PREPARATION AND STUDY OF SOME COMPLEXES OF TRANSITION ELEMENTS WITH POLYDENTATE LIGANDS

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Abstract: *This research includes the preparation of ligands with large cyclic molecules and their interaction with chromium (III), manganese (II), iron (III), cobalt (II), nickel (II), and copper (II). These complexes were characterized using the techniques of elemental microanalysis, electrical molar conductivity, magnetic measurement, infrared spectra, and electronic spectra. From these measurements, it was found that the expected chemical composition of the complexes is* $[M(L)Cl_2]$*, where M = (Mn, Co, Ni, Cu) and L =* $(L_{2,3py}, L_{2,6py})$*, and* $[M(L)Cl_2]Cl$*, where M = (Cr, Fe) and L =* $(L_{2,3py}, L_{2,6py})$*, and that all the complexes have an octahedral structure. The effect of the obtained ligands on the growth of bacteria, namely, strains of Staphylococcus aureus and Klebsiella pneumoniae, was studied. The results indicate that the cobalt (II), nickel (II), and copper (II) complexes of ligand* $L_{2,3}$ *have a greater effect on different types of bacteria compared to the composite of ligand* $L_{2,6}$*, which gave a lower rate of effectiveness.*

Keywords: *Polydentate ligands, metal ions, thiourea, biological activity.*
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Introduction

The study of macromolecules that have certain characteristics—having a large number of atoms and at least three groups of electron donors that can coordinate to form different molecules—is the focus of scientists. It is important to study the methods of obtaining them, obtaining their complexes, studying their properties, and how to benefit from them in various fields [1-3]. For a long time, macromolecules have been referred to as biological structures. Lehn [4] described this term as chemistry beyond the molecules. He also mentioned polycyclic donor filaments, the most common of which are nitrogen, oxygen, and sulfur, which are effective in preparing macrocyclic complexes as they bind with one or more metal ions [5-7]. The great importance of these complexes, especially in life systems, led to their extensive study [8]. Among these naturally occurring complexes are heme, which is found in hemoglobin [9]; enzyme catalase; chlorine, which is found in chlorophyll (which is a complex of magnesium (II)); vitamin B12 (which is a complex of cobalt (II)); and metalloproteins that use binuclear alkaline centers to perform catalytic processes within the human body [10, 11].

In the year 1928, phthalocyanines containing multiple rings within the large ring and four nitrogen donor atoms (tetraamine macrocyclic) were prepared, which can bind with the metal and be a thermally stable complex, and this makes them widely used in the manufacture of wadis, fabrics, etc. [12, 13]. After that, a large number of large cyclic compounds were prepared by a number of researchers and used as ligands to react with metals to form macrocyclic complexes.

Chandra and Gupta [14] were able to prepare monometallic complexes of the elements (copper (II), nickel (II), cobalt (II), and magnesium (II)) with a large cyclic ligand containing donor atoms, namely sulfur, nitrogen, and oxygen. From the condensation of thiodiglycolic acid with thiourea, the complexes with general chemical formula $[Ni(TTC)]X_2$ and $[M(TTC)X_2]TTC$ 1,3,9,11-tetraaza-4,8,12,16-tetraoxo-2,6,10,14-tetrathiacyclohexadecane were diagnosed using nuclear magnetic resonance (H.NMR), infrared spectroscopy, and paramagnetic electron resonance spectroscopy, along with electronic spectroscopy and measurements of magnetic susceptibility and molar electrical conductivity. They concluded that the complexes have an octahedral symmetrical shape and that they are electrolytically inactive, except for the nickel complex (II). It has a planar square structure and is electrolytic with a ratio of 1:2. When the effectiveness of these complexes was studied biologically, it turned out that they are effective against types of bacteria and fungi.

Siddiqi et al. [15] prepared three types of homogeneous mononuclear, polynuclear iron (II) complexes with multiple mononuclear nitrogen atoms $[Fe(C_{20}H_{22}N_6O_4)Cl_2]$, $[Fe(C_{22}H_{28}N_8O_4)CI_2]$, $[Fe_2(C_{26}H_{38}N_{10}O_4)Cl_4]$. The complexes were diagnosed using nuclear magnetic resonance (^{13}C-NMR, ^{1}H-NMR) spectra, electronic spectra, infrared spectroscopy, and measurements of magnetic susceptibility and molar electrical conductivity. It was found that all complexes are arranged in a distorted octahedral symmetrical geometric shape. These complexes are characterized by stability and are not electrically conductive.

In [16], transition element complexes for manganese (II), iron (II), cobalt (II), nickel (II), and copper (II), as well as zinc (II), were obtained, which were prepared with a tetragonal ligand of type (1, 3, 10, 12-tetrazo-4,9,13,18-tetraoxo-2,11-dithioctadecene (cyclic) and dipyridine. The prepared complexes were diagnosed by microanalysis techniques (M), electrical molar conductivity measurements, magnetic sensitivity measurements, and infrared radiation and the electronic spectrum. It was found that the prepared complexes possess an octahedral structure [16].

New complexes were prepared in [17] using some of the elements of the first transition chain—manganese (II), cobalt (II), nickel (II), and copper (II)—with new large macrocyclic biologically active ligands prepared from β-diketone 1-(4-chlorophenyl)-3-(2-hydroxyphenyl) propane-1,3-dione and o-phenylene diamine. Elemental analysis, electrical molar conductivity, magnetic sensitivity, thermal analysis, X-ray diffraction, infrared, nuclear magnetic resonance measurement (1H-NMR), UV-Vis spectra measurement, and spectroscopy of mass were used to describe each complex, recently created macrocyclic ligand that is physiologically active. It was found that the complexes were conductive in a ratio of 1:2 and were highly twisted and hexagonal; they had an octahedral structure. In vitro tests have been conducted to evaluate the ligand and its metal complexes' antibacterial and antifungal capabilities against E. coli, Staphylococcus aureus, Aspergillus niger, and Trichoderma, correspondingly [17].

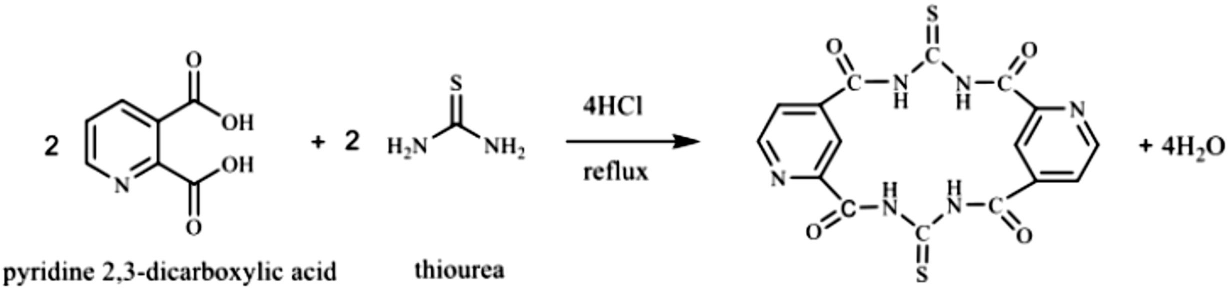
In 2022, in [18], a reaction of ligand N.N (1,3-dithioformylphthalamide) in a ratio of 2:2 with some of the transition elements, including chromium, manganese, iron, cobalt, nickel, copper, and zinc, was conducted. It was established that they are electrical conductors with a ratio of 1:2 and had a tetrahedral structure.

In this study we continue to be interested in the design of new complex compounds formed with certain numerous donating ligands (2,3-dicarboxylic pyridine and 2,6-dicarboxylic pyridine) and the first transition series metal ions (Cr^{3+}, Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, and Cu^{2+}), and we have created a novel type of tetradentate ligand called [N4].

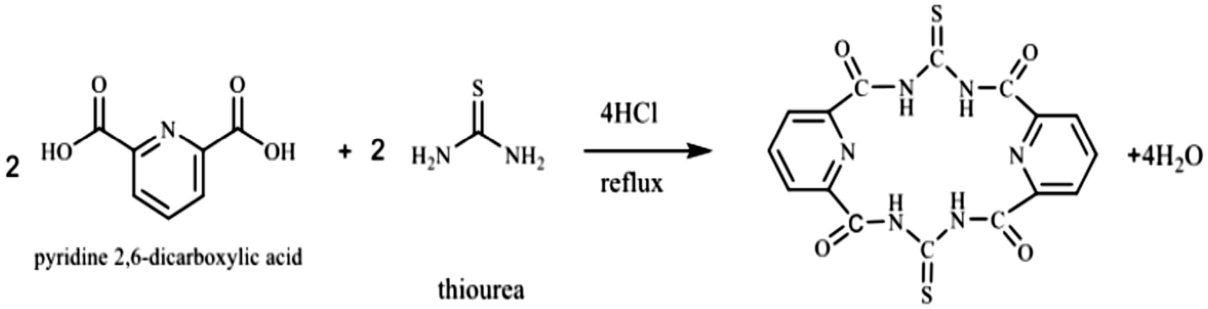
Experimental part

Preparing the ligands ($L_{2,3py}$) and ($L_{2,6py}$): When preparing the ligands, ($L_{2,3py}$) or ($L_{2,6py}$) is dissolved by weighing 1.67 gm (0.01 mol) in 20 ml of hot ethanol, and 0.76 gm (0.01 mol) of thiourea previously dissolved in 20 ml of hot ethanol is slowly added to it. The mixture is refluxed at a temperature of 85 °C for 10 hours and in the presence of 2 ml of HCl. After the time has expired, the solution is cooled. A precipitate appears, which is then filtered, washed with cold ethanol, and dried under high pressure [14] (Scheme below).

M. p. ($L_{2,3py}$) = 253-255 °C; m. p. ($L_{2,6py}$) = 292-295 °C.



4,10-dithioxo-3,5,9,11-tetraaza-1(2,4),7(4,2)-dipyridinacyclododecaphane-2,6,8,12-tetraone



4,10-dithioxo-3,5,9,11-tetraaza-1,7(2,6)-dipyridinacyclododecaphane-2,6,8,12-tetraone

Preparation of the complexes. The ligand (0.001 mol/20 ml) was dissolved in hot ethanol and added to the metal chloride (0.001 mol/20 ml) solution in ethanol, and for 3 hours, the mixture was stirred continuously, and then the solution was cooled to room temperature. A colored precipitate is formed, separated by filtration, rinsed with small amounts of cold ethanol, and dried in a vacuum for several hours [19]. In the same way, other complexes of this type are prepared with different transitional elements.

Biological activity. A preliminary screening for the produced compounds' biological activity was carried out in 100 µg/ml DMF against microorganisms that represent G+ bacteria. Both Staphylococcus aureus and E. coli bacteria grow on nutritional agar. Under septic conditions, sterile agar was poured into petri dishes before spreading one hundred microliters of each normative test organism onto agar plates [19]. Assay plates were used to measure the susceptibility of bacteria to antimicrobial treatments. Incubation took place for 24 hours at 37°C on the plates [19].

Physical measurement. Physical tests were made using a conductivity meter (PMC3) and DMF to measure the electrical molar conductivity of the complexes at room temperature (JENWAY). The concentration used for the measurements was 10^{-3} M. Using a Bruker (Tensor27) spectrophotometer, the FT-IR spectra were measured in the 200-4000 cm^{-1} range. The UV-visible spectrum was measured using a Shimadzu spectrophotometer with quartz cells. By employing a BRUKER BM6 type, the complexes' magnetic readings were assessed using the Faraday method (Cr^{3+}, Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, and Cu^{2+}).

The complexes of Ni^{2+}, Cu^{2+}, and Zn^{2+} were examined using appropriate indicators and standard EDTA solutions [20]. Moreover, UV-visible spectroscopy was employed to measure cobalt [21]. Chloride in the composite was calculated by the Mohr method. Then examined using C.H.N. microanalysis in the labs of Ordu University, Turkey (Table 1).

Electrical molar conductivity. After letting the solution reach thermal equilibrium at 25°C, molar electrical conduction of the produced complexes was measured at a concentration of 10-3 in a dimethyl formamide (DMF) solution [22]. The electrical conductivity measurement findings were found to agree with the suggested structural chemistry formulas for the complexes that were synthesized.

From the measurements, it was shown that the complexes that were prepared fall within the category of complexes with neutral behavior that are non-electrolytic or weakly conductive and with the chemical formula $[M(L_{2,3})Cl_2]$ or $[M(L_{2,6})Cl_2]$. Except for the chromium and iron complexes, they were conductive in a 1:1 ratio and the chemical formula $[M(L_{2,3})Cl_2]Cl$ or $[M(L_{2,6})Cl_2]Cl$ (Table 1).

Magnetic measurements and electronic spectra. The electronic spectra of the prepared complexes were measured within the range of 9090-50000 cm^{-1}. By using the solvent DMF and with a focus on 10-3. The magnetic moments of the formulated complexes were also measured to determine the number of lone electrons present in the complexes. Below is an explanation of the results obtained from these measurements. The values of the magnetic measurements and electronic spectra for the produced complexes are displayed in Table 2.

Results and discussion

Chromium complexes. The magnetic moment of the prepared chromium complexes is found within limits (3.78-3.82 B.M.). These results are compatible with highly Chromium complexes with octahedral electron arrangement (t2g3 eg0) [24]

The electronic spectrum has been measured for chromium (III) complexes. Two complexes demonstrated an absorption band in the region (21276.60-22222.2 cm^{-1}) belonging to (v_3) and referring to the transition ($^4A_2g\rightarrow{}^4T_1g(p)$), and two absorption bands in (15873.02-16129.03 cm^{-1}) belonging to (v_2) where it refers to the transition (($^4A_2g\rightarrow{}^4T_1g(F)$) and ($v_1$) bands belonging to the transition ($^4A_2g\rightarrow{}^4T_1g(F)$), so it was within (9071.2-10845.98 cm^{-1}) that the locations of absorption bands (v_1, v_2, v_3) for the aforementioned chromium (II) complexes agree with chromium's (III) hexagonal complexes of octahedral symmetry [24, 25].

Manganese complexes. The Mn^{2+} complexes prepared showed values ranging between 5.93 and 5.95 M.B., and these values are consistent with the magnetic paths of the manganese (II) complexes with a highly twisted octahedral shape [26]. When measuring the electronic spectrum of manganese (II) complexes, it is not expected that transitions (d-d) will appear in the visible region because they are strictly prohibited and orbitally confined according to Laporte's rule, while absorption bands appear in the region (33557-36496 cm^{1}). These absorptions are most likely representative of charge transfer spectra [27].

Iron complexes. The prepared hexagonal iron (II) complexes showed a magnetic moment of 5.55-5.82 B.M., respectively, and these values are consistent with the magnetic values of the highly spiral octahedral iron complexes [28].

When measuring the electronic spectrum of the prepared hexagonal iron (II) complexes, it showed in the region (9960.02-10964.91 cm^{-1}), which is attributed to the transition (5T2g → 5Eg), which indicates that these complexes take a highly octahedral shape [29].

Cobalt complexes. Show magnetic moments ranging from 4.89 to 4.95 B.M., which are consistent with the value of the magnetic moment for the high-spin octahedral, and the observed increase in the value of the magnetic moment is believed to be due to the presence of the orbital contribution. Cobalt (II) complexes are octahedral, highly spin [30]. The spectra of these compounds show three bands at the wavelengths 19230.70-19455.3 cm^{-1}, 16447.4-16650.4 cm^{-1}, and 9293.7-9671.2 cm^{-1}, indicating an octahedral geometry surrounding the metal ion. These transitions have been given the following designations:

$^4T_1g(F)\rightarrow{}^4T_1g(P)$ (v_3) , $^4T_1g(F)\rightarrow{}^4A_2g(F)$ (v_2) , $^4T_1g(F)\rightarrow{}^4T_2g(F)$ (v_1), respectively [31, 32].

Nickel Complexes: Magnetic values were provided in (3.40 - 3.90 B.M), and these values are compatible with the nickel complexes having an octahedral structure [33]. When the nickel complexes' electronic spectra were measured, three absorption bands were found. The v_3 is responsible for the first one in the region 23809.5 -23970.5 cm^{-1}, according to $^3A_2g(F)\rightarrow T_1g(P)$). The second one was located in the range 14450.8 - 1538.6 cm^{-1} and was assigned to the v_2 ($^3A_2g(F)\rightarrow{}^3T_1g(F)$). The third one, which appears in absorptions ranging from 9451.8 to 10504.2 cm^{-1}, is a member of the v_1 ($^3A_2g(F)\rightarrow{}^3T_2g(F)$). The octahedral hexagonal symmetric compounds with literature are compatible with the adsorption band locations of Nickel (II) complexes [34, 35].

Copper complexes. Copper (II) complexes of hexagonal symmetry prepared showed a magnetic moment ranging between 1.88 and 1.97 B.M., and this indicates that these complexes have an octagonal structure [36]. The wide absorption band that the Cu^{2+} complexes displayed in the range of 16447.4-16778.5 cm^{-1}, which is associated with two or three of the following transitions, is a result of the Jahn-Teller distortion: $2B_1g \rightarrow 2Eg$ (ν_3), $2B_1g \rightarrow 2B_2g$ (ν_2), and $2B_1g \rightarrow 2A_1g$ (ν_1). According to these results, the Cu complexes are octahedral [36, 37].

Infrared spectroscopy. The vibrational spectra of the formulated compound were measured in the range of 400-40000 cm^{-1}. The infrared spectrum (I.R.) of the prepared ligands and their complexes recorded significant bands (vibrations, stretching and bending of the group). These bands are amide I (ν (C=O)), amide II [ν (CN) + ν(N-H)], amide III [δ (N-H)], ν (N-H), ν (C=S), and ν ($C=N_{pyring}$).

It was observed that the frequency of stretching of the ν (N-H) group of the prepared ligands lies between 3415 and 3461 cm^{-1} [38]. Absorption bands also appear at 1344-1410 cm^{-1} and 1574-1593 cm^{-1} due to the frequency of the bonds bending amide III δ (N-H) [39] and amide II ν(C-N+ δN-H) [40]. In the case of complex formation, these bands are noticeably shifted towards a lower frequency. This displacement confirms the occurrence of bonding between the nitrogen and metal atoms of the (N-H) group [41]. ν (C=S) and ν (C=N pyring) stretching vibration bands appeared at (1080-1092 cm^{-1}) [44] and (1456-1493 cm^{-1}) [45], respectively, in the prepared ligands. It was observed that the positions of these bundles did not change significantly in the complexes. The bands of the amide I (ν (C=O)) group appeared at 1618-1631 cm^{-1} in the ligand, and the thioamides I and II may be the cause of the bands at 773-1446 cm^{-1} and 779-1410 cm^{-1}. It was noted that the I and II bands were shifted towards lower frequencies due to the nitrogen group in the ligand being linked to the metal atom when preparing and the C=S group remaining unlinked to the metal [45-47]. The absorber band of the (M-N) group appeared in all the complexes in the range 465-492 cm^{-1}, and this indicates the occurrence of consistency with the metal through nitrogen [48]. Finally, as for the complexes containing chloride in an ionic form outside the coordination sphere, they showed a band in the region (588-623) [49] (Table 3). Fig. 1 represents IR spectra of some prepared complexes.

Table 1. The ligands' and their complexes' physical and analytical information

No.	Compounds	Color	m. p. (°C)	Yield %	Λ_m $cm^2.ohm^{-1}.mol^{-1}$	M% Found (calc.)%	Cl% Found (calc.) %	Found (calc.)%		
								C	H	N
$L_{2,3py}$	$C_7H_5O_4 N_1$	Dark red	253-255	86.4				54.53 (54.86)	2.13 (2.86)	23.95 (24.0)
$L_{2,6py}$	$C_7H_5O_4 N_1$	Dark red	292-295	82.4				54.45 (54.86)	3.06 (2.86)	24.05 (24.0)
1.	$[Cr(L_{2,3py})Cl_2]Cl$	green	> 300	88.7	63.7	-----	18.11 (18.36)	37.80 (37.77)	1.95 (1.96)	16.55 (16.52)
2.	$[Mn(L_{2,3py})Cl_2]$	Dark green	78-79	70.5	35.8	-----	15.72 (14.92)	40.04 (40.34)	2.31 (2.10)	17.80 (17.65)
3.	$[Fe(L_{2,3py})Cl_2]Cl$	Reddish brown	190-192	75.1	76.5	-----	19.89 (20.79)	37.60 (37.48)	1.83 (1.95)	16.33 (16.39)
4.	$[Co(L_{2,3py})Cl_2]$	Maroon	136-138	73.3	33.6	12.10 (12.27)	14.75 (14.79)	39.53 (40.01)	2.13 (2.08)	16.75 (17.50)
5.	$[Ni(L_{2,3py})Cl_2]$	Light orange	> 300	80.4	15.5	13.14 (12.23)	14.07 (14.80)	39.85 (40.03)	1.88 (2.08)	17.25 (17.51)
6.	$[Cu(L_{2,3py})Cl_2]$	Reddish brown	140-142	80.8	39.1	13.36 (13.11)	14.71 (14.65)	39.59 (39.63)	1.94 (2.06)	17.25 (17.34)
7	$[Cr(L_{2,6py})Cl_2]Cl$	Green-brown	120-122	77.0	68.4	-----	19.44 (18.36)	38.01 (37.77)	1.90 (1.96)	16.60 (16.52)
8	$[Mn(L_{2,6py})Cl_2]$	Dark green	> 300	78.1	10.4	-----	15.12 (14.92)	39.95 (40.34)	2.45 (2.10)	17.43 (17.65)
9	$[Fe(L_{2,6py})Cl_2]Cl$	Maroon	240-242d	73.4	66.5	-----	21.48 (20.79)	37.33 (37.48)	1.88 (1.95)	16.35 (16.39)

10	[Co($L_{2,6py}$) Cl_2]	Dark green	132-134	85.5	37.9	11.88 (12.27)	14.44 (14.79)	39.71 (40.01)	1.89 (2.08)	16.99 (17.50)
11	[Ni($L_{2,6py}$) Cl_2]	Red Brown	199-200d	75.3	35.4	11.33 (12.23)	15.21 (14.80)	40.10 (40.03)	2.12 (2.08)	17.33 (17.51)
12	[Cu($L_{2,6py}$) Cl_2]	Dark brown	148-150	86.6	28.4	13.00 (13.11)	14.30 (14.65)	39.47 (39.63)	12.3 (2.06)	17.12 (17.34)

Table 2. Electronic spectrum (in DMF) and magnetic susceptibility moment

No.	Compounds	d-d. transition (cm^{-1})			M_{eff} (B.M)
		ν_1	ν_2	ν_3	
1.	[Cr($L_{2,3py}$) Cl_2]Cl	10845.98	16129.03	22222.2	3.78
2.	[Mn($L_{2,3py}$) Cl_2]	----	----	----	5.93
3.	[Fe($L_{2,3py}$) Cl_2]Cl	9960.02	----	----	5.55
4.	[Co($L_{2,3py}$) Cl_2]	9293.7	16447.4	19455.3	4.89
5.	[Ni($L_{2,3py}$) Cl_2]	10504.2	1538.6	23970.5	3.40
6.	[Cu($L_{2,3py}$) Cl_2]	16447.4	----	----	1.97
7.	[Cr($L_{2,6py}$) Cl_2]Cl	9671.2	15873.02	21276.60	3.82
8.	[Mn($L_{2,6py}$) Cl_2]	----	----	---	5.95
9.	[Fe($L_{2,6py}$) Cl_2]Cl	10964.91	----	----	5.82
10.	[Co($L_{2,6py}$) Cl_2]	9671.2	16650.4	19230.70	4.95
11.	[Ni($L_{2,6py}$) Cl_2]	9451.8	14450.8	23809.5	3.20
12.	[Cu($L_{2,6py}$) Cl_2]	16778.5	----	----	1.88

Table 3. Ligand's customized infrared bands and their complexes

No.	Compounds	ν(C=O) Amide I	N (C=S)	ν(C-N+ δN-H) Amide II	δ (N-H) III	Thioamid I	Thioamid II	ν (N-H)	ν (M- N)	ν ($C=N_{pyring}$)	ν (M- X)
$L_{2,3py}$	$C_7H_5O_4N_1$	1631	1092	1593	1344	773	1446	3415		1493	
$L_{2,6py}$	$C_7H_5O_4N_1$	1618	1080	1574	1410	779	1410	3461		1456	
1.	[Cr($L_{2,3py}$) Cl_2]Cl	1630	1090	1535	1275	729	1421	3188	469	1490	595
2.	[Mn($L_{2,3py}$) Cl_2]	1620	1095	1554	1273	756	1390	3195	476	1495	
3.	[Fe($L_{2,3py}$) Cl_2]Cl	1625	1095	1552	1304	762	1420	3346	471	1498	588
4.	[Co($L_{2,3py}$) Cl_2]	1631	1103	1564	1306	758	1408	3344	474	1500	
5.	[Ni($L_{2,3py}$) Cl_2]	1630	1107	1552	1267	760	1414	3354	465	1483	
6.	[Cu($L_{2,3py}$) Cl_2]	1635	1103	1547	1308	750	1400	3330	476	1512	
7	[Cr($L_{2,6py}$) Cl_2]Cl	1620	1092	1473	1346	760	1348	3250	476	1450	620
8	[Mn($L_{2,6py}$) Cl_2]	1633	1084	1469	1375	769	1375	3386	472	1442	
9	[Fe($L_{2,6py}$) Cl_2]Cl	1618	1074	1480	1354	756	1354	3255	482	1450	623
10	[Co($L_{2,6py}$) Cl_2]	1618	1074	1496	1369	758	1369	3406	492	1460	
11	[Ni($L_{2,6py}$) Cl_2]	1620	1076	1491	1375	766	1375	3344	476	1445	
12	[Cu($L_{2,6py}$) Cl_2]	1620	1086	1427	1340	752	1340	3230	474	1455	

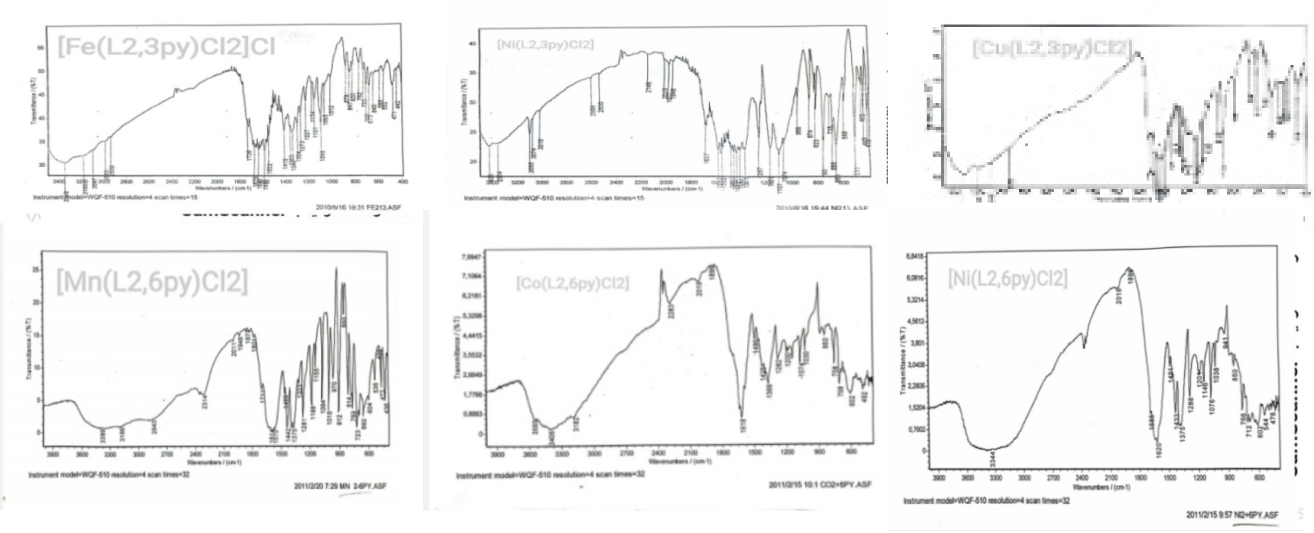


Fig. 1. IR spectra of some prepared complexes

NMR Spectra: Using DMSO-d6 solvent, the ligand's ^{1}H-NMR proton nuclear magnetic resonance spectrum was examined. It revealed two bands: one at $\delta = 9.7$-9 ppm, returning to protons of two imine groups (-NH) and the other at $\delta = 7.3$-8.5 ppm, and back to the protons of the two aromatic rings in prepared ligands [50]. Fig. 2 represents $L_{2,3py}$'s ^{1}H-NMR spectra.

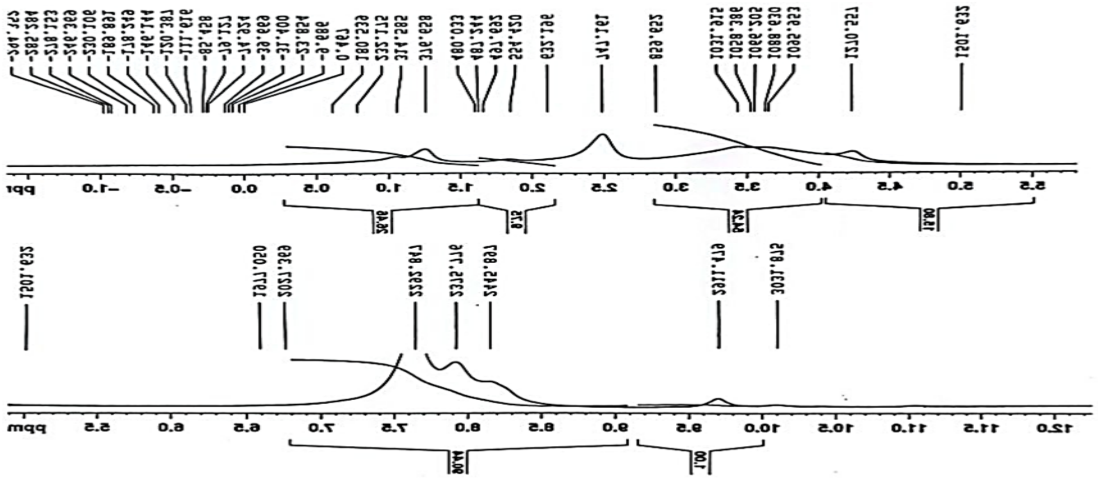


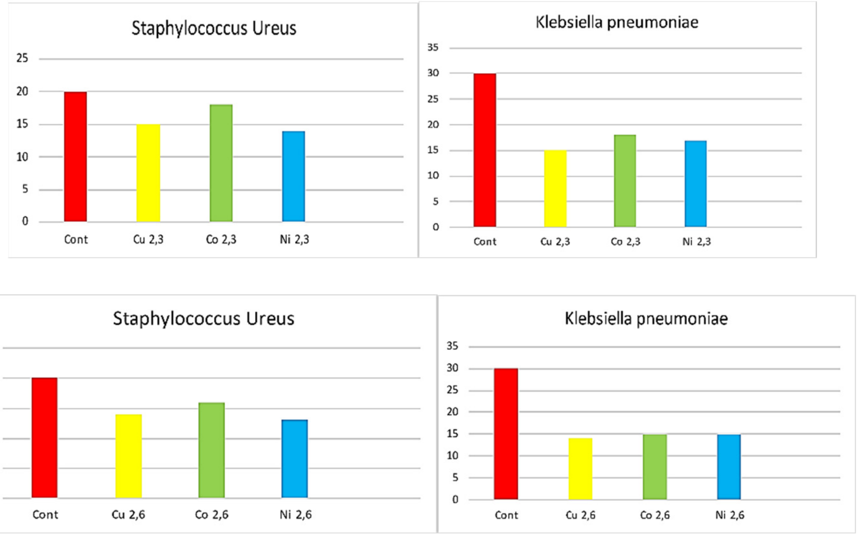
Fig. 2. $L_{2,3py}$'s ^{1}H-NMR spectra

Antimicrobial activity: Analysis was done on the estimated biologic activity of the ligand with complexes against certain species of G(+) bacteria, such as *Staph aureus*, and G(-) bacteria, such as *Klebsiella pneumoniae*. The results are equivalent to the conventional medication (*Ciprofloxacin*) and are contained in Table 4, Fig. 2, and Graph 1 data. The analysis revealed that the activity of their complexes against the bacteria employed in this study is characterized as less than effective when it comes to ciprofloxacin [51, 52, 53].

Table 4. The ligand's antibacterial activity in combination with complexes

No.	**symbol**	**compounds**	***Staphylococcus aurous* (mm)**	***Klebsiella pneumoniae* (mm)**
1	Co2,3	$[Co(L_{2,3py})Cl_2]$	18	18
2	Ni2,3	$[Ni(L_{2,3py})Cl_2]$	14	17
3	Cu2,3	$[Cu(L_{2,3py})Cl_2]$	15	15

4	Co2,6	$[Co(L_{2,6py})\ Cl_2]$	16	15
5	Ni2,6	$[Ni(L_{2,6py})\ Cl_2]$	13	15
6	Cu2,6	$[Cu(L_{2,6py})\ Cl_2]$	14	14
Control			20	30



Graph 1. Antibacterial activity of the compounds**.**

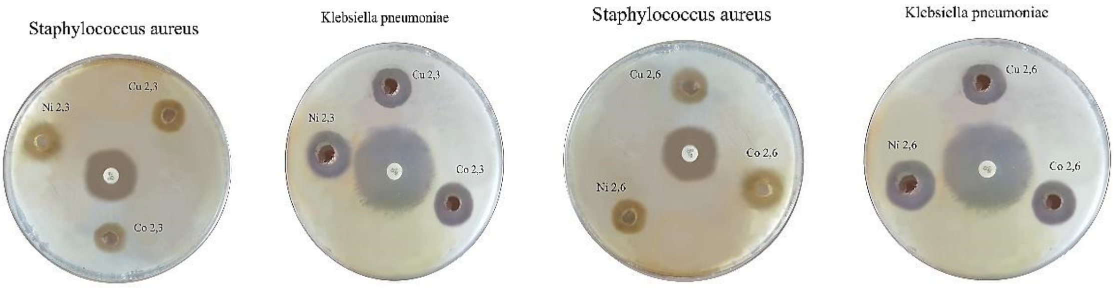


Fig. 3. Antibacterial activity of compounds against (a) *Staphylococcus aureus* and (b) *Klebsiella pneumoniae*

Conclusion

New ligands of type (N4) have been prepared by reacting thiourea with two carboxylic acids. These ligands were then used to prepare new complexes with some transition metals. The prepared complexes were found to be hexagonally coordinated. The coordination is due to four nitrogen atoms with two chloride ions. The measurements of the molar electrical conductivity of the compound suggest that this coordination is associated with the central metal. The biological analysis of the prepared complexes revealed that their activity against bacteria is characterized as less effective than ciprofloxacin.

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