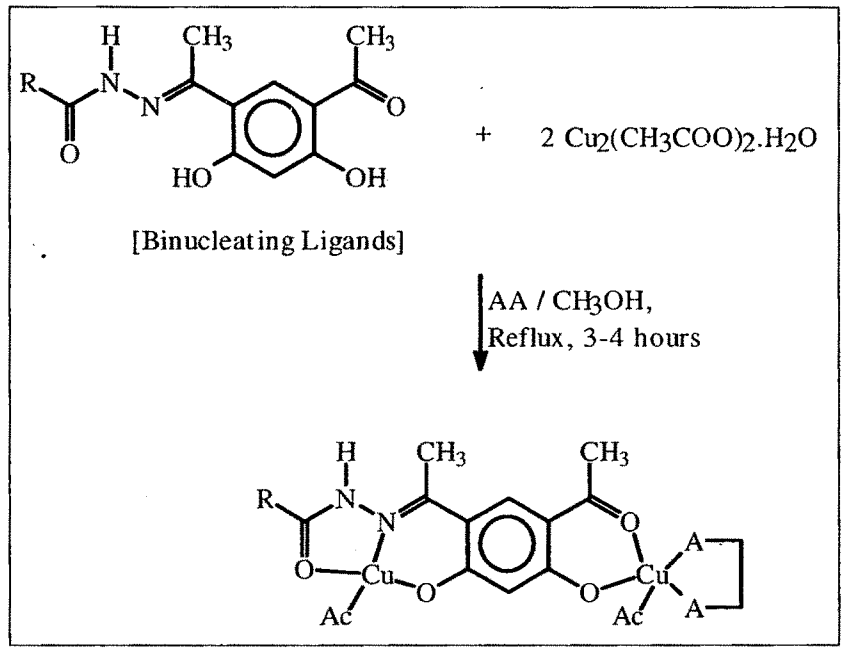
*The values in parentheses are theoretical values calculated for the molecular formulae.

5.2.4 Synthesis of binuclear complexes:

Synthesis of [Cu_2 (bipy)(drBZ)Ac_2]

0.195 g (0.625 mmol) of binucleating ligand, H_2drBZ was dissolved in 15 ml of methanol in a flask equipped with a water condenser and a magnetic stirrer. 0.125 g (0.625 mmol) of copper acetate monohydrate dissolved in 10 ml of methanol was added to the ligand solution. The reaction mixture was allowed to reflux for 1 hour. A 20 ml methanolic solution of 0.098 g (0.625 mmol) 2,2'-bipyridine was added to a solution of 0.124 g (0.625 mmol) copper acetate monohydrate. This resulted in the formation of $[Cu(bipy)]^{2+}$ complex. This solution containing $[Cu(bipy)]^{2+}$ was added to the above refluxing solution over 30 minutes. The reaction mixture was allowed to reflux for 5 hours, at the end which greenish brown coloured microcrystalline compound separated. The reaction mixture was cooled and the solid obtained was washed thoroughly with 30 ml methanol in 5-6 portions and dried in air at 60 – 70 °C.

Complexes (**5-II** to **5-XI**) were synthesized by using a similar procedure and appropriate quantities of binucleating ligands, H_2drBZ, H_2drPAZ, H_2drNZ and H_2drINZ, copper acetate monohydrate and respective secondary ligands, 2,2'-bipyridine, 1,10-phenanthroline, 2-hydroxybenzoic acid or 5-bromo-2-hydroxybenzoic acid (**Scheme 5.2**). The results of the elemental analyses and yields for each complex have been noted in **Table5.2.**



Complexes **5-I, 5-II, 5-III** and **5-IV** : drBz

Complexes **5-V, 5-VI** and **5V-II** : drPAZ

Complexes **5-VIII** and **5-IX** : drNZ

Complexes **5-X and 5-IX** : drINZ

5-I, 5-V, 5-VIII and **5-X** : AA = bipy

5-II, 5-VI, 5-IX and **5-XI** : AA = phen

5-III and 5-VII : AA = 2-hydroxybenzoic acid

5-IV : AA = 5-bromo-2-hydroxybenzoic acid

5-III, 5-IV and **5-VII** : Ac (acetate ion) = 0

5-I, 5-II, 5-V, 5-VI, 5-VIII, 5-IX, 5-X and **5-XI** : Ac (acetate ion) = 2

(Scheme-5.2)

5.2.6 Antibacterial activity test:

As a preliminary screening for antibacterial activity, the binucleating ligands and complexes in dimethylsulfoxide (DMSO) were tested against the gram (+) ve bacteria *S. aureus*, *B. megaterium* and gram (-) ve bacteria *S. typhi*, *S. marsescens* and *P. vulgaris* by well agar diffusion method in vitro. The liquid medium in which the bacterial cultures were to be grown was autoclaved for 15 minutes at 121°C and at 15-psi pressure before inoculation. The bacteria were simultaneously cultured in Luria broth for 24 hours at 37 °C in an incubator. Luria agar was poured into plates and allowed to solidify. The bacterial cultures were spread plated on to the solidified agar plates. The stock solutions of the compounds were prepared by dissolving 5 mg/ml of each compound in DMSO. The test compounds (DMSO solutions) were added to wells made with the help of 8 mm diameter borer on agar plates in sterile conditions. The zone of inhibition around the well was measured in millimeters after 24 hours incubation at 37 °C. DMSO was used as control and ampicillin, tetracycline, gentamicin and chloroamphenicol as standard drugs. All tests were repeated thrice and average of the values were taken as the final results.

5.3 Result and discussion:

Synthesis and characterization of ligands:

The bidentate ligands N-benzoyl-N'-[1-(5-acetyl-2,4-dihydroxy-phenyl)-ethylidene]-hydrazine, N-phenylacetyl-N'-[1-(5-acetyl-2,4-dihydroxy-phenyl)-ethylidene]-hydrazine, N-nicotinoyl-N'-[1-(5-acetyl-2,4-dihydroxy-phenyl)-ethylidene]-hydrazine and N-isonicotinoyl-N'-[1-(5-acetyl-2,4-dihydroxy-phenyl)-ethylidene]-hydrazine were prepared by condensation reaction of 1-(5-Acetyl-2,4-dihydroxy-phenyl)-ethanone and with suitable quantity of hydrazines, benzoyl hydrazine, phenylacetyl hydrazine, nicotonyl hydrazine and isonicotonyl hydrazine respectively. Finally purified ligands were characterized by elemental analysis and FTIR which confirms suggested molecular formula (**Scheme 5.1**).

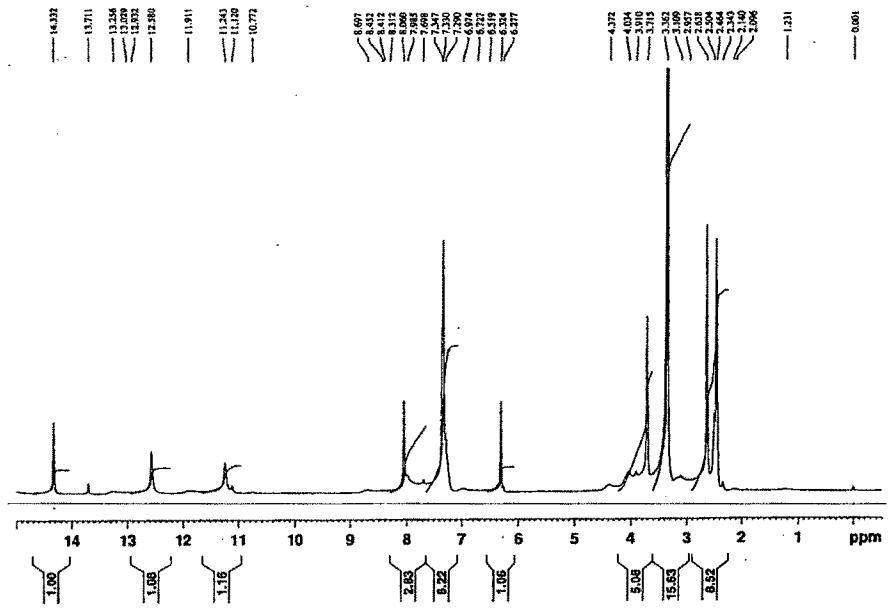


Fig. 5.4.1 ^{1}H NMR of the binucleating ligand, H_2drPAZ.

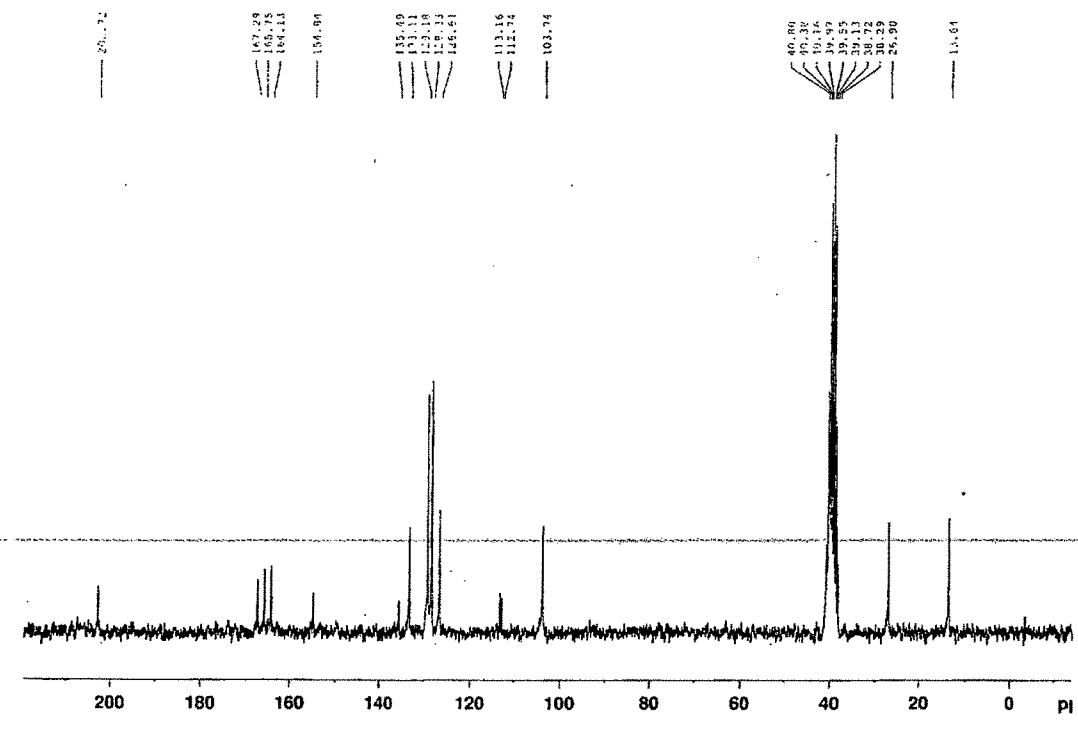
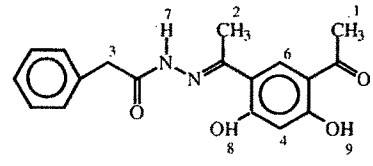


Fig.5.4.2 ^{13}C NMR of the binucleating ligand, H_2drPAZ.

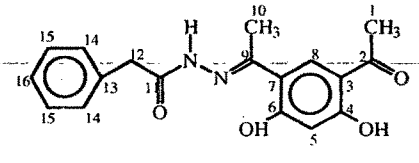
The ligand N-phenylacetyl-N'-[1-(5-acetyl-2,4-dihydroxy-phenyl)-ethylidene]-hydrazine (H_2drPAZ) was characterized by ^{1}H NMR, ^{13}C NMR in DMSO. The spectrum is shown in **Fig. 5.4.1** and **Fig. 5.4.2**. The chemical shift values corresponding to various types of protons are recorded in **Table 5.2.1** and **Table 5.2.2** which confirm the formation of H_2drPAZ.



(Types of proton in the ligand, H_2drPAZ)

Table 5.2.1 ^{1}HNMR of binucleating ligand, H_2drPAZ in DMSO.

Proton type	**Chemical shift , δ (ppm)**	**No. Proton**
CH_3 (1)	2.464	3
CH_3 (2)	2.638	3
CH_2 (3)	3.715	2
ArH (4)	6.324	1
ArH (phenyl)	6.974	1
ArH (phenyl)	7.330	4
ArH (6)	8.060	1
NH (7)	11.243	1
OH (8)	13.029	1
OH (9)	14.332	1



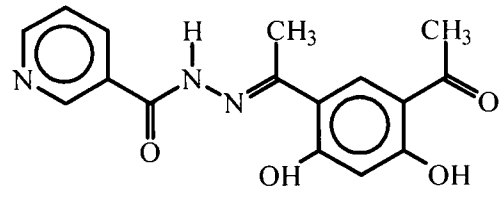
[Types of carbon in the ligand, H_2drPAZ].

P1Th
11A1C

Table 5.2.2 ^{13}C NMR of binucleating ligand, H_2drPAZ in DMSO.

Carbon type	Chemical shift (ppm)	δ	No. Carbon
C (1)	26.90		1
C (2)	201.32		1
C (3)	133.11		1
C (4)	154.84		1
C (5)	113.67		1
C (6)	164.13		1
C (7)	135.79		1
C (8)	112.78		1
C (9)	167.29		1
C (10)	13.64		1
C (11)	165.67		1
C (12)	103.74		1
C (13)	126.64		1
C (14)	129.18		1
C (15 & 16)	128.33		3

The ligand, N-Nicotinoyl-N'-[1-(5-acetyl-2,4-dihydroxy-phenyl)-ethylidene]-hydrazine, (H_2drNZ) was also characterized by ^1H NMR in DMSO. The spectrum shown in **Fig. 5.5.1** and **Fig. 5.5.2.** The chemical shift values and the assignment to various protons are summarized in **Table 5.3.** These are self explanatory and confirm the formation and structure of H_2drNZ.



[Structure of the binucleating ligand, H_2drNZ)].

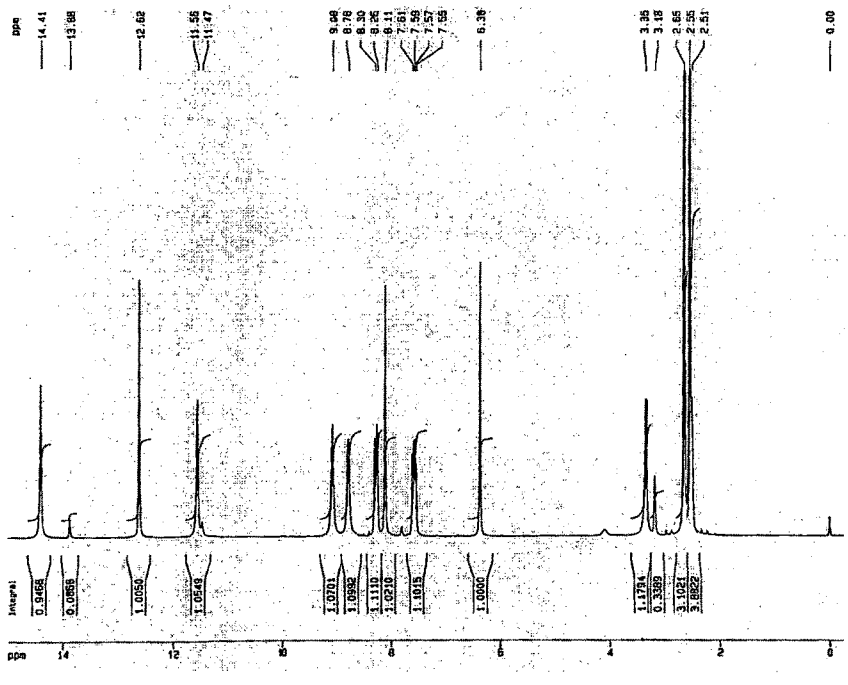


Fig. 5.5.1 ^{1}H NMR of the binucleating ligand, H_2drNZ.

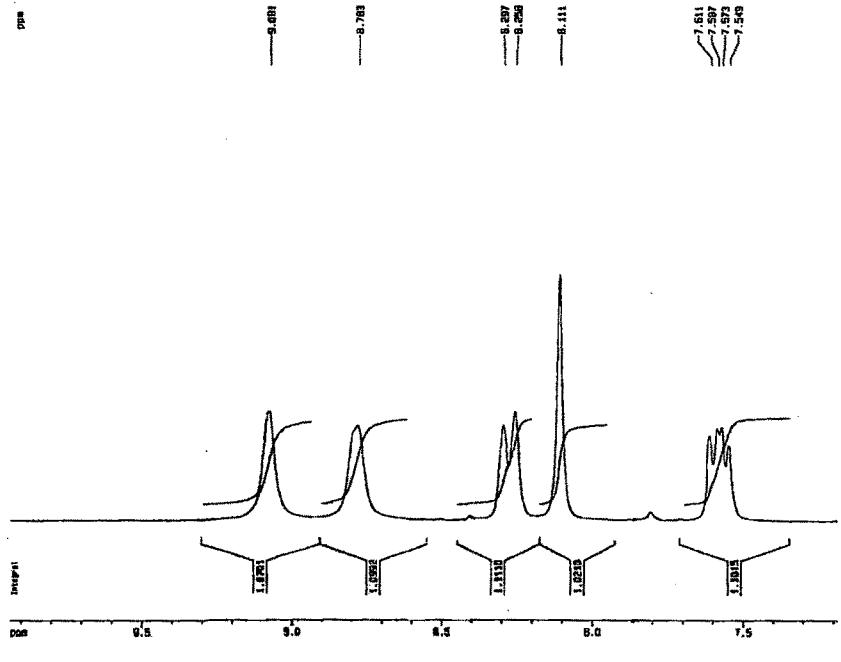


Fig.5.5.2 ^{1}H NMR of the binucleating ligand, H_2drNZ(Expanded) .

Table 5.3 ^{1}HNMR of binucleating ligand, H_2drNZ in DMSO.

Proton type	**Chemical shift, δ (ppm)**	**Splitting pattern**	**No. Proton**
CH_3	2.55	singlet	3
CH_3	2.65	singlet	3
ArH	6.38	singlet	1
ArH	8.11	singlet	1
PyH	7.59	doublet	1
PyH	8.26	doublet	1
PyH	8.78	singlet	1
PyH	9.08	doublet	1
OH	11.56	singlet	1
OH	12.62	singlet	1
NH	14.41	singlet	1

The values of elemental analysis of binuclear complexes given in **Table 5.4**, are agreeable with the suggested molecular formulae (**Scheme 5.2**). The complexes **5-I, 5-II, 5-V and 5-VI** are found to be soluble in DMF. Hence, the conductivity studies were carried out in a mmolar solutions in DMF. All the four complexes have molar conductivity values < 0.01 $\Omega^{-1}M^{-1}cm^2$, indicating that the two acetates are directly coordinated to the metal ions in the axial position. Complexes, **5-VIII, 5-IX, 5-X** and **5-XI**, were insoluble in suitable solvents and hence conductivity measurements could not be performed. Complexes **5-III, 5-IV** and **5-VII** were non ionic in nature.

The TGA curves in the temperature range 24 – 1000 °C show that the metal complexes are thermally stable up to 100 °C. Dehydration is characterized by endothermic peaks at the temperature 125°C for complexes **5-I, 5-II, 5-V, 5-VI, 5-VII, 5-VIII** and **5-X**. The loss of water molecules takes place in the lower temperature range around 125°C, indicating that the water molecule is present outside the coordination sphere as water of crystallization or is held by hydrogen bond formation with oxygen atom of the ligand. Another loss of water molecules for complexes **5-III, 5-VII, 5-VIII, 5-IX** and **5-XI** in the range of 150 – 250°C, corresponds to the loss of coordinated water as demonstrated by weight loss in TGA.

Table 5.4: Preparative yields, elemental analysis, magnetic moment and TGA data for binuclear complexes.

Comp No.	Complexes	Yield (%)	Elemental analysis Found (Calc.) C (%)	H (%)	N (%)	μ (BM)	Temp. (°C)	% weight loss Obsd. (calc)
5-I	$[Cu_2(bipy)(drBZ)Ac_2].H_2O$	62	50.89	3.71	8.05	1.95	120	3.5 (2.5)
	$C_{31}H_{30}N_4O_9Cu_2$		(51.02)	(4.11)	(7.68)			
5-II	$[Cu_2(phen)(drBZ)Ac_2].H_2O$	67	52.30	3.58	8.10	2.11	125	3.0 (2.39)
	$C_{33}H_{30}N_4O_9Cu_2$		(52.58)	(3.72)	(7.44)			
5-III	$[Cu_2(salac)(drBZ)].H_2O$	76	47.71	3.13	5.19	1.72	231	3.4 (3.04)
	$C_{24}H_{20}N_2O_8Cu_2$		(48.72)	(3.38)	(4.74)			
5-IV	$[Cu_2(Brsalac)(drBZ)]$	67	45.76	3.30	5.36	1.66	-	-
	$C_{24}H_{17}N_2O_7BrCu_2$		(44.81)	(2.60)	(5.02)			
5-V	$[Cu_2(bip)(drPAZ)Ac_2].H_2O$	47	51.78	3.71	8.61	2.22	125	3.1 (2.42)
	$C_{32}H_{32}N_4O_9Cu_2$		(51.68)	(4.30)	(7.54)			
5-VI	$[Cu_2(phen)(drPAZ)Ac_2].H_2O$	46	53.81	3.67	7.88	1.92	121	2.3 (2.35)
	$C_{34}H_{32}N_4O_9Cu_2$		(53.19)	(4.17)	(7.30)			
5-VII	$[Cu_2(salac)(drPAZ)].3H_2O$	53	46.16	3.67	4.94	2.03	123	3.7 (2.80)
	$C_{25}H_{26}N_2O_{10}Cu_2$		(46.79)	(4.06)	(4.37)		146	5.7 (5.62)
							251	8.3 (8.42)

Table 5.4 continued.....

Comp No.	Complexes	Yield (%)	Elemental analysis Found (Calc.) C (%)	H (%)	N (%)	μ (BM)	Temp. (°C)	% weight loss Obsd.(calc)
5-VIII	$[Cu_2(bip)(drNZ)Ac_2].2H_2O$	53	47.68	3.79	9.88	1.88	120	2.1 (2.40)
	$C_{30}H_{31}N_5O_{10}Cu_2$		(48.12)	(4.14)	(9.36)		181	3.5 (4.80)
5- IX	$[Cu_2(phen)(drNZ)Ac_2].H_2O$	53	50.76	3.35	9.80	1.89	149	3.2 (2.38)
	$C_{32}H_{29}N_5O_9Cu_2$		(50.92)	(3.58)	(9.28)			
5-X	$[Cu_2(bip)(drINZ)Ac_2].2H_2O$	48	48.27	3.83	10.00	1.81	130	4.7 (4.81)
	$C_{30}H_{31}N_5O_{10}Cu_2$		(48.12)	(4.14)	(9.36)			
5-XI	$[Cu_2(phen)(drINZ)Ac_2].2H_2O$	41	48.89	3.71	10.02	1.97	200	5.2 (4.70)
	$C_{32}H_{31}N_5O_{10}Cu_2$		(49.74)	(4.01)	(9.07)			

5.3.1 Electronic spectra:

The electronic spectra of the complexes in methanolic solutions exhibit a broad band in the region 608 – 736 nm and three bands at 225, 300 and 375 nm. The bands around 225 and 300 nm can be attributed to interaligand $\pi \rightarrow \pi^*$ transition in the pyridyl ring and the imine function of the binucleating hydrozone and secondary ligands. The band around 375 nm indicate $n \rightarrow \pi^*$transition in the amide moiety. The band in the region 608 – 736 nm region corresponds to the ligand field transitions and can be assigned to $d_{xy} \rightarrow d_{x2-y2}$, $d_{yz} \rightarrow d_{x2-y2}$, $d_{xz} \rightarrow d_{x2-y2}$ and $d_{z2} \rightarrow d_{x2-y2}$ transitions in an elongated square based pyramidal geometry resulting due to coordination of acetate. (**Table 5.5**)

Table 5.5 Absorptions in the electronic spectra of the ternary binuclear complexes in methanolic solutions.

Complexes	**Intraligand and CT transitions (λ in nm)**	**LF trans. (λ in nm)**
$[Cu_2(bipy)(drBZ)Ac_2].H_2O$	234, 297, 340, 355, 372, 410	618
$[Cu_2(phen)(drBZ)Ac_2].H_2O$	226, 273, 295, 339, 354, 375, 392	614
$[Cu_2(salac)(drBZ)].H_2O$	233, , 292, 355, 372, 390	608
$[Cu_2(Brsalac)(drBZ)]$	232, 292, 355, 372, 390	618
$[Cu_2(bipy)(drPAZ)Ac_2].H_2O$	238, 258, 298, 312, 335, 368	609
$[Cu_2(phen)(drPAZ)Ac_2].H_2O$	225, 274, 293, 322, 335, 368, 390	625
$[Cu_2(salac)(drPAZ)].3H_2O$	235, 286, 320, 335, 356, 388	628
$[Cu_2(bipy)(drNZ)Ac_2].2H_2O$	228, 244, 300, 312	635
$[Cu_2(phen)(drNZ)Ac_2].H_2O$	225, 272, 294, 306	685
$[Cu_2(bipy)(drINZ)Ac_2].2H_2O$	236, 244, 254, 283, 314	736
$[Cu_2(phen)(drINZ)Ac_2].2H_2O$	214, 272, 294, 342	725

5.3.2 IR Spectra:

The IR spectra of the complexes in the region 400 – 4000cm^{-1} are very rich. The most important IR absorption frequencies among these are as follows.

All the complexes contain water molecule in the empirical formula, the existence of water molecules is shown by absorptions due to O-H stretching and bending vibrations are observed at - 3600 cm^{-1} and - 1300 cm^{-1} respectively. The broad band due to the presence of water molecule masks the band due to phenolic –OH group.

Absorption due to the stretching of the amide N-H occurs between 3404 – 3475 cm^{-1} in the free ligand and in the complexes. In the free ligands, the bands between 1664 – 1690 cm^{-1} are due to >C=O stretching of the amide or ketonic group. On complexation this ν(>C=O) shifts to lower frequencies, i.e. 1594 – 1654 cm^{-1}. In the ligands, imine band ν >C=N is observed between 1636 – 1645 cm^{-1}. These are observed at lower energies in complexes i.e. between 1535 – 1599 cm^{-1}. The shift in >C=O (amide or ketonic) and >C=N (imine) towards lower energy in the complexes compared to the ligands and almost unaffected amide N-H stretching frequency indicate that the imine nitrogen and amide or ketonic oxygen are involved in coordination with metal ion where as amide nitrogen does not take part in the binding with metal ion.

The absorption due to –COO$^-$ (carboxylate anion) ions were observed between 1362 – 1370 cm^{-1} region. It confirmed that the acetate ions are inside the coordination sphere and directly attached to the central metal ion [37]. In the complexes **5-III, 5-IV** and **5-VII** the absorptions at 1367, 1366 and 1368 cm^{-1}, respectively, can be assigned to the carboxylate ion and indicate that 2-hydroxybenzoic acid (complexes **5-III** and **5-VII**) and 5-bromo-2-hydroxybenzoic acid (complex **5-IV**) are attached directly to copper ion through carboxylate anion. In all the complexes characteristic bands appeared between 3030 – 3125 cm^{-1} due to aromatic C-H stretching. In the complex

5-IV bands appear at 609 cm^{-1} due to C-Br stretching, indicating the presence of 5-bromo-2-hydroxybenzoic acid (**Fig. 5.6.1** to **Fig. 5.6.15**, **Table 5.6**).

Table: 5.6 The IR absorption frequencies (cm^{-1}) in the binuclear complexes.

Comp No.	**$\bar{\nu}$ (-NH) (cm^{-1})**	**aromatic stretching $\bar{\nu}$ (-C-H) (cm^{-1})**	**$\bar{\nu}$ (>C=O) (cm^{-1})**	**$\bar{\nu}$ (>C=N) (cm^{-1})**	**$\bar{\nu}$ ($-COO^-$) (cm^{-1})**
5-I	3448	3060	1654	1595	1364
5-II	3432	3058	1654	1593	1365
5 -III	3435	3060	1634	1599	1367
5-IV	3434	3095	1634	1590	1366
5-V	3422	3060	1600	1537	1365
5-VI	3433	3059	1594	1535	1365
5-VII	3424	3040	1601	1538	1368
5-VIII	3448	3065	1638	1592	1369
5-IX	3435	3060	1638	1540	1369
5-X	3433	3055	1638	1575	1362
5-XI	3434	3094	1628	1586	1370

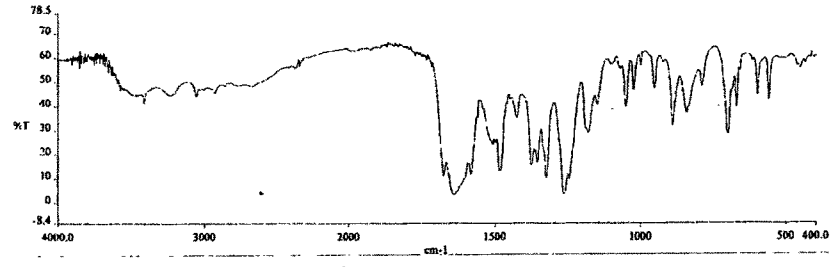


Fig. 5.6.1 FTIR spectrum of the binucleating ligand, H_2drBZ.

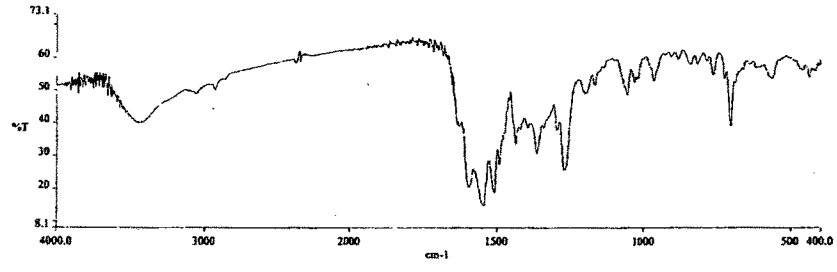


Fig. 5.6.2 FTIR spectrum of the binuclear complex, $[Cu_2(bipy)(drBZ)Ac_2].H_2O$.

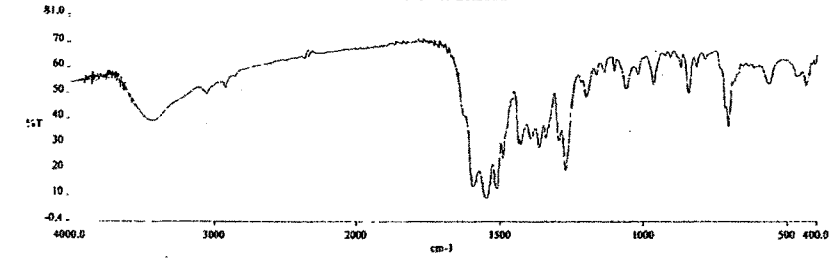


Fig. 5.6.3 FTIR spectrum of the binuclear complex, $[Cu_2(phen)(drBZ)Ac_2].H_2O$

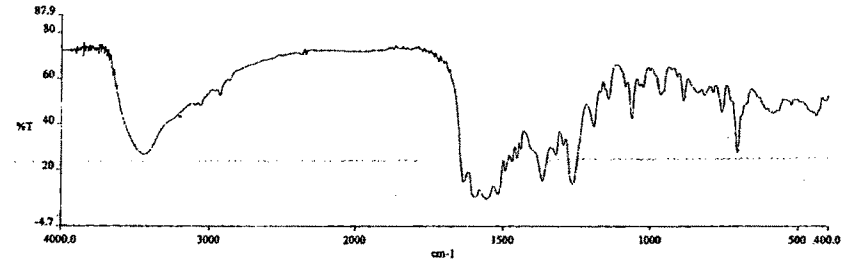


Fig. 5.6.4 FTIR spectrum of the binuclear complex, $[Cu_2(salac)(drBZ)].H_2O$.

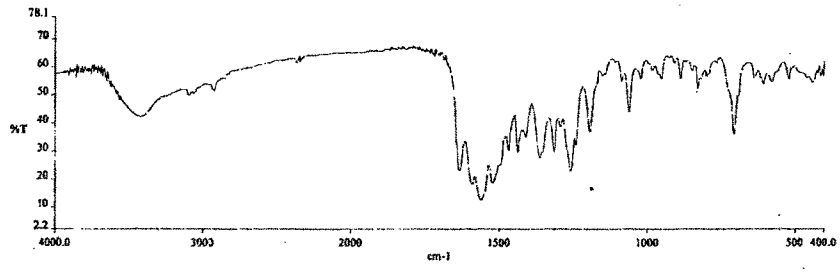


Fig. 5.6.5 FTIR spectra of binuclear complex, $[Cu_2(Brsalac)(drBZ)]$.

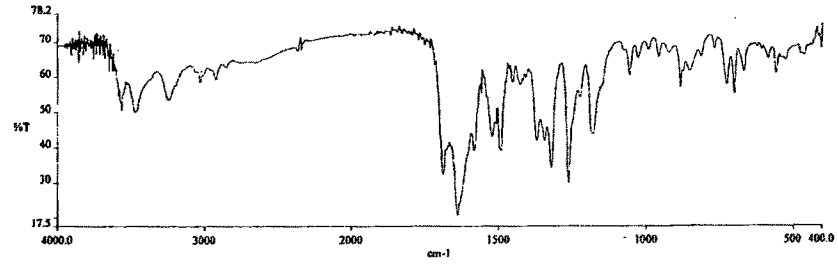


Fig. 5.6.6 FTIR spectrum of the binucleating ligand, H_2drPAZ.

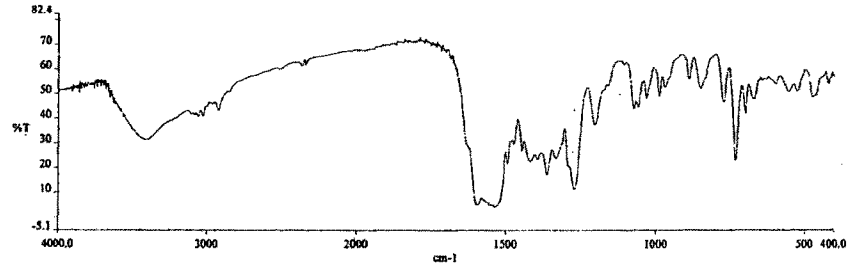


Fig. 5.6.7 FTIR spectrum of the binuclear complex, $[Cu_2(bipy)(drPAZ)Ac_2].H_2O$.

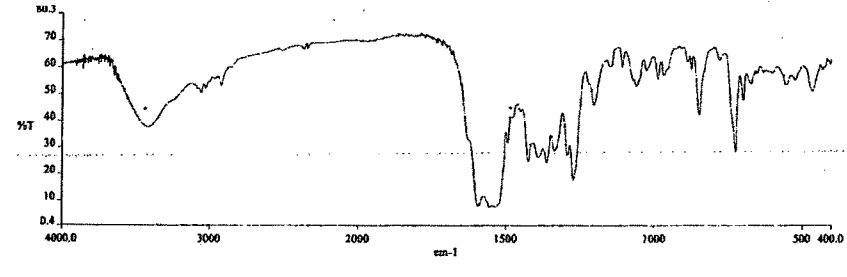


Fig. 5.6.8 FTIR spectrum of the binuclear complex, $[Cu_2(phen)(drPAZ)Ac_2].H_2O$.

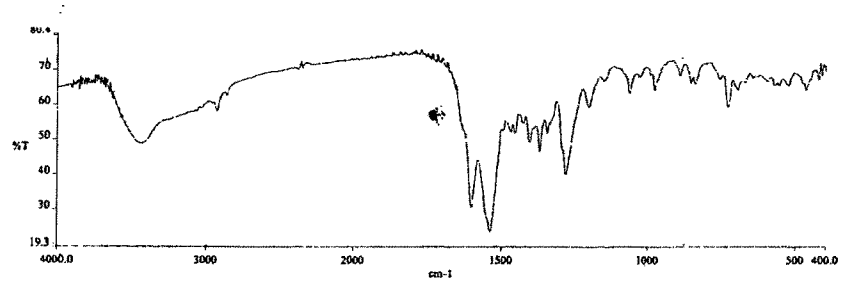


Fig. 5.6.9 FTIR spectrum of the binuclear complex, $[Cu_2(salac)(drPAZ)].3H_2O$.

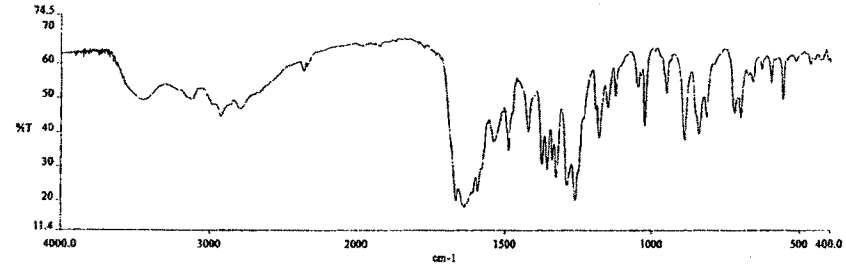


Fig. 5.6.10 FTIR spectrum of the binucleating ligand, H_2drNZ.

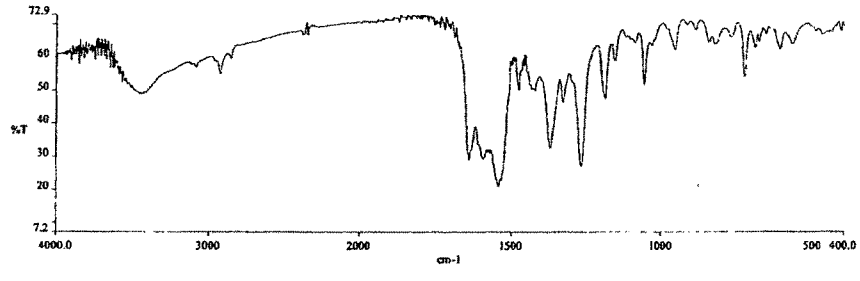


Fig. 5.6.11 FTIR spectrum of the binuclear complex, $[Cu_2(bipy)(drNZ)Ac_2].2H_2O$.

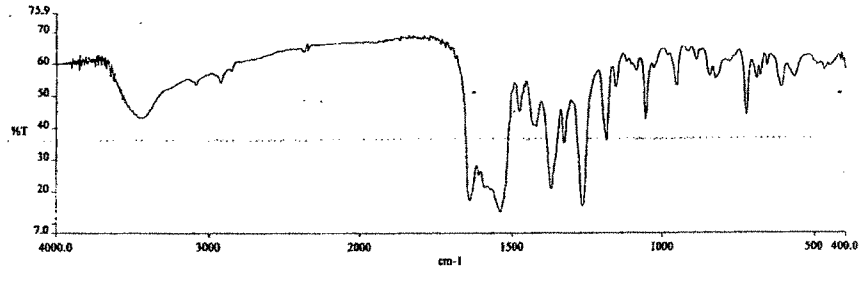


Fig. 5.6.12 FTIR spectrum of the binuclear complex, $[Cu_2(phen)(drNZ)Ac_2].H_2O$.

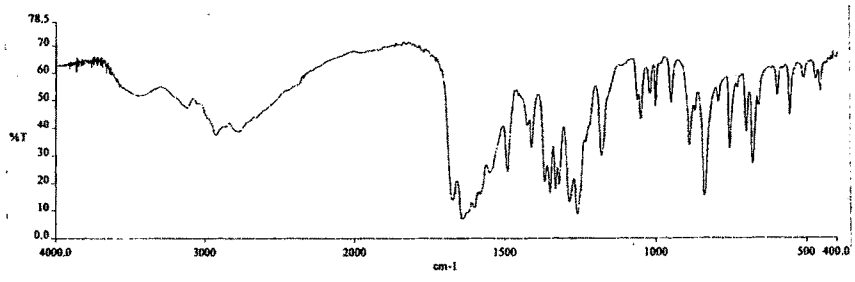


Fig. 5.6.13 FTIR spectrum of the binucleating ligand, H_2drINZ.

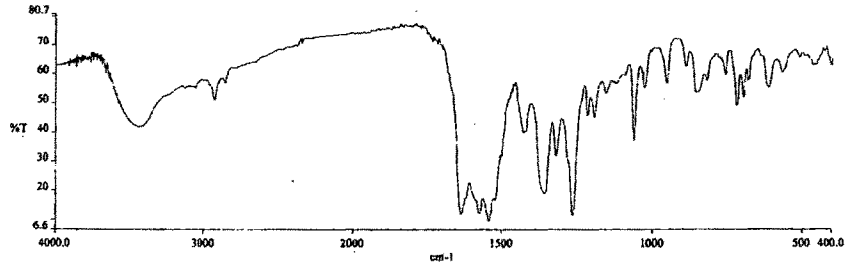


Fig. 5.6.14 FTIR spectrum of the binuclear complex, $[Cu_2(bipy)(drINZ)Ac_2].2H_2O$.

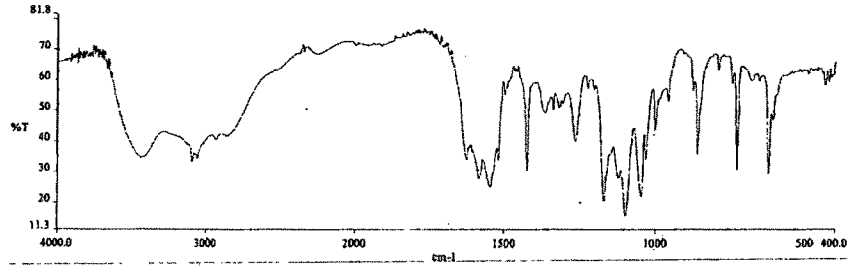


Fig. 5.6.15 FTIR spectrum of the binuclear complex, $[Cu_2(phen)(drINZ)Ac_2].2H_2O$.

5.3.3 Mass spectra:

The FAB mass spectrum of the complex, $[Cu_2(bipy)(drPAZ)Ac_2].H_2O$ consists of parent binuclear mono cation $[Cu_2(bipy)drPAZ]^+$ at m/z = 606 (80%). The peak corresponding to the parent binuclear dication $[Cu_2(bipy)drPAZ]^{2+}$ is observed at m/z = 303 (26%).

Other important fragments include $[Cu(bipy)HPAZ]^+$ is observed at m/z = 456 (26%) formed on the loss of Cu ion from binuclear complex. Peaks corresponding to $[Cu(HPAZ)]^+$ and $[H_3PAZ]^+$ were observed at m/z = 388 (60%) and m/z = 327 (14%), respectively. The peak at m/z 219 (90%) corresponds to the association of metal ion with bipyridyl ligand, $[Cu(bipy)]^+$. The presence of these peaks confirms the formation of binuclear complexes, (**Table 5.7 and Fig. 5.7**).

The peak corresponding to the fragments of m-nitrobenzyl alcohol and associated products are observed at m/z 136, 137, 154, 289 and 307.These fragments can get associated with various fragments of metal complexes and thus are responsible for the occurrence of widely distributed peaks with low abundance.

Table: 5.7 Fragmentation pattern in the positive ion FAB-MS of $[Cu_2(bipy)drPAZ]^{2+}$ in m-nitrobenzyl alcohol.

m/z (%relative abundance)	**Molecular formula of the fragments**
303 (26%)	$[C_{28}H_{24}O_4N_4Cu_2]^{2+}$ (parent binuclear dication)
606 (34%)	$[C_{28}H_{24}O_4N_4Cu_2]^+$ (Parent binuclear monocation)
608 (30%),	$[C_{28}H_{26}O_4N_4Cu]^+$
546 (8%)	$[C_{28}H_{27}O_4N_4Cu]^+$
544 (22%)	$[C_{28}H_{25}O_4N_4Cu]^+$
458 (14%)	$[C_{21}H_{23}O_4N_4Cu]^+$
456 (26%)	$[C_{21}H_{21}O_4N_4Cu]^+$
410 (12%)	$[C_{20}H_{17}O_3N_3Cu]^+$
388 (60%)	$[C_{18}H_{17}O_4N_2Cu]^+$
327 (14%)	$[C_{18}H_{19}O_4N_2]^+$, (binucleating hydrazine)
219 (90%)	$[C_{10}H_8N_2Cu]^+$

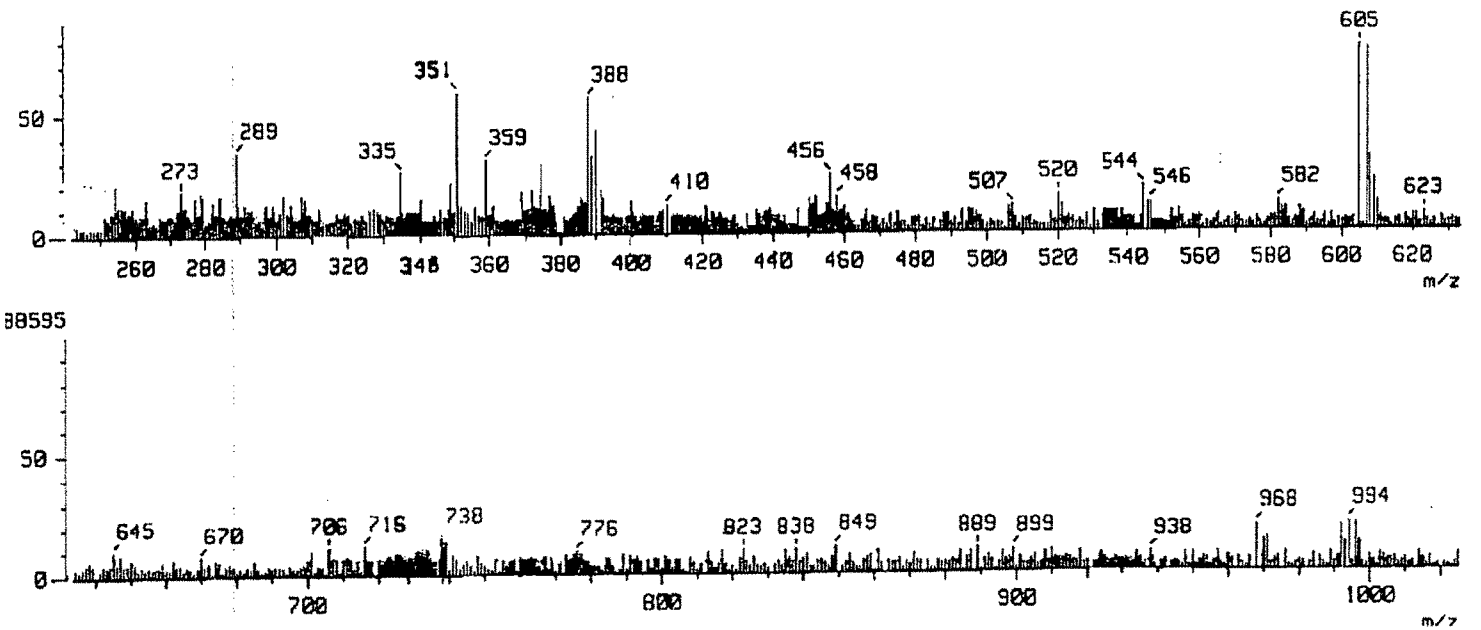
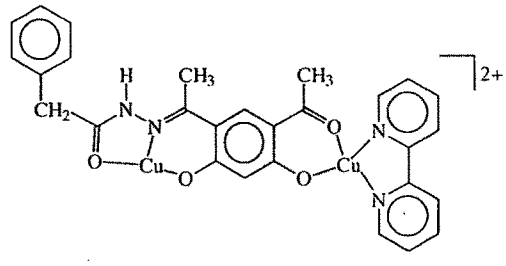
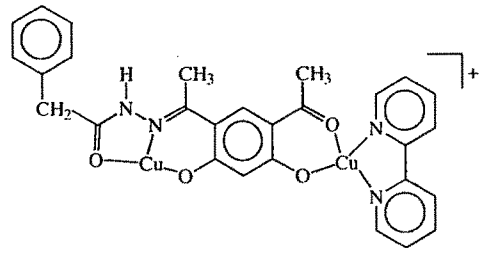


Fig. 5.7, FAB-Mass spectra of binuclear complex, $[Cu_2(bipy)(drPAZ)Ac_2].H_2O$

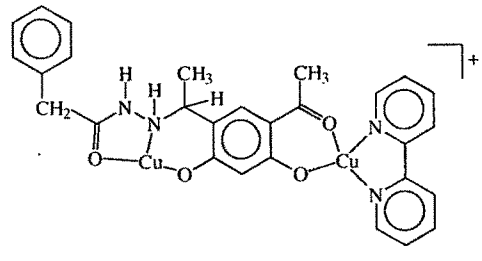
Possible structure of $[Cu_2(drPAZ)(bipy)]^{2+}$ and the corresponding fragments in FAB mass:



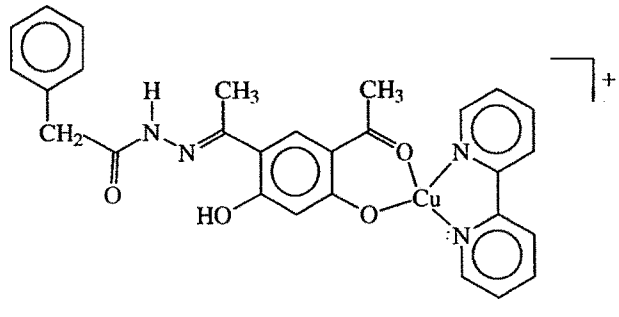
m/z 302 (80%), $[C_{28}H_{24}O_4N_4Cu]^{2+}$



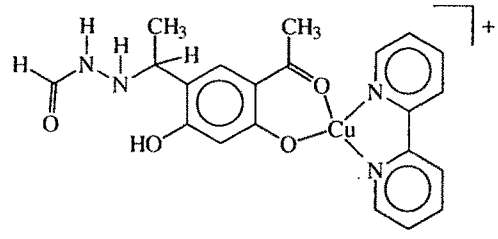
m/z 606 (34%), $[C_{28}H_{24}O_4N_4Cu]^{+}$



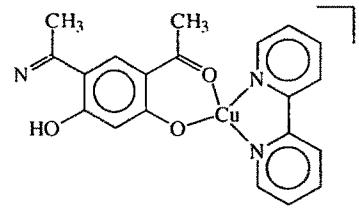
m/z 608 (30%), $[C_{28}H_{26}O_4N_4Cu]^{+}$



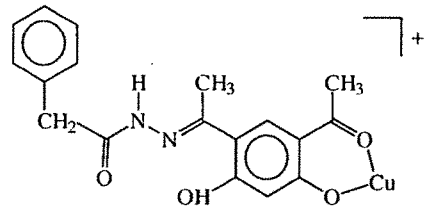
m/z 544 (22%), $[C_{28}H_{25}O_4N_4Cu]^{+}$



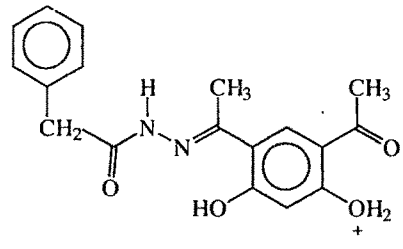
m/z , 456 (26%) $[C_{21}H_{21}O_4N_4Cu]^+$



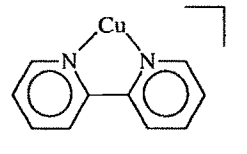
m/z 410 (12%), $[C_{20}H_{17}O_3N_3Cu]^+$



m/z 388 (60%), $[C_{18}H_{17}O_4N_2Cu]^+$



m/z 327 (14%), $[C_{18}H_{19}O_4N_2]^+$



m/z 219 (90%), $[C_{10}H_8N_2Cu]^+$

5.3.4 ESR and Magnetic properties:

X-band ESR spectra of the complex, $[Cu_2(bipy)(drPAZ)Ac_2].H_2O$ as polycrystalline powder, were recorded at room temperature (RT) and at liquid nitrogen temperature (LNT) as frozen solution in DMSO (**Fig. 5.9.1** and **Fig. 5.9.2**). Both are identical indicating indifferent geometry around the metal ion in the polycrystalline state and in the solution. The ESR spectrum of the complex is typically anisotropic due to the combination of lines in the two copper (II) ions in non equivalent geometrical and electronic environments [38] (**Table 5.8**).

The half field transition ($\Delta M_s = 2$) is observed at RT as well as LNT, suggesting a magnetic exchange interaction between two copper (II) ions through the binucleating ligand.

Effective magnetic moment values of the complexes at room temperature range between 1.66 – 2.11 BM per copper (II) ion. These values of magnetic moment indicate weakly antiferromagnetic to ferromagnetic interaction between the two metal centers (**Table 5.4**).

Table: 5.8, ESR of the $[Cu_2(bipy)(drPAZ)Ac_2].H_2O$.

	Room temperature	LNT in (DMSO)
$g^{\parallel}$	2.22606	2.19222
$g^{\perp}$	2.05477	2.05477

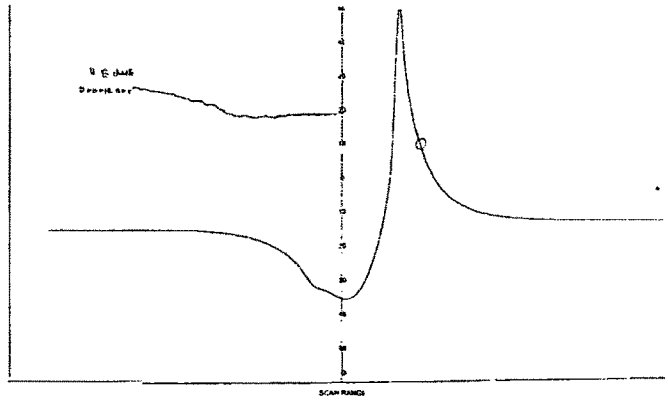


Fig. 5.9.1 ESR of binuclear complex, $[Cu_2(bipy)(drPAZ)Ac_2].H_2O$ at RT.

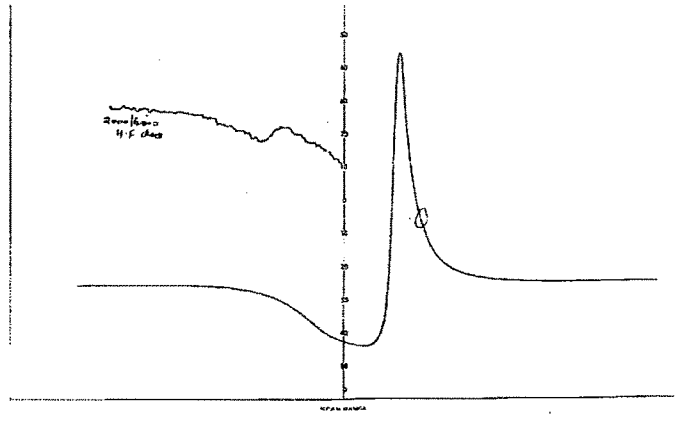


Fig. 5.9.2 ESR of binuclear complex, $[Cu_2(bipy)(drPAZ)Ac_2].H_2O$ at LNT.

5.3.5 Biological activity:

Biological activity of the ligands and their respective copper complexes were examined against *Staphylococcus aureus* and *Bacillus megaterium* which are gram positive organisms and against *Serratia marsescens*, *Proteus vulgaris*, and *Salmonella typhi* which are gram negative organisms. Biological activity of the above mentioned organisms was also carried out against Cu-acetate monohydrate and standard antibiotics like ampicillin, chloramphenicol, kanamycin, streptomycin and tetracycline **(Table 5.9, Fig. 5.10.1 to Fig. 5.10.4)**

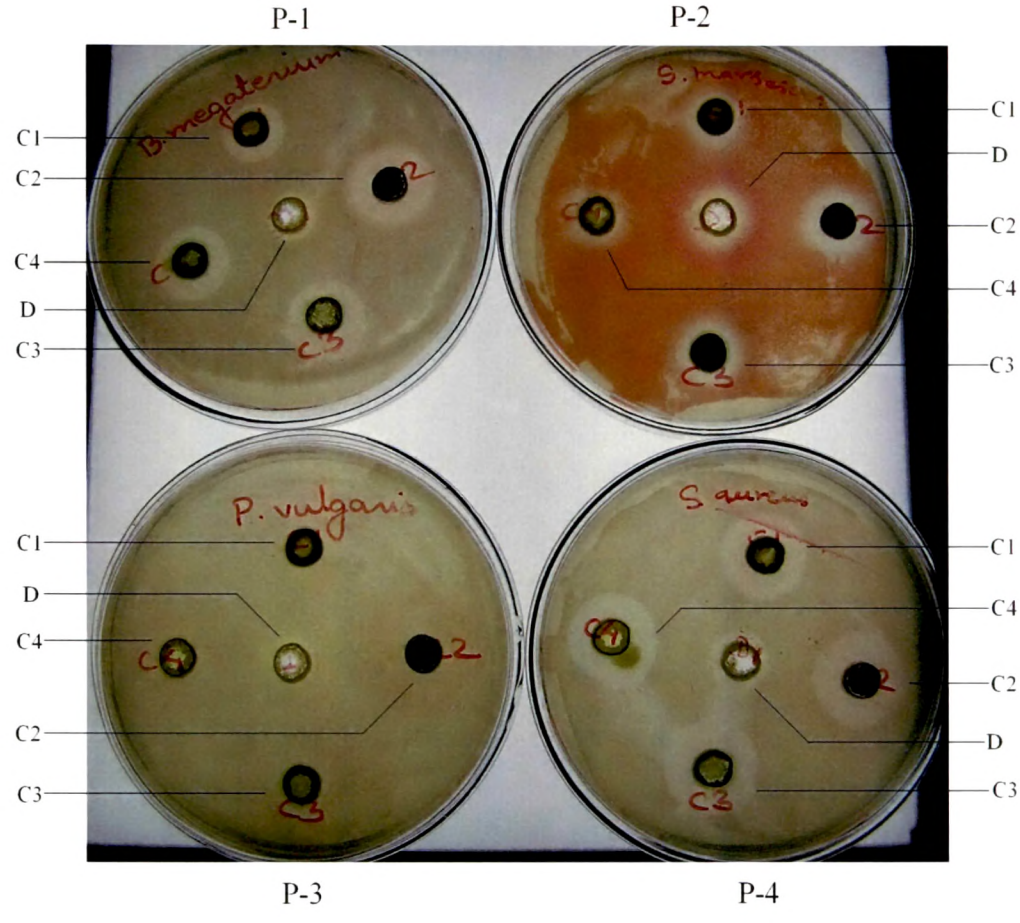


Fig.5.10.1

Inhibition of bacterial growth by ligand, H_2drBZ (D) and binuclear complexes $[Cu_2(bipy)(drBz)Ac_2].H_2O$ (C1), $[Cu_2(phen)(drBz)Ac_2].H_2O$ (C2), $[Cu_2(salac)(drBz)].H_2O$ (C3), $[Cu_2(Brsalac)(drBz)]$ (C4). Plate-1: *B. megaterium*, plate-2: *S. marsescens*, plate-3: *P. vulgaris*, and plate-4: *S. aureus*.

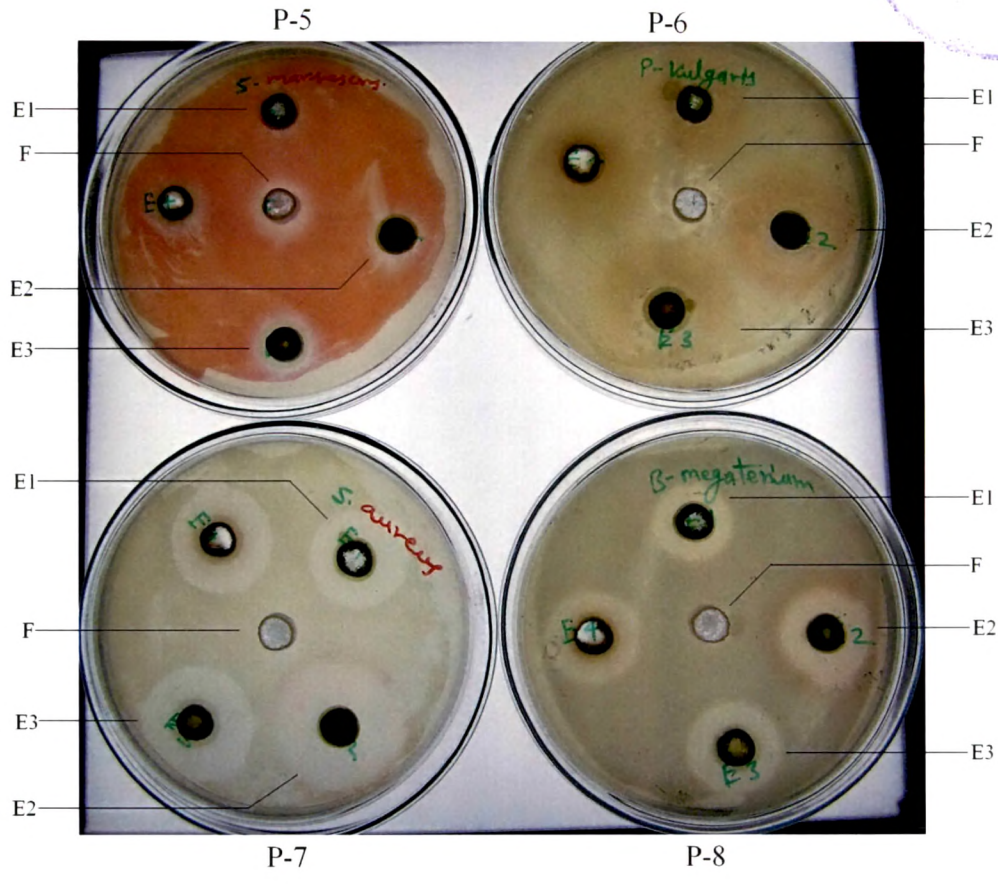


Fig. 5.10.2

Inhibition of bacterial growth by ligand, H_2drPAZ (F) and binuclear complexes [Cu_2(bipy)(drPAZ)Ac_2].H_2O (E1), [Cu_2(phen)(drPAZ)Ac_2].H_2O (E2) and [Cu_2(salac)(drPAZ)].3H_2O (E3). Plate-5: *S. marsescens*, plate-6: *P. vulgaris*, plate-7: *S. aureus* and plate-8: *B. megaterium*.

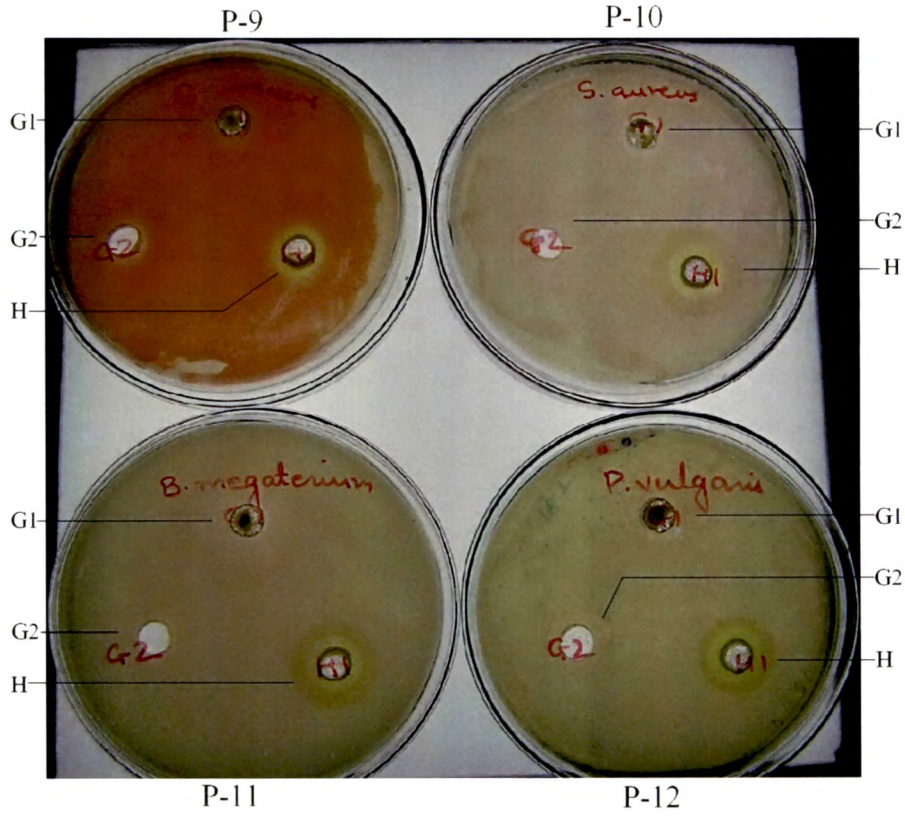


Fig. 5.10.3

Inhibition of bacteria by ligand, H_2drNZ (H) and binuclear complexes $[Cu_2(bipy)(drNZ)Ac_2].2H_2O$ (G1) and $[Cu_2(phen)(drNZ)Ac_2].H_2O$ (G2), Plate-9: *B. megaterium*, plate-10: *S. marsescens*, plate-11: *P. vulgaris*, and plate-12: *S. aureus*.

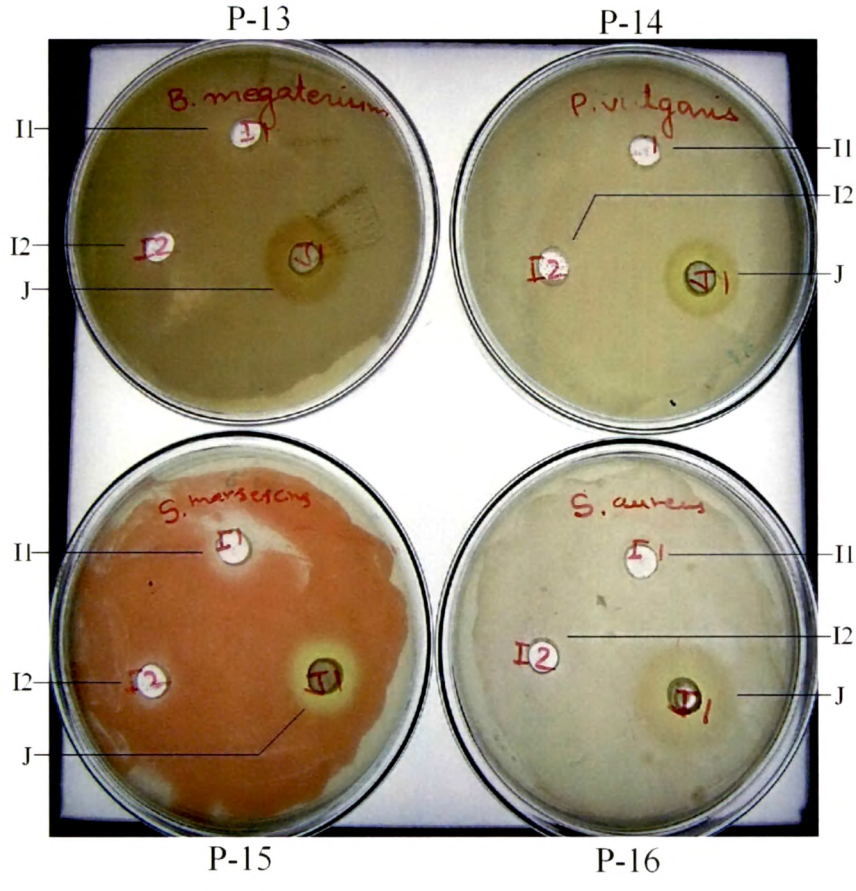


Fig. 5.10.4

Inhibition of bacteria by ligand, H_2drINZ (J) and binuclear complexes $[Cu_2(bipy)(drINZ)Ac_2].2H_2O$ (I1) and $[Cu_2(phen)(drINZ)Ac_2].2H_2O$ (I2), plate-13: *B. megaterium*, plate-14: *P. vulgaris*, plate-15: *S. marsescens* and plate-16: *S. aureus*.

Table: 5.9 Antibacterial activities of ligands and complexes (Zone formation in mm).

Compounds	*S. aureus*	*B. megaterium*	*S. marsescens*	*P. vulgaris*	*S. typhi*
Ligand, H_2drBZ	13	12	15	-	-
5-I	20	17	13	-	-
5-II	21	20	14	15	-
5-III	20	19	14	-	-
5-IV	20	18	12	-	-
Ligand, H_2drPAZ	-	-	14	-	-
5-V	23	18	11	-	-
5-VI	27	25	13	14	-
5-VII	26	21	14	-	-
Ligand, H_2drNZ	16	12	14	-	-
5-VIII	-	-	-	-	-
5-IX	-	-	-	-	-
Ligand, H_2drINZ	-	-	15	16	-
5-X	-	-	13	-	-
5-XI	-	-	12	-	-
Ampicillin	26	12	31	22	36
Chloroamphenicol	22	40	40	30	32
Kanamycin	28	32	35	25	29
Streptomycin	30	25	36	-	30
Tetracyclin	30	34	25	20	32

Ligand, H_2drBZ and its complexes (**5-I, 5-II 5-III & 5-IV**) showed biological activity against *Staphylococcus aureus*, *Bacillus megaterium* and *Serratia marsescens.* Ligand, H_2drPAZ and its complexes (**5-I, 5-II, 5-III & 5-IV**) did not show any biological activity against *Proteus vulgaris*, and *Salmonella typhi* which are gram negative organisms. Biological activity showed by complexes of ligand, drBZ is higher as compared to the ligand, H_2drBZ itself.

Complexes of ligand, H_2drPAZ (**5-V, 5-VI & 5-VII**) showed biological activity against *Staphylococcus aureus*, *Bacillus megaterium* and *Serratia marsescens* but the ligand, H_2drPAZ itself did not show any activity as such.

The case of ligand, H_2drNZ and its complexes is completely opposite to that of ligand, H_2drPAZ. Ligand, H_2drNZ showed biological activity against *Staphylococcus aureus*, *Bacillus megaterium* and *Serratia marsescens* but its complexes (**5-VIII & 5-IX**) did not show any biological activity.

Ligand, H_2drINZ and its complexes (**5-X & 5-XI**) showed biological activity only against *Serratia marsescens*. Ligand, H_2drINZ and its complexes (**5-X & 5-XI**) did not show any biological activity against *Staphylococcus aureus*, *Bacillus megaterium*, *Proteus vulgaris*, and *Salmonella typhi*.

Biological activity was showed against *Staphylococcus aureus* and *Bacillus megaterium* which are gram positive organisms and against *Serratia marsescens*, *Proteus vulgaris*, and *Salmonella typhi* which are gram negative organisms when treated with Cu-acetate monohydrate and standard antibiotics like ampicillin, chloramphenicol, kanamycin, streptomycin and tetracycline.

Generally, stating the ligands, H_2drBZ, H_2drPAZ and their complexes showed good biological activity against gram positive *Staphylococcus aureus* and *Bacillus megaterium*. However, the ligands H_2drNZ, H_2drINZ and their complexes showed poor or no biological activity against gram positive as well as against gram negative organisms. The biological activity showed by the complexes was much better than their ligands. Similar findings have been reported by Nishat et al [39, 40] and Vuckovic et al [41] regarding complexes and their ligands. The biological activity showed by the ligands and their complexes was either comparable or mediocre as compared to the biological activity against known standard antibiotics.

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