

Metal-assisted assembly of dinuclear metal(II) dithiocarbamate Schiff-base macrocyclic complexes: Synthesis and biological studies

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Abstract

The synthesis of dinuclear transition metal(II) dithiocarbamate (dtc)-based macrocyclic and their characterisation are described. The bimetallic dithiocarbamate-based complexes were prepared *via* a one-pot reaction using bis-amine-Schiff base, CS₂, KOH and metal chloride. The mode of bonding and overall geometry of the dinuclear complexes were determined through IR, UV-Vis, NMR, and mass spectral studies, magnetic moment measurements, elemental analysis, metal content, and conductance. These studies revealed binuclear complexes of the general formulae [M₂(L)₂] with tetrahedral geometries for Co^{II} and Zn^{II} complexes, while square planar geometries have been suggested for Ni^{II} and Cu^{II} complexes. Biological activity of the ligand and its metal complexes against gram positive bacterial strain *Staphylococcus aureus* and gram negative bacteria *Escherichia coli* revealed that the metal complexes become more potentially resistive to the microbial activities as compared to the free ligand. However, these metal complexes do not exhibit any effects on the activity of *Pseudomonas aeruginosa* bacteria. There is therefore no inhibition zone.

Keywords: Dithiocarbamates; Transition metals; One-pot reaction; Structural and biological studies

1. Introduction

The development of metal-directed self-assembly based on transition metals and multidentate ligands has been the subject of extensive research due to their potential applications in supramolecular and materials science [1-4]. One approach in the use of metal-directed self-assembly techniques is to develop a facile route to novel host macrocyclics capable of binding charged and neutral guest substrates [5]. Depending on the coordination fashion of the ligand and preferred metal coordination geometry, different synthetic strategies have been developed, and unusual molecular architectures capable of encapsulating guest molecules in a selective manner are reported. Dithiocarbamates (dtc) are versatile ligands which have been extensively investigated with regard to their numerous applications in different areas such as materials science, medicine, agriculture and supramolecular chemistry [6-8]. The dithiocarbamate (dtc) moiety has been shown to form strong chelate complexes with a wide range of transition metal and main group elements. Such complexes have had numerous uses for example; they have acted as lubricants,

antioxidants and accelerators for rubber vulcanisation [7, 9]. One potential application of multifunctional dithiocarbamate ligands is their use in the design and fabrication of new supramolecular structures with unusual optical and electrochemical properties [10]. In addition, the incorporation of redox-active dtc- complexes into the framework of a macrocyclic system enables the possibility of using the host as an electrochemical sensor for guest substrates [5, 11]. In this paper, we report here one-pot template preparation of new dimeric assemblies of dithiocarbamate-based complexes and their antimicrobial activities.

2. Experimental

2.1. Materials

All reagents were commercially available and used without further purification. Solvents were distilled from appropriate drying agents immediately prior to use.

2.2. Physical measurements

Elemental analyses (C, H and N) were carried out on a Heraeus instrument (Vario EL).

Melting points were obtained on a Buchi SMP-20 capillary melting point apparatus and are uncorrected. IR spectra were recorded as KBr discs using a Shimadzu 8300 FTIR spectrophotometer in the range (4000-400) cm^{-1} . Electronic spectra were measured in the region (200-900) nm using 10^{-3} M solutions in DMF at 25°C using a Shimadzu 160 spectrophotometer. Mass spectrum for the free ligand was obtained by positive Fast Atom Bombardment (FAB) and was recorded on a VG autospec micromass spectrometer. ^1H NMR spectrum was acquired in DMSO- d_6 solution using a Bruker AMX400 MHz spectrometer with tetramethylsilane (TMS) as an internal standard for ^1H NMR. Metals were determined using a Shimadzu (A.A) 680 G atomic absorption spectrophotometer. Chloride was determined using potentiometer titration method on a (686-Titro processor-665Dosimat-Metrohm Swiss). Conductivity measurements were made with DMF solutions using a Jenway 4071 digital conductivity meter and room temperature magnetic moments were measured with a magnetic susceptibility balance (Jonson Matthey Catalytic System Division).

3. Synthesis

3.1. Preparation of the free ligand L

The free dithiocarbamate Schiff-base macrocyclic ligand, potassium 2,2'-(1E,1'E)-(1,2-diphenylethane-1,2-diylidene)bis(azan-1-yl-1-ylidene)bis(2,1-phenylene)dicarbamodithioate, was prepared in two steps as follows:

3.1.1. Preparation of bis-amine-Schiff base

A solution of phenylenediamine (2 mmol) in methanol (15 mL) was added slowly to a mixture of benzil (1 mmol) dissolved in methanol (20 mL). The reaction mixture was refluxed for 2 h, and then stirred at room temperature for a further 1 h. A white solid was collected by filtration, recrystallised from a mixture of hot methanol / H_2O , and dried under vacuum for 24 h to give the required compound as a white solid. Yield (66%), m.p = 165 °C. IR data (cm^{-1}): 3410, 3396 $\nu(\text{N-H})$; 3026, 3055 $\nu(\text{C-H})$; 1618 $\nu(\text{C=N})$; 1597 $\delta(\text{N-H})$; 1500, 1450 $\nu(\text{C=C})$.

3.1.2. Preparation of the free ligand

A mixture of bis-amine-Schiff base (1 mmole) in methanol (80 mL) was allowed to stir at room temperature for 15 min. KOH (2.2 mmole) was added and the solution was stirred for 20 min. On addition of CS_2 (2.2 mmol), a yellow solution was developed which was allowed to reflux for 1 h, and then stirred at room temperature for 8 h. A beige solid was collected by filtration, and then dried under

vacuum for 24 h. Yield (65%), mp = 192-195 °C. IR data (cm^{-1}): 3383 $\nu(\text{N-H})$; 3028, 3057 $\nu(\text{C-H})$; 1655, 1636 $\nu(\text{C=N})$; 1593 $\nu(\text{N-H})$; 1500 $\nu(\text{C=C})$; 1442 $\nu(\text{C-N})$; 1274, 977 $\nu(\text{CS}_2)$ as; 1006 $\nu(\text{CS}_2)$ s. The positive (FAB) mass spectrum of L showed the parent ion peak at m/z 618.15 (22.50 %) corresponding to $(\text{M})^+$ and the following fragments; 657.25 (28 %) $[\text{M}+\text{K}]^+$, 509.53 (18 %) $[\text{M}-(\text{K}_2\text{S})]^+$, 386.11 (100%) $[\text{M}-(\text{K}_2\text{S}+\text{C}_2\text{H}_2\text{S}_3)]^+$, 309.63 (100%) $[\text{M}-(\text{K}_2\text{S}+\text{C}_2\text{H}_2\text{S}_3+\text{C}_6\text{H}_5)]^+$.

3.2. General one pot synthesis of the complexes

A methanolic solution (20 mL) of the metal salt (1 mmol) (metal salts are hydrated chlorides except zinc as the anhydrous chloride) was stirred into a methanolic solution of bis-amine-Schiff base compound (1 mmol), KOH (2.2 mmol) and carbon dioxide (2 mmole) in methanol (40 mL). The reaction mixture was refluxed under N_2 for 2 h, resulting in the formation of a solid mass which was filtered, collected and recrystallised from hot methanol, and then dried under vacuum. Elemental analysis data, colours, and yields for the complexes are given in (Table 1).

3.3. Synthesis of $[\text{Zn}^{\text{II}}_2(\text{L})_2]$ from the free ligand

After (1 mmol) of ZnCl_2 was dissolved in methanol (20 mL), a solution of the free ligand (1.1 mmol) in MeOH (15 mL) was added. The reaction mixture was refluxed under N_2 for 1 h, resulting in the formation of a solid mass which was filtered, collected and recrystallised from hot methanol, and then washed with ether (10 mL) and dried under vacuum. All the spectroscopic data were identical to $[\text{Zn}^{\text{II}}_2(\text{L})_2]$ prepared *via* one pot method.

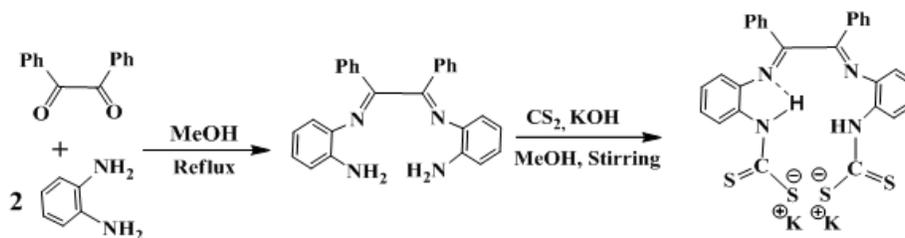
3.4. Determination of bacteriological activity

Bioactivities were investigated using agar-well diffusion method [12]. The wells were dug in the media with the help of a sterile metallic borer with centres at least 24 mm. Recommended concentration (100 μL) of the test sample 1 mg/mL in DMSO was introduced in the respective wells. The plates were incubated immediately at 37°C for 20 hours. Activity was determined by measuring the diameter of zones showing complete inhibition (mm). In order to clarify the role of DMSO in the biological screening, separate studies were carried out with the solutions alone of DMSO and they showed no activity against any bacterial strains. All these complexes were found to be potentially active against these bacterial strains, except for the strain of *Pseudomonas aeruginosa*.

Table 1. Colours, yields, elemental analyses, and molar conductance values.

Compound	Colour	Yield (%)	m.p	Found (Calcd.) (%)					$\Lambda_{25}(\text{cm}^2\Omega^{-1}\text{mol}^{-1})$
				M	C	H	N	Cl	
L	Beige	66	192-195	-	51.2 (50.9)	4.7 (4.9)	6.5 (6.6)	-	-
$[\text{Co}^{\text{II}}(\text{L})_2]$	Red brown	53	310*	10.1 (9.8)	55.8 (56.1)	3.9 (3.4)	8.9 (9.3)	Nil	1.7
$[\text{Ni}^{\text{II}}(\text{L})_2]$	Green	58	270*	9.5 (9.8)	56.5 (56.1)	3.8 (3.4)	9.1 (9.4)	Nil	3.6
$[\text{Cu}^{\text{II}}(\text{L})_2]$	Dark green	60	200*	10.2 (10.5)	55.7 (55.6)	3.2 (3.3)	9.3 (9.2)	Nil	5.9
$[\text{Zn}^{\text{II}}(\text{L})_2]$	Pale yellow	59	130	11.3 (10.8)	55.4 (55.5)	3.7 (3.3)	9.0 (9.2)	Nil	14.6

(*) decomposed

**Scheme 1.** Synthesis route of ligand.

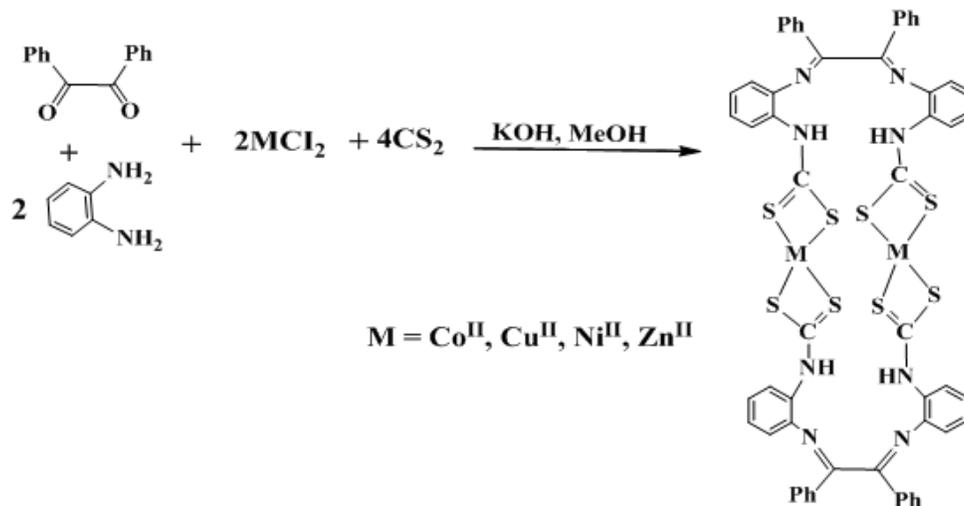
4. Results and Discussion

Bimetallic dithiocarbamate macrocyclic complexes were designed from bis-amine separated by an aromatic-imine spacer. This spacer conferred a degree of rigidity upon the ligand, thus pre-organising it for self-assembly. The resulting bis-amine-imine Schiff-base was then reacted with base, carbon disulphide and metal(II) salt to yield the dinuclear macrocyclic complex. In these template reactions metal centres play a key role in assisted self-assembly forming bimetallic dithiocarbamate macrocyclic complexes. The parent bis-amine-Schiff base was synthesised *via* a condensation reaction of benzil with *o*-phenylenediamine in methanol medium and then reacted with CS_2 in presence of KOH to give the free ligand with a good yield (Scheme 1). The ligand was characterised by elemental analysis, IR and mass spectra. Metal-directed self-assembly of the desired dinuclear macrocyclic M(II)-dtc (where M = Co^{II} , Ni^{II} , Cu^{II} and Zn^{II}) complexes was performed *via* the initial reaction of the bis-amine-imine with potassium hydroxide and carbon disulphide (Scheme 2). This generated the potassium bis-dtc salt that was not usually isolated. Addition of $\text{M}^{\text{II}}\text{Cl}_2$ to the solution resulted in the formation of the desired macrocyclic dtc complexes. The dinuclear dtc-

based macrocyclic complexes were recrystallised from hot methanol. The complexes are air stable solid, completely soluble in DMF, DMSO and hot MeOH, and not soluble in other organic solvents. All attempts to isolate crystals suitable for X-ray single crystal diffraction analysis were unsuccessful. However, we reported the preparation of the free ligand and its Zn-complex to confirm the proposed structure, ligand and metal complexes, and to support the validation of the one-pot preparation method. The molar conductance of solutions of the complexes in DMF is indicative of their non-electrolytic nature [13].

4.1. IR and NMR spectra

Important infrared bands of the ligand and its metal complexes together with their assignments are collected in Table 2. IR spectrum of the free ligand shows bands due to $\nu(\text{CS}_2)$, $\nu(\text{C}=\text{N})$ and $\nu(\text{N}-\text{H})$. The spectrum displays bands at 1655 and 1633 cm^{-1} assigned to the $-\text{Ph}-\text{C}=\text{N}(\text{imine})$, indicating the azometine bands are nonequivalents. This is perhaps due to the intra-hydrogen bonding between the hydrogen of the N-H and the nitrogen of the C=N groups (Scheme 1). The IR spectra of the dinuclear macrocyclics M(II)-dtc gave evidence for the formation of the dithiocarbamate functions and their coordination



Scheme 2. Synthesis route of complexes formation *via* one pot method.

Table 2. IR frequencies (cm^{-1}) of the compounds.

Compound	$\nu(\text{N-H})$	$\nu(\text{C=N})_{\text{imin}}$	$\nu(\text{-N-C-S})$	$\nu(\text{CS}_2)_{\text{as}}$	$\nu(\text{CS}_2)_{\text{s}}$	$\nu(\text{M-S})$
L	3028	1636, 1655	1442	1274, 977	1006	-
$[\text{Co}^{\text{II}}_2(\text{L})_2]$	3203	1631	1510	1260, 981	1058,	385, 425
$[\text{Ni}^{\text{II}}_2(\text{L})_2]$	3226	1629	1479	1301, 989	1055	354, 428
$[\text{Cu}^{\text{II}}_2(\text{L})_2]$	3236	1634	1486	1268, 1007	1053	389, 405
$[\text{Zn}^{\text{II}}_2(\text{L})_2]$	3205	1631	1520	1250, 982	1045	366, 452

to the dimetal fragments. The bands resulting from the stretching vibrations of the -C-N-S bonds at $1479\text{--}1520\text{ cm}^{-1}$ have wave numbers that are intermediate when compared to those reported for C-N single bonds ($1250\text{--}1350\text{ cm}^{-1}$) and C=N double bonds ($1630\text{--}1690\text{ cm}^{-1}$), suggesting partial double bond character and, therefore, partial delocalisation of π -electron density within the dithiocarbamate functions [14]. For the CS_2 groups two bands were observed, $\nu(\text{CS}_2)_{\text{as}}$ and $\nu(\text{CS}_2)_{\text{s}}$ at ($1250\text{--}1301, 981$) and $1006\text{--}1058\text{ cm}^{-1}$, respectively which are characteristic for an anisobidentate chelation mode of the ligand to the metal atoms [15]. The bands at $1629\text{--}1634\text{ cm}^{-1}$ are assigned to $\nu(\text{C=N})$ stretching of the non-coordinated imine group, indicating the azomethine groups are equivalent due to the rigidity that occurs upon complex formation. The disappearance of the hydrogen bonding interaction between the hydrogen of the amine group (N-H) and the nitrogen on the imine moiety (C=N), compared with that observed in the free ligand is also relevant in this. At lower frequency the complexes exhibited two sets of bands at $354\text{--}385$ and $405\text{--}425\text{ cm}^{-1}$ which are

assigned to the $\nu(\text{M-S})$ vibrational mode [16, 17], and supporting the anisobidentate chelation mode of the ligand.

In this work the predicted ^1H NMR spectrum of the free ligand was generated using CS Chem 3D Ultra Molecular Modeling and Analysis Program [18]. The aim of this was to compare the chemical shifts of different protons with that recorded for metal complexes, (Figure 1). The predicted ^1H NMR spectrum of the free ligand showed peaks at; δ_{H} 7.9 (4H), 7.5 (6H), 7.20 (2H, m), 7.1 (2H), 6.9 (4H, m), 4.1 (2H, s, N-H). However, the ^1H NMR spectrum of the complex $[\text{Zn}_2^{\text{II}}(\text{L})_2]$ in DMSO-d_6 showed peaks of coordinated ligand, shifted downfield and observed at; δ_{H} (400 MHz, DMSO-d_6): 8.1 (4H, m, Ar-H); 7.9 (4H, d, d J_{HH} 8.5 Hz, Ar-H); 7.5 (8H, m, Ar-H); 7.3 (10H, m, Ar-H); 7.1 (2H, m, Ar-H); 6.6 (4H, m, Ar-H); 6.4 (4H, m, Ar-H); 4.6 (4H, s, N-H). The ^1H NMR spectrum of the complex $[\text{Ni}_2^{\text{II}}(\text{L})_2]$ in DMSO-d_6 showed peaks observed at; δ_{H} (400 MHz, DMSO-d_6): 8.18 (4H, m, Ar-H); 7.98-7.89 (4H, d, 8.7 Hz, Ar-H); 7.765 (2H, d, d, J_{HH} 7.6 Hz, Ar-H); 7.377 (6H, m, Ar-H); 7.295 (4H, m, Ar-H); 7.25 (4H, m,

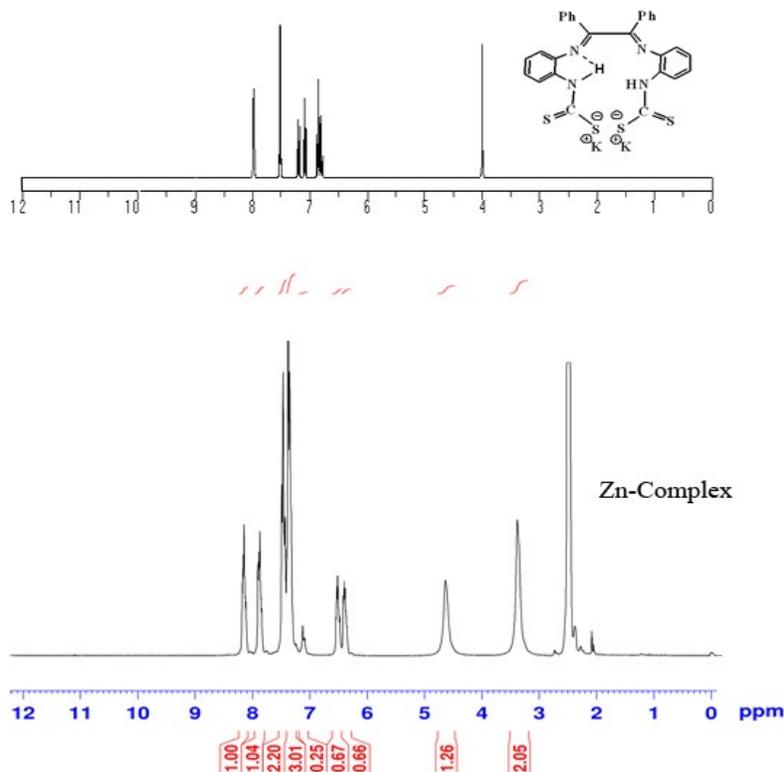


Figure 1. NMR spectra; the predicted ^1H NMR of the free ligand and the measured ^1H NMR of Zn-complex in DMSO- d_6 solvents.

Ar-H); 7.02-6.97 (2H, m, Ar-H) 6.78-6.67 (6H, m, Ar-H); 6.615 (4H, m, Ar-H). The observed chemical shift of N-H at 4.5 ppm revealed that there is no interaction occurred between the hydrogen of the amine group and the solvent. The splitting pattern of the complexes shows that rigidity is generated in the molecule as a result of coordination. In addition, the NMR spectrum of Ni-complex confirms the diamagnetism of the nickel atom. The NMR spectra revealed the stability of the complexes in DMSO solutions.

4.2. Electronic spectra and magnetic moments

The electronic spectra of the bimetallic macrocyclic complexes exhibited bands around (301-322) and (341-388) nm related to intra-ligand $\pi \rightarrow \pi^*$ and charge transfer (CT) transitions, respectively (Table 3). The electronic spectra confirm the stability of these complexes in DMF solutions and supported the stability of complexes in the NMR solution. The structures of complexes in solutions are in accord with their structures in the solid state. The electronic spectrum of the Co(II) complex is consistent with tetrahedral assignment [19-21]. The magnetic moment of this complex is typical for a tetrahedral structure. The Ni(II) complex is diamagnetic suggesting a square planar

geometry [17, 19]. The electronic spectrum of this complex was consistent with this assignment. The Cu(II)-complex gave a brown colour in DMF solutions indicating further coordination to solvent molecules. The spectrum of the Cu(II) complex displayed three absorption bands in the visible region. These bands could be attributed to ($^2\text{B}_{1g} \rightarrow ^2\text{E}_g$), ($^2\text{B}_{1g} \rightarrow ^2\text{B}_{2g}$) and ($^2\text{B}_{1g} \rightarrow ^2\text{A}_{2g}$) transitions of distorted octahedral Cu(II) complexes [19, 22, 23]. The magnetic moment value of the green Cu(II) complex, as well as the other analytical data, are in agreement with square planar structures [19-21]. The spectrum of the Zn(II) complex exhibited bands assigned to ligand $\pi \rightarrow \pi^*$ and L \rightarrow M charge transfer [16-21]. This complex is diamagnetic as expected. The metal normally prefers tetrahedral coordination.

4.3. Antimicrobial activity

The free dithiocarbamate Schiff-base macrocyclic ligand and its metal complexes were screened against *Staphylococcus aureus*, *Escherichia coli* and *Pseudomonas aeruginosa* to assess their potential as an antimicrobial agent by disc diffusion method. The measured zone of inhibition against the growth of various microorganisms is listed in Table 4. It is found

Table 3. Magnetic moment and u.v-vis spectral data in DMF solutions.

Compound	μ_{eff} (BM) (per atom)	Band position (λ , nm)	Extinction coefficient ϵ_{max} (dm ³ mol ⁻¹ cm ⁻¹)	Assignments
[Co ^{II} (L) ₂]	3.88	309	590	$\pi \rightarrow \pi^*$
		388	880	CT
		425	98	${}^4T_{1g}^{(F)} \rightarrow {}^4T_{1g}^{(P)}$
		668	38	${}^4T_{1g}^{(F)} \rightarrow {}^4A_{2g}^{(F)}$
[Ni ^{II} (L) ₂]	diamagnetic	322	780	$\pi \rightarrow \pi^*$
		366	1100	CT
		414	101	${}^1A_{1g} \rightarrow {}^1B_{1g}$
		655	47	${}^1A_{1g} \rightarrow {}^1A_{2g}$
[Cu ^{II} (L) ₂]	1.81	303	220	$\pi \rightarrow \pi^*$
		353	229	CT
		455	380	${}^2B_{1g} \rightarrow {}^2E_g$
		656	45	${}^2B_{1g} \rightarrow {}^2B_{2g}$
		795	18	${}^2B_{1g} \rightarrow {}^2A_{2g}$
[Zn ^{II} (L) ₂]	Diamagnetic	301	780	$\pi \rightarrow \pi^*$
		341	1235	CT

Table 4. Antibacterial activities for dithiocarbamate-Schiff-base macrocyclic complexes.

Compounds	<i>Staphylococcus aureus</i>		<i>Escherichia coli</i> (-)		<i>Pseudomonas aeruginosa</i> (-)	
	5mM	10mM	5mM	10mM	5mM	10mM
Free ligand	-	+	-	+	-	-
[Co ^{II} (L) ₂]	++	+++	+	++	-	-
[Ni ^{II} (L) ₂]	++	+++	+	++	-	-
[Cu ^{II} (L) ₂]	++	+++	+	++	-	-
[Zn ^{II} (L) ₂]	-	+	++	+++	-	-

(-) = No inhibition = inactive, (+) = (2-4) mm = active, (++) = (5-7) mm = more active, (+++) = (8-13) mm = highly active

that the metal complexes have higher antimicrobial activity than the free ligand. Hence complexation increases the antimicrobial activity. Such increased activity of the metal complexes can also be explained on the basis of chelation theory [24, 25]. According to this, the chelation reduces the polarity of the metal atom mainly because of the partial sharing of its positive charge with donor group and possible π -electron delocalisation over the whole ring. This increases the lipophilic character of the metal chelate system which favours its permeation through lipid layer of the cell membranes. The mode of action of compounds may involve the (CS₂) and (C=N) groups with active centres of cell constituents resulting in the interference with normal cell process. Furthermore, it was found that the complexes have long-lasting antimicrobial activities due to their thermal stabilities

6. Conclusions

The synthesis and coordination chemistry of some bimetallic dithiocarbamate Schiff-base macrocyclic complexes are reported. Two synthetic routes were followed in this work; a one-pot reaction using bis-amine-Schiff base compound, CS₂, KOH and metal chloride, and the synthesis of the free ligand and then the synthesis of its metal complexes. The mode of bonding and overall structure of the complexes were determined through physico-chemical and spectroscopic methods. These results revealed the preparation of four coordinated complexes. Biological activity of the ligand and its metal complexes against gram positive bacterial strain *Staphylococcus aureus* and gram negative bacteria *Escherichia coli* showed that the metal complexes became more active against bacterial strains. However, these metal complexes do not

affect the activity of *Pseudomonas aeruginosa* bacteria.

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