Synthesis, Spectral Characterization and Biological Activity of new niii, Coii and Cuii Complexes with Thiosemicarbazide Ligand

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Abstract
The research included the preparation and characterization of the new thiosemicarbazide ligand; N1-(dimethylcarbamoyl)-lhydrazine-1,2-bis (carbo-thiomide) (L). Three transition metal complexes were isolated from the mixing of the title ligand with the metal ions of (Ni(II), Co(II) and Cu(II)). The reaction was performed by mixing metal:ligand in a 1:1 mole ratio using EtOH as the medium. The chemical formula of L complexes is presented as follows; [LNiCl2H2O], [LCoCl2H2O] and [LCuCl2H2O], The entity of the expected structure of the ligand and its metal complexes were illustrated through a range of physicochemical techniques. These include; FT-IR electronic spectra, 1H- and 13 C- NMR spectra, elemental analysis (CHNS), chloride content, metal content, melting point, molar conductivity and magnetic susceptibility measurements. The spectral and analytical analyses concluded the isolation of six-coordinate complexes for the (Ni(II), Co(II) and Cu(II) with a distorted octahedral geometry about the centre atom. The anti-bacterial activity (G+ and G- bacterial) was explored.
Keywords: Synthesis, antibacterial activity, metal complexes

1. Introduction

The chemistry of nitrogen, oxygen and sulfur heteroatom-containing aromatic compounds represents an interesting area of research [1]. The most important aspect of these compounds is highlighted by their role in being used as chelating agents, as they can interact with transitional elements [2]. Compounds containing nitrogen, oxygen, and sulfur are considered an important class of organic compounds that played an important role in the development of organic chemistry [3] and inorganic and coordination chemistry [3]. Further, researchers have implemented several synthetic routes to improve the preparation methods of organic ligands and their stability including their metal complexes. These factors played role in the development of organic and coordination chemistry [4,5]. Heterocyclic compounds represent materials that contain at least one heteroatom, and the most common heterocyclic atoms are nitrogen, oxygen and sulfur. Compounds that are derived from thiosemicarbazide are interesting reagents as they consist of the hard site (nitrogen) and the soft site (sulfur). Subsequently, these compounds (the organic and their metal complexes) are potential agents that use in medicine and the pharmaceutical industry. These compounds exhibit a wide range of activity against diseases and are used as antimicrobials and insecticide agents [6,7]. More, heterocyclic compounds are used as antifungal [8], antibacterial [9], anticancer [10] and anti-inflammatory [11], anti-tubercular [12] and anti-HIV [13], as well as analytical and environmental chemistry [14]. The chemistry of heterogeneous organic species and complexes remains one of the hot research areas that influenced the concern of organic, inorganic and coordination chemists. This work represents the synthesis and spectral characterization of a new thiosemicarbazide ligand namely; N1-(dimethylcarbamoyl)-hydrazine-1,2-bis (carbo-thiomide) (L) and its metal complexes with M(II) ions (Ni,Co and Cu). More, the antibacterial evaluation of the ligand and its metal complexes is explored.

2. Experimental

Elemental analysis was carried out using a Carlo Erba 1108 Elemental Analyzer (Milan, Italy). The infrared (IR) spectrum was recorded as KBr and CsI pellets using a Perkin Elmer Spectrum GX spectrophotometer (Perkin Elmer, Waltham, MA, USA). NMR spectra (1H, 13C- NMR) were acquired in DMSO-d6 solutions usinga Bruker-400MHz for 1H-NMR and 100.61 MHz for 13C-NMR with tetramethylsilane (TMS) as an internal reference for 1H NMR.

Synthesis of N¹-(dimethylcarbamoyl)-hydrazine-1,2-bis (carbo- thioamide) (L)

The ligand was prepared according to the method reported in [15] and as follows

A mixture of dimethyl carbamoyl chloride (1.07g, 10mmol) and ammonium thiocyanate (0.76 g, 10mmol) in acetonitrile (40mL) was heated at reflux for 1h. The reaction mixture was cooled to room temperature and then filtrated off. thiosemicarbazide (0.91g, 10 mmol) in acetonitrile (20mL) was added to the filtrate and the mixture was refluxed for 2h. Upon cooling, a white solid was formed which was

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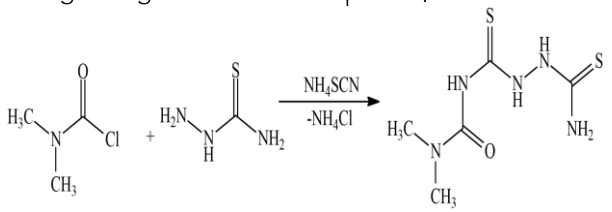
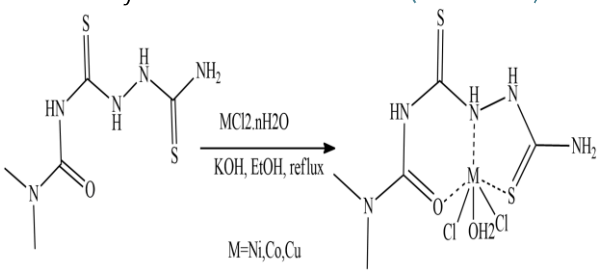
collected by filtration washed with acetonitrile (10mL) and dried in a desiccator over anhydrous silica gel to give the title compound, Scheme 1.



Scheme 1: Synthetic route of ligand.

Synthesis of complexes

In a 100mL of a round-bottomed flask was mixed N1-(dimethylcarbamoyl)-lhydrazine-1,2-bis(carbothioamide) (L) (0.470g, 2mmol) dissolved in ethanol (10mL). A solution of KOH (0.011g, 2mmol) dissolved in ethanol (10mL) was added dropwise to the L solution. The resulting mixture was refluxed for 1h and then an ethanolic solution (10mL) of the title metal ions MCl2.6H2O (2 mmol) (M(II)= Ni,Co or Cu) was added dropwise. The resulting coloured solution was allowed to reflux for 2h and then cooled to room temperature. The metal complexes were collected by filtration and air-dried (Scheme 2).



Scheme 2: Synthetic route of complexes

3. Results and Discussion

FT-IR spectrum of L

The solid-state infrared spectrum of the prepared ligand, Figure1, was recorded in the range of 4000-400 cm-1. The main FTIR bands of the ligand are presented in Table (1). The FTIR spectrum of thiosemicarbazide ligand showed bands around (3371– 3100), 802 and 755cm-1 assigned to ν(N-H) and ν(C=S)thiosemicarbzid and (C=S)thiocyanat5, respectively [16,17]. Bands detected at 1165 and 1002cm-1 were attributed to ν(C-N) and ν(N-N), respectively. The ν(C=O) of the carbamoyl group appeared at 1625 cm-1 [18].

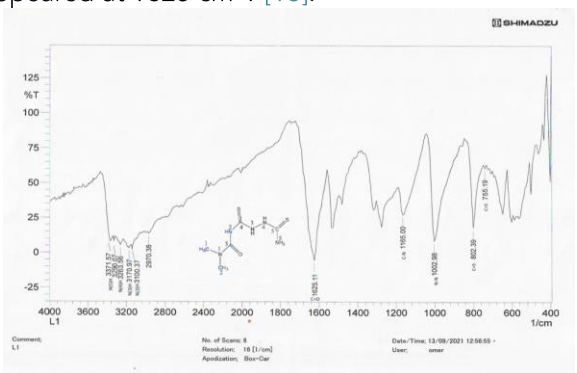


Figure 1. The FTIR spectrum of N1-dimethylcarbamoyl)-hydrazine-1,2-bis (carbo- thioamide)(L)

3-1-2 U.v. Spectrum of Ligand

The UV spectrum for L, Figure 2, showed a high-intensity absorption peak at 277 which is attributed to the ligand field (an overlap of π →π* transitions) [19,20].

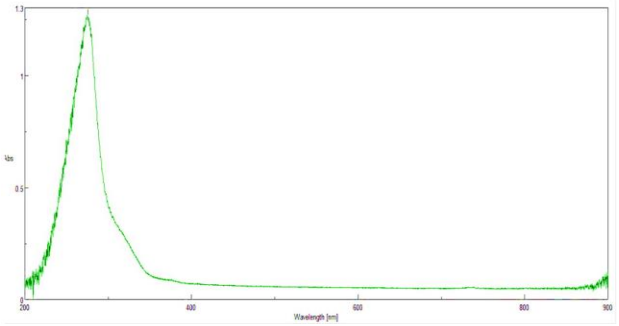


Figure-2. Electronic spectrum of Ligand L in DMSO Solvent

3.1.3 Nuclear Magnetic Resonance (NMR) spectra of Ligand

The ^{1}H-NMR spectrum of N^{1}-dimethylcarbamoyl)-hydrazine-1,2-bis (carbo- thioamide) in DMSO-d6 solvent is presented in Figure 3. The singlet peak at 8.54ppm equivalent to one proton is related to [1H, N(2)H, s]. A singlet peak at 7.46ppm which is equivalent to two protons is attributed to [2H, N(3,4)H, s] [21]. The singlet peak at 7.10ppm equivalent to two protons is related to [2H, N(5)H, s] [22]. The chemical shifts in the aliphatic that are detected as a singlet at 2.80ppm are due to [6H, C(1,2)H, s] [21].

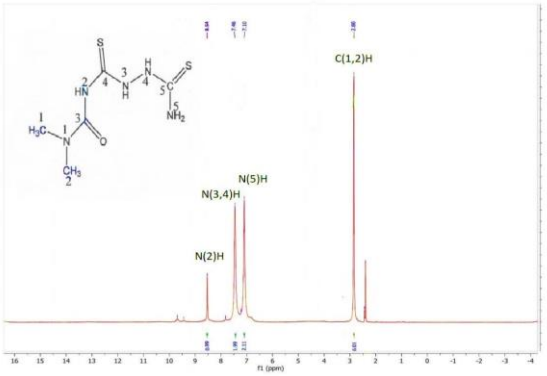


Figure 3. 1H NMR of N1-(dimethylcarbamoyl)-hydrazine-1,2-bis

(carbo- thioamide)(L)

The 13C NMR spectrum of the ligand in DMSO-d6 is shown in Figure 4. The spectrum of L1 showed downfield shifts at 181.13 and 178.10 ppm assigned to the thione carbon (C=S) for thiocyanate and thiosemicarbazide, respectively. The slight difference in the chemical shifts of these peaks in the spectrum of the ligand is due to the different environments around the (C=S) groups. The spectrum indicated a signal at 156.53 ppm attributed to the carbonyl of the amide group. The aliphatic carbons signals of the CH3 (C1,2) appeared as expected at 34.99ppm. All 13C-NMR chemical shift positions of the ligand are in agreement with values reported in other thiosemicarbazide ligands [23].

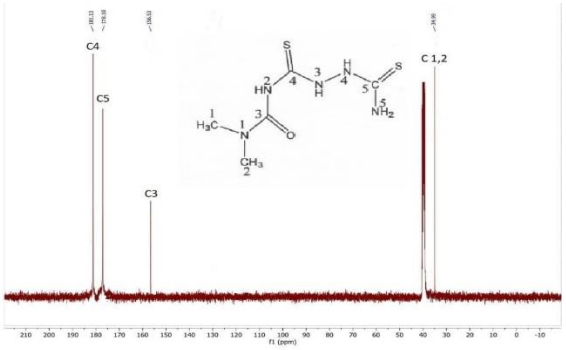


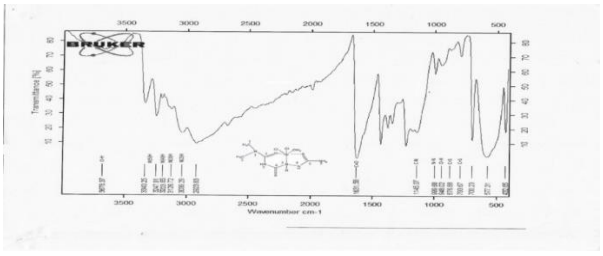
Figure 4. ^{13}C NMR spectrum of N^1- dimethylcarbamoyl)-N^2-methylhydrazine-1,2-(carbothioamide)

FT-IR spectra of the prepared complexes

Figures 3-5 to 3-7 show the FT-IR spectra of complexes 1, 2 and 3, while Table (3-1) includes the assignment of the distinct bands. the FTIR spectra in the complexes of Ni(II), Co(II) and Cu(II) showed peaks related to v(O-H) stretches around 3678, 3500 and 3595 cm-1, respectively. These peaks were assigned to the OH of the aqua molecule [24,25,26]. The spectra revealed bands in the range 3350-3039 cm-1 that were attributed to the v(N-H). These bands were shifted to lower wavenumber, compared with that observed in the range 3371-3100cm-1 in the spectrum of the free ligand [27], Table 3-1. The band detected at 1625 cm-1 in the free ligand, Figure 1, that related to the v(C=O) carbonyl has appeared in the lower and higher range at 1635-1608cm-1 in the spectra of the complexes (1, 2 and 3). The shift of the carbonyl bands is related to the involvement of this moiety in the coordination with the metal centre [28,29]. The FTIR spectra of complexes revealed bands in the range 1145-1135 cm-1 that attributed to the v(C- N) group. These bands were shifted to a lower and higher wavenumber, compared with that observed at 1165cm-1 in the free ligand confirming the involvement of this group in the coordination. The complexes display a band in the range 1010-999cm−1 due to ν(N–N). This band appeared at a higher and lower wavenumber compared with that detected at 1002cm−1 in the free ligand [30]. The band that was assigned to the v(C=S)thiosemicarbazide group was detected in the range 876–757cm-1 in 1, 2 and 3. This band suffered a shift to the lower and higher wavenumber, compared with that observed at 802cm-1 in the ligand [31]. The band that related to the v(C=S) thiocyanate group at 755 cm-1 in the free ligand appeared at a lower and higher wavenumber, in the range 793-694cm-1, in the spectra of the complexes, confirming the involvement of this v(C=S)thiocyanate group in the coordination. The spectra of metal complexes revealed additional peaks between 600-200cm -1 that were not presented in the spectrum of the ligand. Peaks correlated to v(Ni-N), v(Co-N) and v(Cu- N) were detected at 439, 478 and 464cm-1, respectively [25,26]. Bands detected at 586, 609 and 601, cm-1 assigned to v(Ni-O), v(Co-O) and v(Cu-O), respectively.Peaks detected at 331, 331 and 347cm-1 were correlated to v(Ni-S), v(Co-S) and v(Cu-S), respectively. The FT-IR spectra revealed bands that belong to v(Ni- Cl), v(Co- Cl) and v(Cu- Cl) at 316, 316 and 327cm-1, respectively [32,33].

Table 3.1 Principal FTIR bands of ligand and complexes (cm-1)

NO	O-H	νN(5)H	νN(4)H	νN(3)H	νN(2)H	ν(C=O) carbomyl	ν(C-N)	ν(N-N)	ν(C=S) thiosemicarbazide	(C=) Thiocyanat	ν(M-O)	(M-N) ν	ν(M-S)	(M-Cl) ν
L	-	3371 3290	3263	3170	3100	1625	1165	1002	802	755	-	-	-	-
C1	3678	3340 3247	3203	3126	3039	1631	1145	999	876	793	586	439	331	316
C2	3500	3350 3278	3200	3100	3075	1608	1135	1007	757	694	609	478	331	316
C3	3595	3340 3290	3248	3140	3086	1635	1141	1010	874	759	601	464	347	327



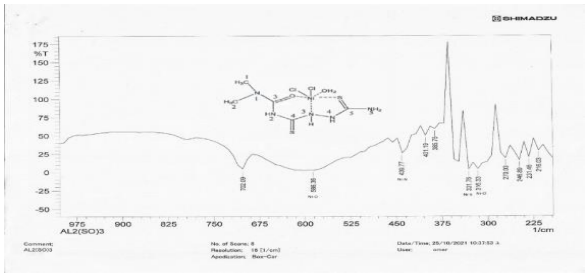


Figure (3-5) The Infrared spectrum of [LNiCl₂H₂O]

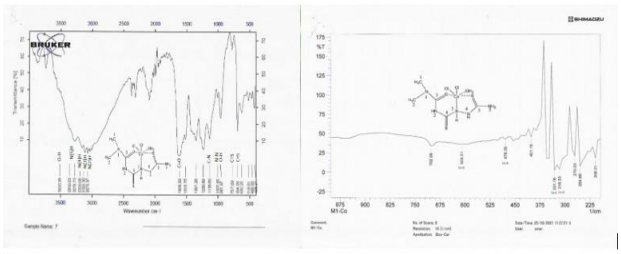


Figure (3-6) The Infrared spectrum of [LCoCl₂H₂O]

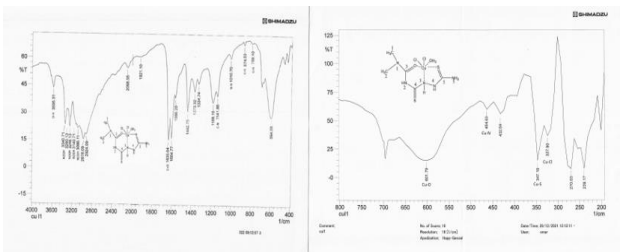


Figure (3-7) The Infrared spectrum of [LCuCl₂H₂O]

3-2-2 U.v.-Vis Spectra of the complexes

The electronic absorption spectra of complexes were determined in DMSO solutions (con. = 1x 10-3 M) . The electronic spectra of the metal complexes of Ni(II) , Co(II) and Cu(II) are exhibited in Figures (3-8), (3-9) and (3-10), respectively. The spectra indicated peaks, see Table (3-2), around 290-284nm related to the overlap of π → π* (ligand field transitions). The spectra of 1, 2 and 3 showed an extra peak about ca.315nm assigned to charge transfer (C.T) [34-37]. In the d-d region of the Ni(II) complex, bands observed at 610 and 1030nm correlated to 3A2g→3T1g and 3A2g→3T2g, respectively indicating a distorted octahedral geometry about the metal centre [38]. Peaks at 334 and 599 nm in the spectrum of Co referred to n→ π*and 4T1g→4A2g, confirming a distorted octahedral geometry around the metal centre [39,40]. The peak at 695nm in the spectrum of Cu(II) is referred to 2B2g →2A1g transition confirming a distorted octahedral geometry around the metal centre [41].

Table (3-2): UV-visible spectrum of ligand and complex

Complex	λ nm	cm-1 λ	εmax (dm3 mo-1cm - 1)	Assignment	Suggested geometry
L	277	36101	1300	π → π*	
C^1	284 610 1030	35211 16393 9708	930 30 30	π → π* 3A2g→3T1g 3A2g→3T2g	Octahedral
C^2	334 595	29940 16806	70 1000	n→ π* 4T1g→4A2g	Octahedral
C^3	290 396 695	34482 25252 14388	1100 006 20	π → π* n → π* 2B2g →2A1g	Octahedral

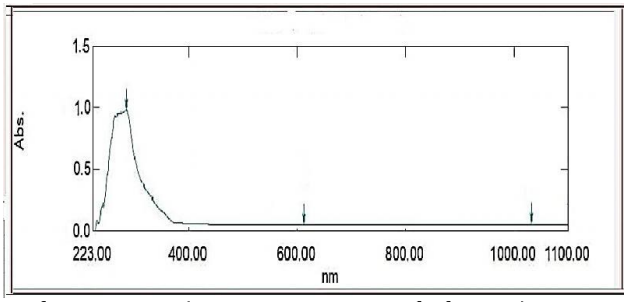


figure (3-8): Electronic spectrum of of [LNiCl2H2O]

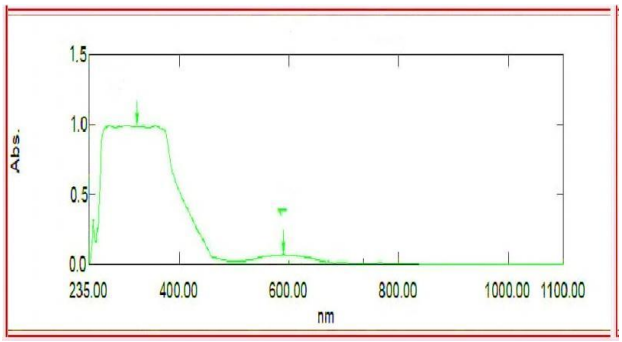


figure (3-9): Electronic spectrum of of [LCoCl2H2O]

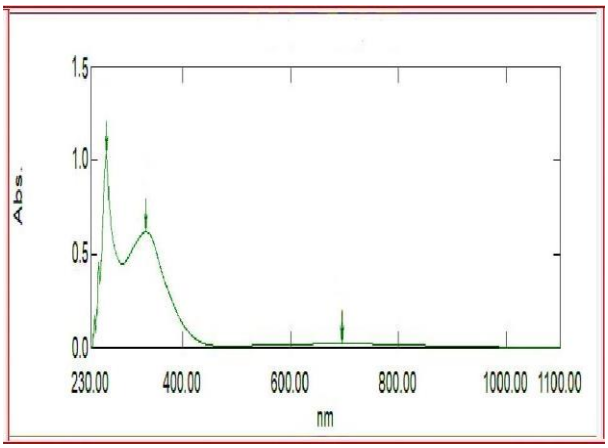


figure (3-10): Electronic spectrum of of [LCuCl2H2O]

Biological Activity

The ligand and its metal complexes were examined for their microbiological activity against a type of isolate of Gram-positive bacteria (Staphylococcus aureus) and a dye-negative bacteria (Escherichia Coli).

Table3.3 Biological activity values of some prepared compounds against isolates of pathogenic bacteria

Compound	Concentration (mg/ml)	Staphylococus aureus (G+)	Escherichia Coli (G-)
L	50 25 12.5	32 27 18	29 19 14
C1	50 25 12.5	23 16 R	26 22 16
C2	50 25 12.5	31 24 18	23 17 13
C3	50 25 12.5	25 19 15	22 19 15

The antibacterial activity was performed using a disc diffusion method. The in vitro antibacterial studies were conducted at a range of concentrations of 50mg/ml, 25mg/ml, and 12.5mg/ml, against

pathogenic bacterial strains. Clarithromycin (10 µg/disc) was used as a positive control and polymyxin B as the negative control. The agar media was prepared by pouring the nutrient agar solution into the sterilized Petri dishes. All bacteria were cultured in the nutrient broth and incubated at 37°C for 24 h, and then the cultures were spread on the surface of the nutrient agar. Discs of 5mm diameter were cut out of Whatman No.1 filter paper and autoclaved at 15psi for 15 min under aseptic conditions. When a filter paper disc is impregnated with a chemical and placed on agar, the chemical will diffuse from the filter paper into the agar. The diffusion will place the chemical in the agar only around the disc. The solubility of the chemical and its molecular size will determine the size of the area of chemical infiltration around the disc if it is susceptible to the chemical. The area of no growth is known as the 'zone of inhibition'. A loopful of an overnight slant culture of the test organism was inoculated to 5µL of 140 sterile physiological salines to make a uniform suspension. This suspension culture was surface spread on a nutrient agar plate by swabbing with a sterile cotton swab to get a uniform lawn culture. The discs with test samples prepared as mentioned above were placed on the swabbed surfaces of the plates (5 discs per plate), using sterile forceps. The plates were incubated at 37°C for 24 hours and then checked for zones of inhibition around the discs. Regarding the biological activity of Escherichia coli, L and C1, in the first concentration 50, The biological activity of the tested compounds against Staphylococcus aureus indicated the free ligand and complex 2 showed good activity against this type of bacteria, while the rest of the complexes showed medium activity and the C1 in the third concentration indicated no activity against this type of bacteria

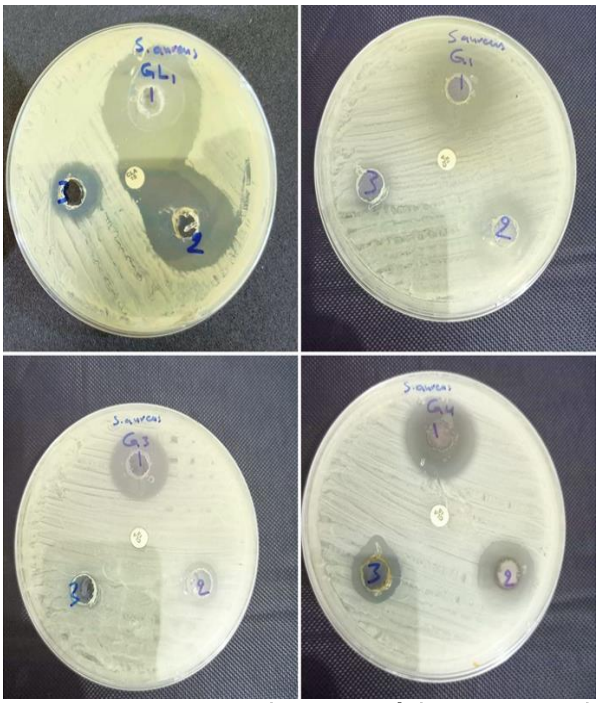


Figure (3-11): Antiviral activity of the compounds against Staphylococcus aureus of the L ligand and its complexes [C1, C2, C3]

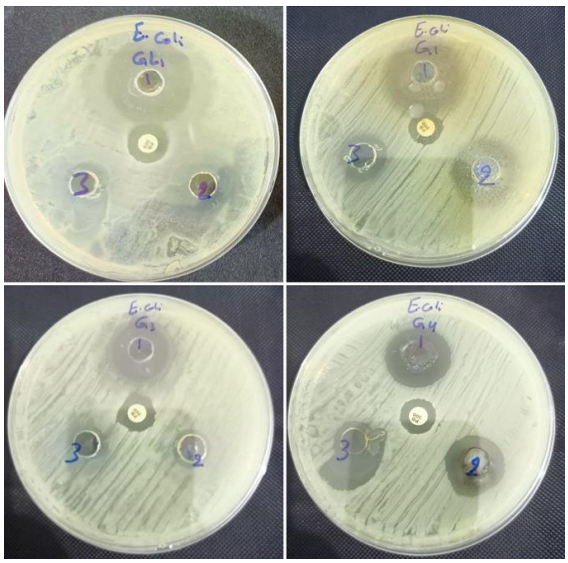


Figure (3-12): Antiviral activity of the compounds against Escherichia coli of the L ligand and its complexes [C_1, C_2, C_3]

4. Conclusions

The synthesis and characterisation of N1-(dimethylcarbamoyl)-hydrazine-1,2-bis (carbo-thiomide) (L) and its new metal complexes are reported. The reaction of the ligand with Ni(II), Co(II) and Cu(II) metal ions in a 1:1 (L:M) mole ratio resulted in the isolation of monomeric complexes. The chemical structure of compounds and overall bonding behaviour of the complexes were confirmed through physicochemical techniques. The characterisation data confirmed the isolation of six-coordinate monomeric complexes of the general formula; [LNiCl2H2O], [LCoCl2H2O] and [LCuCl2H2O] . The biological activity of the ligand and its complexes against (G+ and G-) bacterial was tested.

Acknowledgements

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