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Original Research Article

Synthesis, Characterization, Biological Activity, and Scanning Electron Microscopy Studies of Schiff Base Binuclear Complexes Co (II), Cu (II), Cd (II), and Pt (II) Derivative from Tolidine with Salicylaldehyde

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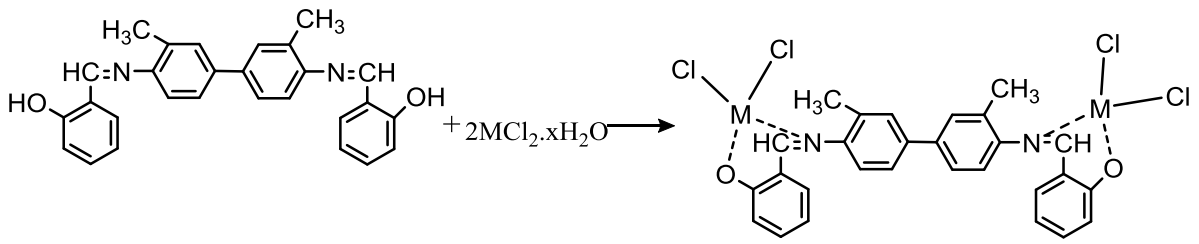
ABSTRACT

In this study, binuclear complexes with the general formula [M_2LCl_4] were prepared, which were derived from salsaldehyde with 3,3′-Dimethyl-[1,1′-biphenyl]-4,4′-diamine (toluidine) and metal ions M= Co (II), Cu (II), Cd (II), and Pt (II) in a ratio (2:1) (metal: ligand). These complexes were characterized by elemental analysis (CHN), UV-Visible, FT-IR, ^{1}H-NMR, and magnetic susceptibility, scanning electron microscopy (SEM), and molar conductivity. All complexes are non-electrolytic as the measurements confirmed that the complexes have a square planar structure. SEM showed that the complexes were of nanometric structure. The biological activity of the prepared complexes was tested to inhibit the growth of three types of bacteria: *Escherichia coli*, *Pseudomonas aeruginosa*, and *Staphylococcus aureus*.

GRAPHICAL ABSTRACT



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Introduction

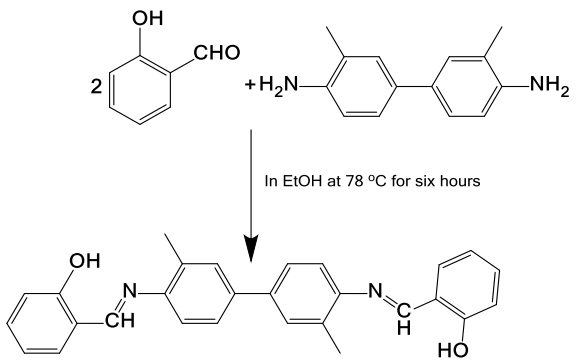
Schiff bases are organic compounds resulting from the reaction of an aldehyde or a ketone with primary amines to give the imine functional group, which can coordinate with metals due to the presence of a lone pair on nitrogen atom. They may be monodentate or polydentate, depending on the number of donor atoms in the ligand [1,2]. The presence of the C=N functional group gives Schiff's bases great importance in various industrial, agricultural, and nanotechnology applications [3]. Many Schiff base complexes have been given sufficient attention by chemists all over the world [4]. Complexes derivative from Schiff bases have been widely used in biological applications, like inhibition of bacterial growth and treatment of cancerous diseases [5]**.** The current study depicts the coordination behavior of the complexes of Co (II), Cu (II), Cd (II), and Pt (II) that derived from the condensation of 3,3'-dimethyl-4,4'-diaminobiphenyl with salicylaldehyde and in a ratio (2:1). Studying the effect of its complexes on three types of bacteria: *Escherichia coli, Pseudomonas aeruginosa,* and *Staphylococcus aurous* and comparing their effectiveness with chloramphenicol, and gentamycin antibiotics**.**

Materials and Mthods

The chemical substances used were of high purity and used without purification. The chemicals: salicylaldehyde, orthotolidine, glacial acetic acid, and $CoCl_2.6H_2O$ from (Sigma), $CuCl_2.2H_2O$, $CdCl_2$, and $PtCl_2$ (BDH), absolute ethanol, diethyl ether. Melting points were measured by an electro thermal 9300 instrument. Elemental analyses were performed using an elementar vario ELIII device. Conductivity measurements were done by conductivity meter (Cond 7Il0) with DMSO solutions, the magnetic susceptibility was measured at 25 °C using a magnetic susceptibility balance (Sherwood scientific). The FT-IR spectra carried out ALPHA II FTIR Spectrometer from Bruker Optics was measured in the range 400-4000 cm^{-1}. The electronic spectra were measured using UV Tg +92 spectrophotometer device with a measurement range of (190-1100) with 10^{-3} M solutions of DMSO at 25 °C. ^{1}H-NMR spectra were recorded in DMSO-d_6 solutions using Varin 500 MHz spectrometers. Scanning electron microscope was done by a ZEISS MODEL SIGMA VP device in Iran.

Synthesis of Schiff base 3,3-dimethyl- N,N'-bis[(E)-Arylmethylidene]biphenyl-4,4'- diamine (L)

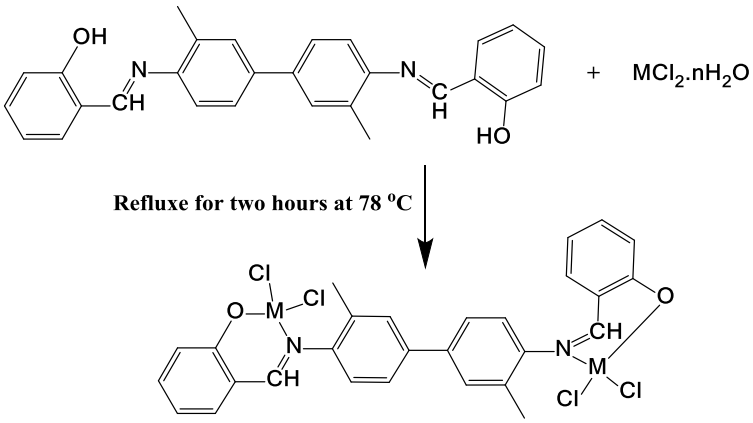
Salicylaldehyde (0.5 g, 4 mmol) was dissolved in absolute ethanol 15 mL and added dropwise to orthotolidine (0.424 g, 2 mmol) in absolute ethanol 20 mL with 5 drops of glacial acetic acid as catalyst. The mixture was refluxed for six hours at 78 °C. During the reflux time the solution volume was reduced until a light-yellow precipitate product appeared, and then the resultant product was collected, recrystallized with cooled ethanol, washed with diethyl ether, and dried at 50 ºC to produce 90% yield of L with melting point of 195-197 °C (Scheme 1).



Scheme 1: Synthesis of 3,3-dimethyl- *N,N'*-bis[(*E*)-Arylmethylidene]biphenyl-4,4'- diamine (L)

Synthesis of Complexes[$M_2(L)Cl_4$], M = Co (II), Cu (II), Cd (II), and Pt (II)

Divalent metals salt (1.0 mmol, 0.237 g, 0.170 g, 0.183 g, or 0.266 g) were dissolved in a hot mixture of water and ethanol (1:1) 25 mL. The free ligand (0.5 mmol, 0.21 g) was dissolved in hot ethanol 25 mL. Furthermore, divalent metal solutions were added gradually with stirrer to the free ligand solution and refluxed for two hours at 78°C. The resultant complexes were precipitated, filtered, and dried under vacuum to produce pure complexes in the general formula [$M_2(L)Cl_4$], where M = Co (II), Cu (II), Cd (II) or Pt (II). Moreover, physical appearance, melting point, and micro analysis for the elements, conductivity, and yield are listed in Table 1 (Scheme 2).



Scheme 2: Synthesis process of Co (II), Cu (II), Cd (II), and Pt (II) complexes

Table 1: Physical properties, analytical, and molar conductivity data of the prepared ligands and their complexes

No.	Compounds	Yield %	Color	M.P °C	Molar ʌ cond./ mol^{-1}, cm^{-1} hom	C% cal	H% cal	N% cal
						(C%) found	(H%) found	(N%) found
1	L	90%	Light yellow	195-197	8.25	6.65 (6.68)	5.70 (5.52)	79.9 (79.7)
2	[$Co_2(L)Cl_4$]	75%	Green	278-280	10.16	4.11 (4.15)	3.52 (3.47)	49.4 (49.2)
3	[$Cu_2(L)Cl_4$]	80%	Orange	260-262	22.50	3.78 (3.76)	3.24 (3.21)	45.4 (45.29)
4	[$Cd_2(L)Cl_4$]	77%	Yellow	273-275	19.42	3.55 (3.53)	3.04 (3.10)	42.6 (42.7)
5	[$Pt_2(L)Cl_4$]	70%	Brown	290-292	23.11	2.94 (2.86)	2.52 (2.54)	35.2 (35.1)

Anti-bacterial activity

The inhibitory activity of the prepared complexes was tested against three types of bacteria. *E.Coli*, *Pseudomonas aeruginosa*, and *Staphylococcus aureus*. Bacterial media were inoculated in broth (inoculation medium). The medium was inoculated by incubation at 37°C for 24 hours, and then the inoculation medium containing the culture medium was added, in a sterile manner, i.e. the nutrient medium for 24 hours and mixed well to obtain a uniform distribution. Thereafter, the solution (25 ml) was poured into each Petri dish, and then left at room temperature. The wells (6 mm) were cut into agar plates. Using sterile tubes, the wells are filled with (0.1 ml) of the prepared complexes that were dissolved in dimethyl sulfoxide and left for one hour. Next, they were incubated at 37°C for 24 hours, and then the diameter of inhibition zones was read. The minimum inhibitory concentrations were determined using the serial dilution method

Results and discussion

Molar conductivity

The molar conductivity of the prepared complexes was measured at (0.001 M or 1 mM) in DMSO solvent. The lower values of conductivity $ohm^{-1}.cm^{2}.mol^{-1}$) for all complexes indicate that the complexes are non- electrolytic, as presented in Table 1 [6].

UV-Visible spectra and magnetic properties

The electronic spectra of the $[Co_2(L)Cl_4]$complex showed three peaks at 885 nm, 397 nm, and 250 nm which are assigned to the $^4A_2$ (F) → $^4T_1$ (P), n→π*, and MLCT transitions, respectively. These values confirm that the complex is tetrahedral geometry around the Co (II) [7,8]. The value of the magnetic moment ٤,٢٣ B.M shows that the tetrahedral has a high value indicate second order orbital contribution [8], as provided in Table (2). The $[Cu_2(L)Cl_4]$complex showed three peaks at 525, 290, and 260 nm which are assigned to the $^2B_{1g}\rightarrow{}^2E_{2g}$,$^2B_{1g}\rightarrow{}^2A_{1g}$, n→π*, and MLCT transitions, respectively. These values are attributed to the fact that the complex took the form of a square planar geometry around of copper (II) [9,10]. It was found that the value of the magnetic moment is (1.78) B.M and confirming that the shape is square planar geometry [8]. The spectra of the cadmium (II) complex show two bands 306 nm and 242 nm, that are attributed to n→ π*and π→ π*.The electronic spectra of $[Pt_2(L)Cl_4]$ complexes exhibited bands 670, 530, and 265 transitions related to $^1A_{1g}\rightarrow{}^1T_{1g}$, $^1A_{1g}\rightarrow{}^1T_{2g}$, and MLCT charge transfer of square planar environment [11]. The UV-Vis data are indicated Table 2 (Figures 1-3).

Table 2: Electronic spectra and magnetic moments of the prepared complexes

No.	Compounds	wave length (nm)	Wave number (cm^{-1})	Electronic Transitions	μ_{eff} B.M	Geometric structure
1	$[Co_2(L)Cl_4]$	885 397 250	11299 25189 40000	$^4A_2$ (F) → $^4T_1$ (P) $n \rightarrow \pi^*$ MLCT	3.97	Tetrahedral
2	$[Cu_2(L)Cl_4]$	525 290 260	19048 34483 38462	$^2B_{1g}\rightarrow{}^2E_{2g}$ $^2B_{1g}\rightarrow{}^2A_{1g}$ LCT	1.88	Square planer
3	$[Cd_2(L)Cl_4]$	306 242	32680 41322	$n \rightarrow \pi^*$ MLCT	Dia	Tetrahedral
4	$[Pt_2(L)Cl_4]$	760 530 265	13158 18868 37736	$^1A_{1g}\rightarrow{}^1T_{1g}$ $^1A_{1g}\rightarrow{}^1T_{2g}$ MLCT	Dia	Square planer

Dia=diamagnetic

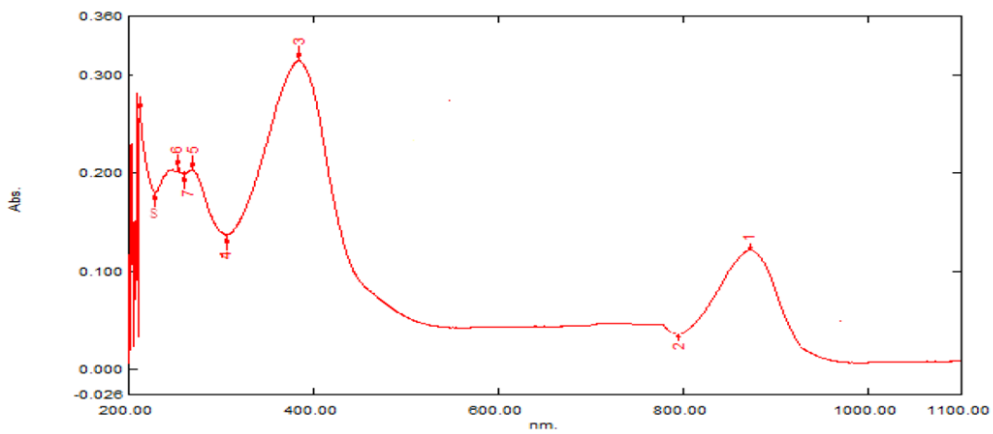


Figure 1: UV-Vis spectrum of the $[Co_2(L)Cl_4]$ complex

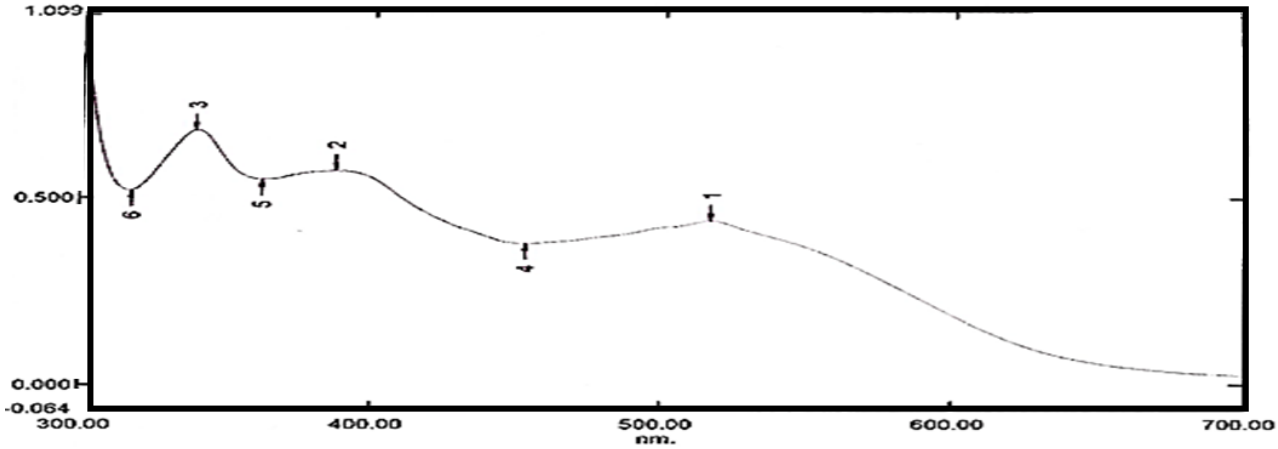


Figure 2: UV-Vis spectrum of the [$Cu_2(L)Cl_4$] complex

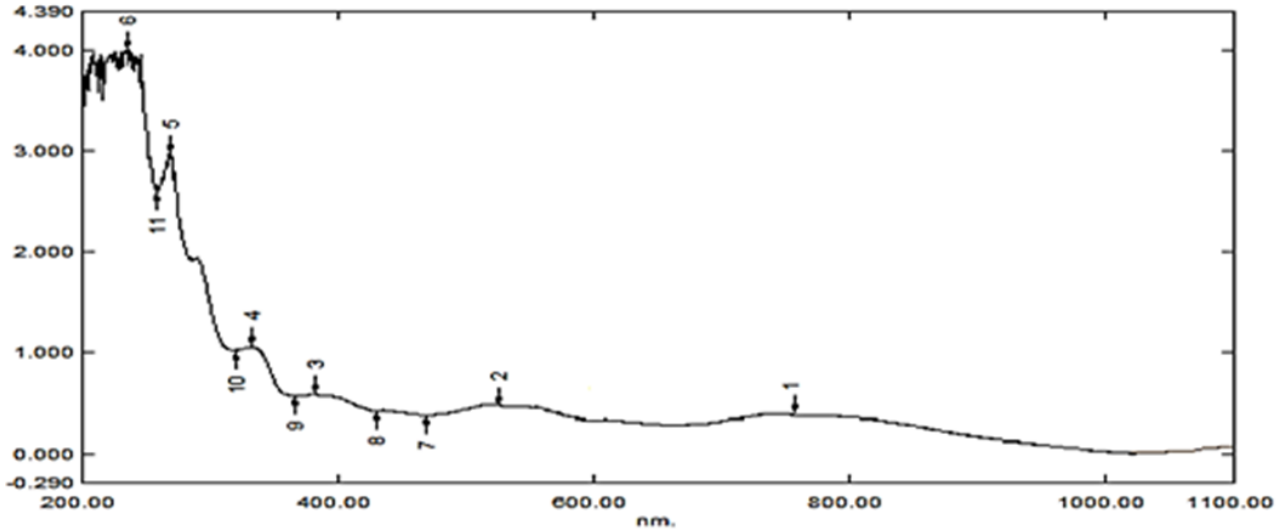


Figure 3: UV-Vis spectrum of the [$Pt_2(L)Cl_4$] complex

FT- IR spectral studies

The complexes showed characteristic absorption bands similar to the absorption peaks of the ligands, with a slight difference in the values which indicates chelation [12-14]. The complexes spectra displayed peaks at (1624-1626) cm^{-1} and (424-429) cm^{-1} due to γC=N of azomethine nitrogen and (M-N), respectively [15,16]. The absence of absorption bands at 3400 of phenolic hydrogen in the complexes indicates the coordination of metals with ligand and the absorption bands are shown in Table 3 (Figures 4-7).

Table 3: FT-IR data of ligands and their metal complexes

No.	Compounds	υ(C=H) cm^{-1}	υ(C-H) υArom cm^{-1}	υ(C-H) υAliph. cm^{-1}	υ(O-H) cm^{-1}	υ (M–N) (azomethine) cm^{-1}
1	L	1610 ,1584	3072	2894	3440	----
2	[$Co_2(L)Cl_4$]	1624, 1593	3072	2896	-----	416
3	[$Cu_2(L)Cl_4$]	1626,1594	3085	2896	-----	429
4	[$Cd_2(L)Cl_4$]	1625,1593	3072	2998	-----	424
5	[$Pt_2(L)Cl_4$]	1625,1574	3072	2963	------	424

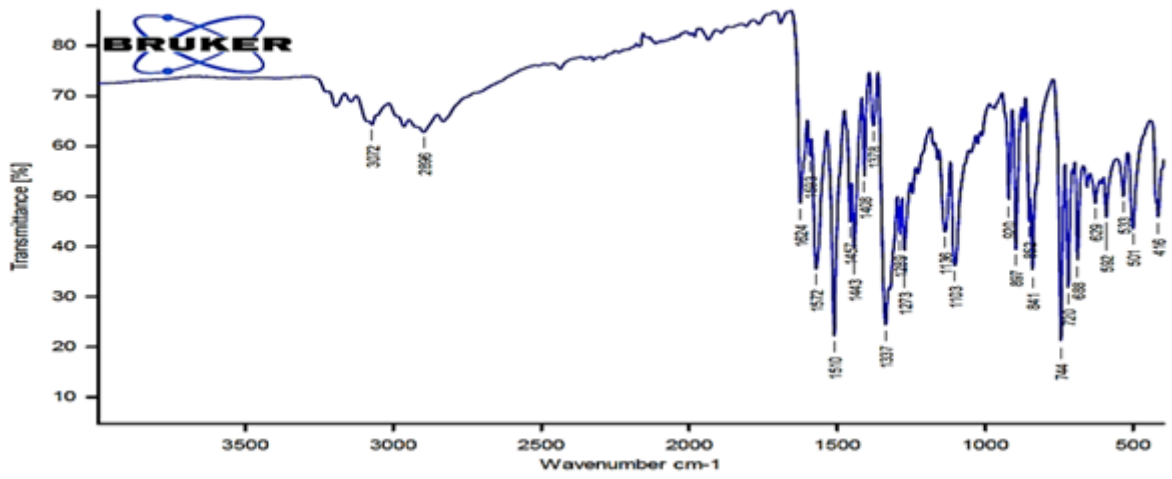


Figure 4. IR spectrum of complex $[Co_2(L)Cl_4]$

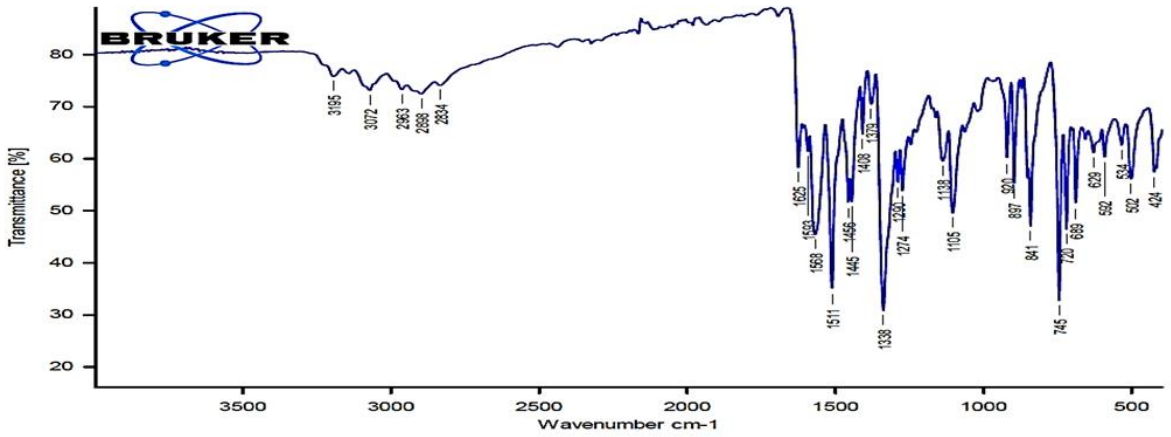


Figure 5: IR spectrum of complex $[Cu_2(L)Cl_4]$

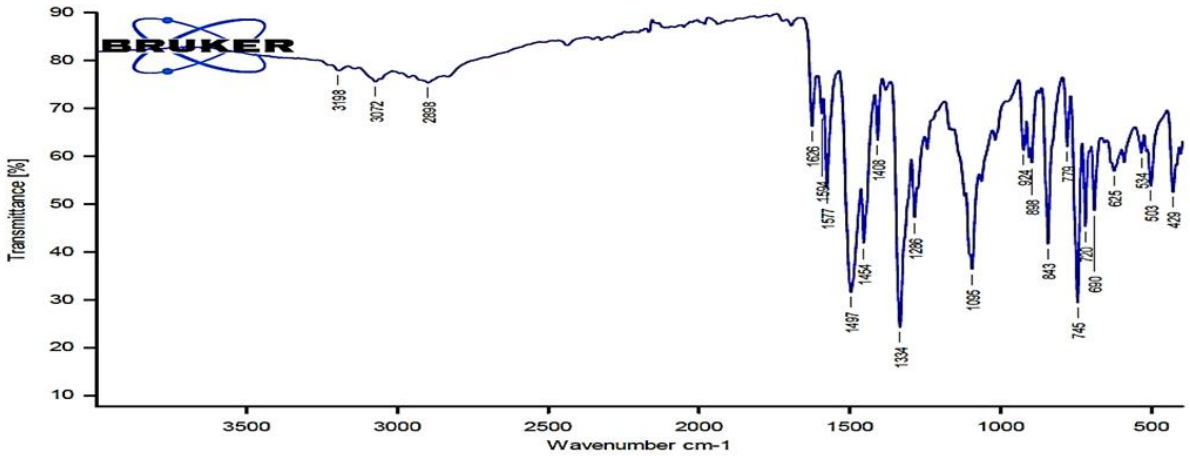


Figure 6: IR spectrum of complex $[Cd_2(L)Cl_4]$

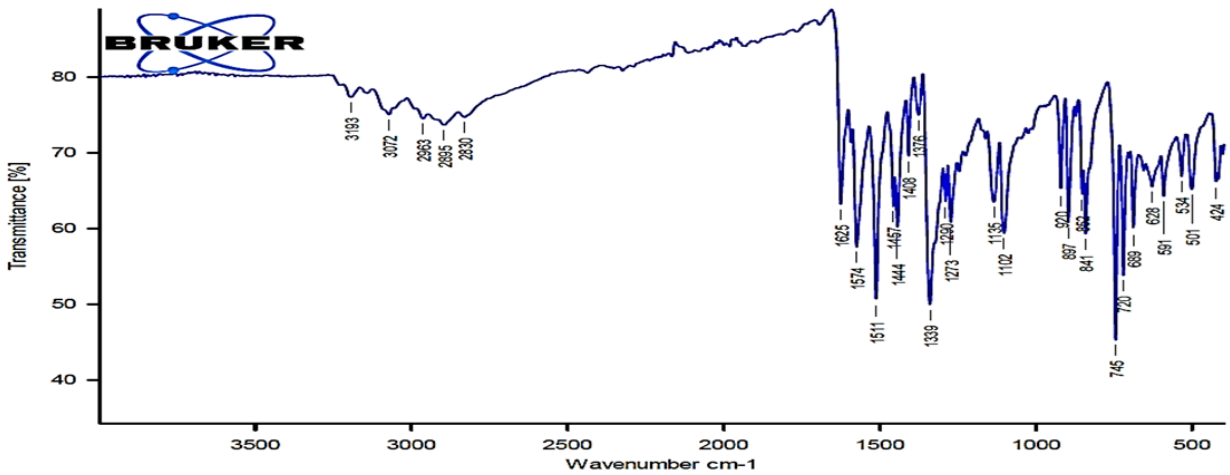


Figure 7: IR spectrum of complex $[Pt_2(L)Cl_4]$.

^{1}H-NMR spectral studies

NMR spectroscopy measurements are very important in the diagnosis of organic and inorganic compounds, as they give important evidence to the nature of the chemical composition in solution [17]. Figure 8 depicts 1H-NMR (DMSO-500MHz) δ= 11.728 (s, 2H, 2*OH), 7.69-7.87 (m, 14H, of phenyl groups, 2.30-2.51(m, 6H, 2*CH3), and (2H, 2CH=N) (Figure 8).

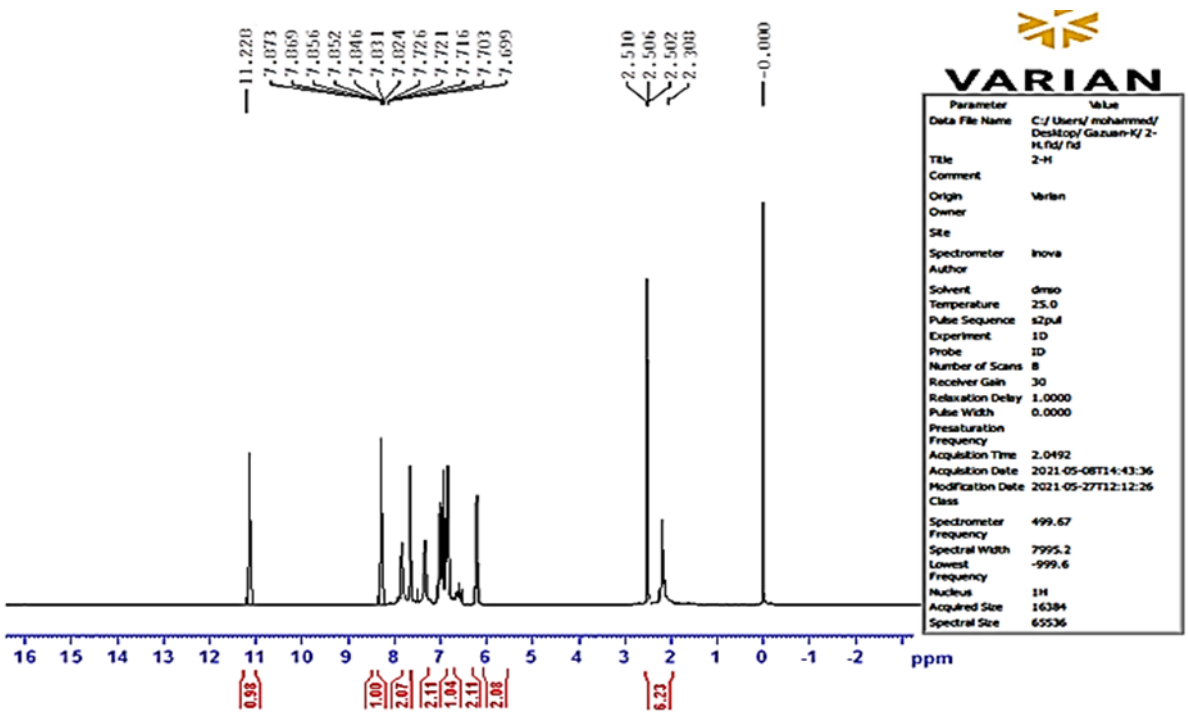


Figure 8: ^{1}H-NMR spectrum of ligand

Determination of antibacterial activity

The effect of the prepared complexes$[Co_2(L)Cl_4]$, $[Cu_2(L)Cl_4]$, $[Cd_2(L)Cl_4]$, and $[Pt_2(L)Cl_4]$ on three types of bacteria: *Escherichia coli*, *Staphylococcus aureus*, and *Pseudomonas aeruginosa* were studied, and dimethyl sulfoxide (DMSO) was used as a solvent [18,19]. A control model was performed for the solvent, which gave an activity greater than compared with the antibiotics Chloramphenicol and Gentamycin as follows:

For *Escherichia coli* bacteria (Gram-negative), the $[Co_2LCl_4]$ complex showed low activity at

concentrations of 50 and 100 µg/ml and high activity at concentrations of 150 µg/ml, while its complex $[Cu_2(L)Cl_4]$ showed a high inhibitory ability from the other complexes at concentration 150 µg/ml against *Pseudomonas aeruginosa*. For *Staphylococcus aureus*, the $[Pt_2(L)Cl_4]$ complex showed high inhibition activity, from other complexes [20], as indicated in Table 4 (Figure 9).

Table 4: Inhibiting activity of synthesized compounds comparison with antibiotics (inhabiting diameter mm)

Compounds	*Bacteria* *E.coli*			*Bacteria* *Pseudomonas aeruginosa*			*Bacteria* *Staphylococcus aureus*		
	Zone of Inhibition (mm)								
	Conc. (µg/m) 50	Conc. (µg/m) 100	Conc. (µg/m) 150	Conc. (µg/ml) 50	Conc. (µg/m) 100	Conc. (µg/ml) 150	Conc. (µg/ml) 50	Conc. (µg/ml) 100	Conc. (µg/ml) 150
$[Co_2LCl_4]$	24	30	55	10	12	25	11	22	38
$[Cu_2LCl_4]$	13	33	44	23	42	54	15	27	42
$[Cd_2LCl_4]$	16	25	45	7	13	26	17	24	37
$[Pt_2LCl_4]$	5	33	62	2	6	5	13	33	65
Chloramphenicol (30 mg/disc)	16			18			15		
Gentamycin (10 mg/disc)	14			13			15		

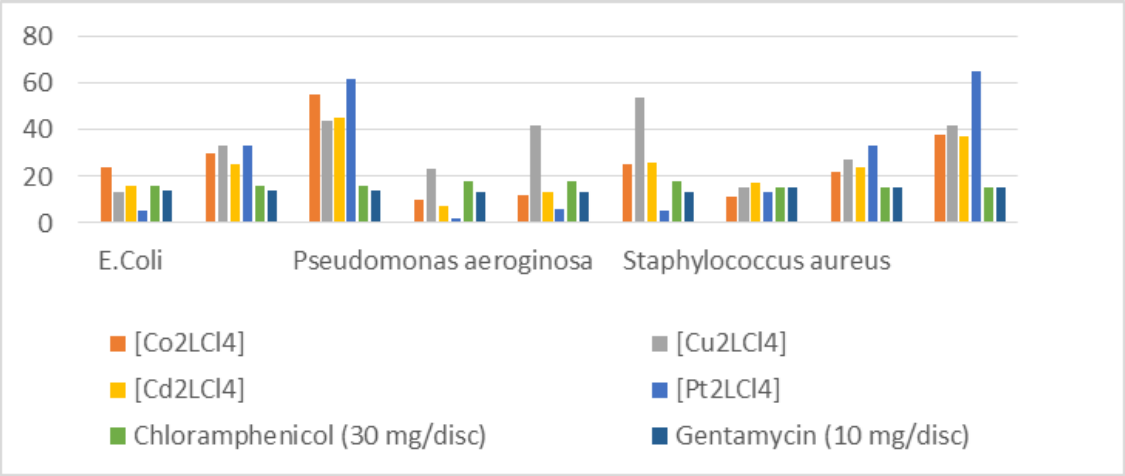


Figure 9: Graphical representation of biological activities of complexes against three bacteria

Scanning electron microscopy (SEM) studies

The SEM micrographs of complexes are presented in Figure 10. The SEM image of these complexes molecules are arranged in plate-shaped structure [13]. The particle size of the prepared complexes was on the order of a few microns in diameter. Therefore, particles whose size is close to or less than 100 nm, that is agglomerates of larger size, have been also observed [7] (Figure 10).

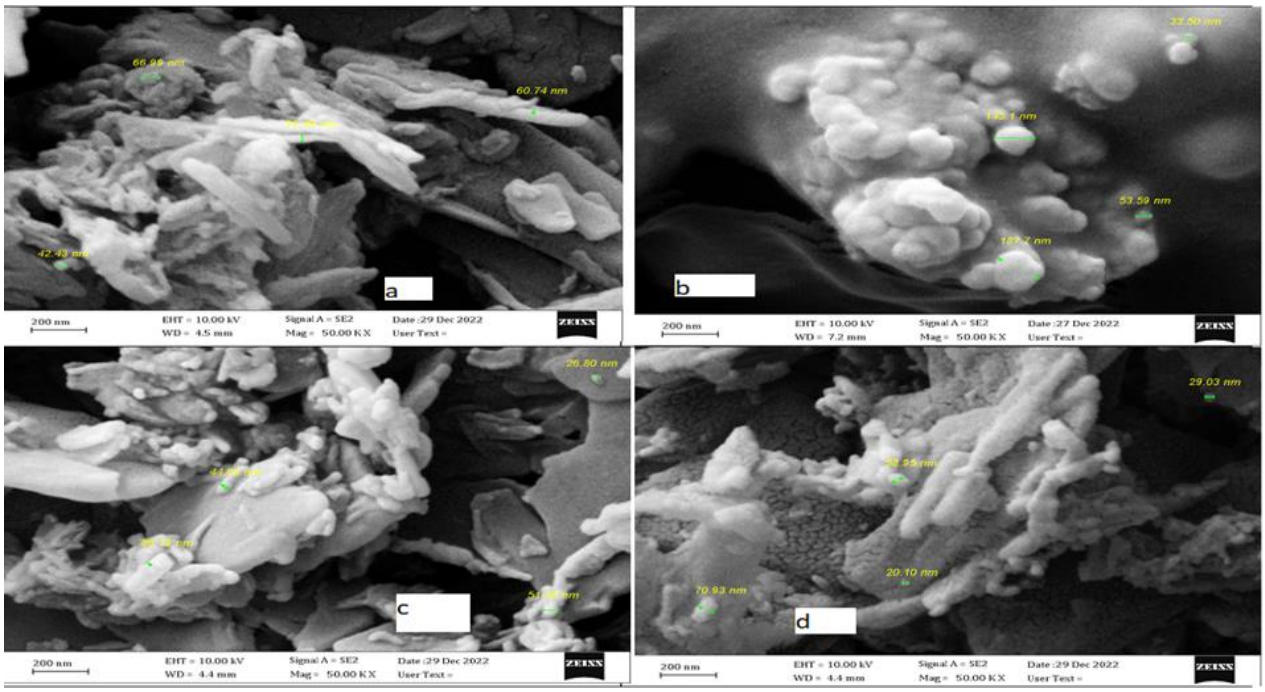


Figure 10: SEM image of (a) $[Co_2(L)Cl_4]$, (b) $[Cu_2(L)Cl_4]$, (c) $[Cd_2(L)Cl_4]$, and (d) $[Pt_2(L)Cl_4]$ complexes

Conclusion

In this study, binuclear Schiff base complexes were prepared. The measurements which confirms the tetrahedral geometry around Co(II) and Cd(II) as well as the square planar geometry around Cu(II) and Pt(II). The molar conductance confirms the non-electrolytic of complexes. The biological effectiveness study also confirmed that the Pt(II) complex at a 150 (μ/ml) concentration had the highest effect on the *E.coli* and *Staphylococcus aureus* bacteria, and the Cu(II) complex had the best effect on the *Pseudomonas aeruginosa* bacteria. The SEM study showed that morphology particles of the complexes are different in size and are within the range of nanoparticles.

Disclosure Statement

No potential conflict of interest was reported by the authors.

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Authors' Contributions

All authors contributed to data analysis, drafting, and revising of the paper and agreed to be responsible for all the aspects of this work

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