Synthesis, X-Ray Crystal Structure, Bactericidal and Kinetic Study of some Mononuclear Zinc and Mercury Complexes Supported by Bisaroylhydrazone Derivatives

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Abstract

This work includes the synthesis of two derivatives of cyclohexane bisaroylhydrazone: (L_1) and (L_2). These compounds were synthesized via the condensation reaction of 1,2-cyclohexanedione with an appropriate hydrazide derivative in acidic medium. The prepared ligands were reacted with zinc chloride or mercury chloride under ambient conditions. Consequently, mononuclear type complexes: $[Zn(L_1)Cl_2]$ **(1)**, $[Zn(L_2)Cl_2].CH_3CN$ **(2)**. $[Hg(L_1)Cl_2]$ **(3)** and $[Hg(L_2)Cl_2].CH_3CN$ **(4)** were obtained. Different techniques have been used to characterize the prepared organic ligands and their metal complexes (X-ray single crystal crystallography and microelemental analyses in addition to infrared, nuclear magnetic resonance, X-ray powder diffraction, Ultraviolate-visible-Near infrared, and mass spectroscopes). Depending upon the X-ray crystallography, it seems that the obtained products of **1, 2, 3** and **4** are mononuclear complexes. Each structure comprises a $[M\ (L)]^{2+}$ core. The kinetic of complex formation of **2** was investigated and the results are investigated and compare with that of **4.** The study showed in general, the formation of **2** and **4** in one phase with a first-order type reaction. Antibacterial activities of all the prepared compounds against some pathogenic bacteria (*Staphylococcus aureus* and *Escherichia coli*) were evaluated, which exhibit a good growth inhibitory activity. [DOI: 10.22401/ANJS.22.1.03]

Keywords**:** Mononuclear complexes, Bisaroylhydrazone, Kinetic studies.

Introduction

In general, there has been an increased interest in hydrazide and their derivatives, particularly in the last few years, related to their coordinative and pharmacological activity as well as their use in analytical chemistry as metal-extracting agents [1–11]. These compounds possess diverse biological and pharmacological properties such as antimicrobial, anti-inflammatory, analgesic, antifungal, anti-tubercular, antiviral, anticancer, antiplatelet, antimalarial, anticonvulsant, cardio protective, antihelmintic, antiprotozoal, anti-trypanosomal, antischistosomiasis..etc.

Benzohydrazide and their derivatives are poly-functional molecules (containing multi-functional groups in their structures like –CO, –NH– and $–NH_2$). Due to that, a wide range of compounds have been prepared based on benzohydrazide derivative [1,4,6,9,11]. Among all of these, aroylhydrozones (Schiff bases) represent one of the most known and important compounds. These compounds possessing an azomethine -NHN= CH - proton constitute an important class of compounds for different biological activities : antimicrobial, anticovulsant, analgesic, antiplatelet, anti-inflammatory, anti-tubercular, anticancer and antitumor as well as a new drug development [6–8, 11].

Reaction of aroylhydrazide with di-aldehyde or di-ketone produces bisaroylhydrazones [3,12–14]. Bisaroylhydrazones are known to be a class of versatile ligands, capable of generating different molecular architectures (even have been used as starting materials for the formation of 1,2,3,4- tetrazine, 1,3,4-oxadiazine or 1,2,3-triazine derivatives [12]).

This work is focus on the synthesis of new bisaroylhydrazone derivatives and study their coordination behavior toward Zn(II) and Hg(II) ions as a part of our continuation work in this field [15,16]

Experimental

Materials and instruments

All the reagents that are used in this work are purchased from commercial sources (Sigma-Aldrich Co. and Alfa Aesar Co.). ^1H and $^{13}C\{^1H\}$NMR spectra were measured in DMSO–d_6 using a Bruker 400 MHz spectrometer. Mass spectra of the ligands were

obtained using Orbitrap LTQ XL-Thermo Fisher scientific mass spectrometer. Infrared spectra were performed using a Vertex 70-FTIR spectrometer. Electronic spectra were carried out with a Shimadzu UV-3101PC spectrophotometer for (1×10^{-3} M) of the samples in DMSO at RT. EuroEA Elemental Analyzer was used to determine the elemental analyses (C, H and N). While (Zn and Hg) were measured with a 7300 V ICP-OES PerkinElmer-Optima Spectrometer. X-ray powder diffraction patterns were obtained with a Stoe Powder Diffractometer System Stadi P., using Cu-Ka radiation (λ = 1.54178 Å).

Synthesis of ligands (general procedure)

A mixture of an appropriate hydrazide derivative (1.46g, 10.7mmol for benzhydrazide) and (1.78g, 10.7mmol for 4-methoxybenzhydrazide), 1,2-cyclohexanedione (0.6g, 5.35mmol) and glacial acetic acid (2ml) in methanol ($35cm^3$) was reflux for 5h. The light yellow microcrystalline powder that deposited is filtered and washed with CH_3OH. Yields: (1.40g, 90% for L_1) and (1.70g, 93% for L_2). Microelemental analysis% calculated (found): for L_1: C 68.9 (68.8), H 5.8 (5.8), N 16.1 (16.1), for L_2: C 64.7 (64.6), H 5.9 (5.8), N 13.7 (13.5). Spectroscopic data for L_1: ^{1}H NMR spectrum δ/ppm: cyclohexane protons: 1.74 (4H, m, CH_2), 2.63 (2H, t, J_{HH} = 3.1 Hz, CH_2), 2.83 (2H, t, J_{HH} = 3.1 Hz, CH_2); other protons: 7.52–8.22 (10H, m, aromatic protons), 11.15 (1H, s, NH-keto form), 14.45 (1H, s, OH-enol form). $^{13}C\{^1H\}$NMR spectrum δ/ppm: 21.54–34.24 (cyclohexane carbons), 128.88–133.44 (aromatic carbons), 153.55 (C=N), 163.74 (C=O). Mass spect. (m/z): 348. IR spectrum υ/cm^{-1}: 3217 (w-m, υ(NH)), 3060 (w, υ(C−H aromatic)), 2960 (w, υ_{as}(C−H) of CH_2), 2876 (w, υ_s(C−H) of CH_2), 1656 (s, υ(C=O)), 1602, 1578 (m, υ(C=C aromatic)), 1518 (m, υ(C=N)). Spectroscopic data for L_2: ^{1}H NMR spectrum δ/ppm: cyclohexane protons: 1.75 (4H, m, CH_2), 2.63 (2H, t, J_{HH} = 3.1 Hz, CH_2), 2.83 (2H, t, J_{HH} = 3.1Hz, CH_2); other protons: 3.85 (6H, s, OCH_3), 7.03–8.22 (8H, m, aromatic protons), 10.95 (1H, s, NH-keto form), 14.34 (1H, s, OH-enol form). $^{13}C\{^1H\}$NMR spectrum δ/ppm: 21.77–34.43 (cyclohexane carbons), 56.18 (OCH_3), 114.36–131.16 (aromatic carbons), 153.17 (C=N), 163.13 (C=O). Mass spect. (m/z): 408. IR spectrum υ/cm^{-1}: 3365 (w-m, υ(NH)), 3059 (w, υ(C−H aromatic)), 2986 (w, υ_{as}(C−H) of CH_3), 2946 (w, υ_{as}(C−H) of CH_2), 2873 (w, υ_s(C−H) of CH_3), 2833 (w, υ_s(C−H) of CH_2), 1678 (s, υ(C=O)), 1602, 1575 (m, υ(C=C aromatic)), 1528 (m, υ(C=N)), 1240 (vs, υ(C−O)).

Synthesis of metal complexes

[Zn(L_1)Cl_2] compound (1)

$ZnCl_2$ (0.05 g, 0.367 mmol) was dissolved in CH_3CN ($6cm^3$) and added to L_1 (0.127 g, 0.367 mmol) in CH_3CN ($35cm^3$). After couple of days yellow crystals formed which are filtered and washed with CH_3CN. Yield: 0.125g, 59%. Microelemental analysis% calculated (found): C49.6(49.4), H4.2(4.4), N11.6(11.5), Zn13.5(13.3). ^{1}H NMR spectrum δ/ppm: cyclohexane protons: 1.74 (4H, m,CH_2), 2.64 (2H, t, J_{HH} = 3.1 Hz, CH_2), 2.83 (CH_2, t, 2H, J_{HH} = 3.1 Hz); other protons: 7.50–8.19 (10H, m, aromatic protons), 11.14 (1H, s, NH-keto form), 14.41 (1H, s, OH-enol form). $^{13}C\{^1H\}$NMR spectrum δ/ppm: 22.42–35.13 (cyclohexane carbons), 129.79–134.32 (aromatic carbons), 154.53 (C=N), 164.64 (C=O). IR spectrum υ/cm^{-1}: 3196 (w-m, υ(NH)), 3064 (w, υ(C−H aromatic)), 2957 (w, υ_{as}(C−H) of CH_2), 2880 (w, υ_s(C−H) of CH_2), 1667 (s, υ(C=O)), 1600, 1583 (m, υ(C=C aromatic)), 1531 (m, υ(C=N)).

[Zn(L_2)Cl_2].CH_3CN compound (2)

$ZnCl_2$ (0.06 g, 0.431mmol) was dissolved in CH_3CN ($6cm^3$) and added to L_2 (0.176g, 0.431mmol) in CH_3CN ($35cm^3$). After couple of days yellow crystals formed which are filtered and washed with CH_3CN. Yield: 0.135g, 62.7%. Microelemental analysis% calculated(found): C49.2(49.1), H4.6(4.5), N12.0(11.6), Zn11.2(11.0). ^{1}H NMR spectrum δ/ppm: cyclohexane protons: 1.74 (4H, m, CH_2), 2.62 (2H, t, J_{HH} = 3.1 Hz, CH_2), 2.82 (2H, t, J_{HH} = 3.1Hz, CH_2); other protons: 3.85 (6H, s, OCH_3), 7.03–8.23 (8H, m, aromatic protons), 10.95 (1H, s, NH-keto form), 14.34 (1H, s, OH-enol form). $^{13}C\{^1H\}$NMR spectrum δ/ppm: 21.54–34.19 (cyclohexane carbons), 55.93 (OCH_3), 114.15–130.96 (aromatic carbons), 151.33 (C=N), 162.91

(C=O). IR spectrum υ/cm^{-1}: 3365 (w-m, υ(NH)), 3068 (w, υ(C−H aromatic)), 2977 (w, υ_{as}(C−H) of CH_3), 2935 (w, υ_{as}(C−H) of CH_2), 2870 (w, υ_s(C−H) of CH_3), 2831 (w, υ_s(C−H) of CH_2), 1666 (s, υ(C=O)), 1602, 1576 (m, υ(C=C aromatic)), 1528 (m, υ(C=N)), 1250 (vs, υ(C−O)).

[Hg(L_1)Cl_2] compound (3)

$HgCl_2$ (0.10g, 0.360mmol) was dissolved in CH_3OH (6cm^3) and added to L_1 (0.125g, 0.360mmol) in CH_3OH (40cm^3). The mixture has been stirred for few minutes and a huge amount of precipitate formed. This precipitate was isolated and the clear solution was kept closed. After couple of days, yellow small crystals were deposited, which were filtered and washed with CH_3OH. Yield: 0.17g, 63.8%. Microelemental analysis% calculated (found): C38.8(38.9), H3.3(3.2), N9.0(9.1), Hg32.4(32.2). ^{1}H NMR spectrum δ/ppm: cyclohexane protons: 1.75 (4H, m, CH_2), 2.91 (4H, t, J_{HH} = 3.2 Hz, CH_2); other protons: 7.50–8.20 (10H, m, aromatic protons), 11.14 (2H, s, NH). ^{13}C{^{1}H}NMR spectrum δ/ppm: 22.33–35.26 (cyclohexane carbons), 127.67–134.47 (aromatic carbons), 155.77 (C=N), 160.56 (C=O). IR spectrum υ/cm^{-1}: 3230 (w-m, υ(NH)), 3054 (w, υ(C−H aromatic)), 2948 (w, υ_{as}(C−H) of CH_2), 2866 (w, υ_s(C−H) of CH_2), 1664 (s, υ(C=O)), 1600, 1575 (m, υ(C=C aromatic)), 1534 (m, υ(C=N)).

[Hg(L_2)Cl_2].CH_3CN compound (4)

The synthetic procedure of this compound can be found in our previous article [7]. Yield: 0.17g, 66.3%. Elemental analysis (%) calc. (found): C 40.0 (39.9), H 3.8 (3.7), N 9.7 (9.5), Hg 27.8 (27.5). ^{1}H NMR spectrum δ/ppm: cyclohexane protons: 1.80 (4H, m, CH_2), 2.91 (4H, t, J_{HH} = 3.1 Hz CH_2); other protons: 3.86 (6H, s, OCH_3), 7.09–7.93 (8H, m, aromatic protons), 11.54 (2H, s, NH). ^{13}C{^{1}H}NMR spectrum δ/ppm: 21.21–32.56 (cyclohexane carbons), 54.41 (OCH_3), 112.66–129.31 (aromatic carbons), 151.18 (C=N), 161.28 (C=O). IR spectrum υ/cm^{-1}: 3263 (w-m, υ(NH)), 3071 (w, υ(C−H aromatic)), 2972 (w, υ_{as}(C−H) of CH_3), 2946 (w, υ_{as}(C−H) of CH_2), 2879 (w, υ_s(C−H) of CH_3), 2840 (w, υ_s(C−H) of CH_2), 1657 (s, υ(C=O)), 1598, 1575 (m, υ(C=C aromatic)),1528 (m, υ(C=N)), 1248 (vs, υ(C−O)).

X-Ray Crystallography

Crystals of the prepared compounds were analyzed and data were collected with MoKα radiation on a Bruker APEX II system [17]. COSMO was used to determine the strategy of the data collection [18] and the integration was carried out with SAINT [19]. The corrections of multi-scan absorption were carried out with SADABS [20]. The structures of the prepared compounds were solved and refined with SHELXTL [21]. Crystal and refinement data for **1–4** are given in Table 1.

Kinetic Studies

This study was carried out using an Applied Photophysics SX.18MV stopped-flow spectrophotometer. The solutions of Zn(II) ion and L_2 in acetonitrile were prepared under N_2 atmosphere and used within 30 minutes of preparation. Origin lab software was used to fit the absorbance-time traces to exponential curves. The obtained rate constants (k_{obs}) showed in the figures are the average of at least three experiments. All experiments were performed under pseudo-first-order conditions with the concentration of L_2 in an excess over the concentration of the Zn(II) ion.

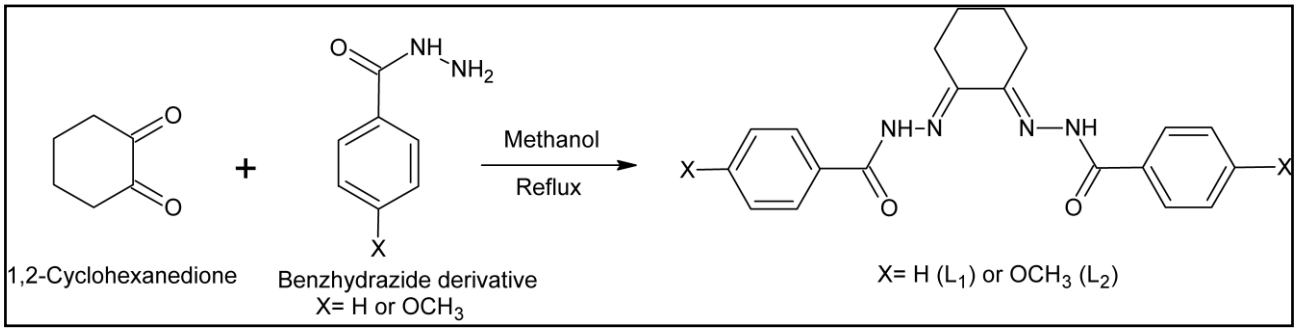
Bactericidal screening

Antibacterial activities of all the prepared compounds against some pathogenic bacteria (*Staphylococcus aureus* and *Escherichia coli*) were evaluated by the disc diffusion method. The concentration of the solutions of compounds in DMSO is (1×10^{-4} M). DMSO was used as control and gentamicin as the standard drug. The inhibition zones were measured after 24 h.

Results and Discussion

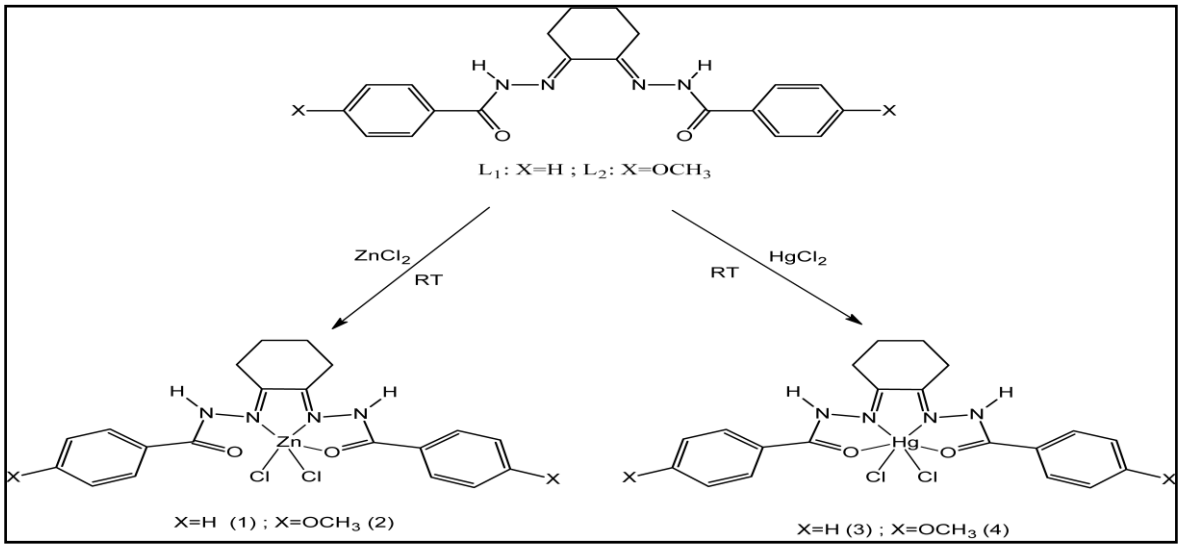
Synthesis and characterization of the prepared compounds

L_1 and L_2 were synthesized by the condensation of an appropriate benzhydrazide derivative (benzhydrazide or 4-methoxybenzhydrazide) and 1,2-cyclohexanedione in methanol, Scheme (1).



Scheme (1): General route for the preparation of ligands (L_1 and L_2).

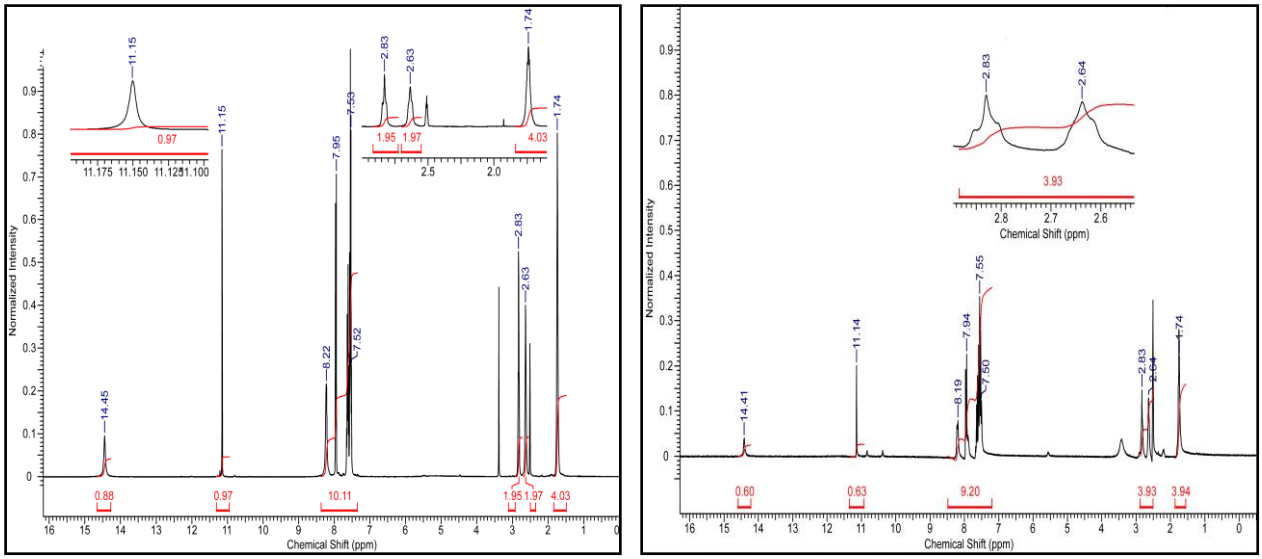
The reaction of equimolar amount of L_1 or L_2 and $HgCl_2$ or $ZnCl_2$, produced mononuclear type complexes: $[Zn(L_1)Cl_2]$ **(1)**, $[Zn(L_2)Cl_2].CH_3CN$ **(2)**. $[Hg(L_1)Cl_2]$ **(3)** and $[Hg(L_2)Cl_2].CH_3CN$ **(4)**, Scheme **(2)**.



Scheme (2): Synthetic diagram for the preparation of metal complexes.

Different techniques have been used to characterize the prepared organic ligands and their metal complexes (X-ray single crystal crystallography and microelemental analyses in addition to infrared, nuclear magnetic resonance, X-ray powder diffraction, Ultra violate-visible-Near infrared, and mass spectroscopies). The ^1H and ^{13}C NMR spectra of L_1, L_2, **1**, **2**, **3** and **4** in general showed signals related to the proton and carbon nuclei, see experimental part. ^1H NMR of these compounds displayed two triplet and one mutiplet signals at the chemical shifts range: (1.74 – 2.85) ppm which can be attributed to the cyclohexyl protons. The multipet that appeared at the range (6 – 8) ppm is assigned to the aromatic protons. The spectra also showed the appearance of two singlet signals at different chemical shifts which are due to the NH-keto and OH-enol forms, for instant see Fig.(1). The infrared spectra of the organic ligands and their metal complexes showed several absorptions, belonging to υ(NH) and υ(C=O) [22]. Moreover, the υ(C=N) that appeared in the spectra of the free ligands is found to be shifted either at lower or higher frequencies. This may indicates that the azomethane nitrogen atom is involved in the coordination. UV-Vis-NIR spectra of L_1 and L_2 displayed in general, two main absorption peaks at the ranges: (273–283 nm, ε_{max}= 14,000–14,190 $dm^3. mol^{-1}. cm^{-1}$) and (338–344 nm, ε_{max}= 7,200–7,800 $dm^3. mol^{-1}. cm^{-1}$) attributable to the π-π* and n-π* transitions, respectively. The spectra of all the prepared complexes **(1–4),** caused bathochromic shift of ligand band related to the π-π* transition. This band was appeared at the range: (335–342 nm,

ε_{max}= 15,600–18,200 dm^3. mol^{-1}. cm^{-1}). No band related to n-π* transition could be clearly observed in these spectra except in **4**, which shows a shoulder with low intensity, detected at (430 nm, ε_{max}= 1,180 dm^3. mol^{-1}. cm^{-1}). So, the band related to n-π* in these compounds may be obscured by π-π* band. New band were observed in all spectra of the prepared complexes at the range: (385–450 nm, ε_{max}= 10,200–11,000 dm^3. mol^{-1}. cm^{-1}). These bands were assigned to charge transfer transition. No d-d transitions are detected in the spectra of metal complexes, because of filled d–orbitals [23].

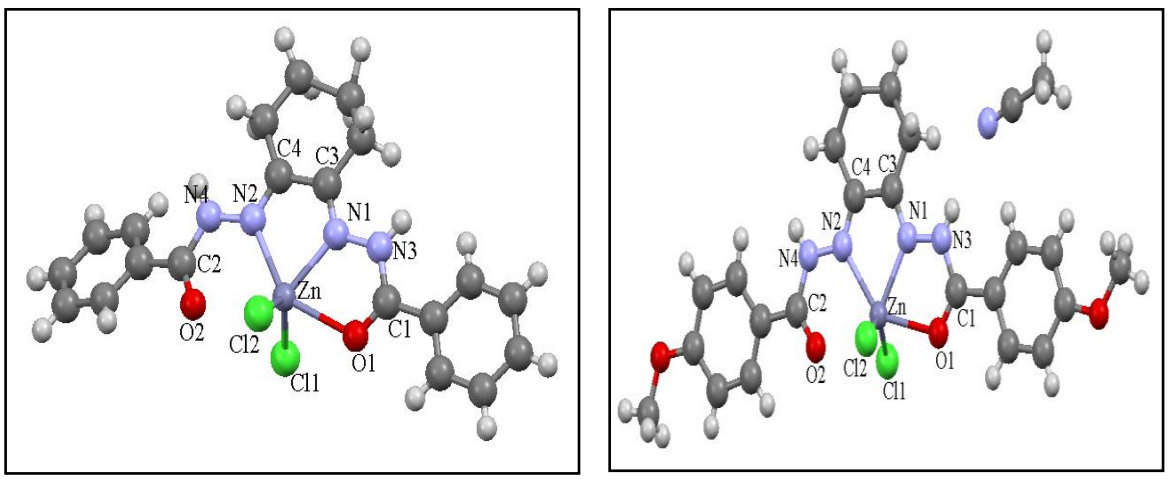


(i) (ii)

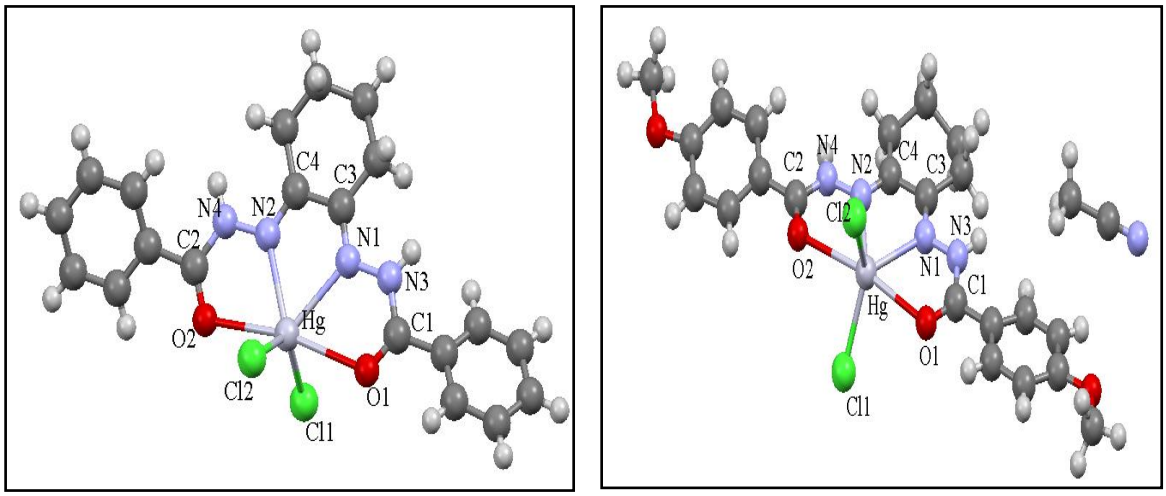
Fig.(1): (i) ^{1}HNMR spectrum of L_1 (ii) ^{1}HNMR spectrum of 1.

X-ray structures of mononuclear-zinc and mononuclear-mercury complexes

Figures 2 show the x-ray crystal structures of $[Zn(L_1)Cl_2]$ **(1)**, $[Zn(L_2)Cl_2].CH_3CN$ **(2)**. $[Hg(L_1)Cl_2]$ **(3)** and $[Hg(L_2)Cl_2].CH_3CN$ **(4)**. In general, the structure of each complex comprises the $[M(L)]^{2+}$ core (L: L_1 or L_2, M= Zn^{2+} or Hg^{2+}). Furthermore, it is clearly seen from this figure that L_1 and L_2 are behave as planar quadridentate ligands. The zinc complexes are found to be five coordinate with square-based pyramidal (one oxygen atom and two nitrogen atoms of bishydrazone ligand, and two chloro atoms), while the mercury complexes are six coordinate with octahedral geometry (two oxygen atoms and two nitrogen atoms of bishydrazone ligand, and two chloro atoms). Full details of the bonds length for compounds **1** to **4** are listed in Tables (2 and 3). The XRD pattern obtained experimentally is quite close to that obtained from the x-ray crystal data of the compounds (for example see Fig.(3).



(A) (B)



(C) (D)

Fig.(2): X-ray crystal structures of 1 (A), 2 (B), 3 (C) and 4 (D).

Table (1)
Crystal data and experimental details for 1, 2, 3 and 4.

	1	**2**	**3**	**4**
Crystal size (mm^3)	0.12 × 0.11 × 0.10	0.13 × 0.13 × 0.11	0.12 x 0.10 x 0.08	0.32 x 0.26 x 0.12
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic
Space group	P1	P1	P1	P1
Unit cell dimensions (Å, °):				
a	9.0312(2)	10.1345 (3)	9.0881(2)	11.2103(15)
b	10.5576(2)	10.7268 (3)	10.3420(3)	11.8606(16)
c	11.6525(2)	13.5438 (4)	11.2757(3)	19.223(3)
α	86.050(1)	77.386(1)	81.983(2)	86.901(5)
β	82.484(1)	70.445(1)	80.153(2)	76.165(4)
γ	80.855(1)	65.529(2)	83.188(1)	75.252(4)
Volume ($Å^3$)	1086.18(4)	1257.33(6)	1029.09(5)	2399.9(6)
Temperature (K)	133(2)	133(2)	133(2)	120(2)
F(000)	496	604	596	1364
Absorption coefficient (mm^{-1})	1.400	1.231	7.763	6.676
Theta range for data collection (°)	2.57 to 27.48	2.10 to 27.48	1.85 to 27.48	1.09 to 32.60
Reflections collected	7692	9514	6183	51449
Independent reflections	4898 R(int) = 0.0172	5598 R(int) = 0.0230	4600 R(int) = 0.0441	13435 R(int) = 0.0480
Trans max/min	0.7456 / 0.6342	0.7456 / 0.6640	0.7456/ 0.3763	0.5013 / 0.2238
Final R indices [I>2sigma(I)]	R1 = 0.0307 wR2 = 0.0672	R1 = 0.0315 wR2 = 0.0716	R1 = 0.0558 wR2 = 0.1331	R1 = 0.0245 wR2 = 0.0481
indices (all data)	R1 = 0.0339 wR2 = 0.0693	R1 = 0.0357 wR2 = 0.0745	R1 = 0.0694 wR2 = 0.1432	R1 = 0.0360 wR2 = 0.0515

Table (2)
Selected bond lengths in 1 and 2.

	1	2
Zn(1) – O(1)	2.3711(14)	2.3704(14)
Zn(1) – N(1)	2.1293(16)	2.1600(15)
Zn(1) – N(2)	2.2154(15)	2.2135(16)
Zn(1) – Cl(1)	2.2268(5)	2.2366(5)
Zn(1) – Cl(2)	2.2419(5)	2.2595(5)
C(3) – N(1)	1.2811(3)	1.2887(2)
C(4) – N(2)	1.2944(2)	1.2924(2)
C(1) – N(3)	1.3623(3)	1.3765(2)
C(2) – N(4)	1.3782(2)	1.3894(2)
C(1) – O(1)	1.2189(2)	1.2229(2)
C(2) – O(2)	1.2150(2)	1.2190(2)
C(3) – C(4)	1.4894(2)	1.4920(2)
N(1) – N(3)	1.3741(2)	1.3645(2)
N(2) – N(4)	1.3665(2)	1.3688(2)

Table (3)
Selected bond lengths in 3 and 4.

	3	4
Hg(1) – O(1)	2.7329(8)	2.674(2)
Hg(1) – O(2)	2.6960(10)	2.652(2)
Hg(1) – N(1)	2.4743(8)	2.452(2)
Hg(1) – N(2)	2.4240(10)	2.446(2)
Hg(1) – Cl(1)	2.4039(3)	2.4137(6)
Hg(1) – Cl(2)	2.3986(2)	2.3779(6)
C(3) – N(1)	1.2921(15)	1.291(3)
C(4) – N(2)	1.2871(14)	1.281(3)
C(1) – N(3)	1.3635(15)	1.381(3)
C(2) – N(4)	1.3717(14)	1.376(3)
C(1) – O(1)	1.2266(13)	1.211(3)
C(2) – O(2)	1.2299(13)	1.218(3)
C(3) – C(4)	1.4823(14)	1.480(4)
N(1) – N(3)	1.3509(12)	1.362(3)

Antibacterial study

Wide spectrum of biological activities of hydrazide and hydrazone type compounds are already reported in the literatures which showed the remarkable properties of such compounds, for example see reference 24. In this work, the prepared organic ligands and their metal complexes displayed an interesting biological activity against *Staphylococcus aureus* and *Escherichia coli* bacteria. The percentage of inhibition of growth was about 73–83%, see Fig.(4).

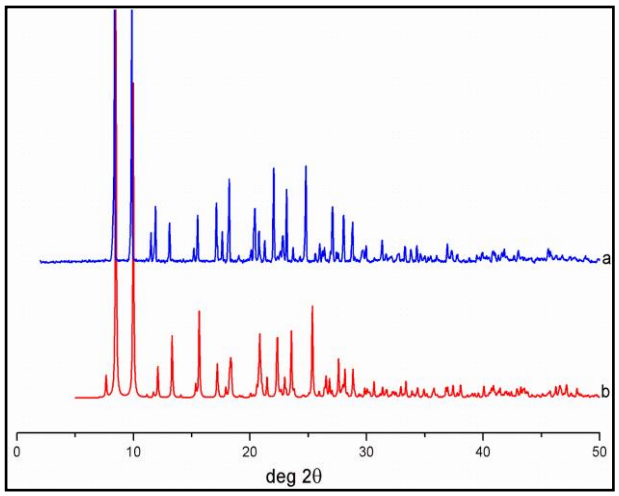


Fig. (3): X-ray diffraction patterns of 1: (a) pattern that obtained experimentally; (b) pattern that calculated from the x-ray data.

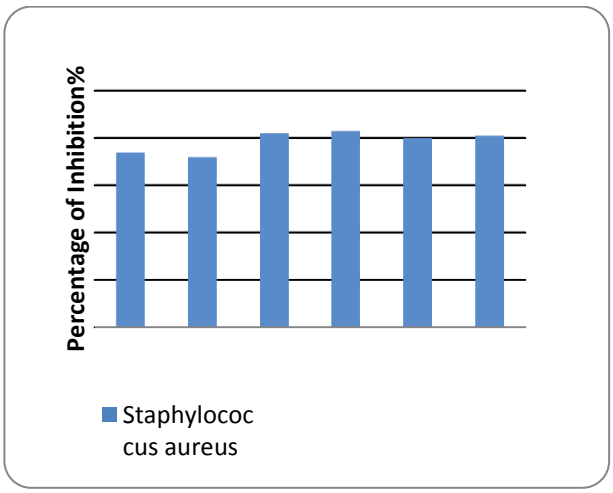


Fig.(4): Percentage of inhibition of some pathogenic bacteria by the prepared compounds.

Kinetics studies

Stopped-flow spectrophotometry was used to study the kinetics of the reactions between L_2 and Zn(II). The reactions were studied under pseudo-first-order conditions with $[L_2] \geq 10[Zn^{2+}]$ monitoring the reaction at λ = 430 nm. Fig.(5), shows that the absorbance-time traces is fitted to a single exponential curve, which indicates a first-order of the reactions depending upon the concentration of zinc ion. This was confirmed in studies where the concentration of zinc ion was varied in the range: 0.2–1.0 mmol dm^{-3} and the concentration of L_2 was 10 mmol dm^{-3}, but nevertheless, the values of the observed rate constants (k_{obs}) for each reaction were almost constant. The reactions displaying a first-order dependence on the concentration of L_2, as

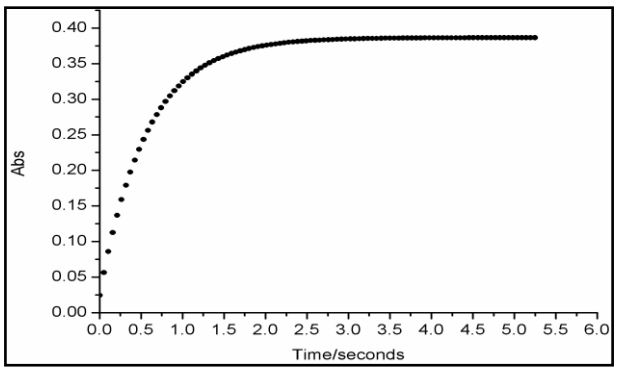
typified by the plot shown in Fig.(5) and the corresponding rate law in equation (1). As in our previous work [15,16, 25,26]**,** the initial binding of L_2 to $[Zn(NCMe)_4]^{2+}$ by replacement of one of the coordinated CH_3CN molecules represents the rate-limiting step of the chelate formation. The mechanism for such a reaction is focus on the generation of $[Zn(NCMe)_{(n-1)}]^{2+}$ (with a vacant site at which L_2 can bind (Scheme 3a)) through the dissociation of a coordinated solvent from $[Zn(NCMe)_n]^{2+}$. The full rate law for this mechanism is shown in equation (2). When the concentration of L_2 is small, k_{-1} [MeCN] > k_2 [L_2] the rate law would simplify to that shown in equation (3), which is of the same form as observed experimentally in eqn (1) ($k_a = k_1 k_2 / k_{-1}$ [MeCN]).

$$- d[Zn^{2+}]/dt = k_a [L_2][Zn^{2+}] \quad \text{.....(1)}$$

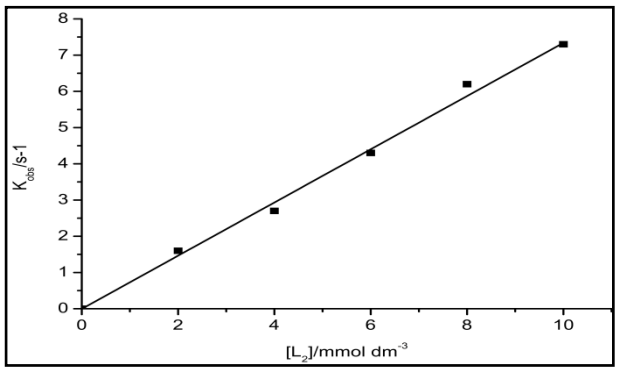
$$- d[Zn^{2+}]/dt = k_1 k_2 [L_2][Zn^{2+}] / k_{-1} [MeCN] + k_2 [L_2] \quad \text{.....(2)}$$

$$- d[Zn^{2+}]/dt = k_1 k_2 [L_2][Zn^{2+}] / k_{-1} [MeCN] \quad \text{.....(3)}$$

Our previous study [15,16] reports the kinetic of the reaction of L_2 with Cu^{2+} [15] or with Hg^{2+} [16]. In case of Hg^{2+}, the story is quite similar to that of Zn^{2+}, except that the rate constant of the formation of mercury complex (**4**) is lower than that of zinc complex (**2**). All attempts to study the kinetics of the reactions between L_1 and metal ions (Zn^{2+} or Hg^{2+}), were unsuccessful, because of the lack solubility of L_1 in acetonitrile!

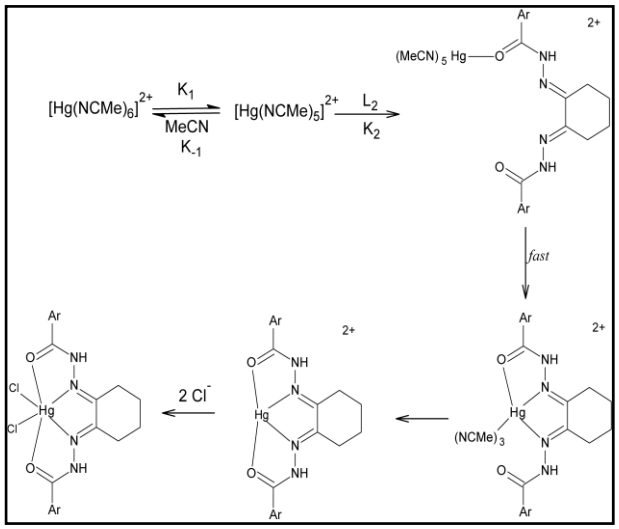


(i)

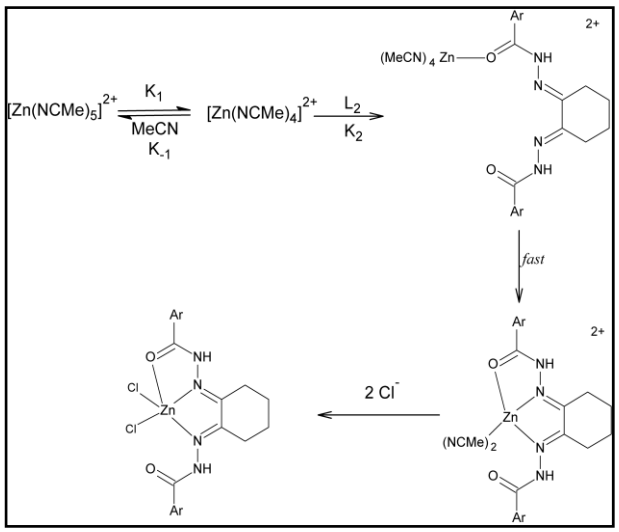


(ii)

Fig.(5): Kinetic studies for the formation of 2 i) Curve of the absorbance as a function of time ii) the first order dependence of the k_{obs} on the concentration of L_2 ($k_{obs}=7.4x10^2[L_2]$).



(i)



(ii)

Scheme (3): Kinetic mechanisms for the formation of 2 (i), and 4 (ii).

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