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**DRUG SYNTHESIS**

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**SYNTHETIC, STRUCTURAL AND BIOLOGICAL  
PROPERTIES OF BINUCLEAR COMPLEXES  
WITH SOME SCHIFF BASES**

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**Abstract:** The complexes of Co(II), Ni(II) and Cu(II) with N,N'-bis-[5-X-salicylidene]-4,4'-diaminodibenzyl, abbreviated as H<sub>2</sub>-XSaIPDADB (X = -H, -CH<sub>3</sub>, -Br) have been synthesized and investigated by elemental analysis, electrical conductance, magnetic, spectral and thermal studies. The molar conductivity data indicate that the complexes are non-electrolytes. Analytical data support 1:1 (M:L) stoichiometry. The reflectance spectra along with the magnetic data suggest pseudo-tetrahedral geometry for the complexes. The Schiff bases function as tetradentate ligands coordinating through ON-NO donor system. Substitution in the phenyl ring of the complexes produces shift in the azomethine  $\nu(\text{C}=\text{N})$  stretching vibrational frequency, which is related to the Hammett's substituent parameter ( $\sigma$ ). The <sup>1</sup>H-NMR data reveal that all Schiff bases exist in enol-iminic form. Various ESR parameters for copper complexes have been calculated. The compounds have been screened for their biological activities.

**Keywords:** N,N'-bis-[5-X-salicylidene]-4,4'-diaminodibenzyl, Schiff bases, biological activity

The chemistry of transition metal complexes with Schiff base ligands is attracting increasing attention by chemists and has undergone a spectacular growth during the last few years due to their involvement in catalytic processes and discovery that proteins and enzymes require two or more metal ions for their activity. Schiff bases have remarkable property of forming complexes and serve as excellent chelating ligands and have been used (1) as analytical reagents for the spectrophotometric determination of metal ions. Schiff base metal complexes have broad applications as catalysts in chemical and petrochemical industries (2, 3) and in biological processes (4). Synthesis of complexes using tetradentate Schiff base ligands has aroused much interest in recent times, particularly with a view to examine their structural diagnosis and biological activity. The azomethine metal complexes have been found to be active against different type of bacteria (5, 6). We have reported earlier mononuclear complexes prepared from tetradentate Schiff base ligands (7). This paper describes the synthetic, structural and biological properties of binuclear Co(II), Ni(II) and Cu(II) complexes of Schiff bases derived from condensation of 4,4'-diaminodibenzyl with salicyl-

aldehyde, 5-methylsalicylaldehyde and 5-bromosalicylaldehyde.

**EXPERIMENTAL****Materials**

4,4'-Diaminodibenzyl was obtained from M/s Fluka Chemicals. Co(OAc)<sub>2</sub>·4H<sub>2</sub>O, Ni(OAc)<sub>2</sub>·6H<sub>2</sub>O, Cu(OAc)<sub>2</sub>·H<sub>2</sub>O, salicylaldehyde and all other chemicals were of analytical reagent grade. The 5-methylsalicylaldehyde and 5-bromosalicylaldehyde were prepared by the Duff reaction (8). The solvents were purified and doubly distilled before use.

**METHODS**

## Synthesis of the ligands

The required Schiff bases were obtained by reacting the calculated quantities of 4,4'-diaminodibenzyl (0.1 mol) and corresponding aldehyde (0.2 mol) in ethanolic medium. The reaction mixture was refluxed for 3 h. It was cooled and the solid obtained was filtered, washed with ethanol and dried in air. The ligands so obtained were recrystallized from xylene as microcrystalline compounds. The yields were around 90%.

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### Synthesis of complexes

In a typical reaction, the ligand (0.01 mol) suspended in DMF was added to 0.02 M NaOH solution. The suspension was stirred with heating on water bath whereupon a reddish brown solution was produced. The contents were cooled to room temperature, and a solution of metal acetate (0.01 mol) in DMF was added dropwise. The resulting mixture was stirred for 3 h with heating on a water bath. The product was filtered by suction, washed with ethanol and dried *in vacuo*.

### Analyses

The compounds were analyzed for C, H, N while the metal contents in the complexes were estimated by standard methods. The molar conductance values at room temperature were measured in DMF ( $10^{-3}$  M) on an Elico digital direct reading conductivity meter model CM-180. Room temperature magnetic susceptibility measurements were made on solid samples, by a Gouy method using  $\text{Hg}[\text{Co}(\text{SCN})_4]$  as the calibrant. The optical density (OD) of test solutions for antifungal activity were recorded on a spectrophotometer (Elico-Model CL-24). The diffuse reflectance spectra of the chelates in solid state were recorded on a Shimadzu UV-2100 spectrophotometer. FTIR spectra were recorded on a Perkin-Elmer FTIR spectrophotometer model 1600 using KBr pellets. The  $^1\text{H-NMR}$  spectra were recorded on Varian XL-500 MHz instrument in  $\text{DMSO-d}_6$  solvent using TMS as the internal standard. The ESR spectra of Cu(II) complexes were recorded on Varian-E line, E-112 electron spin resonance spectrometer at room temperature in polycrystalline state using TCNE marker. Thermogravimetric data were obtained from an assembly by recording the change in weight on increasing the temperature from room temperature with a heating rate of  $10^\circ\text{C min}^{-1}$  in air.

### Antimicrobial screening

The antimicrobial activity of the compounds under investigation were studied using two types of the pathogenic bacteria *Escherichia coli* and *Staphylococcus aureus* by paper disc method. The tube dilution method was used to assay antifungal activity against pathogens of rice *Pyricularia oryzae* and *Helminthosporium oryzae*. The *in vitro* screening for the antitubercular activity was examined using the highly virulent  $\text{H}_{37}\text{R}_v$  strain of *Mycobacterium tuberculosis* as test organism. The compounds were tested in Youman's liquid medium (9).

### Paper Disc Diffusion Method

This method was used to study the antibacterial activity of the complexes against some of the pathogenic bacteria. In this method, 0.1 mL of inoculum of the test organism was spread uniformly on the surface of the agar medium in a Petri plate using a spreader. The sterilized Whatman filter paper discs of 5 mm diameter were dipped into the solution in DMF ( $10^{-3}$  M) and then were placed on the surface of the agar. Up to four discs in each plate were used. The plates were incubated at  $37^\circ\text{C}$  for 24 h. During incubation, the complex diffuses from the filter paper into the agar. The activity of the complexes was assessed by measuring the diameter of the inhibited zone in millimeters (mm). The results were compared against those of control (tetracycline), which was screened simultaneously. DMF, used as blank, was also run to know its activity.

### Tube Dilution Method

This method was used to study the antifungal activity of the complexes against some of the pathogenic fungi. Fungus inoculum was prepared by inoculating the selected fungus into sterilized Sabouraud's broth to which 0.1 mg/mL of streptomycin was added to prevent bacterial contamination. After sporulation, the spores were harvested in the same media by gentle stirring using magnetic stirrer and the spore suspension was poured into another sterile flask.

To a 5 mL of Sabouraud's broth contained in a 15 mL Corning test tube, 0.1 mL of the test solution of the complex in DMF was added. It was autoclaved at 15 lb pressure for 15 min. The tubes were then cooled and were inoculated with 0.1 mL of spore suspension. The tubes were kept on a rotary shaker and incubated at room temperature for 24 h. The percentage growth of the fungus was calculated after determining the optical density (OD) of the solution on a spectrophotometer (Elico-Model CL-24) at 530 nm with an inoculated Sabouraud's broth as blank. The growth of the fungus in the tube, which contained none of the antifungal agent, was assumed as 100%. The results were compared against those of the control (amphotericin), which was screened simultaneously.

## RESULTS AND DISCUSSION

The complexes are intense colored and thermally stable at room temperature, non-hygroscopic, insoluble in water and show varying but low solubility in common organic solvents but sparingly sol-

uble in DMF. The analytical data (Table 1) for ligands and their complexes are consistent with proposed structures and indicate that the complexes have 1:1 metal-ligand stoichiometry. The molar conductance value of  $10^{-3}$  M solution of the complexes in DMF was found in the range 0.26-0.37  $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$  indicating their non-electrolytic nature (10).

#### $^1\text{H-NMR}$ spectra

The salient features of  $^1\text{H-NMR}$  spectra of the Schiff bases are discussed. The multiplet signals corresponding to aromatic protons occur between 6.83-7.45 ppm and absorption signals due to methylene ( $-\text{CH}_2-$ ) protons occur in the range 2.95-3.04 ppm. The resonance signals due to  $\text{CH}_3$  protons present in  $\text{H}_2-\text{CH}_3\text{SalPDADB}$  are observed at 1.98 ppm. The most direct and effective method of investigating tautomeric equilibrium is PMR spectroscopy. In the spectra of  $\text{H}_2-\text{HSalPDADB}$ ,  $\text{H}_2-\text{CH}_3\text{SalPDADB}$  and  $\text{H}_2-\text{BrSalPDADB}$ , the azomethine protons ( $-\text{CH}=\text{N}-$ ) exhibit a chemical shift respectively at 8.64, 8.78 and 8.54 ppm, typical of the enolic form (11). The sharp low field signals for the two phenolic protons were found, respectively, at 13.34, 13.46 and 13.29 ppm. This shows that the Schiff bases form intramolecular hydrogen bonds (12) involving the phenolic proton and the

azomethine nitrogen atom, thus implying a phenol-iminic structure (Figure 1).

#### Infrared spectra

The IR spectra of the ligands and their metal complexes are complex and it is not possible to assign all the bands without ambiguity. However, structurally important bands (Table 2), which provide unequivocal evidence regarding the structural features and manners of their bonding with metal ions, have been evaluated on the basis of the known infrared spectra of the related compounds. Some common features of the IR spectra are noteworthy:

1. The medium intense and broad band at around  $2920\text{ cm}^{-1}$ , showing the existence of intramolecular H-bonding (13) between the phenolic oxygen and azomethine nitrogen,  $\nu(\text{OH})$  ( $\text{OH}\dots\text{N}$ ). This band is absent in the spectra of complexes indicating that the phenolic  $-\text{OH}$  groups are deprotonated and the Schiff bases are dibasic.

2. The presence of a strong band in the spectra of  $\text{H}_2-\text{HSalPDADB}$ ,  $\text{H}_2-\text{CH}_3\text{SalPDADB}$  and  $\text{H}_2-\text{BrSalPDADB}$ , respectively, at  $1284$ ,  $1287$  and  $1278\text{ cm}^{-1}$  is typical of phenolic C-O stretching band, and indicates the presence of an enol-iminic structure (14) in salicylidene. This band of the ligands shows marked shift of  $35-50\text{ cm}^{-1}$  to higher wave

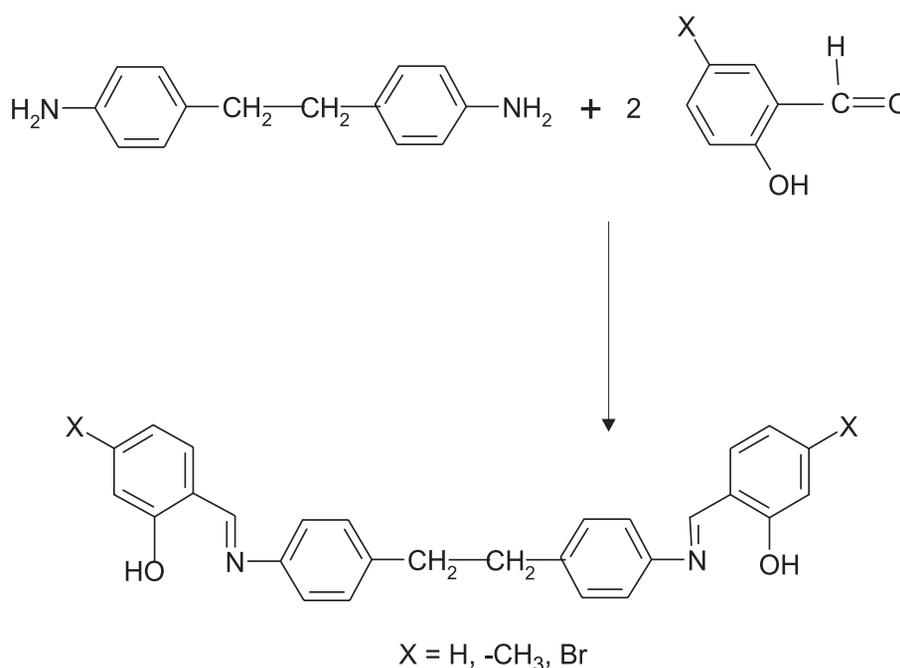


Figure 1. Proposed structure and schematic representation for the formation of Schiff base ligands.

Table 1. Analytical data and physical properties of ligand and metal complexes.

Compound	Color	Decomp. temp./ M. p. (°C)	Elemental analysis: found (calculated) (%)				Molar conduct. mhos cm <sup>2</sup> mol <sup>-1</sup>
			M	C	H	N	
H <sub>2</sub> -HSalPDADB	yellow	232*	–	79.9 (80.0)	5.9 (5.7)	6.8 (6.7)	–
Cu <sub>2</sub> (HSalPDADB) <sub>2</sub>	purple	>310	12.8 (12.9)	70.0 (69.8)	4.9 (4.6)	5.6 (5.8)	0.37
Ni <sub>2</sub> (HSalPDADB) <sub>2</sub>	green	>350	12.1 (12.3)	69.9 (70.5)	4.3 (4.7)	6.1 (5.9)	0.35
Co <sub>2</sub> (HSalPDADB) <sub>2</sub>	brick-red	>300	12.5 (12.3)	70.2 (70.4)	4.8 (4.6)	5.8 (5.9)	0.26
H <sub>2</sub> -CH <sub>3</sub> SalPDADB	yellow	258*	–	80.2 (80.4)	6.4 (6.3)	6.1 (6.2)	–
Cu <sub>2</sub> (CH <sub>3</sub> SalPDADB) <sub>2</sub>	brown	>306	12.7 (12.5)	70.9 (70.7)	4.9 (5.1)	5.2 (5.5)	0.26
Ni <sub>2</sub> (CH <sub>3</sub> SalPDADB) <sub>2</sub>	light green	>341	11.4 (11.7)	71.3 (71.4)	5.2 (5.2)	5.8 (5.6)	0.34
Co <sub>2</sub> (CH <sub>3</sub> SalPDADB) <sub>2</sub>	red	>287	11.6 (11.7)	71.4 (71.3)	5.5 (5.2)	5.7 (5.6)	0.29
H <sub>2</sub> -BrSalPDADB	yellow	271*	–	58.0 (58.2)	4.0 (3.9)	5.1 (4.9)	–
Cu <sub>2</sub> (BrSalPDADB) <sub>2</sub>	brown	>312	9.5 (9.6)	52.7 (52.6)	2.9 (3.1)	4.4 (4.4)	0.28
Ni <sub>2</sub> (BrSalPDADB) <sub>2</sub>	light green	>343	9.6 (9.4)	52.9 (53.0)	3.5 (3.2)	4.2 (4.5)	0.37
Co <sub>2</sub> (BrSalPDADB) <sub>2</sub>	reddish brown	>279	9.1 (9.3)	52.7 (52.9)	3.2 (3.2)	4.9 (4.5)	0.33

\* Melting point

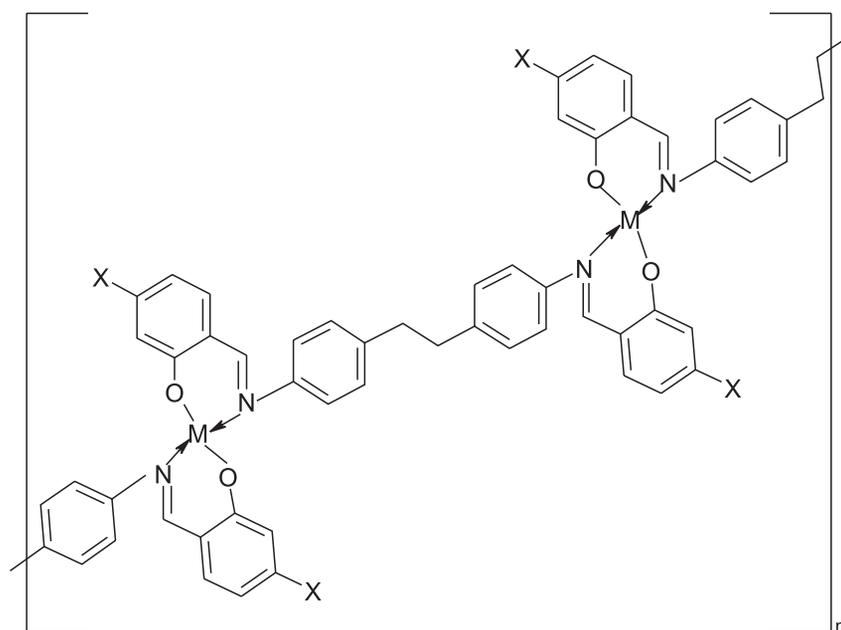


Figure 2. Proposed structure for the Cu(II), Ni(II) and Co(II) complexes of N, N'-bis[5-X-salicylidene]-4, 4'-diaminodibenzyl.

number in the complexes indicating metal-oxygen bonding. This view is further supported by the appearance of a band corresponding to  $\nu(\text{M-O})$  in the complexes (15).

3. The ligands show an intense band due to  $\nu(\text{C=N})$  of azomethine group at around  $1618 \text{ cm}^{-1}$  consistent with the iminic absorption at  $1610\text{-}1630 \text{ cm}^{-1}$  of free salicylidenic Schiff bases (16). In all the metal complexes this band undergoes a shift to lower energy, indicating coordination of the azomethine nitrogen with metal ions which is further reflected by the appearance of new bands due to  $\nu(\text{M-N})$  at low wave number region (17).

4. The infrared spectra also show the effect of substitution as the  $\nu(\text{C=N})$ ,  $\nu(\text{C-O})$  and intramolecular hydrogen bonding are affected by substitution in the phenyl ring moiety of the parent ligand. With the introduction of an electron withdrawing group like bromide, the strength of hydrogen bonding decreases. This can be noticed in their spectra where the  $-\text{OH}$  bond frequency moves to higher wave number side. The  $\nu(\text{C=N})$  is affected by substitution in the phenyl moiety of the parent ligand. In the metal chelates there are both  $\sigma$  and  $\pi$  interactions and  $\nu(\text{C=N})$  decreases in the order  $\text{CH}_3 > \text{H} > \text{Br}$  which is consistent with the Hammett's  $\sigma$  values (18) (Me:0.07, H:0, Br:0.39). The electron releasing substituent, like methyl, tends to increase the electron density on the nitrogen atom of  $-\text{CH=N}-$ , thereby facilitating strong  $\sigma$  and poor  $\pi$  interactions.

5. In addition to above bands, the IR bands due to phenyl ring systems between  $1350\text{-}1600 \text{ cm}^{-1}$  which are almost unaffected in the metal complexes,

have been assigned to aromatic  $\nu(\text{C=C})$ . The bands near  $1600 \text{ cm}^{-1}$  are assigned to aromatic ring, which are found to overlap with strong absorption band due to  $\nu(\text{C=N})$  azomethine group.

6. The spectra show the absence of absorption bands due to water molecules in the chelates.

7. The significant shift of free ligand  $\nu(\text{C=N})$  to lower wave number side and  $\nu(\text{C-O})$  towards higher wave number side in the complexes point to the bonding of the ligand to metal ion through phenolic oxygen and azomethine nitrogen and support the tetradentate nature of the ligands.

#### Magnetic and electronic studies

The room temperature magnetic moment values per metal ion (Table 3) of Co(II) complexes fall in the range of 4.25-4.38 B.M. Although the values of high spin octahedral and tetrahedral cobalt complexes overlap considerably, tetrahedral Co(II) complexes generally have low  $\mu_{\text{eff}}$  values, often in the range of 4.2-4.5 B. M. The  $\mu_{\text{eff}}$  values for the corresponding octahedral complexes fall around 4.8 B.M. The observed magnetic moments of the present Co(II) complexes are in consistence with the reported magneton values of known pseudo-tetrahedral complexes (19). This is further supported by the spectral data. The diffuse reflectance spectra of the Co(II) complexes show two absorption bands, a weak shoulder at around  $11000 \text{ cm}^{-1}$  and broad band near  $15000 \text{ cm}^{-1}$  which may be assigned to the transition  ${}^4\text{A}_2 \rightarrow {}^4\text{T}_1(\text{F})$  and  ${}^4\text{A}_2 \rightarrow {}^4\text{T}_1(\text{P})$ , respectively. For tetrahedral environment there are three possible transitions. The  $\nu_1$  band occurs at low energies and is not observed in all

Table 2. Selected IR bands ( $\text{cm}^{-1}$ ) of ligand and metal complexes.

Complexes	$\nu(\text{C=N})$	$\nu(\text{C-O})$	$\nu(\text{OH}\cdots\text{N})$	$\nu(\text{M-O})$	$\nu(\text{M-N})$
$\text{H}_2\text{-HSalPDADB}$	1619 s	1284 s	2918 b	-	-
$\text{Cu}_2(\text{HSalPDADB})_2$	1610 s	1327 s	-	555 m	456 m
$\text{Ni}_2(\text{HSalPDADB})_2$	1610 s	1325 s	-	552 m	453 m
$\text{Co}_2(\text{HSalPDADB})_2$	1609 s	1321 s	-	554 m	470 m
$\text{H}_2\text{-CH}_3\text{SalPDADB}$	1622 s	1287 s	2915 b	-	-
$\text{Cu}_2(\text{CH}_3\text{SalPDADB})_2$	1613 s	1327 s	-	556 m	450 m
$\text{Ni}_2(\text{CH}_3\text{SalPDADB})_2$	1611 s	1325 s	-	548 m	446 m
$\text{Co}_2(\text{CH}_3\text{SalPDADB})_2$	1610 s	1338 s	-	570 m	425 m
$\text{H}_2\text{-BrSalPDADB}$	1618 s	1278 s	2920 b	-	-
$\text{Cu}_2(\text{BrSalPDADB})_2$	1609 s	1320 s	-	547 m	451 m
$\text{Ni}_2(\text{BrSalPDADB})_2$	1604 s	1312 s	-	553 m	447 m
$\text{Co}_2(\text{BrSalPDADB})_2$	1601 s	1310 s	-	550 m	452 m

m: medium, s: strong, b: broad

Table 3. Magnetic moments and diffused reflectance spectral data (cm<sup>-1</sup>) of metal complexes.

Complexes	<sup>3</sup> T <sub>1</sub> → <sup>3</sup> T <sub>2</sub> (F)*	<sup>3</sup> T <sub>1</sub> → <sup>4</sup> A <sub>1</sub> (F)	<sup>3</sup> T <sub>1</sub> → <sup>3</sup> T <sub>1</sub> (P)	Dq	B'	β	μ <sub>eff</sub> (B.M)
Ni <sub>2</sub> (HSalPDADB) <sub>2</sub>	5389	10869	16103	538.9	882.5	0.849	3.49
Ni <sub>2</sub> (CH <sub>3</sub> SalPDADB) <sub>2</sub>	5671	10964	16319	567.1	893.7	0.853	3.53
Ni <sub>2</sub> (BrSalPDADB) <sub>2</sub>	5208	10526	15980	520.8	745.6	0.729	3.18
Complexes	<sup>4</sup> A <sub>2</sub> → <sup>4</sup> T <sub>2</sub> (F)*	<sup>4</sup> A <sub>2</sub> → <sup>4</sup> T <sub>1</sub> (F)	<sup>4</sup> A <sub>2</sub> → <sup>4</sup> T <sub>1</sub> (P)	Dq	B'	β	μ <sub>eff</sub> (B.M)
Co <sub>2</sub> (HSalPDADB) <sub>2</sub>	5555	11245	14281	555.5	590	0.619	4.38
Co <sub>2</sub> (CH <sub>3</sub> SalPDADB) <sub>2</sub>	5563	11371	14918	556.3	597	0.651	4.25
Co <sub>2</sub> (BrSalPDADB) <sub>2</sub>	5498	11487	14815	549.8	565	0.593	4.37

\* calculated values

Table 4. Magnetic moments, diffused reflectance ESR data of copper complexes.

Complex	μ <sub>eff</sub> (B.M.)	Band positions (ν) (cm <sup>-1</sup> )	ESR Parameters					
			g <sub>  </sub>	g <sub>⊥</sub>	g <sub>0</sub>	A <sub>  </sub> (×10 <sup>-4</sup> )(cm <sup>-1</sup> )	A <sub>⊥</sub> (×10 <sup>-4</sup> )(cm <sup>-1</sup> )	A (×10 <sup>-4</sup> )(cm <sup>-1</sup> )
Cu <sub>2</sub> (HSalPDADB) <sub>2</sub>	1.79	14,018; 10,243	2.19	2.08	2.12	45.16	36.84	39.6
Cu <sub>2</sub> (CH <sub>3</sub> SalPDADB) <sub>2</sub>	1.81	14,359; 10648	2.13	2.01	2.04	59.4	48.2	55.9
Cu <sub>2</sub> (BrSalPDADB) <sub>2</sub>	1.75	14,238; 10500	2.20	2.00	2.07	53.9	44.6	48.4

Table 5. Biological activity of the compounds.

Compound	Antimicrobial activity (% zone of inhibition)		Antifungal activity (% zone of inhibition)		Antitubercular activity (MIC) in μg/mL
	1	2	3	4	5
H <sub>2</sub> -HSalPDADB	19	18	55.7	60.1	47
Cu <sub>2</sub> (HSalPDADB) <sub>2</sub>	15	16	70.8	73.5	39
Ni <sub>2</sub> (HSalPDADB) <sub>2</sub>	14	13	53.7	51.3	34
Co <sub>2</sub> (HSalPDADB) <sub>2</sub>	20	19	61.9	23.7	25
H <sub>2</sub> -CH <sub>3</sub> SalPDADB	23	21	43.6	48.9	36
Cu <sub>2</sub> (CH <sub>3</sub> SalPDADB) <sub>2</sub>	17	19	73.1	67.8	33
Ni <sub>2</sub> (CH <sub>3</sub> SalPDADB) <sub>2</sub>	16	13	46.6	57.4	54
Co <sub>2</sub> (CH <sub>3</sub> SalPDADB) <sub>2</sub>	27	24	59.5	18.3	21
H <sub>2</sub> -BrSalPDADB	18	20	43.7	46.6	49
Cu <sub>2</sub> (BrSalPDADB) <sub>2</sub>	14	15	67.5	71.3	43
Ni <sub>2</sub> (BrSalPDADB) <sub>2</sub>	10	12	51.7	54.4	38
Co <sub>2</sub> (BrSalPDADB) <sub>2</sub>	18	20	62.5	24.9	27

1 – *E. coli*, 2 – *S. aureus*, 3 – *P. oryzae*, 4 – *H. oryzae*, 5 – *M. tuberculosis* (H<sub>37</sub>Rv)

cases. Hence, the value  $\nu_1$ , B' and  $\beta$  have been calculated (20).

All the Ni(II) complexes are paramagnetic and show the magnetic moments in the range 3.18 – 3.53 B.M. As the magnetic moment values are greater than spin-only value but lower than those expected for a tetrahedral, these complexes are assigned to have pseudo-tetrahedral geometry (21). The reflectance spectra show two absorption bands:

one at around 16000 cm<sup>-1</sup> and the other in the range 10526-10964 cm<sup>-1</sup>, assignable to <sup>3</sup>T<sub>1</sub> → <sup>3</sup>T<sub>1</sub>(P) and <sup>3</sup>T<sub>1</sub> → <sup>3</sup>A<sub>2</sub>(F) transitions (22), respectively. The low energy band  $\nu_1$  is not clearly observed in the spectra; hence the values of Dq, B and  $\beta$  have been obtained (23) on the basis of the observed transitions. The values of B' and  $\beta$  (Table 3) suggest appreciable amount of covalent character in the M-L bond.

The observed magnetic moment values per Cu(II) ion (Table 4) are in the range 1.75-1.81 B.M. which are very close to the spin only value for one unpaired electron (1.73 B.M), which indicates that the orbital contribution is almost quenched by the crystalline field. The  $\mu_{\text{eff}}$  values of the present complexes are comparable to those of an analogous series of binuclear pseudo-tetrahedral Cu(II) complexes reported earlier (24). The magnetic moment values (Table 4) are normal at room temperature indicating negligible or non-observable magnetic interaction. The recent reports on binuclear Cu(II) complexes with biphenyl moieties as bridging units have shown that a considerable amount of anti-ferromagnetic interaction exists between the two Cu(II) centers through  $\sigma$  overlap super exchange mechanism (25, 26). The normally expected exchange mechanism involving conjugated  $\pi$ -delocalization has been shown to be energetically unfavored, even though a partial contribution by this mechanism is not ruled out. The possible superexchange interaction via a  $\pi$ -delocalized electron cloud of the biphenyl moiety is broken by the presence of two  $sp^3$  carbon atom between the two 1,1'- $sp^2$  carbons of the bridging phenyl moieties.

The diffuse reflectance spectra of Cu(II) complexes show two bands; a low energy, less intense one at around 10500  $\text{cm}^{-1}$  and a relatively more energetic, intense and broad one at around 14000  $\text{cm}^{-1}$ . Planar Schiff base copper(II) complexes are known to have only one band around 15000  $\text{cm}^{-1}$  while the tetrahedral ones are known to have a transition around 12000  $\text{cm}^{-1}$ . An extra low intensity band, assigned to  $dx^2-y^2 \rightarrow dyz$  transition, has been reported for certain Cu(II) Schiff base complexes with pseudo tetrahedral geometry (26). The fact that the band at around 14000  $\text{cm}^{-1}$  (Table 4) in the present Cu(II) complexes is of lower energy than that expected for the square planar Cu(II) centers and that a low energy (10500  $\text{cm}^{-1}$ ) band is present, indicates a pseudo-tetrahedral geometry around the Cu(II) center which is further supported by ESR spectral studies.

#### ESR spectral studies

The X-band room temperature polycrystalline ESR spectra of Cu(II) complexes show well resolved parallel and perpendicular parts. No  $\Delta M_s = \pm 2$  transition at half field is observed indicating the absence of intramolecular or intermolecular antiferromagnetic interactions. There are a few examples of pseudo-tetrahedral complexes of Cu(II) which do not show any hyperfine ESR spectra (19, 26). This absence of hyperfine splitting is attributed to dipolar

line broadening and to the much reduced nuclear hyperfine coupling constant for pseudo-tetrahedral Cu(II) complexes.

According to Kivelson and Neimen (27), the most sensitive function is  $g_{\text{II}}$  which is the best indicator of the covalent character. The observed  $g_{\text{II}}$  values are less than 2.3 and are in agreement with the covalent character of the metal-ligand bond. On this basis, the covalent character should increase in the order  $-\text{CH}_3 > -\text{H} > -\text{Br}$  chelates of copper(II). This order satisfactorily correlates with electron density at the phenolic oxygen, which shows the same trend.

Furthermore, deviation from planar to tetrahedral geometry is reflected in  $A_{\text{II}}$  and  $A_0$  values (28). In case of severe distortion from square planar geometry towards tetrahedral one, the  $A_0$  values are lowered by nearly two to three times. The  $A_0$  values (Table 4) for the present complexes compare very well with the values reported (29) for the pseudo-tetrahedral Cu(II) complexes. It is important to note that  $A_{\text{II}}$  values are nearly half of the monomer value and supports a binuclear structure (Figure 2) for Cu(II) complexes. These observations support the previously discussed results that the Cu(II) ion environment is highly distorted towards tetrahedral configuration and shows the geometry around Cu(II) center as pseudo-tetrahedral.

#### Thermogravimetric analysis

Thermal decomposition studies were made by heating the compounds to various temperatures starting from room temperature. The temperature was allowed to increase at the rate of 10°C  $\text{min}^{-1}$ . The decomposition temperatures (>250°C) of the chelates indicate that they are thermally stable suggesting stronger metal-ligand bonding. The decomposition temperature indicates that for the various metal complexes, the thermal stability increases in the order  $\text{Ni} > \text{Cu} > \text{Co}$ , consistent with the observation of Goodwin and Bailar (30). The thermal curves of metal complexes are single stepped, indicating the gradual decomposition of the ligand after the decomposition point, leaving metal(II) oxide as the ultimate product of heating. The perusal of thermograms of metal chelates shows absence of water molecules in the metal complexes, which further supports the infrared spectral studies.

#### Biological properties

The results of the preliminary study on antimicrobial activity against the bacterial strains indicate that most of the compounds are less to highly active.

However, these microorganisms show general resistance to some of the Ni(II) complexes. Amongst all the metal complexes, the Co(II) complexes are more active than the other metal complexes, which may be possibly due to the low oxidation potential of Co(II). Thus, while coordination to Co(II) appears to enhance the activity, complexation with Ni(II) seems to have negative effect on the activity of the parent ligands. The present compounds are much less active compared to standard compound like tetracycline.

The Schiff base ligands and their metal complexes were tested for the antifungal activity against the pathogens of rice *Pyricularia oryzae* and *Helminthosporium oryzae* by tube dilution method. Co(II) complexes were found to be effective against *Pyricularia oryzae* but inactive against *Helminthosporium oryzae*. The Ni(II) complexes exhibit normal results against both the fungal pathogens. The Cu(II) complexes shows remarkable fungitoxicity against both the organisms under study.

The *in vitro* screening for the antitubercular property of the compounds indicated that the Co(II) complexes were found to be more effective where all other compounds showed average antitubercular activity. The results of antibacterial properties are summarized in Table 5.

The studies show enhancement of the activity of the ligands on complexation and hence on chelation, which reduces considerably the polarity of the metal ions in the complexes (31). This is due mainly to the partial sharing of its positive charge with the donor group and possible  $\pi$ -electron delocalization over the whole chelate ring system through  $p\pi$  or  $d\pi$ - $d\pi$  interactions of the orbitals of the ligands and metal ions, which in turn increases the hydrophobic character of the chelate and thus enables its permeation through the lipid layer (cell membrane) of microorganisms.

## CONCLUSIONS

Based on the above discussion and information available in the literature, the following brief conclusions may be drawn.

1. The magnetic moment values, together with the electronic spectral data, are in favor of a pseudo-tetrahedral stereochemistry of the metal complexes.
2. The analytical data show the presence of one metal ion per ligand molecule, with a polymeric structure.
3. The antibacterial activity of compounds shows that they are most effective against selected

bacterial strain and the results are comparable to the commercially available compounds.

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