Specroscopic and Biological Activity Studies of Thiadiazole Ligand Type N_2O and its Complexes with Fe(II), Co(II) and Ni(II)

Hasan A. Hasan, Ali H. Samir and Wurood Ali Jaafar Al-Saedi
Department of Chemistry–College of Education Ibn al-Haitham–University of Baghdad

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الخلاصة

في هذا البحث تم إستخدام المشتق [2-amino-5-mercapto-1,3,4-thiadiazole][S] لتحضير الليكاند الثلاثي السن [2-(2-Hydroxy-benzylidine)amino-5-thiol-1,3,4-thiadiazole][HL] من نوع (N_2O).

تم تصعيد الليكاند بإستخدام الايثانول كمذيب مع املاح الايونات [Fe(II) و Co(II) مع Ni(II)] بنسبة 2:1 (M:L) بوجود هيدروكسيد البوتاسيوم كقاعدة لتكوين المعقدات. تم تشخيص المعقدات بالطرق الطيفية (الاشعة تحت الحمراء والاشعة فوق البنفسجية–المرئية مع الامتصاص الذري) وقياسات محتوى الكلوريد و التوصيلية الكهربائية مع درجة الانصهار. هذه الدراسات بينت ان الشكل الهندسي هو ثماني السطوح لمعقدات [Fe(II) و Co(II) مع Ni(II)] بالصيغة العامه $[M(L)_2]$ أما قياسات الفعالية البيولوجية فأظهرت ان معقد الحديد فعال تجاه Bacillus(G+) strain بينما بقية المعقدات لم تظهر أي فعالية تجاه نوعين من البكتريا .Bacillus(G+) and Pseudomonase(G-)strains .

ABSTRACT

In this work, the precursor [2-amino-5-mercapto-1,3,4-thiadiazole][S] has been used in the synthesis of new tridentate ligand [2-(2-Hydroxy-benzylidine)amino-5-thiol-1,3,4-thiadiazole][HL] type (N_2O).

The ligand was refluxed in ethanol with the metal ions [Fe(II), Co(II) and Ni(II)] salts, using KOH as a base in (2:1) molar ratio to give the complexes. These complexes were characterised by atomic absorption(A.A), F.T.I.R, ultraviolet visible(U.V-Vis) spectroscopies, along with conductivity, chroride content and melting point measurement. These studies revealed an octahedral geometries for Fe(II), Co(II) and Ni(II) complexes with the general structure $[M(L)_2]$. The Fe(II) complex exhibited biological activity against the Bacillus(G+) strain, while the other complexes have no biological activity against the two types of bacteria the Bacillus(G+) and the Pseudomonase(G-) strains.

INTRODUCTION

Since thiadiazoles have a variety of potential biological activities and utilities as technologically useful materials, a number of methods for their preparation have been developed. A useful preparative method for 2-amino-5-mecapto-1,3,4-thiadiazole was developed by Guha(1) by treating thiosemicarbazide with carbon disulphide and potassium hydroxide. Hetero cyclic amines(2,3) have been widely used for the synthesis of new Schiff's bases.

Azoles, thiadiazole and their derivatives continue to draw the attention of synthetic organic and inorganic chemists due to the large group of compounds possessing a wide spectrum of uses. Heterocyclic compounds possessing the 1,3,4-thiadiazole ring system has shown antifungal, bacteriostatic as well as antihelmintic effects(4,5). Compounds containing the mentioned ring also exhibit anti-inflammatory, antimicrobial properties(6) in addition to the depression effect on the central nervous system(7). All the tested thiodiazole compounds are less active than oxacillin, which is currently used as clinical antibiotic(8). In the recent past, number of studies has highlighted the use of azo compounds and its complexes with transition metals in various significant applications(9).

MATERIALS AND METHODS

All chemicals used supplied from Fluka and Merck companies and used without any further purification. Infrared spectra were performed using a Shimadzu (FT–IR)–8400S spectrophotometer in the range (4000 – 400 cm^{-1}). Spectra were recoded as potassium bromide discs at Ibn-sina company. The electronic spectra of the compounds were obtained using a (U.V.–Visible) spectrophotometer type Shimadzu 160, in the range (200–900 nm) using quartz cell of (1.0)cm length with concentration (10^{-3}) mole L^{-1} of samples in DMF at 25°C, and electrical conductivity measurements of the complexes were recorded at (25ºC) for (10^{-3}–10^{-5})M solutions of the samples in DMF using a PW 9526 digital conductivity meter. The chloride content determined using potentiometric titration method on 686–Titro Processor–665 Dosim A–Metrohm/Swiss, and melting points were obtained using an electrothermal apparatus Stuart melting point, and metals were determined with a Shimadzu (A.A.) 680G atomic absorption spectrophotometer, all measurements were obtained in Ibn Sina company.

1- Preparation of [2-amino-5-mercapto-1,3,4-thiadiazole][S]

A mixture of (2.0g, 20mmol.) of thiosemicarbazide and (2.33g, 20mmol.) of anhydrous sodium carbonate was dissolved in 25ml of absolute ethanol 99.9%. To this solution (3.2g, 40mmol.) of carbon disulphide was added.

The resulting mixture was heated under reflux for 7hrs., and the reaction mixture was then allowed to cool down to room temperature. Most of solvent was removed under reduced pressure and the residue was dissolved in distilled water 20ml, after which it was carefully acidified with cold concentrated hydrochloric acid to give a pale yellow precipitate. The crude product was filtered and washed with cold water, recrystallized from ethanol to give the desired product as yellow needles, with a yield of (1.6g, 67%) and a m.p. of (229-230)^{o}C(10).

2-Preparation of 2-(2-Hydroxy-benzylidine)amino-5-thiol-1,3,4-thiadiazole [HL].

A mixture of compound [S] (0.2g, 1mmol.), absolute ethanol (99.9%, 25ml.) and the appropriate salicyldehyde (0.12g, 1mmol.) in acidic medium was refluxed in a water bath for (4-5)hrs., and the reaction mixture was then allowed to cool at room temperature and the precipitate was filtered, dried and recrystallized from ethanol (50%) to give a yellow crystals, with a yield of (75%) and a m.p. of (241-243)^{o}C.

3- Preparation of the Fe(II) **complex** (1)

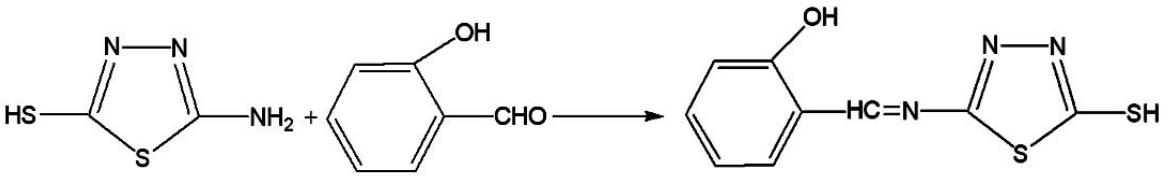
A solution of (0.06g, 0.4mmol.) of dehydrated iron(II) chloride dissolved in(10 ml.) ethanol was added dropwise to a solution of [HL] (0.2g, 0.8mmol.) dissolved in (15ml.) ethanol, the pH of the reaction mixture was adjusted by adding potassium hydroxide in equivalent quantity, and the reaction mixture was allowed to reflux for 2hrs. A dark brown precipitate was formed, which was filtered off, washed several times with absolute ethanol and dried. The yield was (0.17g, 85%) of the title complex, which has a m.p. of (300^{o}C)dec.

4- Preparation of the Co(II) complex (2) and Ni(II) complex (3)

A similar method to that mentioned for the preparation of the Fe(II)(1) complex was used to prepare the complexes of [HL] with Co(II) and Ni(II) ions.

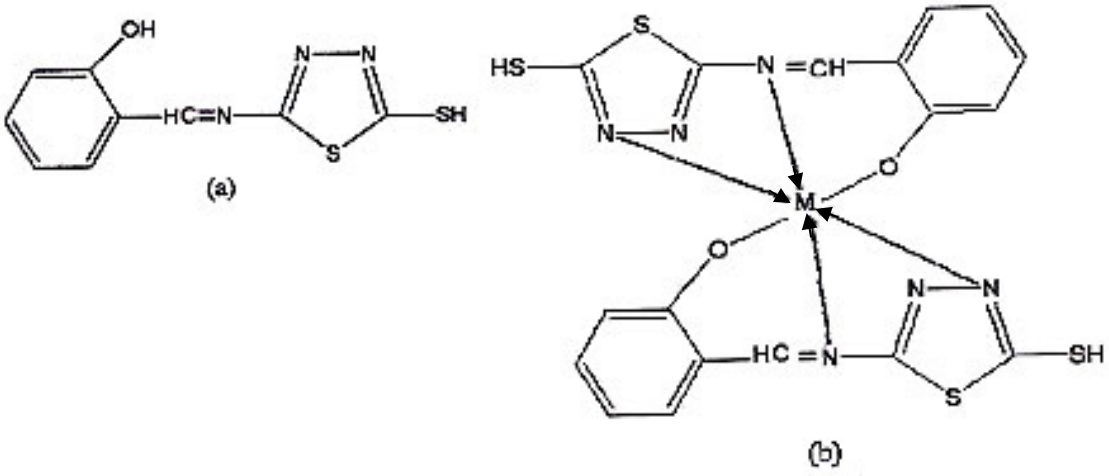
RESULTS AND DISCUSSION

The ligand [HL] was obtained in high yield by the condensation reaction using one equivalent of compound [S] and one equivalent of salisaldehyde, where a potentially tridentate new cyclic ligand type N_2O donor atoms have been synthesised. The ligand contains one labile proton [HL] and by removing this proton an anionic(-1) tridentate system is formed. The ligand was prepared according to the general route shown in the Scheme (1).



Scheme (1)
General route for the preparation of the ligand [HL]

All complexes were prepared with similar methods by refluxing the ligand [HL]
(Scheme 2a) with the corresponding metal chloride salt in ethanol, as a solvent, and potassium hydroxide as a base where the pure complexes were formed (Scheme 2b).



Scheme (2)
Chemical structures of the ligand [HL] (a) and the synthesised complexes (b)

Infrared spectral data

I.R. spectral data for the ligand [HL] and (1), (2) and (3) complexes are shown in Fig.(1). The important infrared bands for the ligand and the produced complexes with their assignments are listed in Table (1).

The I.R. spectrum for [HL] displayed band at (2873)cm^{-1} assigned to the iminic ν(C-H) stretching and a broad band at (3236)cm^{-1} which can be attributed to ν(OH) stretching and the absence of this band in all complexes indicates the deprotonation followed by complexation(11). The I.R. spectra showed a weak band at (2360)cm^{-1} for the ligand and all complexes which can be attributed to ν(S-H) stretching, while the ligand displayed a band at (902)cm^{-1} due to (-S-C-S)(12)stretching vibration.

On the other hand, the band at (1604)cm^{-1} which attributed to the iminic ν(C=N) exocyclic stretching in the spectrum of the free ligand, was shifted to a higher frequency and appeared at (1635, 1608 and 1608)cm^{-1} for the complexes (1), (2) and (3) respectively, indicating weak coordination of nitrogen of the imine group to the metal atoms(13).

The ligand exhibit significant stretching band at (1273)cm^{-1}, this indicated the presence of (=N-N=C-) cyclic group(10).

The band at (1570)cm^{-1} due to the ν(C=N) endocyclic stretching vibration (near the S-H group) and have tautomerism with the (S-H) in the free ligand was shifted to a lower frequency and appeared at (1504, 1516 and 1539)cm^{-1} for complexes (1), (2) and (3) respectively, assigned to the ν(C=N) stretching of reduced bond order. This can be attributed to delocalisation of the metal electron density to the π-system of the ligand(14,15).

The band at (1249)cm^{-1} which is due to the ν(C-O) stretching vibration in the free ligand was shifted to lower frequency and observed at (1242, 1203 and 1203)cm^{-1} for complexes (1), (2) and (3) respectively, This shift in the ν(C-O) vibration confirms the coordination of the ligand through the oxygen atom to the metal ion(16,17). Finally the complexes exhibited bands at the range (486-497) and (524-547)cm^{-1} which could be assigned to the ν(M-N) and ν(M-O) stretching vibration modes respectively(13). Due to the larger dipole moment change for ν(M-O) compared with ν(M-N), the ν(M-O) band usually appears at higher frequency than the ν(M-N) band(18).

Table -1: I.R. spectral data of the synthesised compounds

Compound	$\upsilon_{(C=N)}$ Exocyclic	$\upsilon_{(C=N)}$ Endocyclic	$\upsilon_{(O-H)}$	$\upsilon_{(N-H)}$	$\upsilon_{(C-O)}$	$\upsilon_{(S-H)}$	$\upsilon_{(M-O)}$	$\upsilon_{(M-N)}$
[HL]	1604	1570	3236	3479	1249	2360	-	-
$[Fe(II)(L)_2]$	1635	1504	-	3414	1242	2360	540	478
$[Co(II)(L)_2]$	1608	1516	-	3479	1203	2360	547	486
$[Ni(II)(L)_2]$	1608	1539	-	3414	1203	2360	524	497

(U.V.-Vis.) spectra

(U.V.-Vis.) spectra and molar conductivity measurement for complexes (1), (2) and (3) are shown in Table (2), and the U.V.-Vis. spectra are shown in Fig.(2). The U.V.-Vis. spectrum of complex (1), exhibited a high intensity peak at (314)nm related to the intraligand (n→ π*) transition, and peak at (692)nm related to ($^5T_2g \rightarrow {}^5Eg$) transition, suggesting an octahedral geometry around the iron(II) ion(19,20). The U.V.-Vis. spectrum of complex (2), exhibited a peak at (326)nm due to the (n→ π*) transition and peak at (351)nm which refer to the (C.T.) transition and a peak at (412)nm due to ($^4T_1g^{(f)} \rightarrow {}^4T_1g^{(p)}$) transition, suggesting an octahedral geometry around the cobalt(II) ion(19,21). The U.V.-Vis. spectrum of

complex (3) exhibited peaks at (238) and (345) nm due to the ($\pi \rightarrow \pi^*$) and (C.T.) transitions, while the peak at (680)nm may due to the ($^3A_2g \rightarrow {}^3T_1g^{(f)}$) transition, suggesting an octahedral geometry around the nickel(II) ion(19,21).

The molar conductance of the complexes in (DMF) lie in the (7.48-51) $S.cm^2.mole^{-1}$ range, indicating their non-electrolytic behavior(22).

Table -2: (U.V.-Vis.) spectral data and molar conductivity in DMF solution.

Compound	λ	Assignments	Λ_m S.cm^2 mol^{-1}	Ratio	Suggested structure
$[Fe(II)(L)_2]$	319 692	$n \rightarrow \pi^*$ $^5T_2g \rightarrow {}^5Eg$	51	neutral	octahedral
$[Co(II)(L)_2]$	326 351 412	$n \rightarrow \pi^*$ C.T. $^4T_1g^{(F)} \rightarrow {}^4T_1g^{(P)}$	14.28	neutral	octahedral
$[Ni(II)(L)_2]$	238 345 680	$\pi \rightarrow \pi^*$ C.T. $^3A_2g \rightarrow {}^3T_1g^{(F)}$	7.48	neutral	octahedral

BIOLOGICAL SCREENING: THE ANTIBACTERIAL ACTIVITY TEST

In our study the synthesised compounds have been screened for their antibacterial activity against the Bacillus(G+) and Pseudomonase(G-) strains by the agar diffusion technique(23). Each of the compounds was dissolved in DMF to give a final concentration of (0.001)mg/ml, and from the data shown in Table (3), and [Figs.(3 and 4)], the Fe(II) complex exhibited a biological activity against the Bacillus(G+) strain [inhibition zone = 1.3cm] only, while the other complexes have no biological activity against the two types of bacteria [inhibition zone = zero].

Table -3: The biological activity of the synthesised complexes

compound	Bacillus (G+)	Pseudomonase (G-)
$[Fe(II)(L)_2]$	+	-
$[Co(II)(L)_2]$	-	-
$[Ni(II)(L)_2]$	-	-

Table (4) represented below shows the chloride content, melting point, atomic absorption and some other physical properties for the ligand and the synthesised complexes.

Table -4: Results of elemental analysis and physical properties for the ligand and the synthesised complexes

compound	M.wt	Yield %	Color	m.p.	Metal Found, (calculate)	Cl^- content
[HL]	237	75	Pale yellow	241-243	-	-
$[Fe(II)(L)_2]$	527.85	85	Dark brown	300 dec.	10.2 (10.5)	Nil
$[Co(II)(L)_2]$	530.93	68	Green	287 dec.	10.9 (11.09)	Nil
$[Ni(II)(L)_2]$	530.69	50	Yellow orange	300 dec.	10.8 (11.05)	Nil

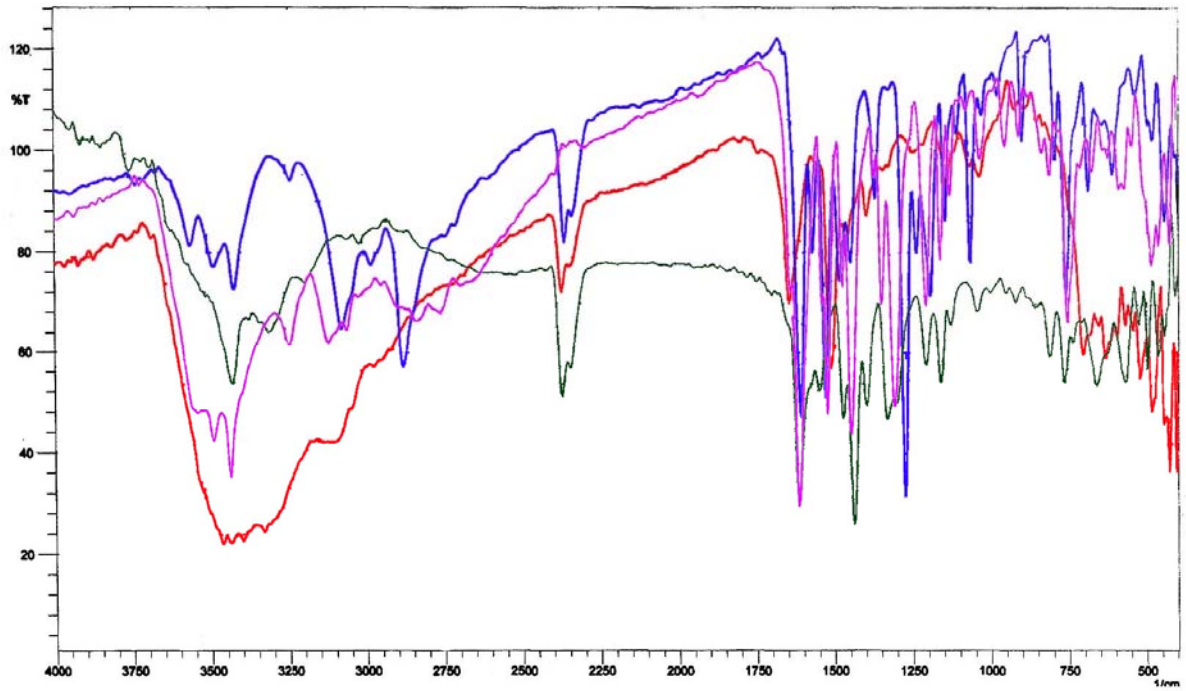


Fig. -1: The I.R Spectra of :
Ligand [HL]
$[Fe(II)(L)_2]$ complex
$[Co(II)(L)_2]$ complex
$[Ni(II)(L)_2]$ complex

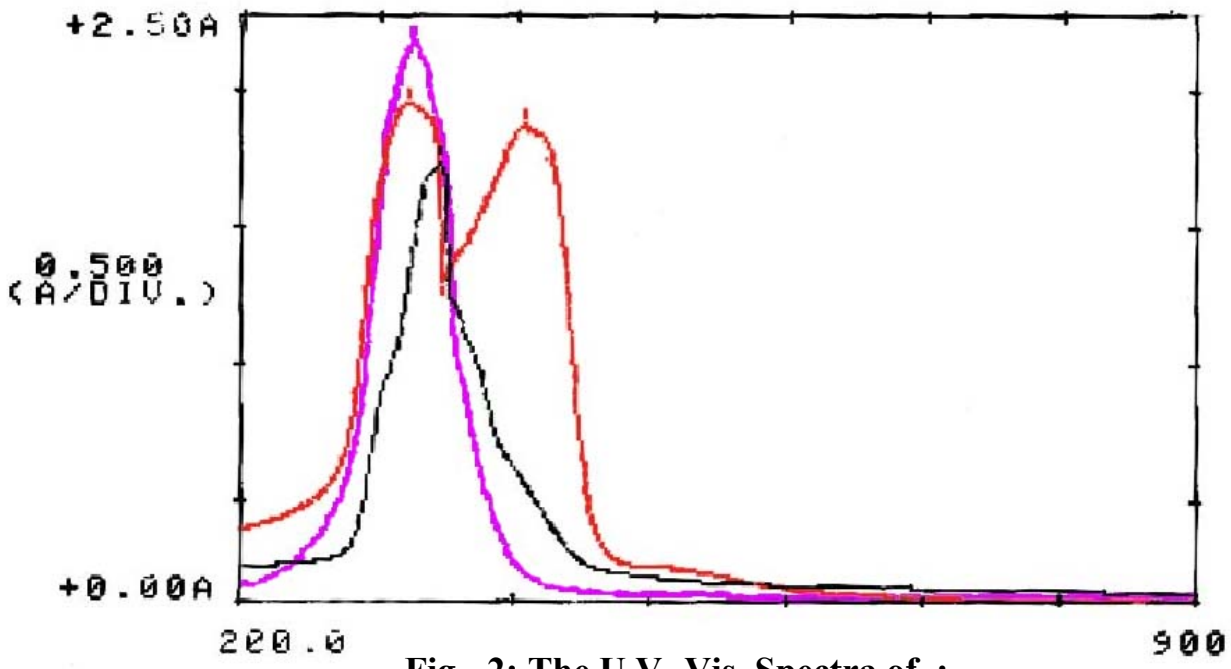


Fig. -2: The U.V.-Vis. Spectra of :
$[Fe(II)(L)_2]$ complex
$[Co(II)(L)_2]$ complex
$[Ni(II)(L)_2]$ complex

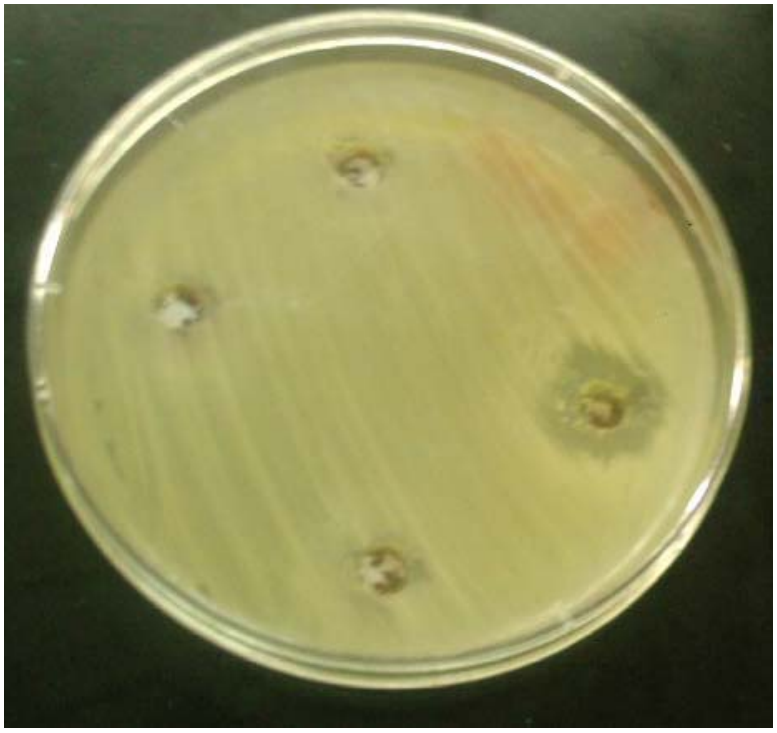


Fig. -3: Effect of the complexes towards the

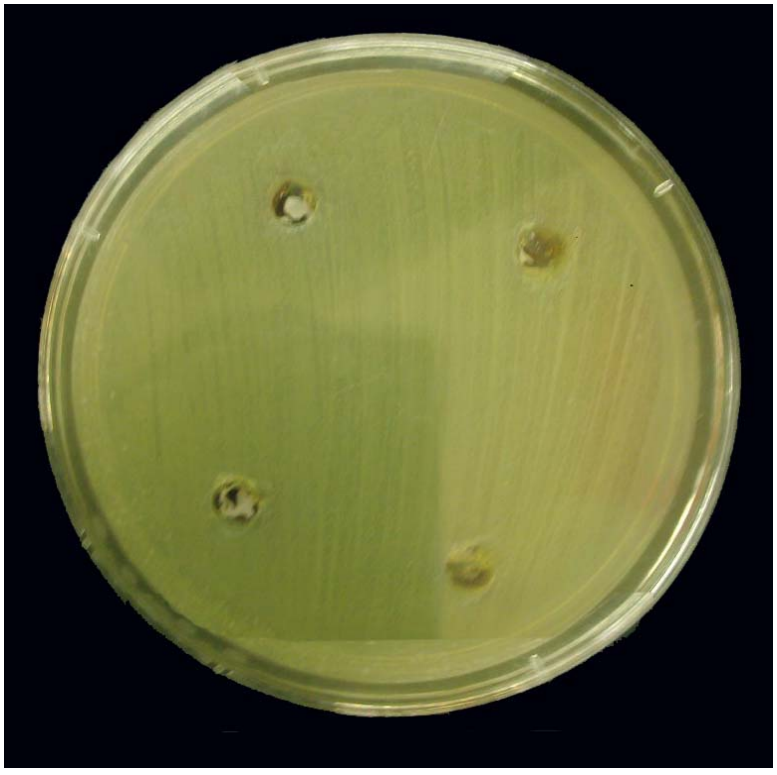


Fig. -4: Effect of the complexes towards the

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