



Research Article

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Synthesis, characterization and biological study of some new metal-azo chelate complexes

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ABSTRACT

Four metal-azo chelate complexes of Co(III), Ni(II), Cu(II) and Zn(II) have been synthesized from the azo ligand 1-[(6-Methyl-2-benzothiazolyl)-azo]-2-naphthol-4-sulfonic acid (BANS) and characterized by elemental analysis, spectral (Mass, IR, and UV-Vis for azo ligand), magnetic moment measurements and molar conductance studies. The electronic absorption spectra and magnetic susceptibility measurements of chelate complexes indicate octahedral geometry for all prepared complexes. The important infrared (IR) spectral bands corresponding to the active groups in the ligand and its solid complexes under investigation were studied and implies that (BANS) is coordinated to the metal ions in a mono negative tridentate manner. Finally the invitro biological screening effects of this azo ligand and its chelate complexes were tested against the bacterial species *Staphylococcus aureus*, *Enterococcus*, *Streptococcus viridians*, *Escherichia coli*, *Pseudomonas aeruginosa* and *Klebsiella pneumonia* and fungal species *Aspergillus niger* and *Aspergillus flavus* by well diffusion method. The antimicrobial activity data showed that chelate complexes are more than of the free ligand.

Key words: Thiazolyl azo ligand (BANS), Complexes of Co(III), Ni(II), Cu(II) and Zn(II), Biological study

INTRODUCTION

A large number of multidentate ligands have been synthesized and investigated for metal binding characteristics. Several such ligands possessing (–N=N–) grouping are known as azo ligands [1-3]. Thiazolylazo ligands are organic compounds easily prepared by the diazotization of 2-aminothiazole and its derivatives. The intermediary diazotate form is highly reactive that it has to be coupled with phenolic or other aromatic substances in alkaline solutions at low temperature (0 °C to –5 °C) to yield azo dyes [4-6]. This type of molecules has several advantages. Some of them are used as analytical reagents [7,8], non-linear optics [9,10], and another of them have also proved to be particularly useful as disperse dyes [11]. For a thiazolylazo ligand which has a hydroxyl group in the *ortho* position relative to the azo group, the metal ion is bonded to the oxygen of the hydroxyl group, the azo group and the nitrogen atom of the hetero cyclic thiazole ring, forming to five-membered chelate rings [12]. The metal complexes with organic molecules containing nitrogen, sulfur and oxygen including the study of the biological activity are great interesting [13-15].

This paper describe the synthesis characterization and biological study of new cobalt (III), nickel (II), copper (II) and zinc(II) chelate complexes with the azo ligand, (BANS= H₂L).

EXPERIMENTAL SECTION

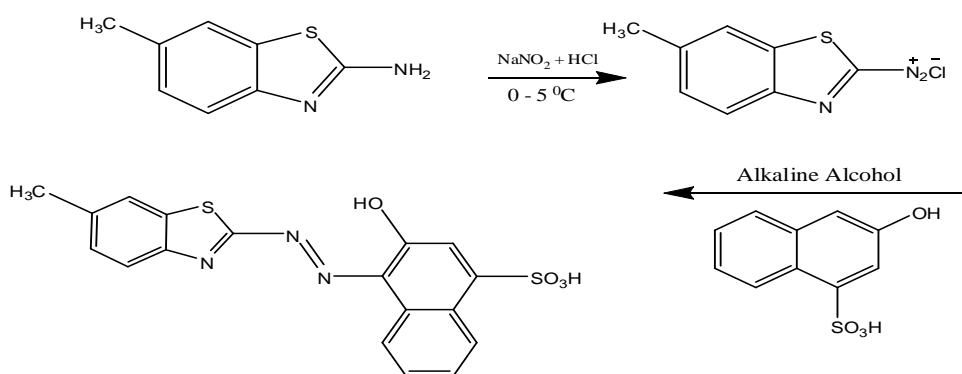
Materials and measurements

All reagents and solvents were obtained from commercial sources and used as received. Mass spectrum of ligand was recorded on mass spectrometer agilent technologies 5975 at 70 ev and MSD energy. Elemental analyses were carried out by means of Micro analytical unit of 1108 C.H.N Elemental analyzer. IR spectra were recorded using

KBr discs $4000\text{--}400\text{ cm}^{-1}$ on FT-IR Testscan Shimadzu model 8000. UV – Vis. Spectra were recorded in ethanol on Shimadzu model 1700 UV–Vis Spectrophotometer. Magnetic susceptibilities were measured as powder samples using Faraday method, Balance Magnetic (Sherwood Scientific) was employed for this purpose. The diamagnetic corrections were made by Pascal's constants [16]. The metal content of the complexes was measured using atomic absorption technique by (Phoenix-986 AA). Molar conductance measurements were determined in DMF by using a Inolab Multi 740, WTW 82362 Weilhiem conductivity meter. pH measurements were carried out using WTW pH meter model 720. Stuart melting point SMP10 was used to measure the melting points of the ligand and its complexes.

Synthesis of 1-[(6-Methyl-2-benzothiazolyl)-azo]-2-naphthol-4-sulfonic acid

(BANS = H_2L) azo ligand was prepared according to the following general procedure [17] (Scheme.1), 2-amino-6-methylbenzothiazole (1.64 g, 10mmol) was dissolved in 30 ml of water and 6 ml of concentrated hydrochloric acid. The filtered solution was diazotized at ($-5\text{ }^\circ\text{C}$) 12 ml of aqueous (1.0 M) sodium nitrite. The resulting diazonium chloride solution was added drop wise with string to the 2-naphthol - 4- sulfonic acid (2.24 g, 10 mmol) dissolved in 200 ml alkaline ethanol cooled below 0°C . After leaving in the refrigerator for 24 hour, the mixture was acidified with dilute hydrochloric acid until (pH = 6). The precipitate was filtered off, and recrystallized twice from hot ethanol, and dried in a vacuum desiccator.



Scheme.1: Syntheses of the (BANS = H_2L) ligand

Synthesis of the metal complexes

The metal chelate complexes were synthesized by reacting (0.5 mmole) ethanolic solutions of each metal(II) chloride 10 ml separately with 50 ml ligand solution of (BANS = H_2L) (0.399 g, 0.1 mmol) in hot ethanol in 1:2 (M : L) molar ratio and were refluxed for 30 min. The complexes were precipitated after cooling the reaction mixture at room temperature and were filtered. The pure products were obtained by washing the compound twice with hot ethanol and finally with diethyl ether, and dried in a desiccator over anhydrous CaCl_2 at room temperature.

Antimicrobial activity studies

Antibacterial activity

The invitro antibacterial effects of the synthesized the ligand and its metal complexes were tested against six pathogenic bacteria representative three Gram-positive bacteria namely Staphylococcus aureus, Enterococcus and Streptococcus viridians and three Gram-negative bacteria namely Escherichia coli, Pseudomonas aeruginosa and Klebsiella pneumonia by agar well diffusion method using Muell-Hinton agar (MHA) as medium [18]. Wells of 6 mm in diameter were made in the agar plates by using sterile cork borer, then agar surfaces were inoculated with each bacterium. The tested compounds were dissolved in dimethyl sulfoxide (DMSO) to obtain a solution 1000 ppm concentration. The plates were incubated at $37\text{ }^\circ\text{C}$ for 24 hour during which activity was evidenced by the presence of a zone of inhibition surrounding the well, the zones of inhibition formed were measured in mm. Each experiment was performed in triplicate and the average of three age of the three determinations was recorded.

Antifungal activity

The antifungal activity of the ligand and their metal complexes were evaluated in (DMSO) against two fungal, namely, Aspergillus niger and Aspergillus flavus by agar well diffusion method [19] at 10, 100 and 1000 ppm concentrations with triplicate determinations in each case. The average percentage inhibition was calculated using the following formula [19,20]. Inhibition (%) = $(C-T) 100 / C$.

Were C is diameter of colony fungus in center plates and T is diameter of the colony fungus in the test plates.

RESULTS AND DISCUSSION

Azo ligand characterization

The azo ligand (H_2L) is subjected to elemental analyses. The results of elemental analyses (C, H and N) with molecular formula and the melting points are presented in Table 1. The results obtained are in good agreement with those calculated for the suggested formula. The sharp melting point indicating the purity of this ligand. The Scheme of the thiazolyl azo compound syntheses is given by Scheme.1. The structure of this ligand is also confirmed by Mass and IR spectra, which will be discussed in detailed manner together with its metal chelate complexes later.

Table.1: Some physical properties and analytical data of ligand (BANS) and its chelate complexes

No	Compound	Color	m.p C°	Yield %	Molecular formula (Mot. Wt)	Found (Calc.)%			
						C	H	N	M
1	(BANS = H_2L)	Orange	182- 183	67	$C_{18}H_{13}N_3S_2O_4$ (399.23)	54.58 (54.13)	3.17 (3.25)	10.65 (10.52)	—
2	$[Co(HL)_2]Cl$	Dark red	223d	64	$C_{36}H_{24}N_6S_4O_8ClCo$ (890.38)	48.29 (48.51)	2.58 (2.69)	9.63 (9.43)	683 (6.61)
3	$[Ni(HL)_2]$	Deep brown	290-291	68	$C_{36}H_{24}N_6S_4O_8Ni$ (854.69)	50.47 (50.62)	2.74 (2.80)	9.93 (9.82)	6.64 (6.86)
4	$[Cu(HL)_2]$	Purple	250-251	72	$C_{36}H_{24}N_6S_4O_8Cu$ (859.54)	50.43 (50.25)	2.68 (2.79)	9.82 (9.77)	7.57 (7.38)
5	$[Zn(HL)_2]$	Red	215-216	75	$C_{36}H_{24}N_6S_4O_8Zn$ (861.38)	50.37 (50.15)	2.66 (2.78)	9.84 (9.75)	7.75 (7.59)

Mass spectrum of azo ligand (BANS)

The mass spectrum of the free ligand, confirms the proposed formula by showing a molecular ion peak (m/z) at 399 (M^+) with a relative intensity 18% corresponding to the ligand moiety [$(C_{18}H_{13}N_3O_4S_2)$ atomic mass 399 u], and the main mass fragmentation of the azo ligand is given in the Fig.1. The series of peaks in the range i.e. 77, 127, 162, 164, 207, 222 and 237 etc, may be assigned to various fragments.

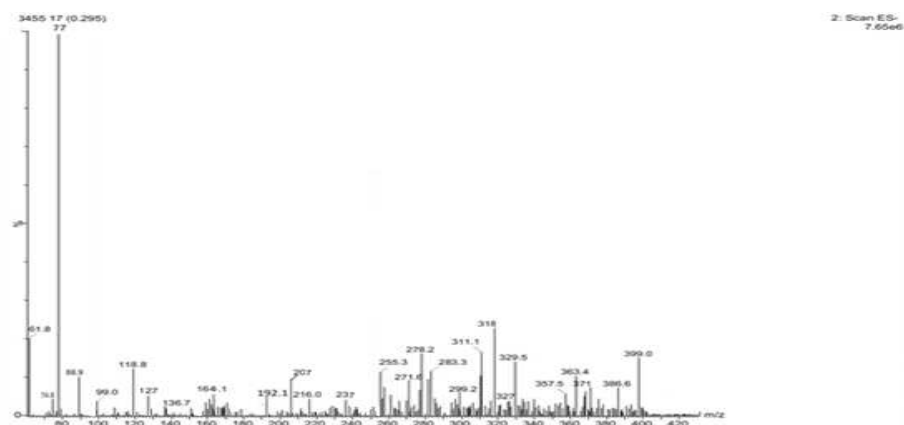


Fig.1: The mass spectrum of azo ligand (BANS)

Infrared spectra

The infrared spectra of the free azo ligand (BANS) and its metal complexes with Co(III), Ni(II), Cu(II) and Zn(II) are given in Table 2. These spectra are complicated owing to the extensive overlap of number of bands arising from ν (O—H), ν (C=N), ν (—N=N—) and other bands due to the phenyl and thiazole rings which appeared in the region below 1595 cm^{-1} . The comparisons between the IR spectral data of the free ligand with that of its complexes are discussed as follows:

1- The spectrum of azo ligand shows a very broad and weak absorption band around 3450 cm^{-1} due to the ν (O—H) of hydroxyl and sulfonic groups. This suggests a strong intermolecular hydrogen bonding [21]. The bands around $(3420 - 3400)\text{ cm}^{-1}$ in all chelate complexes spectra indicates non-involvement of sulfonic group in coordination, and is in accordance with earlier reports [22-23].

2- The weak bands which observed at 3105 cm^{-1} and 2960 cm^{-1} in the ligand spectrum are due to ν (C—H) aromatic and aliphatic respectively. These bands are stable in position in both ligand and metal complexes [24].

3- The spectrum of ligand shows absorption band at 1595 cm^{-1} due to $\nu(\text{C}=\text{N})$ of thiazole ring [25]. This band is observed with a little change in shape and shifted to lower frequencies ($1585 - 1575$) cm^{-1} in complexes. These differences may suggest the linkage of metal ions with nitrogen of heterocyclic thiazole ring [21].

4- The azo group ($-\text{N}=\text{N}-$) appears at 1520 cm^{-1} in the free ligand spectrum. This band has been shifted to a lower frequencies ($1500 - 1490$) cm^{-1} and also reduced in intensity in complexes spectra, this means that some linkage of metal ions with nitrogen atom of azo group which is the farthest of thiazol ring takes place[26].

5- The weak band at 1250 cm^{-1} has also been appeared in the ligand spectrum which is due to $\nu(\text{C}-\text{S})$ of thiazole ring [27]. The fixed position of this band in all chelate complexes means that the sulfur atom of heterocyclic ring does not participate in coordination [21].

6- Finally, the IR spectra of the complexes exhibited new non-ligand bands in the range ($445 - 430$) cm^{-1} and in the range ($435 - 420$) cm^{-1} assigned as $\nu(\text{M}-\text{O})$ and $\nu(\text{M}-\text{N})$ stretching vibrations, respectively. There fore, it can be concluded that (BANS) ligand binds to the metal ions through phenolic oxygen, nitrogen of azo group and thiazole ring nitrogen and the ligand behaves as mono negative tridentate ligand [28].

Table. 2: Characteristic IR absorption bands of azo ligand (BANS) and Its chelate complexes in cm^{-1} units

No.	Compound	$\nu(\text{O}-\text{H})$	$\nu(\text{C}=\text{N})$	$\nu(\text{N}=\text{N})$	$\nu(\text{C}-\text{S})$	$\nu(\text{M}-\text{O})$	$\nu(\text{M}-\text{N})$
1	H_2L	3450 wbr.	1595 m	1520 m	1250 w	—	—
2	$[\text{Co}(\text{HL})_2]$	3400 Wbr	1575 m	1495 m	1245 w	545 w	435 w
3	$[\text{Ni}(\text{HL})_2]$	3410 Wbr	1575 m	1490 m	1250 w	540 w	425 w
4	$[\text{Cu}(\text{HL})_2]$	3420 Wbr	1580 s	1495 m	1250 w	530 w	430 w
5	$[\text{Zn}(\text{HL})_2]$	3410 Wbr	1585 m	1500 m	1245 w	545 w	420 w

$\text{H}_2\text{L} = (\text{BANS})$, w=weak, s=strange, m= medium, br=broad

Metal: ligand ratio

The (metal: ligand) ratios of complexes were determined by molar ratio method at fixed concentration and pH at wavelengths of maximum absorption. The results are given in Table 3, the ligand was found to form (2: 1) chelates with all metal ions, and these results are in agreement with the values reported for some thiazolyazo phenol complexes [29].

Molar Conductance Measurements

The metal-azo complexes were dissolved in DMSO and the molar conductivities of (10^{-3} M) of their solutions were measured at room temperature. The conductance values of the Co(III) complexes support their electrolytic nature (1:1) types while Ni(II), Cu(II) and Zn(II) complexes are non ionic in nature and non electrolytes. The data are listed in Table 3.

Magnetic measurement and Electronic spectra

The spectral data and the magnetic moment of syntheses complexes are listed in Table.3. The magnetic moment of the Cobalt (II) has been found to be diamagnetic and the low spin behavior of this complex indicates that Co(II) ion is oxidized to Co(III) during complexation. The change of the oxidation state agrees with earlier observation that the aqueous solution of Co(II) salts are spontaneously oxidized to Co(III) in the presence of strong ligand such as thiazolyazo compounds [30]. The electronic spectrum of this complex shows two absorption bands at 556 nm 17985 cm^{-1} and 441 nm 22675 cm^{-1} they are assigned to $^1\text{A}_1\text{g} \rightarrow ^1\text{T}_1\text{g}$ and $^1\text{A}_1\text{g} \rightarrow ^1\text{T}_2\text{g}$ transitions respectively, which are characteristic of octahedral stereo chemistry [31]. For the Nickel (II) complex, its magnetic moment (3.10 B.M), and (d→d) spectrum of this complex show bands at 989 nm 10110 cm^{-1} , 523 nm 19120 cm^{-1} and 316 nm 31645 cm^{-1} , which are suggesting the existence of $^3\text{A}_2\text{g} \rightarrow ^3\text{T}_2\text{g}(\text{F})$, $^3\text{A}_2\text{g} \rightarrow ^3\text{T}_1\text{g}(\text{F})$ and $^3\text{A}_2\text{g} \rightarrow ^3\text{T}_1\text{g}(\text{p})$ transitions respectively with an octahedral spatial configuration [32]. The magnetic moment value of the copper (II) complex (1.71 B.M) suggests the presence of one unpaired electron in this complex. It's electronic spectrum shows band centered at 675 nm 14815 cm^{-1} which may assigned to $^2\text{E}_2\text{g} \rightarrow ^2\text{T}_2\text{g}$ transition in distorted octahedral environment [33]. Zinc (II) complex is diamagnetic and the electronic spectrum of this chelate compound exhibit high intense charge transfer transition in the visible region 570 nm 17543 cm^{-1} which is assigned to (MLCT) [34].

Table 3 : Electronic Spectra, Conductivity measurements, Magnetic moment, Metal : Ligand ratios and Optimal pH values of metal-azo complexes

Complex	Absorption bands (cm ⁻¹)	Transition	Conductivity S.cm ² .mol ⁻¹	μ_{eff} B.M	Metal:Ligand	Optimal pH
[Co(HL) ₂]Cl	17985	¹ A _{1g} → ¹ T _{1g}	75.84	dia	(1 : 2)	7.0
	22675	¹ A _{1g} → ¹ T _{2g}				
[Ni(HL) ₂]	10110	³ A _{2g} → ³ T _{2g} (F)	6.34	3.09	(1 : 2)	8.5
	19120	³ A _{2g} → ³ T _{1g} (F)				
	31645	³ A _{2g} → ³ T _{1g} (p)				
[Cu(HL) ₂]	14815	² E _g → ² T _{2g}	7.93	1.76	(1 : 2)	6.0
[Zn(HL) ₂]	570	C.T	11.53	dia	(1 : 2)	7.5

According to these results the structural formula of syntheses complexes in this paper may be proposed as shown in Fig. 2.

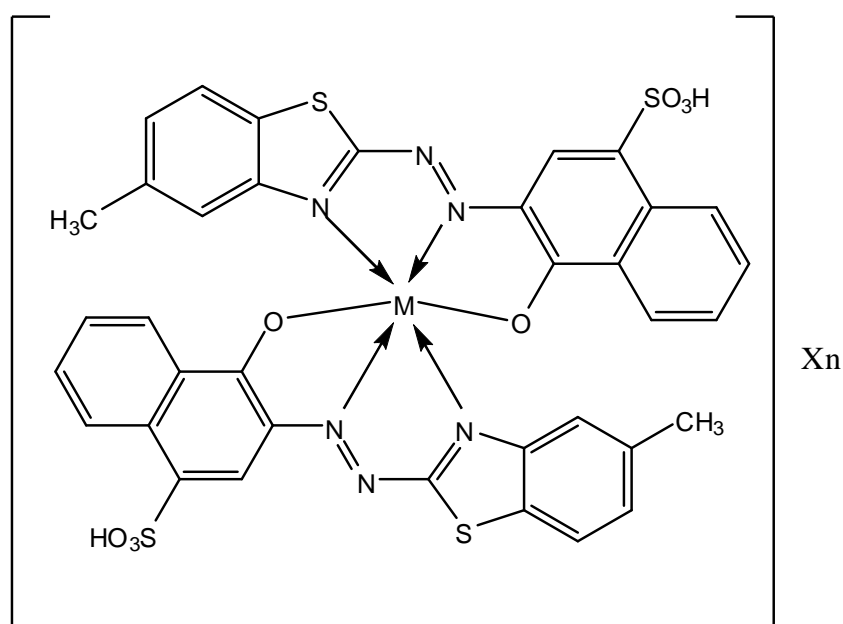


Fig. 2 : structural formula of Metal complexes

$M = \text{Co(III)}, \text{Ni(II)}, \text{Cu(II)}, \text{Zn(II)}$, where $M = \text{Co}$ $X = \text{Cl}$ $n = 1$

Antimicrobial activity studies

The antibacterial effect of the azo ligand (BANS) and chelate complexes have been tested for invitro growth inhibitory against both Gram-positive and Gram-negative bacteria. All of tested compounds exhibited a remarkable antibacterial activity against tested bacteria. The results are listed in Table.4, and its statistical presentation is shown in Fig. 3 shows that the metal complexes are more active than the free ligand and such enhanced activity of metal chelates is due to the lipophilic nature of the metal ions in complexes [35]. It also suggests that the complexes posses antibacterial activity inhibiting multiplication process of the microbes by blocking their active sites [36]. The ligand shows slight effect against all tested bacteria strains except *S.aureus* and *E.coli* moderate activity. The cobalt(III) complex was exhibited moderate activity to most bacteria with the exception of *P.aeruginosa* slight effect, the nikle(II) complex was exhibited higher antibacterial activity against all bacteria except *P.aeruginosa* and *K.pneumonia* moderate effect. The Cu(II) and Zn(II) complexes were moderate effect against all tested bacteria. From *invitro* antifungal activity Table. 5 data reveals that the metal complexes indicates higher antifungal activity than the free ligand. A comparative study of the compounds was shown significant toxicity at 1000 ppm con. , all species of fungi. However, all metal complexes are more active than the free ligand and antifungal activity decrease on dilution. Also, it was observed that compounds exhibit more significant effect *A.niger* than *A.flavus*. The variation in the activity of different complexes against tested microbial depends on either the impermeability of cells of the microbes or difference in ribosomes of microbial cell [37]. The higher biological activity of metal complexes than that free ligand can be explained on the basis of Overtone's concept and Tweedy's chelation theory [38]. On chelation, metal ion polarity is reduced to a greater extent due to the overlapping of the ligand orbital and partial sharing of positive charge of metal ion with donor groups [39]. Further, the delocalization of the π -electron is increased over the whole chelate sphere and enhances the lipophilicity of the complex. The lipophilic nature of the central metal atom is also increased upon chelation, which subsequently favors the permeation through the lipid

layer of cell membrane [40]. The differences in antimicrobial activity is due to the nature of metal ions and also the cell membrane of the microorganisms.

Table 4 : Antibacterial activity data (zone of inhibition in mm) of the ligand and their metal complexes

Compound Bacteria	G (+ve)			G (-ve)		
	<i>S.aureus</i>	<i>Entro.</i>	<i>S.viridan</i>	<i>E-coli</i>	<i>P.aeruginosa</i>	<i>K.pneumonia</i>
BANS	++	+	+	++	+	+
[Co(BANS) ₂]Cl	++	++	++	++	+	++
[Ni(BANS) ₂]	+++	+++	+++	+++	++	++
[Cu(BANS) ₂]	++	++	++	++	++	++
[Zn(BANS) ₂]	++	++	++	++	++	++

Note: High activity = +++ inhibition zone > 12mm Moderate = ++ inhibition zone = 9-12mm and Slight = + inhibition zone = 6-8mm

Table 5: Antifungal activity data of the ligand and their metal complexes

Compound Fungi	Average percentage inhibition (%) after 72h					
	<i>A.flavus</i>			<i>A.niger</i>		
	10	100	1000	10	100	1000
BANS	30	42.2	48.9	37.8	47.8	56.7
[Co(BANS) ₂]Cl	47.8	55.7	66.7	54.1	63.3	67.6
[Ni(BANS) ₂]	53.3	56.7	64.4	57.8	64.4	76.7
[Cu(BANS) ₂]	56.7	59.9	62.2	55.6	60	68.9
[Zn(BANS) ₂]	45.6	54.1	58.9	53.3	57.8	61.1

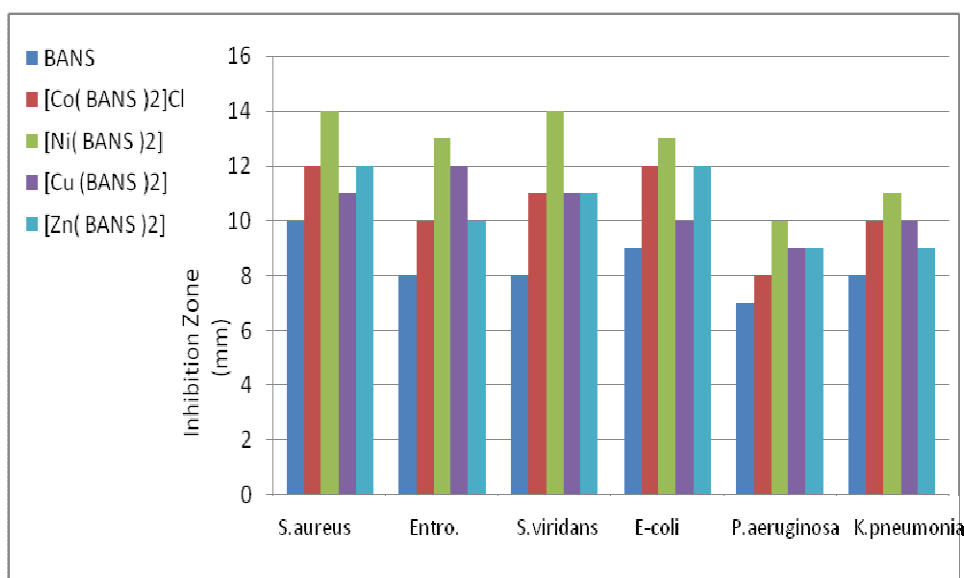


Fig.3 : Statistical representation for antibacterial activity of ligand (BANS) and its metal complexes

CONCLUSION

The spectral, molar conductance and magnetic studies of the synthesized thiazolyl azo ligand and its metal-azo chelate complexes of Co(III), Ni(II), Cu(II) and Zn(II) have shown octahedral geometry. The ligand acts as mono anionic tridentate ligand. The complexes are biologically active and show enhanced antimicrobial activity compared to free ligand.

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