

Synthesis ,charactrazion and biological studies of metalscomplexes with Schiff base from sulfadiazine and teraphthaldyhyde

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Abstract:

Some new complexes of Schiff base ligand derived from sulfadiazine and terephthalaldehyde with Cu(II), Ni(II), Fe(II) ions were synthesized and characterized by UV-Vis spectral analysis, Fourier transform infrared spectroscopy (FT-IR), ^1H - NMR, biological activity. The UV-Visible spectrophotometric analysis revealed 1:2 (metal-ligand) stoichiometry for all complexes and assigned an octahedral geometry. While the appearance of $\nu(\text{O-H})$ due to water molecules in all complexes and the lowering shift of the stretching frequency of the $\nu(\text{CH=N})$ azomethine band in the ligand after complexation, the Schiff base ligand showed higher significant activity against one or more bacterial compared with complexes.

Keywords : Sulfadiazine , Schiff base ,metal complexes, biological activity.

INTRODUCTION

Schiff bases derived from amino and carbonyl compound are an important class of ligands that coordinate to metal ions via azomethine nitrogen and have been extensively. In azomethine derivatives, the $-\text{CH=N}-$ linkages is essential for biological activity[1], several azomethine were reported to possess a remarkable antibacterial, antifungal, anticancer and diuretic activities, Schiff bases have wide application in food chemistry[2], dye industry, analytical chemistry, catalysis, fungicidal, agrochemical and biological activities, sulfa drugs which were the synthetic antimicrobial agents from p-amino benzenesulphonamide[3] and are primarily bacteriostatic in action, their antibacterial activity is thought to arise from similarity of their structure to the p-amino benzoic acid found in bacterial for folic acid synthesis[4], the sulpha drugs can be enhanced upon coordination with a suitable metal ion[5,6], Schiff bases are among the most studied sulfa drug derivatives which have been used for numerous biological applications[7,8]. In this paper, we therefore, present the synthesis, characterization and biological studies Cu(II), Fe(II), and

Ni(II) complexes of Schiff base derived from sulfadiazine and terephthalaldehyde.

EXPERIMENTAL

Chemicals

Sulfadiazine (Fluka), terephthalaldehyde (Fluka), Copper Sulfate. pentahydrate, Nickel sulfate. heptahydrate and Iron sulfate. heptahydrate (Fluka), Ethanol absolute, DMF, and Acetic acid (BDH).

Instruments

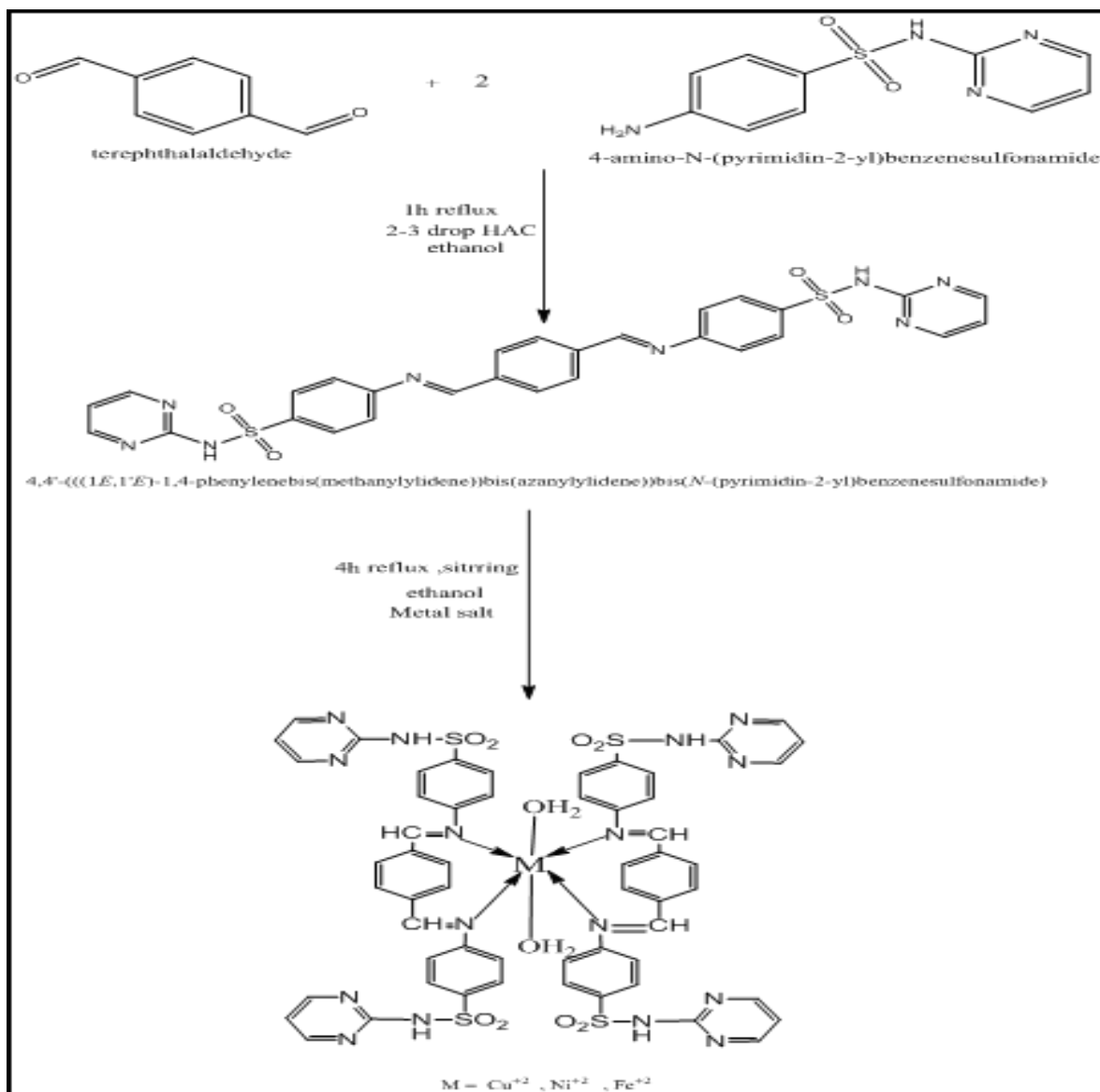
Melting points were recorded on Gallenkamp melting points apparatus without correction, IR Spectra were measured on Shimadzu 8400S spectrophotometer as KBr pellets in the region $4000-600\text{cm}^{-1}$, UV-Vis spectrometer Cary(100) conc The ^1H NMR spectra were recorded in DMSO- d_6 on Bruker 500MHz spectrometer using TMS an internal standard. Molar conductivities of 10^{-3} M solutions of the solid complexes in DMF were measured on the using Jenway 4010 conductivity meter, Magnetic measurements were measured by the Gouy method at room temperature using a magnetic susceptibility balance (Johnson Matthey alfa product, Model No. MKI).

Synthesis of Schiff bases ligand (S_2T)

Schiff base was prepared by dissolving (0.5 g, 2mmol) of sulfadiazine in 50ml absolute ethanol and (0.134g, 1mmol) terephthalaldehyde in 50ml absolute ethanol in 250ml round flask, the mixture was heated with reflux for 4 hours, during which the color of the solution changes to pale green. The formed pale green solid product was left to coagulate, then filtered off and was recrystallized from absolute ethanol. the yield was (88%), its melting point was 298°C Scheme(1)..

General procedures for synthesis of the metal complexes

The following general procedures were used for preparing all of the complexes under investigation like that of Cu(II) complex: A solution of the $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (0.249 g, 2mmol) in 25ml absolute ethanol was added to solution of ligand (S_2T) (1.068 g, 1mmol) 25ml absolute ethanol with the molar ratio 2:1 (ligand : metal) the reaction mixture was heated to reflux for 24h. The color of solution was green in the beginning of reaction and then became pale green at the end the reaction, on cooling solid formed, the solid separated was filtered and washed with ethanol and then air-dried, the yield were between (62-84%) Scheme(1).



Scheme(1) synthesis of schiff base ligand and metal complexes

Biological activity

Antibacterial activity was determined by using Mueller Hinton agar, Petri plates were prepared by pouring 10 ml of Mueller Hinton agar and allowed to solidify, Plates were dried and 100 μ l of inoculum's suspension (approximately 10^6 cfu/ml of bacteria) was poured and uniformly, Whatman filter paper discs(5mm) were impregnated with 2 ml of ligand and complexes at concentration (10^{-3} M) and used to fill hole bored by cork borer in the inoculated agar. All the plates were incubated at 37 °C for 24 hours to obtain maximum growth in the culture media. For this concentration, the diameter of inhibition zone of growth minus the diameter of the disc was measured to estimate the degree of antibacterial activity ,by using DMF solvent[9,10].

Results and discussion

The schiff base of sulfadiazine ligand (S_2T) was prepared by the condensation of sulfadiazine with terephthalaldehyde in the molar ratio 2:1, the ligand (S_2T) was reacted with $Cu(II)$, $Ni(II)$, $Fe(II)$ ions to yield corresponding metal complexes (scheme 1), the physical data of ligand and corresponding transition metal complexes were listed in (table 1).

Electronic spectra

Electronic spectra of the ligand (S_2T) were recorded in DMF, and exhibited absorption bands at 254, 298, 310 nm, 39370, 33557, 3225 cm^{-1} . The first band corresponds to transitions of the phenyl rings [11]. The second band corresponds to the $\pi \rightarrow \pi^*$ of the azomethine groups $-CH=N-$. The last band corresponds to the $n \rightarrow \pi^*$ due to the non-bonding electrons on the oxygen and nitrogen atoms [12]. The electronic spectra of S_2T Cu complexes dissolved in DMF (Table 1), which exhibited shift toward high wavelength and due to bands assigned to $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$ transition as well as band due to ${}^2E_g \rightarrow {}^3T_{2g}$. The electronic spectra of S_2T Ni complex show absorption band at 26881 cm^{-1} which due to ${}^3A_{2g} \rightarrow {}^3T_{2g}$ while S_2T Fe complex exhibited band at 28169 cm^{-1} due to ${}^5A_{1g} \rightarrow T_{2g}(G)$ [13,14].

Table (1): The physical data obtained for the schiff base and complexes

No	Formula of ligand and complexes	colour	M.P	Yield	nm λ	Electronic spectral data cm^{-1}	${}^m\Delta_{O_h}$ cm^{-1}	μ_{eff} BM
1	$C_{28}H_{22}N_8O_4S_2$ S_2T	Pale green	298	88%	2982 54 310	39370, 33557 32258	-	-
2	$[Cu(C_{56}H_{45}N_{16}O_{10}S_4)(H_2O)_2]$ S_2T Cu	Dark green	352	72%	254 310	39370, 33557	1.32	1.99
3	$[Ni(C_{56}H_{45}N_{16}O_{10}S_4)(H_2O)_2]$ S_2T Ni	white	368	60%	254 310	39370 26881	2.5	2.3
4	$[Fe(C_{56}H_{45}N_{16}O_{10}S_4)(H_2O)_2]$ S_2T Fe	Yellow	386	63%	254 310	39370 28169	3.46	5.3

Infrared spectra

The vibrational modes of infrared spectrum of the ligand (S_2T) and metal complexes, assignments were listed in (Table 3), the N-H asymmetric and N-H symmetric vibrations observed between ($3259-3105\text{cm}^{-1}$) [15]. the bands ($-\text{CH}=\text{N}-$) in the ligand (S_2T) due to 1651cm^{-1} while the lowering shift of the stretching frequencies of the band occurs at $1627-1626\text{cm}^{-1}$ after complexation indicating the coordination of azomethine nitrogen atom to metal ions [16]. The band observed at ($1336-1153$) of the ($\text{O}=\text{S}=\text{O}$). A new band in the region (623cm^{-1}) due to (M-N) in all complexes, the weak bands around ($3584-3421\text{cm}^{-1}$) indicate the presence of water molecules to complexes [17].

Table (2) shows the famous IR frequencies of important bands of functional groups

compound	H_2O water	N-H sulpha	(C-H) str. Aromatic	(C-H) Alph	(HC=N)) str. cm^{-1}	C=N pyridine	SO_2 Asym. Sym.
S_2T	-	3259	3076 m	2937 as 2872 s	1651s	1577s	1323 1153
$S_2T\text{ Cu}$	3421 _w	3259	3039 m	2935 as 2875 s	1627s	1581s	1330 1157
$S_2T\text{ Ni}$	3584 _w	3259	3084 m	2931 as 2866 s	1627s	1581s	1334 1159
$S_2T\text{ Fe}$	3430 _w	3259	3041m	2941 as 2864 s	1626s	1577s	1336 1157

S=strong, w=weak, m=medium

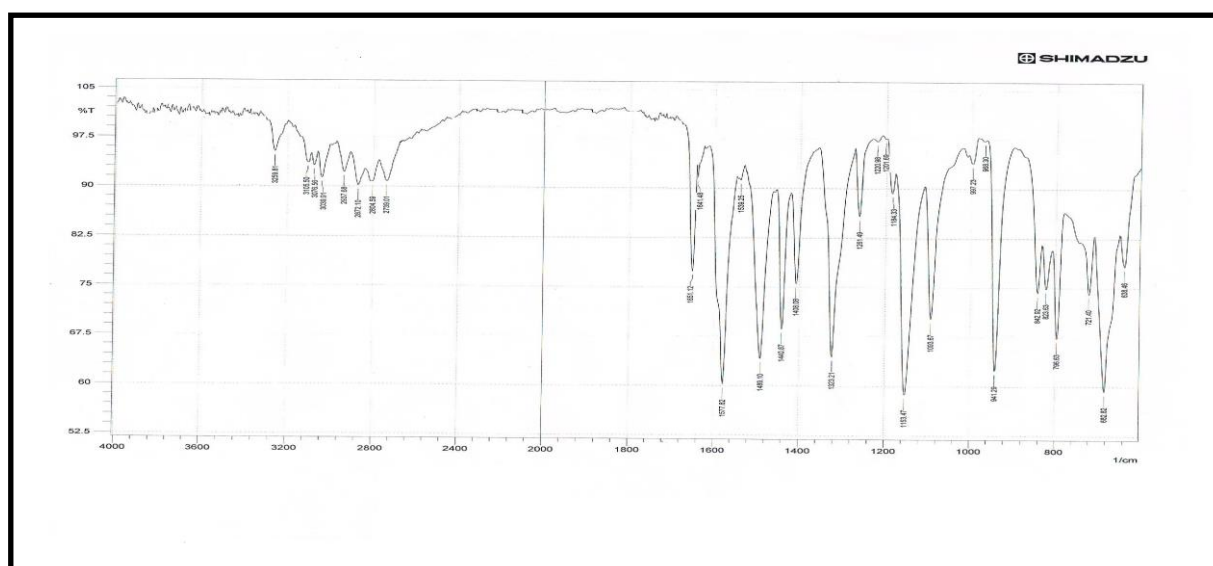
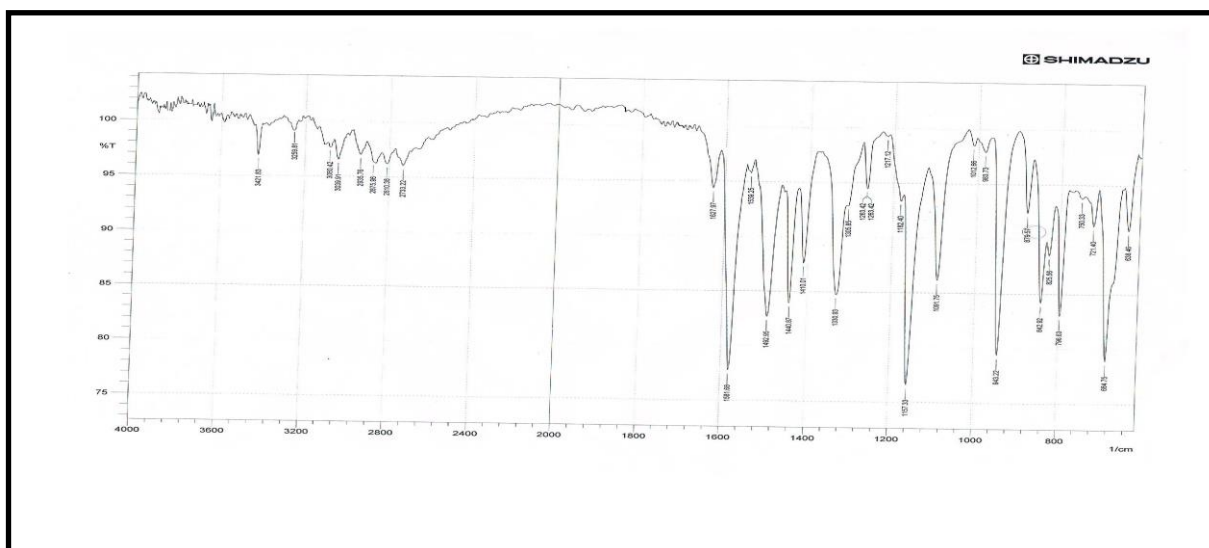


Figure 1: FT-IR Spectrum of ligand (S₂T)Figure 2: FT-IR Spectrum of complex(S₂T Cu)

Molar conductance

The observed molar conductance of all complexes in 10^{-3} M DMF solution at room temperature are listed in (Table 1) are found within the range of $1.32\text{--}3.46\text{ Ohm}^{-1}\cdot\text{m}^2\cdot\text{mole}^{-1}$ showing their non-electrolytic nature. The measured values of the magnetic moment μ_{eff} for complexes (Table 1), were 1.99, 2.3 and 5.3 B.M. respectively, indicating the octahedral structure [18]. The magnetic moment values measured were suggesting the possibility of the octahedral structures.

¹H-NMR spectra

¹H-NMR chemical shifts (ppm) of the ligand(S₂T) in DMSO-d₆ fig(3) the single observed at $\delta 10.25$ ppm was due to NH proton of NHSO₂ moiety[19]. While the signal at $\delta 10.14$ ppm attributed to NH proton of was assigned to the azomethine group (-CH=N-)[20], the aromatic protons in the region $\delta 6.57\text{--}8$ ppm and Pyrimidine ring protons appear at $\delta 8.08\text{--}8.76$ ppm.

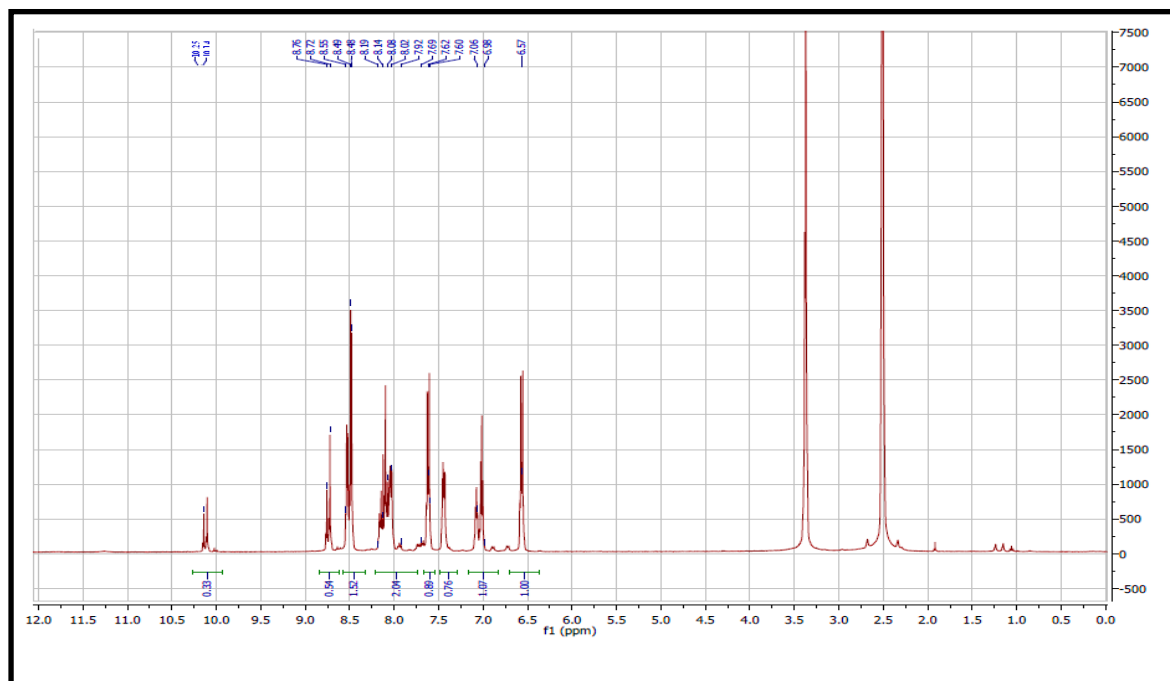


Figure 3: ¹H-NMR Spectrum of ligand(S₂T)

Biological activity

The antibacterial activity of ligand (S₂T) and complexes Cu(II), Ni(II), Fe(II), was determined against three bacterial strains which are listed in table (3). The results show that the complexes Cu(II), Ni(II), Fe(II) did not have any activity at concentration (10⁻³ M) compared with ligand, which showed activity against *Bacillus* with a zone of inhibition (15 mm) than that of *Staphylococcus* (10mm) and *E. coli* (12mm) at concentration (10⁻³ M) [21-23].

Table (3) : biological activity of ligand (S₂T)

Bacterial	Ligand (S ₂ T)	Diameter of inhibition zone (mm)
		(10 ⁻³ M)
Bacillus	√	15
Stapyllococcus	√	10
E.coli	√	12

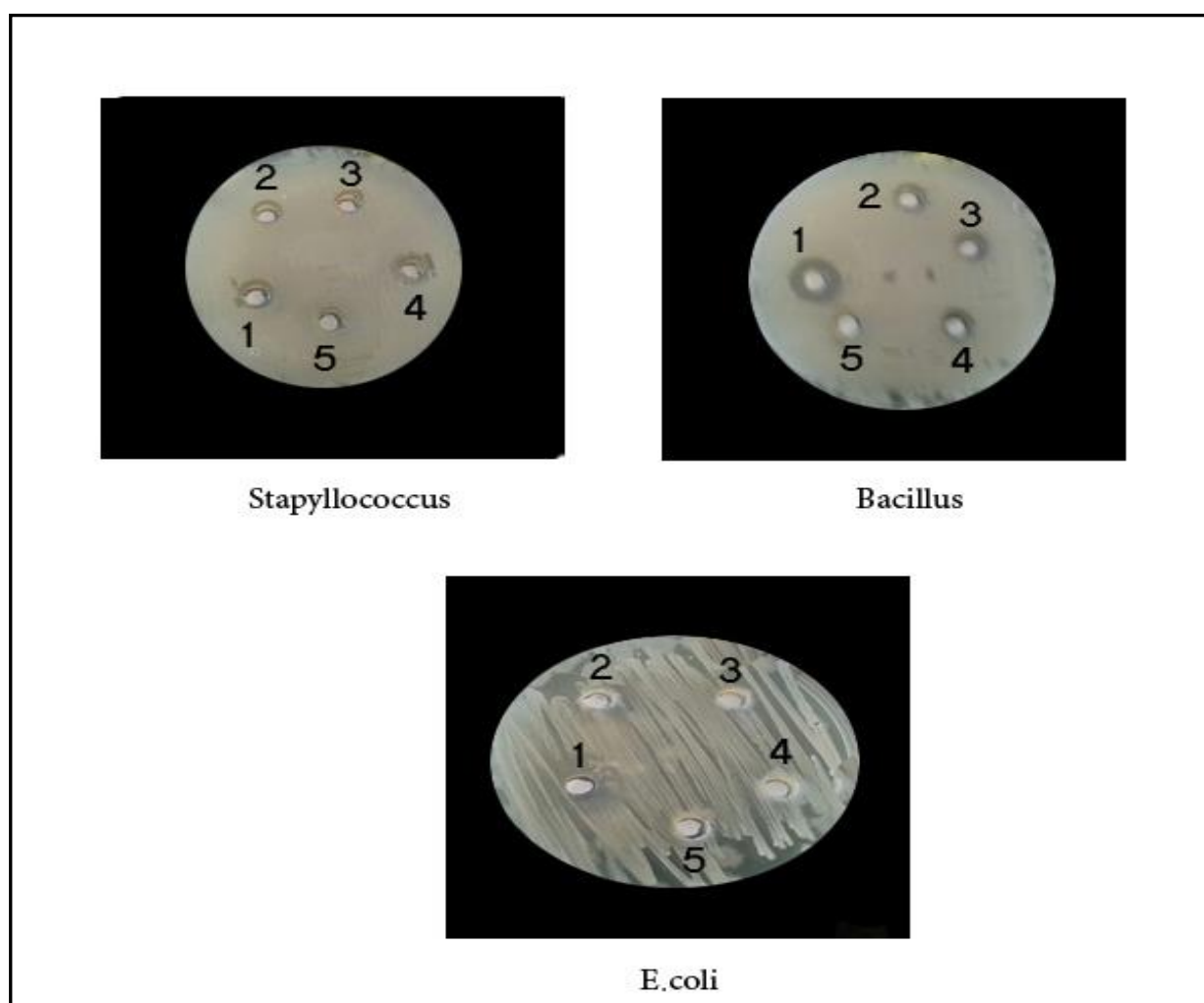


Figure4: biological activity of ligand and complexes

Conclusions

The synthesized Schiff base ligand derived from sulfadiazine has been coordinated with the Cu(II), Ni(II) and Fe(II) metal ions through azomethine-N and water molecules and their structures have been confirmed by analytical and spectral data, IR¹, ¹H-NMR spectra. The magnetic moment results proved that prepared complexes showed octahedral geometry and biological activity of ligand showed higher to significant activity against one or more bacterial compared with complexes.

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