



ISSN (E): 2277- 7695
 ISSN (P): 2349-8242
 NAAS Rating 2017: 5.03
 TPI 2017; 6(5): 90-95
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 www.thepharmajournal.com
 Received: 17-03-2017
 Accepted: 18-04-2017

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Transition metal ion Co^{II} , Ni^{II} , Cu^{II} & Zn^{II} complexes of tridentate ligands (NNO) their synthesis, characterization and biological activities

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Abstract

A series of new Schiff bases were synthesized by combination of 4-(3-nitrophenyl) thiazol-2-amine with hydrox aldehyde (R-H, 5CH₃ and 5Cl). Schiff bases and their transition metal complexes were characterized by elemental analysis, UV-visible, infrared spectra, magnetic susceptibility and conductivity measurement. The transition metal complexes are monomeric and 1:2 stoichiometry having octahedral geometry. The ligands coordinated through oxygen atom of phenolic -OH group and also from thiazole ring nitrogen.

The Schiff bases and their metal complexes were screened for antibacterial and antifungal activity.

Keywords: Schiff base, transition metal ion, biological activity

Introduction

Schiff base are straight forward to prepare, monodentate electron donors with easily-tunable electronic and steric effect thus being versatile. Now a day's active and well-designed Schiff base ligands are considered privileged ligands [1]

Schiff base ligands containing various donor atoms. NOS and ONN type have alternative structure and have attracted the attention of chemist. NOS is an attractive ligands show broad biological activities hence special interest, because of the variety of ways in which they are bonded to metal ions it is known that the existence of metal ions bonded to biologically active compounds may enhance their activities [2, 3] New interesting application found in the field of pesticides and medicine. Ligand ONN is also have alternative structure hence attracted the attention of chemist in various metal complexes with bi and tridentate Schiff base containing nitrogen and oxygen donor atoms play important role in biological system and represent interesting model for metalloenzyme, which efficiently catalyze the reduction of dinitrogen and dioxygen [4-6]

The biological system of 2-amino thiazole and its derivative are well known [7, 8] 2-amino thiazole moiety proven its value in medicinal chemistry has been successfully applied in dopamine against such as B-HT920, PDI 18440 and pramipexole, they widely used as anti-parkinsonian agent [9]. In these cases 2-amino thiazole group interact with nucleic acid to form a stable DNA- drug complex with the aid hydrogen bonds formed between the amino group and the sugar-phosphate chain.

The thiazole moiety of 2-amino thiazole and their derivatives proven their role in medical chemistry and of Schiff base considered as privilege ligand with versatile behaviour. Hence in present communication the selected thiazole moiety i.e.4-(m-Nitrophenyl)-2-aminothiazole and o-hydroxy aldehydes for their synthesis, characterization, spectral studies as well as microbial studies.

Experimental

Synthesis of Schiff base

- a) Synthesis of 4(3-Nitrophenyl)-2-aminothiazole.
4(3-Nitrophenyl)-2-aminothiazole synthesized as reported method [10].
- b) O-hydroxyaldehyde
 1. Salicylaldehyde
 2. 5-methylsalicylaldehyde
 3. 5-chlorosalicylaldehyde

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Synthesis of Schiff base

The Schiff bases have been synthesized by conventional way. A solution of O-hydroxyaldehyde in ethanol was mixed with ethanoic solution of 4-(3-Nitrophenyl)-2-amino thiazole in equimolar quantity. The mixture was refluxed in water bath for 2 hours. The product of Schiff base obtained was filtered and recrystallised from ethanol and dried under vacuum. Purity of the product checked by TLC.

Microwave method

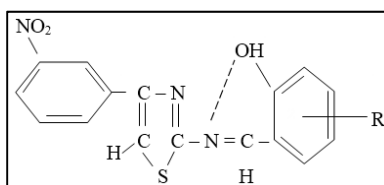
The equimolar ratio (1:1) of 4-(3-Nitrophenyl)-2-aminothiazole and o-hydroxyaldehyde were mixed thoroughly in grinder. The mixture was then irradiated by micro oven by

adding 4-5 ml solvent. The reaction is completed in short time (5-10 min) with excellent yields, then product was recrystallised with ethanol and dried under vacuum. Purity of product was monitored by TLC. The yield of product increase by 10%¹⁰

Following Schiff bases were synthesized.

1. [N-(Salicylidene)-4-(3-nitrophenyl)-2-amino-thiazole] SNPAT
2. [N-(5-Methylsalicylidene)-4-(3-nitrophenyl)-2-amino-thiazole] 5-MSNPAT

[N-(5-Chlorosalicylidene)-4-(3-nitrophenyl)-2-amino-thiazole] 5-CISNPAT



Schiff base

1. SNPAT
2. 5MSNPAT
3. 5CISNPAT

R

1. H
2. 5-CH₃
3. 5-Cl

Synthesis of metal complexes

A ethanoic solution of 25ml of the appropriate metal. Salt^(II) (0.001m) was added to the stirred ethanoic solution (25ml) of respective Schiff (0.002m). The mixture was refluxed for 2 hrs. The resulting mixture was cooled. Filtered and reduced to nearly half its volume. The mixture was kept overnight at room temperature, which result in the formation of solid product, filtered the product by washing number of times with ethanol and crystallized with ethanol. Product of complexes with metal ion Co^{II}, Ni^{II}, Cu^{II} & Zn^{II}.

Microwave Method

The quantity of metal salt and Schiff base (1:2) ratio were mixed thoroughly in grinder. The mixture was then irradiated in the microwave oven by taking 5-7ml solvent. The reaction was completed within short time (5-7 min). The resulting product was recrystallized by ethanol and dried under vacuum. The progress of the reaction and purity of the product was monitored by TLC. The yield of the product increased by 8-10%. Molecular weight of Schiff base and metal complexes were determined by Rast method and elemental analysis of ligand and metal complexes were calculated and found given in table-1.

Table 1: Analytical data of Schiff bases and their metal complexes

Sr. No.	Ligand/ Complexes	Formula Weight	Elemental Analysis Found and (Cal)						Colour and Nature
			M%	C%	H%	S%	N%	Cl%	
1.	SNPAT	325	-	59.10 (59.25)	2.90 (3.08)	9.75 (9.87)	12.80 (12.96)	-	Yellow Crystalline
2.	5MSNPAT	338	-	60.20 (60.35)	3.42 (3.55)	9.37 (9.46)	12.24 (12.42)	-	Yellow Crystalline
3.	5CISNPAT	359	-	53.46 (53.55)	2.39 (2.51)	8.80 (8.92)	11.59 (11.71)	9.81 (9.90)	Yellow Crystalline
4.	Co(C ₁₆ H ₁₀ O ₃ N ₃ S) ₂	708	8.38 (8.47)	54.10 (54.23)	2.70 (2.82)	8.90 (9.03)	13.42 (13.55)	-	Reddish Brown
5.	Co(C ₁₇ H ₁₂ O ₃ N ₃ S) ₂	736	8.07 (8.15)	55.29 (55.43)	3.12 (3.26)	8.55 (8.69)	11.25 (11.41)	-	Reddish Brown
6.	Co(C ₁₆ H ₉ O ₃ N ₃ Cl) ₂	775	7.65 (7.74)	49.41 (49.54)	2.16 (2.32)	8.12 (8.25)	10.70 (10.83)	8.89 (9.03)	Reddish Brown
7.	Ni(C ₁₆ H ₁₀ O ₃ N ₃ S) ₂	707	8.35 (8.42)	54.17 (54.31)	2.70 (2.82)	8.92 (9.05)	11.76 (11.88)	-	Yellow Green
8.	Ni(C ₁₇ H ₁₂ O ₃ N ₃ S) ₂	735	7.89 (8.02)	55.40 (55.51)	3.13 (3.26)	8.62 (8.70)	11.34 (11.42)	-	Yellow Green
9.	Ni(C ₁₆ H ₉ O ₃ N ₃ Cl) ₂	774	7.51 (7.62)	49.50 (49.61)	2.24 (2.32)	8.17 (8.26)	10.76 (10.85)	8.95 (9.04)	Yellow Green
10.	Cu(C ₁₆ H ₁₀ O ₃ N ₃ S) ₂	711	8.74 (8.86)	53.91 (54.00)	2.72 (2.81)	8.94 (9.00)	11.75 (11.81)	-	
11.	Cu(C ₁₇ H ₁₂ O ₃ N ₃ S) ₂	739	8.44 (8.52)	55.12 (55.20)	3.15 (3.24)	8.57 (8.66)	11.28 (11.36)	-	
12.	Cu(C ₁₆ H ₉ O ₃ N ₃ Cl) ₂	778	8.00 (8.09)	49.27 (49.35)	2.22 (2.31)	8.14 (8.22)	10.70 (10.79)	8.81 (8.99)	
13.	Zn(C ₁₆ H ₁₀ O ₃ N ₃ S) ₂	713	9.01 (9.11)	53.77 (53.85)	2.75 (2.80)	8.90 (8.97)	11.71 (11.78)	-	
14.	Zn(C ₁₇ H ₁₂ O ₃ N ₃ S) ₂	741	8.70 (8.77)	55.01 (55.06)	3.18 (3.23)	8.55 (8.63)	11.25 (11.33)	-	
15.	Zn(C ₁₆ H ₁₀ O ₃ N ₃ Cl) ₂	780	8.27 (8.33)	49.17 (49.23)	2.51 (2.56)	8.13 (8.20)	10.70 (10.76)	8.92 (8.97)	

Result and Discussion

The result of microwave synthesis, observed that the reaction was completed in a short time with increasing 10% yields compared to the conventional method.

The Co^{II} , Ni^{II} and Cu^{II} complexes are coloured, solid and stable to wards air and moisture at room temperature. They are soluble in chloroform, benzene, nitro benzene. The elemental analysis data suggest 1:2 (metal-ligand) stoichiometry. The observed molar conductance values ($<10\Omega\text{cm}^2\text{mol}^{-1}$) i.e. low molar conductance in nitrobenzene and molecular weight determination indicates that the complexes are monomeric and non-electrolytic in nature.

Infrared Spectra

The infrared spectra of the Schiff base and their transition metal complexes (Co^{II} , Ni^{II} , Cu^{II} & Zn^{II}) have compared. The band at ~ 1585 $\sim 1510\sim 20$, $\sim 1480\sim 1450\sim 1585\text{m}$, $\sim 1520\text{m}$, $\sim 1450\text{m}$, $\sim 1450\text{m}$ (m-medium) in Schiff bases and their complexes. The Schiff base exhibit V_{OH} , $\text{V}_{\text{C}=\text{N}}$ and $\text{V}_{\text{C}-\text{O}}$ band at ~ 2900 , ~ 1630 and $\sim 1285\text{cm}^{-1}$ respectively. VoH band a

broad and weak bond of phenolic $-\text{O}_\text{H}$ group suggesting that intramolecular hydrogen bonding between $-\text{O}_\text{H}$ group and azomethine nitrogen. The appearance of strong band at $\sim 1630\text{cm}^{-1}$ assigned as azomethine ($\text{V}_{\text{C}=\text{N}}$) linkage^[11-14]

The comparison of infrared spectra of Schiff bases and their transition metal complexes suggest that the lowering of $\text{V}_{\text{C}=\text{N}}$ and shifting of $\text{V}_{\text{C}-\text{O}}$ towards higher frequency the in complexes as compared with the Schiff base. i.e. $\text{V}_{\text{C}=\text{N}}$ $\sim 1630\text{cm}^{-1}$ lowered to 1590cm^{-1} and $\text{V}_{\text{C}-\text{O}}$ $\sim 1280\text{cm}^{-1}$ higher 1325cm^{-1} . Suggest that co-ordination to the central metal takes place through oxygen of the phenolic O_H and nitrogen of the azomethine group¹¹ and nitrogen of thiazole moiety so the ligands behave as tridentate with NNO donor set.

The metal complexes shows high frequency new bands at $\sim 455\sim 470$ and $\sim 535\sim 550\text{cm}^{-1}$. There were in turns assigned to metal oxygen $\text{V}(\text{n}-\text{o})$ and metal-nitrogen $\text{V}_{(\text{M}-\text{N})}$ the absence of V_{OH} frequency in the complexes suggests the involment of phenolic-OH in metal-oxygen bond formation. Ligand frequencies are given in table-2.

Table 2: Infrared Frequencies of Schiff bases (cm^{-1})

Sr. No.	Schiff base	VOH	VC=N	VC-S	Phenyl and thiazole ring vibrations
1.	SNPAT	$\sim 2900\text{bd}$	1630s	1275s	1585m 1520sh 1480s 1450m 1350m 1210m 1180m 1155s
2.	5MSNPAT	$\sim 2900\text{bd}$	1630s	1275s	1585m 1515sh 1480s 1450m 1352m 1215m 1185m 1155s
3.	5CISNPAT	$\sim 2900\text{bd}$	1630s	1275s	1585m 1520sh 1482s 1452m 1355m 1210sh 1180m 1155s

Electronic Spectra

The nature of ligand field around the metal ion has been conclude by reasoning i.e. in logic from the electronic spectra. The electronic spectra of the Co^{II} complexes shows band at ~ 8500 ~ 18000 ~ 21000 and $\sim 26000\text{cm}^{-1}$. Which may be assigned to ${}^4\text{T}_{2\text{g}} \leftarrow {}^4\text{T}_{1\text{g}} (\nu_1)$ ${}^4\text{A}_{2\text{g}} \leftarrow {}^4\text{T}_{1\text{g}} (\nu_2)$ and ${}^4\text{T}_{1\text{g}}(\text{P}) \leftarrow {}^4\text{T}_{1\text{g}} (\nu_3)$ transitions respectively an intense band at 26600cm^{-1} ($\epsilon \sim 1000\text{dm}^3 \text{mole}^{-1}\text{cm}^{-1}$) may be due to ligand to metal (metal-ligand) charge transfer. The spectra suggest an octahedral geometry.

The Ni^{II} complex display three bands at ~ 8400 , ~ 13900 , ~ 25500 and $\sim 27000 \text{cm}^{-1}$. The first three bands corresponding to transition ${}^3\text{A}_{2\text{g}} \rightarrow {}^3\text{T}_{2\text{g}}(\text{p})$, ${}^3\text{A}_{2\text{g}} \rightarrow {}^3\text{T}_{1\text{g}}(\text{f})$ and ${}^3\text{A}_{2\text{g}} \rightarrow {}^3\text{T}_{1\text{g}}(\text{p})$ i.e. ν_1 , ν_2 & ν_3 respectively indicates and

octahedral geometry of the complexes. The band occurring at 27000cm^{-1} is sharp and intense ($\epsilon \sim 1000\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$) and may be due to ligand to metal (metal \leftarrow ligand) charge transfer. Again the spectra suggest an octahedral geometry.

The electronic spectrum of the Cu^{II} complexes shows single broad band at 14500cm^{-1} which correspondence to transition ${}^2\text{E}_\text{g} \rightarrow {}^2\text{T}_{2\text{g}}$. This may assigned an octahedral configuration.^(11,15,16) The Zn^{II} complexes exhibit a high intensity band at $28400\sim 28860\text{cm}^{-1}$ this may assigned to metal-ligand charge transfer and the band exhibit at $13450\sim 15000\text{cm}^{-1}$ due to transition ${}^4\text{T}_{2\text{g}} \leftarrow {}^2\text{E}_\text{g}$ in a distorted octahedral environment.¹¹ The values of various ligand field parameters. 10Dq , B , C , β , $\% \beta$ and ν_3/ν_1 ν_2/ν_1 ν_3/ν_2 were calculated in table no.3 and 3A.

Table 3: Electronic spectral dat of metal complexes Cm^{-1} .

Sr. No.	Metal Complexes	Frequency Cm^{-1} ($\epsilon \text{inmol}^{-1}\text{cm}^{-1}$)	Band Assignment	10Dq	B	C	ν_3/ν_1	ν_2/ν_1	ν_3/ν_2
1.	$\text{CoL}_2 \text{Co}(\text{SNPAT})_2$	8500 18100 21000	${}^4\text{T}_{2\text{g}} \leftarrow {}^4\text{T}_{1\text{g}}$ ${}^4\text{T}_{2\text{g}} \leftarrow {}^4\text{T}_{1\text{g}}$ ${}^4\text{T}_{1\text{g}}(\text{p}) \leftarrow {}^4\text{T}_{1\text{g}}$	9644	327	3831	2.47	2.12	1.16
2.	$\text{NiL}_2 \text{Ni}(\text{SNPAT})_2$	8400 13900 25500	${}^3\text{T}_{2\text{g}}(\text{f}) \leftarrow {}^3\text{T}_{2\text{g}}$ ${}^3\text{T}_{2\text{g}}(\text{f}) \leftarrow {}^3\text{T}_{2\text{g}}$ ${}^3\text{T}_{2\text{g}}(\text{p}) \leftarrow {}^3\text{T}_{2\text{g}}$	8237	864	4002.9	3.03	1.65	1.83
3.	$\text{CuL}_2 \text{Cu}(\text{SNPAT})_2$	13650 16290 26280	${}^2\text{E}_\text{g} \rightarrow {}^2\text{T}_{2\text{g}}$	1337	96.46	446.9	-	-	-

Table 3 A

Sr. No.	Metal Complexes	Frequency Cm^{-1} (cm^{-1})	Covalent factor β	$\% \beta$	LFSE kal mol^{-1}	Geometry
1.	$\text{CoL}_2 \text{Co}(\text{SNPAT})_2$	8500 18100 21000	0.8516	5.63	26.20	Octahedral
2.	$\text{NiL}_2 \text{Ni}(\text{SNPAT})_2$	8400 13900 25500	0.8299	23.98	27.33	Octahedral
3.	$\text{CuL}_2 \text{Cu}(\text{SNPAT})_2$	13650 16290 26280	-		38.67	Octahedral

Magnetic Moments

The values of magnetic moments (Gouy) of Co^{II} , Ni^{II} , Cu^{II} and Zn^{II} metal ion complexes. The Co^{II} complexes lies in the rang 4.5-5.1 BM [17, 18] indicates that Co^{II} complexes having three unpaired electrons and in octahedral environment.

The Ni^{II} complexes lies in the range 2.9-3.1BM [18-20] indicates two unpaired electrons on Ni^{II} ion and in octahedral environment.

The Cu^{II} complexes lies in the range 1.7-1.9 showing one unpaired electrons [21-23] also in distorted octahedral environment.

The Zn^{II} complexes are diamagnetic.

The parameters IR, electronic spectra, magnetic moment and molecular weight the proposed structure for metal complexes are as follow.

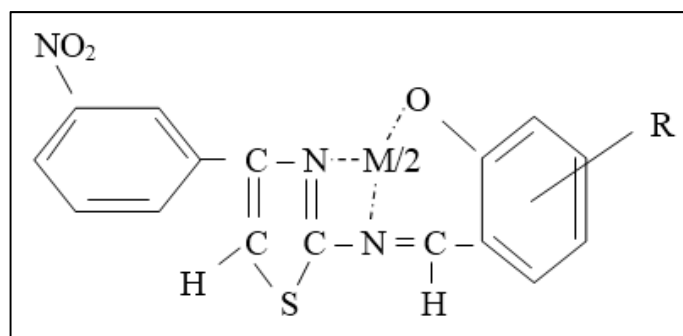


Fig 1: Where M = Co^{II} , Ni^{II} , Cu^{II} and Zn^{II} ions.

Biological Activity

The antibacterial activity of ligand and metal complexes were tested *in vitro* against bacteria. E-coli and staphylococcus aureas by paper disc method²⁴ in 500 and 1000 ppm concentration in DMF compounds are tested. The 10mm diameter whatman paper no. 1 disc were soaked in different solution of compound dried and then placed on the lawn cultures on nutrient agar plate at temperature 37 °C the plates are incubated for 24hr. and the inhibition zone around each disc was measured. The results obtained were compared with standard drug Ampicillin.

For antifungal activity compounds screened against A. flavas and A. niger by mycelia dry weight method²⁵ with glucose nitrate media. The compounds were tested at concentration 500ppm and 1000ppm in DMF and compared with control. The higher inhibition zone of metal complexes than those of the ligands can be explained on the basis of overtones concept and chelation theory. On chelation, the polarity of the metal ion will be reduced to greater extent due to the overlap of the ligand orbital and partial sharing of the positive charge of the metal ion with donor groups. Further, it increases, the delocalization of π electron over whole chelating ring and enhance the penetration of the complexes into lipid membrane and blocking of the metal bonding sites in the enzymes of micro organism. The other factors i.e. solubility, conductivity and bond length between the metal and ligand which increases the activity [26-31]

The several azomethine has been reported to possess remarkable antibacterial, antifungal activities [32-33]

The complexes of metal ion $\text{Vo}(\text{II})$, $\text{Co}(\text{II})$, Ni^{II} , Cu^{II} and Zn^{II} has been studied against several microganism by the well diffusion method. In general the activity order $\text{Cu}^{\text{II}} > \text{Co}^{\text{II}} > \text{Ni}^{\text{II}} > \text{Zn}^{\text{II}} > \text{Vo}^{\text{II}} > \text{ligand}$.³⁴ The investigated antibacterial data reveals that the Co^{II} and Cu^{II} complexes exhibits better antibacterial activity against E-coli and stophylococcus compared to the other compounds. All the metal complexes, metal salt and Schiff bases have bacterial growth inhibition zone in following order.

Metal complexes > Metal salt > Schiff bases The Cu^{II} complexes of Schiff base derived heterocyclic amines and substituted aldehydes and ketones shows the greater antifungal activities compared to the ligand and corresponding metal salt against the Aspergillus niger, Rhizopus stoloniter, Aspergillus flavas, Rhizopctonia bataticola, Condidia alibicans, Fusarium oxysporum, Alternaria, Brassicae and Prenicillum etc.³⁵⁻⁴⁰ The investigated antifungal results show that the Co^{II} and Cu^{II} metal complexes show their greater activity against A. Flavas and A.nigar. In comparison to other metal salt and Schiff base (ligand). All the compounds show fungal growth inhibition zone in following order.

Metal complexes > Metal salt > Schiff bases Antibacterial and antifungal activity inhibition zone shown in table no.4.

Table 4: Antibacterial activity of compounds (diameter of inhibition zone in mm) and antifungal activity in mg C% inhibition) of Schiff base and complexes.

Compounds	Antibacterial activity				Antifungal activity			
	E. Coli		Staphylococcus		Aspergillus Niger		A.Flavas	
	500ppm	1000ppm	500ppm	1000ppm	500ppm	1000ppm	500ppm	1000ppm
Amphicillin	32	35	30	34	70	75	60	65
SNPAT	14	16	10	12	65(14)	68(16)	48(30)	20(55)
5MSNPAT	15	17	12	14	64(13)	67(15)	44(40)	18(60)
5CISNPAT	14	15	13	15	66(15)	65(13)	42(45)	16(65)
Cu(SNPAT) ₂	30	34	21	23	41(47)	15(80)	30(54)	20(67)
Cu(5CISNPAT) ₂	31	35	22	24	40(45)	13(83)	28(60)	18(70)
Cu(5MSNPAT) ₂	28	31	18	23	38(42)	10(86)	25(65)	16(75)
Co(SNPAT) ₂	23	25	15	21	42(40)	18(74)	36(45)	24(60)
Co(5CISNPAT) ₂	24	27	16	22	41(42)	17(78)	34(48)	22(65)
Co(5MSNPAT) ₂	23	26	16	24	40(45)	16(72)	31(55)	20(70)
Ni(SNPAT) ₂	11	17	15	18	40(44)	15(80)	32(51)	22(63)
Ni(5CISNPAT) ₂	10	15	14	17	38(53)	13(78)	30(58)	20(60)
Ni(5MSNPAT) ₂	9	13	12	16	41(45)	12(86)	28(65)	19(65)
Zn(SNPAT) ₂	8	10	9	11	30(80)	34(75)	20(70)	18(65)
Zn(5CISNPAT) ₂	8	11	10	12	28(85)	32(78)	18(75)	18(73)
Zn(5MSNPAT) ₂	7	10	8	10	25(87)	28(82)	15(58)	15(80)

Conclusion

The analytical data and spectral data discussed above suggest that all metal complexes Co^{II}, Ni^{II}, Cu^{II} & Zn^{II} have the proposed geometry is octahedral. Infrared spectra if is assumed that the ligands behave as ONN donor coordinating via-phenolic oxygen, nitrogen of azomethine and nitrogen of thiazole moiety structure illustrated in fig.-1.

The antimicrobial study shows that, metal complexes are more active than ligands. Antibacterial activity Cu^{II} and Co^{II} complexes are more biologically active than Ni^{II} and Zn^{II} complexes. The antifungal activity of these complexes is found to be increases in similar order.

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