Available online www.jocpr.com

Journal of Chemical and Pharmaceutical Research, 2014, 6(7):1697-1703

Research Article

ISSN : 0975-7384
CODEN(USA) : JCPRC5

Preparation, characterization and bioactivity evaluation of Co(II), Ni(II) and Cu(II) complexes containing phthalylsulphathiazole and benzoate ligands

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ABSTRACT

Phthalylsulphathiazole (PST) is a biologically active, monodendate neutral ligand. The present study reveals the microwave assisted preparation, physico-chemical, spectral and biological characterization of Co(II), Ni(II) and Cu(II) complexes with PST and benzoate ion (ben) ligands. The molecular formulae of the complexes were arrived at from the estimation of metals, electrical conductivity, and magnetic moment (μ_{eff}) values. The IR spectral data confirm the entry of the ligands into the coordination sphere. The electronic spectral data indicate the probable geometry of the complexes. The antimicrobial and anti fungal screening of the complexes against the bacteria viz., Staphylococcus sp., Escherichia coli, Proteus vulgaris, Shigella flexneri and Lactobacillus pulgaricus and fungi viz., Candida albicans, Aspergillus oryzae, Aspergillus niger, Aspergillus flavus and Aspergillus sojae were carried out by well diffusion method. The results indicate that Ni(II) complex exhibits enhanced antibacterial activity against Escherichia coli, Proteus vulgaris, Shigella flexneri and Lactobacillus pulgaricus than the pure ligands. Co(II) and Cu(II) complexes have high antibacterial activity against Staphylococcus sp. All the complexes show high anti fungal activity against Candida albicans, Aspergillus oryzae, Aspergillus niger, Aspergillus flavus and Aspergillus sojae. The diphenylpicrylhydrazyl free radical scavenging activity of the above three complexes are found to be nominal.

Key words: Phthalylsulphathiazole, benzoate ion, antibacterial, anti fungal, antioxidantal.

INTRODUCTION

The inorganic elements, other than carbon, nitrogen and oxygen, especially the transition metals[1] are vital to the functioning of biological systems[2]. The bioinorganic chemistry mainly deals with the role of metals and non metals in these systems. It is a highly advanced interdisciplinary science.

Phthalylsulphathiazole (PST)[3] is a biologically active substance and it belongs to sulphonamide group with broad spectrum antimicrobial activities[4]. It can treat different types of infections especially in the treatment of dysentery, colitis and gastroenteritis. Phthalylsulphathiazole contains thiazole, sulphonamide and anilide of phthalic acid groups[5]. Transition metal complexes of phthalylsulphathiazole are very important in the current research due to their enhanced biological activity[6].

Microwave assisted synthesis[7] has gained much attention in recent years. The microwave irradiation is especially used for carrying out chemical transformations since it is almost pollution free, eco-friendly, cheap, less time consuming and offer high yield[8-9] when compared to conventional methods.

The present work aims at the preparation of Co(II), Ni(II) and Cu(II) complexes with phthalylsulphathiazole and benzoate ion as ligands by microwave irradiation and characterization by physico-chemical, spectral and biological methods.

EXPERIMENTAL SECTION

Preparation of complexes

All the chemicals, viz., phthalylsulphathiazole, cobalt(II) nitrate, nickel(II) nitrate, copper(II) nitrate and sodium benzoate were of Analytical reagent grade. The solvents acetonitrile, dimethylsulphoxide, dimethylformamide, ethanol and methanol were of AnalaR grade and used as such.

All the three metal complexes were prepared by adding required mole ratios of phthalylsulphathiazole (5.55 g, 13.77 mmol; 5.55 g, 13.77 mmol and 3.38 g, 8.39 mmol) in 20 ml of methanol and sodium benzoate (1.01 g, 7.01 mmol; 1.00 g, 6.94 mmol and 1.20 g, 8.33 mmol) in 10 ml of ethanol to the methanolic solutions of Co(II) nitrate, Ni(II) nitrate and Cu(II) nitrate (1.00g, 3.44 mmol; 1.0g, 3.44 mmol and 1.00g, 4.14 mmol) respectively followed by microwave irradiation for ~10 seconds after each addition using microwave oven (model: IFB 25PG1S). The precipitated complexes were filtered, washed with ethanol and dried.

Characterization

The estimation of cobalt and copper in the complexes were carried out by volumetric method using EDTA and sodium thiosulphate respectively and nickel by photo-colorimetric method using dimethylglyoxime[10]. The molar conductance measurements of the 10^{-3} M complex in acetonitrile solutions were carried out using Systronic 304 Conductivity meter at 30°C. Magnetic moment of the paramagnetic complexes was recorded using Lake Shore 7410 model Vibrating Sample Magnetometer (VSM) at room temperature. Solid state UV-visible absorbance spectra of all the complexes were carried out using Varian Make, CARY-5000 Model UV-vis Spectrophotometer. The IR spectra of complexes and ligands were recorded on Shimadzu, FT-IR 8400 Spectrometer in 4000-400 cm^{-1} range using KBr pellet technique. Antibacterial[11] and anti fungal activities[12] of the individual ligands and complexes were carried out by well diffusion method. The concentrations of complex/ligand used for antibacterial activities were 25, 50, 75 and 100 μgml^{-1} and those for anti fungal activities were 100, 200 and 400 μgml^{-1}. Antioxidantal activities of the complexes and ligands were carried out by DPPH free radical scavenging method[13] at various concentrations of complex/ligand. The reference standards used for antibacterial, anti fungal and antioxidantal activities were streptomycin, ketoconazole and vitamin-C respectively.

RESULTS AND DISCUSSION

Physico-chemical properties

The cobalt complex was obtained as pale pink colour precipitate with a yield of 73.1%. The metal content was 3.16% against the theoretical 3.08%. The electrical conductivity was 81.23 $ohm^{-1}cm^{2}mol^{-1}$ and the effective magnetic moment was (μ_{eff}) 4.84 BM.

The nickel complex was obtained as pale green colour precipitate with a yield of 73.1%. The metal content was 3.12% as against the theoretical 3.07%. The electrical conductivity was 69.06 $ohm^{-1}cm^{2}mol^{-1}$ and the effective magnetic moment was 3.16 BM.

The copper complex was obtained as greenish blue precipitate with a yield of 70.7%. The metal content was 5.55% as against the theoretical 5.72%. The electrical conductivity was 78.68 $ohm^{-1}cm^{2}mol^{-1}$ and the effective magnetic moment was 1.82 BM.

The results of physico-chemical properties of the three complexes are given in table-1.

Table-1 Physico-chemical properties of Co(II), Ni(II) and Cu(II) complexes

S. No.	Complex	Yield, %	Metal, %		Electrical conductivity, $ohm^{-1}cm^{2}mol^{-1}$	μ_{eff}, BM
			Theoretical	Experi-mental		
1	$[Co(PST)_4(ben)_2]$	73.1	3.08	3.16	81.23	4.84
2	$[Ni(PST)_4(ben)_2]$	73.1	3.07	3.12	69.06	3.16
3	$[Cu(PST)_2(ben)_2]$	70.7	5.72	5.55	78.68	1.82

Based on the metal percentage, the molecular formulae of the three complexes are arrived as $[Co(PST)_4(ben)_2]$, $[Ni(PST)_4(ben)_2]$ and $[Cu(PST)_2(ben)_2]$.

The electrical conductance measurements were low, which indicate that the complexes are non electrolyte in nature and of 1:0 type.

Electronic spectra

UV absorption frequencies obtained at 310 nm, 300 nm and 310 nm (Fig.1) for Co(II), Ni(II) and Cu(II) complexes respectively indicate the charge transfer transition[14].

Magnetic moment

The magnetic moment values[15] of the complexes have been calculated from the following equation,

$$\mu_{eff} = 2.828\ \chi m.T$$

The effective magnetic moment (μ_{eff}) of Co(II) complex 4.84 BM and the λ_{max} value observed at 473 nm corresponds to $^4T_{1g}(P) \leftarrow {}^4T_{1g}(F)$[16-17] indicates distorted octahedral geometry.

The effective magnetic moment (μ_{eff}) of Ni(II) complex, 3.16 BM and the electronic transition $^3T_{1g}(F) \leftarrow {}^3A_{2g}$[18], observed at λ_{max} value 660 nm suggests distorted octahedral geometry for the complex.

The λ_{max} values observed at 710 nm corresponds to $^2E_g \leftarrow {}^2B_{1g}$ $^2B_{2g} \leftarrow {}^2B_{1g}$ and $^2A_{1g} \leftarrow {}^2B_{1g}$ and the effective magnetic moment 1.82 BM for Cu(II) complex shows that the complex is having tetragonally distorted octahedral geometry[19].

The UV-visible spectra for the three complexes recorded are given in fig.1.

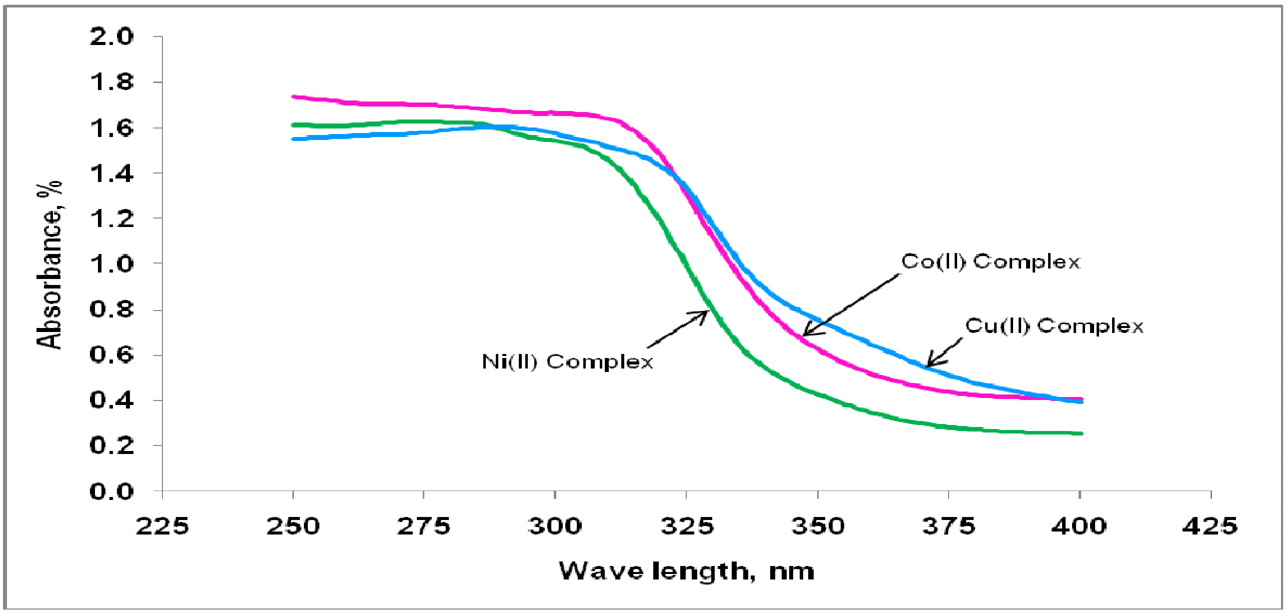

Fig.1 UV-Visible spectra of Co(II), Ni(II) and Cu(II) complexes

IR Spectra

In IR spectrum, the PST ligand exhibited frequencies at 1332cm^{-1}, 1635cm^{-1}and 3144cm^{-1} which are assignable to the **ν**(S=O) stretching, **ν**(C=O) stretching[19] and **ν**(N-H) stretching vibrations respectively. These vibrations are found at the frequencies of 1390 cm^{-1}, 1670 cm^{-1} and 3244 cm^{-1} in Co(II) complex, 1392 cm^{-1}, 1635cm^{-1} and 3141 cm^{-1} in Ni(II) complex and 1400 cm^{-1}, 1585 cm^{-1} and 3107 cm^{-1} in Cu(II) complexes and this ensures the entry of PST in to the coordination sphere.

In the IR spectrum of benzoate ligand, frequencies observed at 1307cm^{-1} and 1602cm^{-1} are assignable to **ν**(C-O) and **ν**(C=C) stretching vibrations. These vibrations are found at the frequencies of 1390 cm^{-1} and 1670 cm^{-1} in Co(II) complex, 1330 cm^{-1} and 1535 cm^{-1} in Ni(II) complex and 1321 cm^{-1}and 1585 cm^{-1} in Cu(II) complexes. This ensures the entry of benzoate ligand into the coordination sphere[20]. The IR spectral data are given in table-2 and the IR spectra recorded are given in fig.2.

Table-2 IR spectral data for Co(II), Ni(II) and Cu(II) complexes and ligands (cm^{-1})

S. No.	Complex/Ligand	ν (S=O) stretch	ν (C=O) stretch (PST)	ν (N-H) stretch (PST)	ν (C-O) stretch (ben)	ν (C=C) stretch (ben)
1	$[Co(PST)_4(ben)_2]$	1390	1670	3244	1390	1670
2	$[Ni(PST)_4(ben)_2]$	1392	1635	3141	1330	1535
3	$[Cu(PST)_2(ben)_2]$	1400	1585	3107	1321	1585
4	PST	1332	1635	3144	-	-
5	ben	-	-	-	1307	1602

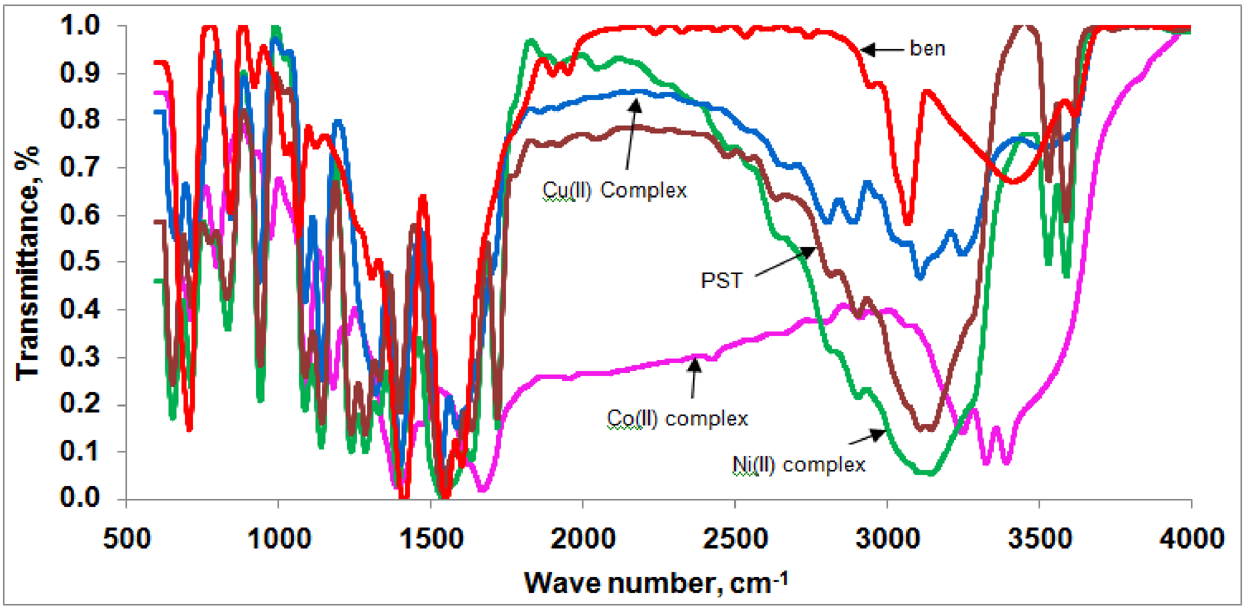

Fig.2 IR Spectra of Co(II), Ni(II) and Cu(II) complexes, PST and ben ion

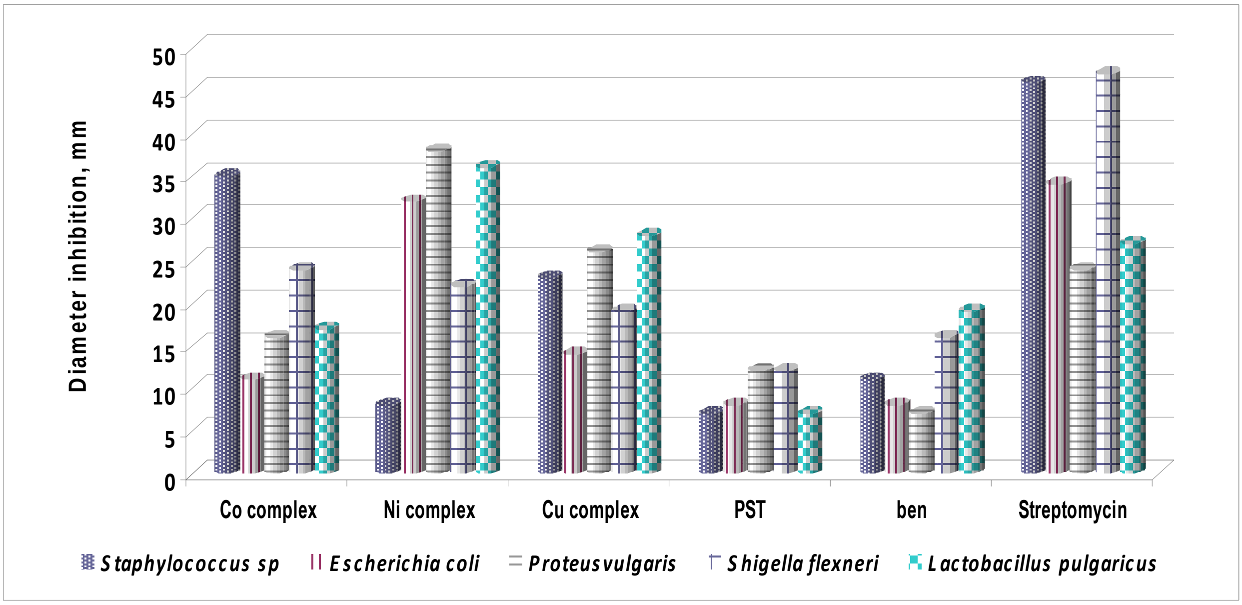

Fig.3 Comparison of antibacterial activities of Co(II), Ni(II) and Cu(II)complexes against pure PST and ben ligands and streptomycin (standard)

Biological activities

Antibacterial activity

All the three complexes exhibit enhanced antibacterial activity than the pure ligands. $[Co(PST)_4(ben)_2]$ is found to be highly active against *Staphylococcus sp* and *Shigella flexneri.* $[Ni(PST)_4(ben)_2]$ shows higher activity against *Escherichia coli*, *Proteus vulgaris* and *Lactobacillus pulgaricus* than the standard, streptomycin. $[Cu(PST)_2(ben)_2]$ exhibits high activity against *Staphylococcus sp., Proteus vulgaris, and Lactobacillus pulgaricus.* The results of antibacterial activities (diameter inhibition) at 100 µgml^{-1} concentration of complex/ligand are given in table-3 and graphically in fig.3.

Table-3 Antibacterial activity of Co(II), Ni(II) and Cu(II) complexes, PST and ben ligands and streptomycin (standard) (Diameter inhibition in mm at 100µgml^{-1} concentration)

S.No.	Complex/Ligand	*Staphylo-coccus sp.*	*Escherichia coli*	*Proteus vulgaris*	*Shigella flexneri*	*Lactobacillus pulgaricus*
1	[Co(PST)$_4$(ben)$_2$]	35	11	16	24	17
2	[Ni(PST)$_4$(ben)$_2$]	8	32	38	22	36
3	[Cu(PST)$_2$(ben)$_2$]	23	14	26	19	28
4	PST	7	8	12	12	7
5	ben	11	8	7	16	19
6	Streptomycin (standard)	46	34	24	47	27

Anti fungal activity

All the three complexes show higher anti fungal activity than PST, but less anti fungal activity when compared to the standard, ketoconazole. [Co(PST)$_4$(ben)$_2$] and [Cu(PST)$_2$(ben)$_2$] showed high activity against *Candida albicans, Aspergillus niger and Aspergillus flavus.* [Ni(PST)$_4$(ben)$_2$] show high activity against *Candida albicans, Aspergillus oryzae* and *Aspergillus sojae.* The results of anti fungal activities (diameter inhibition) at 400 µgml^{-1} concentration of complex/ligand are given in table-4 and graphically in fig.4.

Table-4 Anti fungal activity of Co(II), Ni(II) and Cu(II) complexes, PST and ben ligands and ketoconazole (standard) (Diameter inhibition in mm at 400µgml^{-1} concentration)

S.No.	Complex/Ligand	*Candida albicans*	*Aspergillus oryzae*	*Aspergillus niger*	*Aspergillus flavus*	*Aspergillus sojae*
1	[Co(PST)$_4$(ben)$_2$]	29	16	30	34	4
2	[Ni(PST)$_4$(ben)$_2$]	46	36	13	14	30
3	[Cu(PST)$_2$(ben)$_2$]	39	14	28	26	16
4	PST	4	7	12	8	4
5	ben	22	22	24	16	13
6	Ketoconazole (standard)	86	91	94	89	92

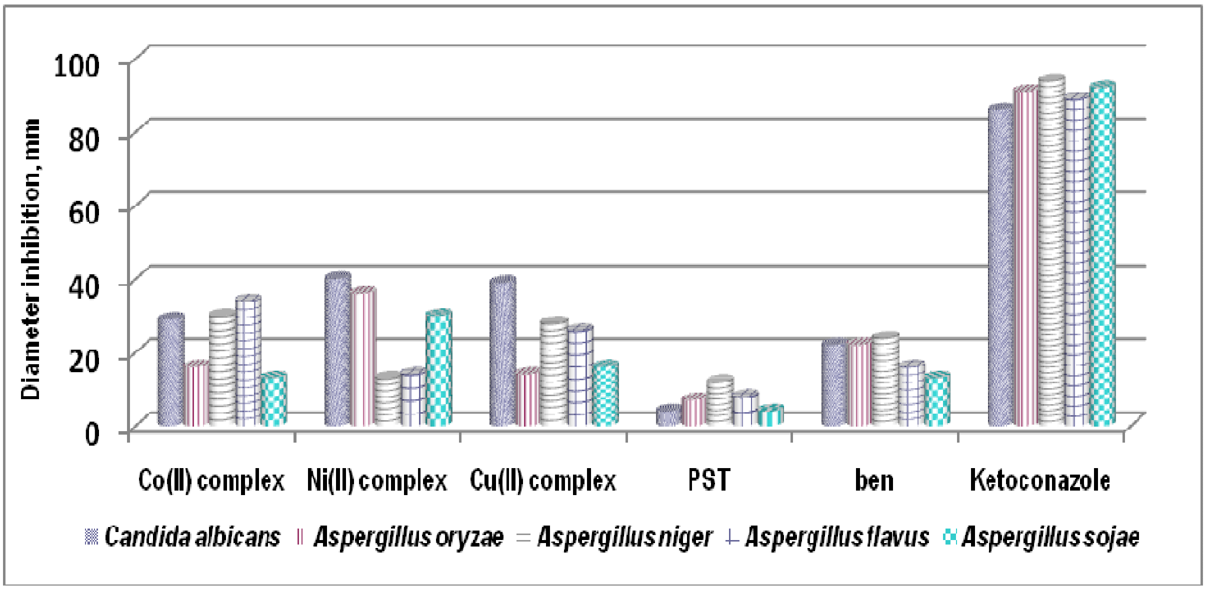

Fig.4 Comparison of anti fungal activities of Co(II), Ni(II) and Cu(II)complexes against pure PST and ben ligands and ketoconazole (standard)

Antioxidant activity

All the three complexes show lower inhibition of DPPH free radical scavenging activity at a concentration of 1000 µgml^{-1} than the standard, Vitamin-C. The rate of increase in the DPPH free radical scavenging activity with increase in complex/ligand concentration is also low. The percentage inhibition of Co(II), Ni(II) and Cu(II) complexes are 22.35, 26.95 and 18.89 respectively. The results of inhibition at various concentrations of complex/ligand are given in table-5 and graphically in fig.5.

Table-5 Antioxidantal activity of Co(II), Ni(II) and Cu(II) complexes DPPH free radical scavenging activity (percentage inhibition)

S. No.	Concentration, µgml^{-1}	Co(II) complex	Ni(II) complex	Cu(II) complex	PST	ben	Vitamin-C
1	1000	22.35	26.95	18.89	13.07	7.66	-
2	500	21.16	22.84	18.45	10.49	5.20	90.23
3	250	20.29	21.86	18.51	2.62	2.98	92.03
4	125	19.75	20.83	18.83	3.03	3.03	93.22
5	62.5	18.99	20.29	15.85	4.12	2.88	93.09
6	31.3	18.72	18.94	16.23	4.01	3.03	88.92
7	15.6	17.97	18.07	15.96	4.22	2.93	75.23
8	7.81	17.53	15.53	14.07	4.12	3.03	38.72
9	3.90	16.24	12.72	11.53	3.96	3.03	25.68
10	1.95	15.42	10.71	7.47	3.86	2.31	11.99

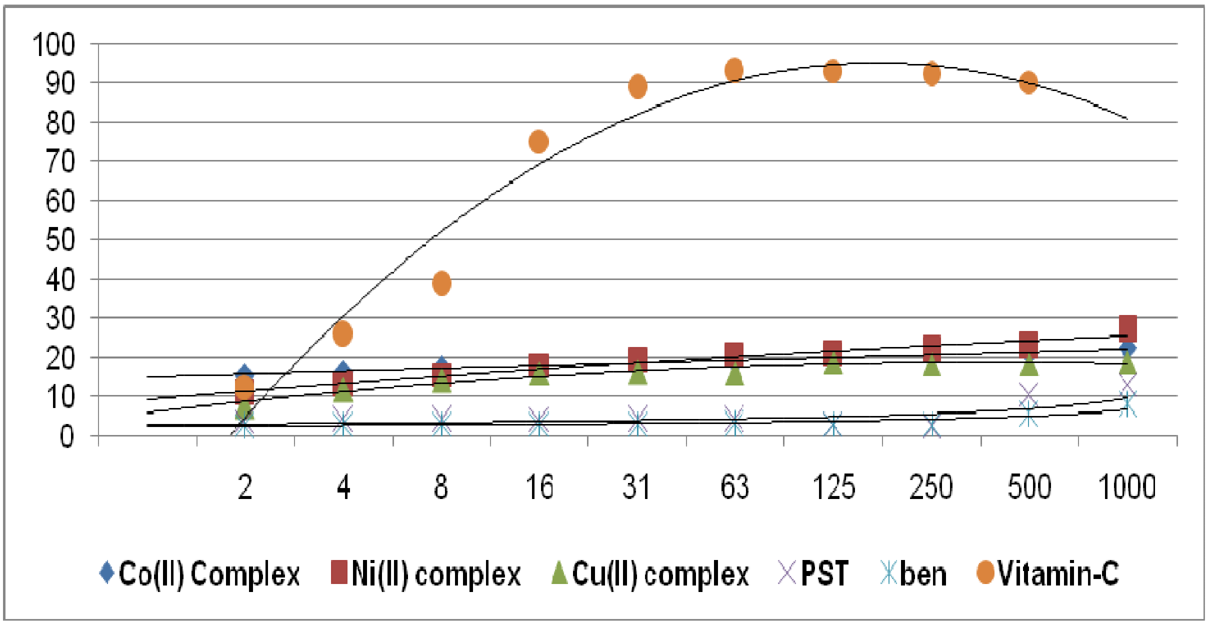

Fig. 5 Antioxidantal activity of Co(II), Ni(II) and Cu(II)complexes against pure PST and ben ligands and Vitamin –C (standard) (Percentage inhibition against concentration of complexes/ligands)

CONCLUSION

From the analytical data, UV-visible and IR spectral studies, the molecular formulae and their probable geometry were arrived at for the complexes. All the three complexes show higher antibacterial activity than pure ligands. Ni(II) complex exhibit higher antibacterial activity against *Proteus vulgaris* and *Lactobacillus pulgaricus* than the standard streptomycin. The anti fungal activities of the complexes are high when compared to PST, but less than ben. The antioxidantal activities of the complexes are low when compared to the standard, Vitamin-C.

Acknowledgements

The authors are thankful to the Principal and Management, Bishop Heber College (Autonomous), Tiruchirappalli for providing the laboratory facilities. They express their gratitude to the Principal and Head of Department of Chemistry, Holy Cross College (Autonomous), Tiruchirappalli for their support. They also thank the Management of Tamilnadu Newsprint and Papers Limited (TNPL), Kagithapuram, Karur for encouragement and support.

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