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SYNTHESIZING PD (II), RU (II) BENZONITRILE-PHENOTHIAZINE DERIVATIVE COMPLEXES AND INVESTIGATING THEIR ANTIBACTERIAL ACTIVITY AND REMOVAL OF SOME HEAVY METALS IN ENVIRONMENTAL SYSTEMS

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Abstract

First, phenol thiazine is reacted with sodium metabisulphite, sodium cyanide, and 4-Formylbenzonitrile to yield the appropriate nitrile. In this study, 4-(cyano(10H-phenothiazin-10-yl)methyl)benzonitrile, a phenothiazine derivative, was synthesized. The stereoscopic shape of the complexes formed around the ionic centers was determined using spectroscopic and physical techniques, including elemental analysis, 1H-NMR and 13C- NMR spectra, FTIR, UV-Vis, metal content, and conductance measurements. After synthesizing the derivatives of the complexes the biological activity of the prepared ligand and its complexes was studied to estimate their potential antimicrobial activity. In general, tests show the ligand and its complexes having good activity against bacteria. The prepared ligand was used to remove heavy metals causing water pollution. Among the heavy elements studied were zinc, lead, and copper. The findings suggest that the prepared complexes may be used to lower concentrations of these elements in water and mitigate their impact on the environment.

Keywords: Transition metal complexes, Physical techniques, Spectral characterization.

تحضير معقدات مشتقات البنزونيتريل- الفينوثيازين Pd(II) وRu(II) ودراسة نشاطها المضاد للبكتيريا وإزالة بعض المعادن الثقيلة في الأنظمة البيئية

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الخلاصة

اولاً يتفاعل الفينوثيازين مع ميتابيسولفيت الصوديوم، وسيانيد الصوديوم، و4-فورمايل بنزو نيتريل لإنتاج مركب النتريل المناسب لاستخدامه في تحضير مشتقات. في هذه الدراسة، تم تصنيع مشتق 4- (10H-phenothiazin-10-yl) methyl) benzonitrile cyano-، وهو أحد مشتقات الفينوثيازين المعقدة. تم تحديد الشكل المجسم للمعقدات المتكونة حول المراكز الأيونية باستخدام مجموعة من تقنيات التحليل الطيفية و التقميات الفيزيائية المهمة، بما في ذلك: تحليل العناصر، وطيف الرنين المغناطيسي وتقنية الاشعة فوق البنفسجية - المرئية وتقنية الاشعة تحت الحمراء UV-Vis ,FTIR, 13C- NMR,1H- NMR والمحتوى المعدني، وقياسات التوصيل الكهربائي والتي تعتبر من اهم الادوات التشخيصية في مجال الكيمياء العضوية. وبعد ان تم تحضير المشتقات المعقدة تمت دراسة النشاط البيولوجي لليكاند المحضر ومعقداته وتقدير نشاطها المضاد للميكروبات. بشكل عام، أظهرت الاختبارات أن الليكاند ومعقداته اظهرت نشاط جيد ضد البكتيريا. وقد اظهرت النتائج امكانية استخدام المعقدات التي تم تحضيرها في هذه الدراسة لإزالة او تقليل بعض العناصر النزرة (الزنك والرصاص والنحاس) من المياه في النظام البيئي.

كلمات مفتاحية: معقدات العناصر الانتقالية، الفعالية المضادة، التشخيص الطيفي.

Introduction

One of the most significant and reliable heterocyclic rings, the phenothiazine nucleus is frequently present in natural goods and pharmaceuticals. It was identified in the 1940s when many scientists were able to identify the biological activities of newer derivatives (10). Phenothiazines are a fascinating class of tricyclic nitrogen-sulfur heterocycles that are rich in electrons and have a wide range of medicinal applications. Various sedatives, tranquilizers, antieplectics, antituberculotics, antipyretics, antitumor agents, bactericides, and parasiticides contain them as their active ingredients (19). Phenothiazine derivatives have been found to have physiological activities as well as being appealing spectroscopic probes in molecular arrangements for photoinduced electron transfer studies and as scientific motif materials due to their reversible oxidative properties that produce deeply colored

radical cations (25). Phenothiazines are widely accessible and reasonably priced. Variations on the phenothiazine nucleus in the substitution pattern can lead to significant differences in activity. These variations are frequently just modest (6). The literature lists a wide range of real-world uses for phenothiazines, with semiconductors, antioxidants, dyes, polymers, and pharmaceuticals being some of the more well-known ones (4). The metal complexing activity of phenothiazine derivatives may be the common chemical source of these interactions. Phenothiazines are physiologically active molecules that can donate electrons via the ring system. Given that phenothiazine complex molecules have a greater biological impact than their parent ligands, the initial coordination sphere of these compounds may be important for biological activity (5).

Pharmaceutical pollution of the environment has drawn a lot of attention in recent decades. Since pharmaceuticals are found in multi-component mixtures of parent compounds, metabolites, and abiotic transformation products (TPs) formed by natural attenuation process and incomplete removal in sewage treatment plants, they are not isolated in the environment. This makes them part of a complex environmental issue (21). Pharmaceuticals derived from phenothiazine are prescribed globally as first-generation antipsychotic, antiparkinson, and antihistamines. Because of their antibacterial activity (either by itself or in conjunction with antibiotics) and potential use as an anti-parasite substitute, these medications have drawn more interest recently. They are also used as an antituberculosis medication. Moreover, medications derived from phenothiazine have been employed as tranquilizers in veterinary care. However, due to their genotoxic qualities, they were prohibited for use in animal production (8 and 24). The research aims to prepare and characterize the ligand and its reaction with metal ions and prove the stereoscopic shape of the resulting complexes their capture of heavy ions.

Materials and Methods

Reagents: The metal ions, phenothiazine, and 4-Formylbenzonitrile were supplied by Aldrich. Every solvent is a pure analytical grade reagent that complies with industry requirements.

Preparation of 4-(cyano(10H-phenothiazin-10-yl)methyl)benzonitrile: After mixing 0.05 mol of sodium metabisulphite with 20 milliliters of water, 0.05 mol of 4-Formylbenzonitrile was added. After 15 minutes, phenothiazine (0.05 mol) was introduced. The reaction mixture was stirred for 30 minutes and allowed to cool in an ice bath. Six hours were spent stirring the mixture after a sodium cyanide solution (0.05 mol) was added drop by drop into 20 mL of water. The reaction flask was left overnight. After being filtered, the finished product was washed with generous amounts of water. Aqueous ethanol was used to recrystallize the dried material (10).

Preparation of complexes: The metal salt was mixed with one mole of the ligand 4-(cyano(10H-phenothiazin-10-yl)methyl)benzonitrile in two equivalents. A container holding a ligand dissolved in 10 milliliters of ethanol was filled with metal chloride (where M= Pd, Ru). After the mixture was refluxed for 4 hours, a colorful

precipitate was produced. This precipitate was filtered, cleaned with methanol and diethyl ether, and allowed to dry at room temperature (2).

Collection and analysis of waste water: A sample of waste water from Heet General Hospital was taken and transferred to the laboratory for the purpose of measuring heavy elements in it through atomic absorption technology. The measurements showed zinc, lead, and copper concentrations at 12.2321 ppm, 28.3551 ppm), and 6.4257 ppm, respectively.

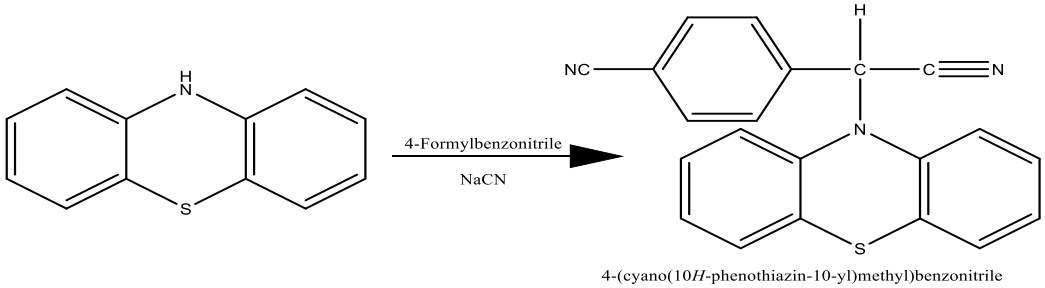
Scavenging of heavy elements by the ligand: About 0.079 g, 0.2 mmol of the prepared ligand was dissolved in 5ml of absolute ethanol and gradually added to 30 ml of water containing heavy metals in a basic medium. After the end of the reaction time, the mixture was left for an hour, where a precipitate was observed to form. The precipitate was filtered and dried. A sample of the solution was taken and the atomic absorption spectrum measured again (1).

The percentage of removal can be calculated using the equation $E(\%) = \frac{Ci-Cf}{Ci} x100$, where E (%) = scavenger percentage
Ci = Initial concentration of elements.

Cf = Final concentration of elements.

Results and Discussion

Phenothiazine derivatives ligand was prepared in this study, as shown in Figure 1. Figures 2 and 3 show the preparation of the complexes.



4-(cyano(10*H*-phenothiazin-10-yl)methyl)benzonitrile

Fig 1: Preparation of the ligand.

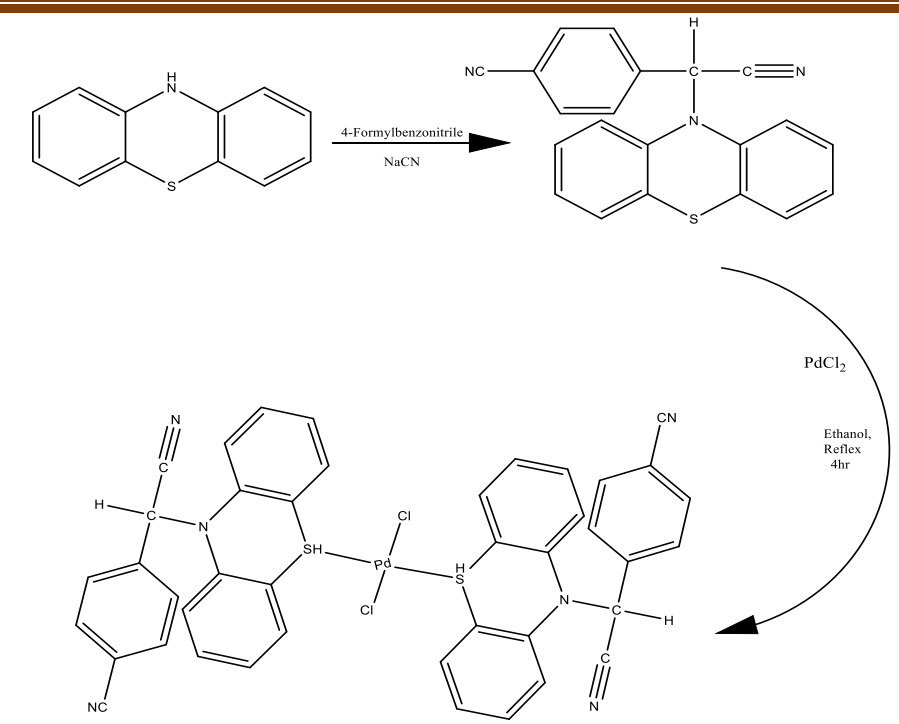


Fig 2: Preparation of Pd Complex.

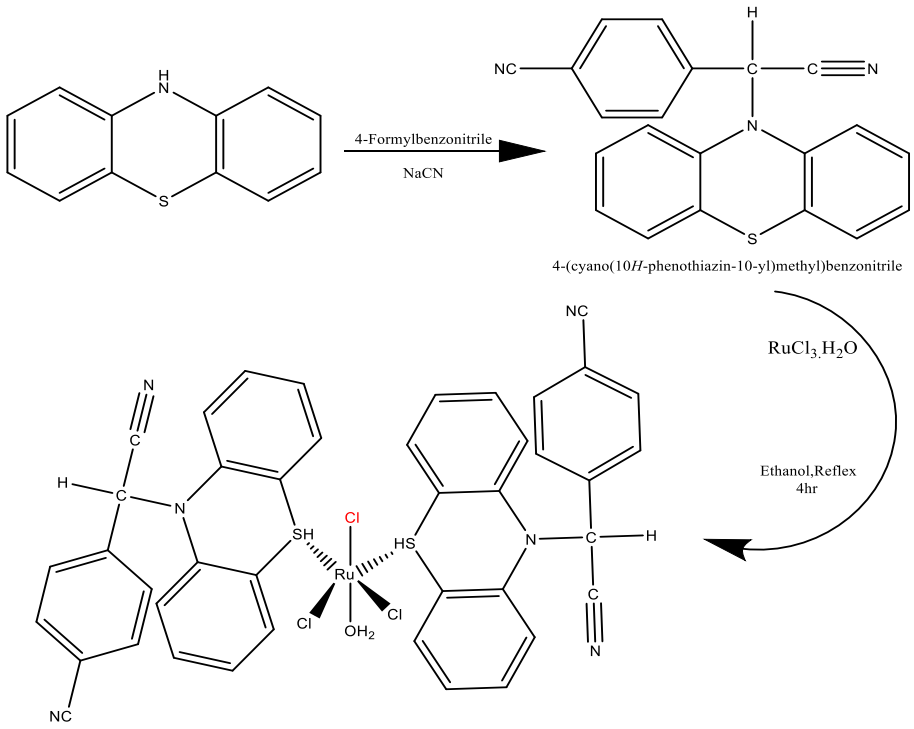


Fig 3: Preparation of Ru Complex.

Table 1: Chemical formula and some physical properties of the prepared complexes.

Chemical formula	M. Weight	% of results	Melting point °C (* Decomposed)	(calcd.) Found (%)			
				C	H	N	M
$C_{21}H_{13}N_3S$	339	79	83	75.44 (74.31)	4.01 (3.86)	9.37 (12.38)	-
$C_{42}H_{28}C_{l2}N_6PdS_2$	858	66	296*	56.73 (58.78)	3.55 (3.29)	9.85 (9.79)	12.25 (12.40)
$C_{42}H_{30}Cl_3N_6ORuS_2$	906	70	>300	57.01 (55.66)	3.30 (3.34)	8.98 (9.27)	10.99 (11.15)

Proton and carbon NMR spectrum of the ligand: The proton spectra of the ligand showed a group of bands appearing (Fig. 4 and Table 2). Also, the carbon of ligand spectra showed a group of bands appearing (Fig. 5 and Table 3).

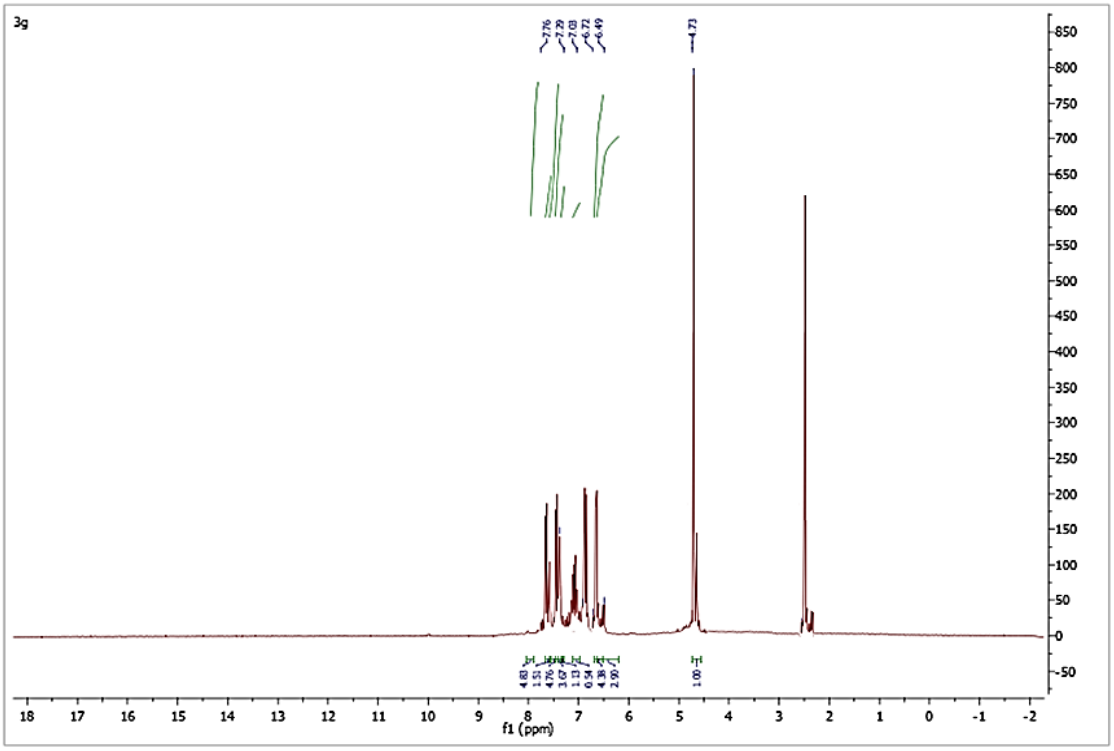


Fig 4: Proton NMR spectrum of the ligand.

Table 2: Proton NMR data of the ligand in DMSO as solvent.

Ligand	Asgmt.	Peaks [ppm]
$C_{21}H_{13}N_3S$	Methylene	4.73
	C─H for (1-benzene)	7.76
	C─H for (1-benzene)	7.29
	C─H for (phenothiazine)	7.03
	C─H for (phenothiazine)	6.72
	C─H for (phenothiazine)	6.49
	DMSO-d6	2.5

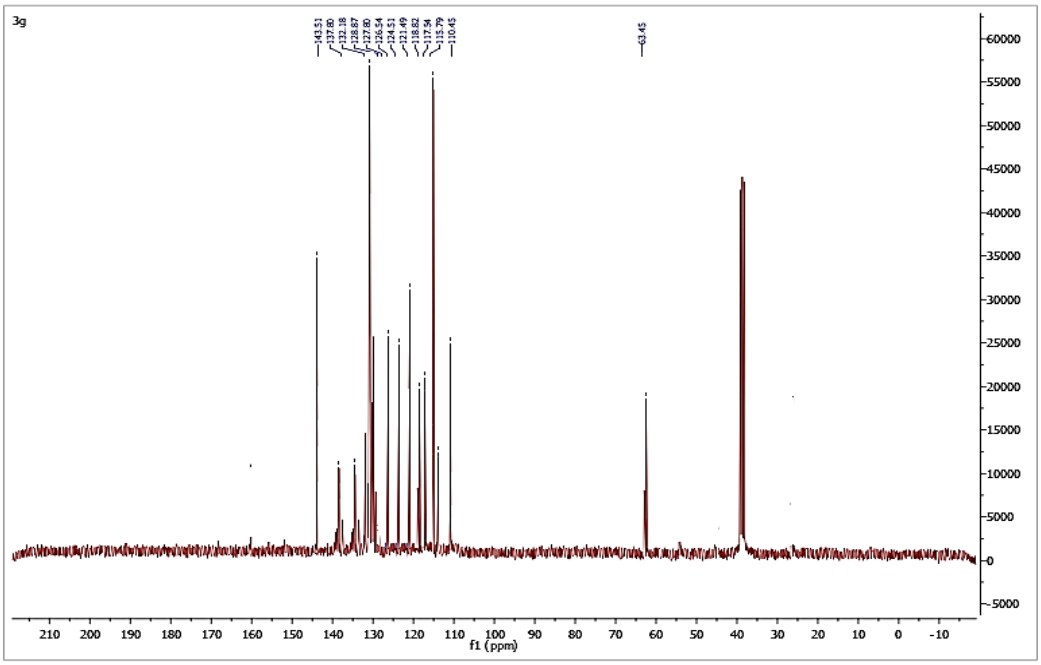


Fig 5: Carbon NMR spectrum of the ligand

Table 3: Carbon NMR data of the ligand in DMSO as solvent.

Ligand	Asgmt.	Peaks [ppm]
$C_{21}H_{13}N_3S$	C for CH methylene	63.45
	C for (benzene ring)	110.45
	C for (benzene ring)	115.79
	C for Nitrile	117.54
	C for Nitrile	118.82
	C for (benzene ring)	121.49
	C for (benzene ring)	124.51
	C for (benzene ring)	126.54
	C for (benzene ring)	127.80
	C for (benzene ring)	128.87
	C for (benzene ring)	132.18
	C for (benzene ring)	137.80
	C for (benzene ring)	143.51
	DMSO	39.9

Infrared spectrum: The band disappeared at roughly 3400 cm^{-1} corresponding to the ligand's (NH) stretching vibrations (20). The (C≡N) group can be identified by the band at 2249 cm^{-1} (14). The (C-H) bond can be known by the band at 3069 cm^{-1} and the (C-N) at 1272 cm^{-1} (7). The aromatic ring (C = C) was assigned to the bands at 3060 cm^{-1}, whereas (C = H) was assigned to the band at 1495 cm^{-1} (12). Following complexation, there were detections of the stretching vibrations M–S and M–Cl at 436, 429 cm^{-1} and 280, 277 cm^{-1}, respectively (3 and 17). The band 839 cm^{-1} was assigned to the v (M-O) vibration (23). Table 4 shows FTIR data for the ligand and its complexes.

Table 4: Spectral FTIR data.

Compounds	ν (C− H); aliphatic	ν (C− H); aromatic	ν (C = C); aromatic	ν(C≡N)	ν(C− N)	ν (M−S)	ν(M−O)	ν(M− Cl)
(L)	3069	3060	1495	2225	1272	-	-	-
[Pd $(L)_2(Cl)_2$]	3053	3056	1490	2225	1275	436	-	280
[Ru $(L)_2(Cl)_2H_2O$]Cl	3016	3054	1491	2225	1270	429	839	277

Ultraviolet-visible spectra: Two absorption peaks in L's UV-Vis spectra were located at (299 nm: 33444 cm^{-1}) and (305 nm: 32786 cm^{-1}), respectively corresponding to the "π→π *" and "n→π *" transitions (16). As seen Table 5, most complexes have an identity to them. The color differences between L and metal salt make them significant coordination markers, and the strength and position of absorption vary throughout the colored transitional metal salt complexes (11).

Table 5: Spectral Uv–Vis data.

Compounds	λ (nm)	ύ (cm^{-1})	Assignment	Suggested Formula
(L)	299	33444	π→π *	
	305	32786	n→π *	
[Pd$(L)_2(Cl)_2$]	266	37593	L. F	square planar
	302	33112	L. F	
	418	23923	C. T overlap $^1A_1g \rightarrow {}^1E_1g$	
	700	14285	$^1A_1g \rightarrow {}^1B_1g$	
[Ru$(L)_2(Cl)_2H_2O$]Cl	257	38910	L. F	Octahedral
	263	38022	L. F	
	399	25062	C. T	
	445	22471	$^5T_2g \rightarrow {}^5Eg$	

Molar conductivities: The Pd II complex's molar conductivity in DMSO is 19.2, showing that it is not an electrolyte (13). The conductance of RuII complex is 35.7. These results show the ionic nature and type 1:1 electrolyte (9).

Bacterial activity: The biological activity of the synthesized ligand and its complexes was investigated utilizing the inhibition method on four different kinds of harmful bacteria (15). Two types of bacteria were gram positive i.e., Bacillus subtilis and Staphylococcus aureus while the second two Psedomonas aeruginosa and Escherichia coli. were gram negative. This is to estimate their potential antimicrobial activity. The part of DMSO in the biological activity shown by separate studies was achieved with the solutions of DMSO alone. It showed no activity against any bacterial strains (18). Inhibition circle diameters in millimeters against the growth of different microorganisms are listed in Table 6.

Table 6: Bacterial activity of ligand and its complexes.

Compounds	*Staphylococcus aureus*	*Bacillus subtilis*	*Pseudomonas aeruginosa*	*Escherichia coli*
Control (DMSO)	–	–	–	–
Ligand	35	37	26	38
[Pd$(L)_2Cl_2$]	30	34	36	25
[Ru$(L)_2(Cl)_2H_2O$]Cl	26	28	25	29

Analysis of heavy elements: Atomic absorption analysis of water containing zinc, lead, and copper was conducted after adding the ligand, and the results showed concentrations of the elements decreasing to 0.2148 ppm, 0.0130 ppm, and 0.1675 ppm from 12.2321 ppm, 28.3551 ppm, and 6.4257 ppm, respectively. This gives a scavenging rate for zinc, lead, and copper of 98.33%, 99.96%, and 98.33, respectively. This is evidence that the prepared ligand is capable of scavenging metal elements and forming complexes (22).

Conclusions

Preparing and diagnosing the 4-(cyano(10H-phenothiazin-10-yl)methyl) benzonitrile ligand and reacting it with metal ions through physical and chemical means revealed the formation of two types of stereoscopic shapes of the complexes i.e., a square planar and an octahedral. In proving this property, heavy ions such as zinc, lead, and copper were scavengers for polluted aqueous media in the form of a precipitate that can be removed. The biological functions of the synthesized phenothiazine ligands and their complexes were also studied.

Supplementary Materials:

No Supplementary Materials.

Author Contributions:

Al-Obaidy: methodology, writing the original draft; Al-Dulymi and Abed: writing, review and editing. All authors have read and agreed to the published version of the manuscript.

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No Informed Consent Statement.

Data Availability Statement:

No Data Availability Statement.

Conflicts of Interest:

The authors declare no conflict of interest.

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