Preparation and Characterization of Schiff Base Ligand Complexes (Dimedone With Thiourea)

Sammer mizher ayash[1], Omar Hamad Shihab[2], Imad (Moh'D Khair) Rashid Hamadneh[3]

[123]*Chemistry department ,college of science, university of anbar , Faculty of science, University of Jordan*

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Dimedone, Thiourea, metal complexes, Schiff base ligand, IC50

ABSTRACT

In this study, eight complexes of this group were prepared by reacting the new ligand prepared from the reaction of dimedone with thiourea with metal chlorides of divalent (Mn, Co, Ni, Cu ,Zn, Cd) and trivalent (Fe, Cr) transition elements. These complexes were characterised by distinctive colours, melting points and solubility, and from the diagnostic results obtained, it was found that the ligand.(1E,5E)-5-carbamothioylimino)-3,3-dimethylcyclohexylidene) thiourea(L2) , that behave as dodecameric ligands with the metal ion, to which they bind through two amine groups. The octahedral shape of the complexes was suggested by IR, UV-visible, molar electrical conductivity, and magnetic susceptibility spectra, all of which indicated paramagnetic properties except for Zn and Cd, which have diamagnetic properties, and molar conductivity showed that all complexes are non-electrolytic except for Fe and Cr. The molecular formula of the complexes forming the group was determined by elemental analysis, where the elemental percentages matched the proposed molecular formula. The results measured the biological efficacy against pathogenic bacteria of the complexes showed varying efficacy. The results of antioxidant efficacy measurement using ethanol showed varying efficacy and were compared with gallic acid using DPPH as a free radical and gave different IC50 values. Density Functional Theory (DFT) measurement results showed that the chemical properties of the prepared complexes were consistent with the results of the practical part.

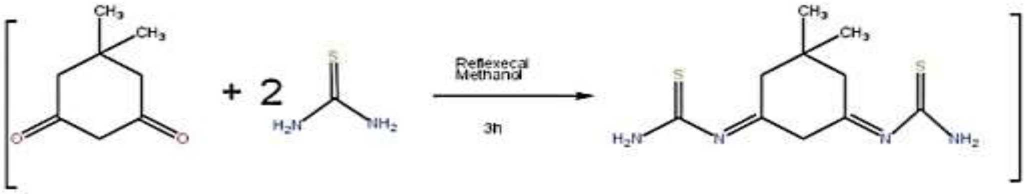
1. Introduction

Coordination chemistry in its modern form has been around for more than a century. Efforts to enumerate and describe what are now called coordination compounds began in the 19th century, and by 1857, Wolcott Gibbs and Frederick Genth published their paper on what they called ammonia and cobalt bases, drawing attention to a class of salts. [1] In 1875, the Danish chemist Jørgensen developed rules to explain the structure of a range of stable compounds that had been discovered, such as those with the formula [$CoCl_3.6NH_3$] - interestingly, Jørgensen spent nearly three decades defending and developing his concepts. [2]Therefore, coordination chemistry has been the focus of attention of researchers in various studies, especially the preparation of the compound [$CoCl_3.6NH_3$] in (1789), and in the second half of the last century it has gained a wide field in chemistry, due to its rapid development in the practical aspect of preparing complex coordination compounds (Coordination Compound) and interpreting the structures of these complexes, which played an important and significant role in various fields such as medicine, industry and agriculture that were tested and confirmed their importance at the present time. [3-5] .

Coordination complexes consist of an atom or ion that accepts a pair of electrons called an acceptor and an atom or ion that provides that pair of electrons called a donor called a ligand, which is part of a neutral molecule such as CO", H_2O and NH_3", or part of an ion such as NH_2CH_2COO- and CO_3-. The acceptor binds to a number of donor atoms that may be identical or dissimilar and the resulting compound may be a positive ion, a negative ion or a neutral molecule. [6,7,8] The formation of complexes is not limited to transition elements only, but the reaction includes symmetrical elements, where metal ions of elements can participate in the formation of complexes as a result of the binding of ions with organic or inorganic ions or molecules called ligands. [9] What distinguishes organic ligands is that they contain active groups whose atoms are electron donors and behave like Lewis bases, and the most famous of these active groups are (C=S, N=O, N=N, NH_2, C=N), in addition to containing active groups that also have a role in increasing the colour intensity of these ligands and their complexes. [10]. The coordination bond is formed by donating an electron pair from a Lewis base ligand to another receptor containing an empty orbital (central metal) Lewis's acid and the new bond formed is called a coordination bond. [11] Schiff bases have been widely used as coordination bond after reacting with organic compounds to form ligands due to the high stability of coordination compounds and their good solubility in common solvents - which have a geometric shape that affects the electronic structure as well. The thermochemical properties of Schiff bases have attracted much attention from researchers due to their ability to coordinate metal ions, leading to the formation of binary, tetra- or octahedral coordination orders in metal chelates containing a donor atom group. [12]

2. Materials and Methods

The ligand L2 resulting from the reaction of thiourea with dimedone was prepared in the following steps: 1.40 gm, 1mmol of dimedone was added to 1.40 gm, 2 mmol of thiourea with 10 drops of ice acetic acid was added as a catalyst and dissolved in 25ml of absolute ethanol. 99.9% high-purity ethanol and the substances were placed together in a 100 mL round bottom flask with continuous stirring. It is placed on the heating device at 80 ^{0}C with the use of a stirrer to ensure the melting of the substances. It is left on heating for 3h using retrograde rectification to form light yellow needle crystals Cooled by an ice bath, the formed crystals were filtered and recrystallized using ethanol. Its melting point is 158-154 ^{0}C as in the following chart:



Scheme 1: (1E,5E)-5-(carbamothioylimino)-3,3-dimethylcyclohexylidene) thiourea

Preparation of L2 ligand complexes:

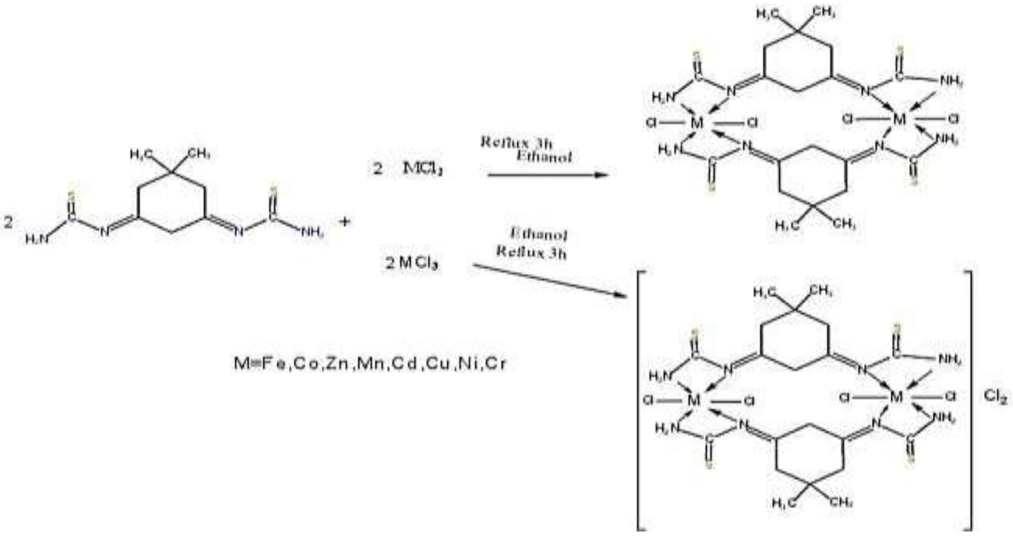
Ligand complexes were prepared from the reaction of previously prepared ligand with metal salts using the following steps:

2.1 Preparation of complexes from the reaction of ligand (L2) with metal ions.

In a 100 ml round bottom flask 0.560 g, 2.0 mmol of L2 dissolved in 20 mL of absolute ethanol to dissolve the ligand with continuous stirring and 0.474 g, 2 mmol of cobalt chloride salt $CoCl_2.6H_2O$ dissolved in 20 mL of absolute ethanol with continuous stirring. The dissolved (L2) was then mixed with the cobalt chloride salt. It was placed on heating using with continuous stirring for 3h. It was heated to 70 ^{0}C. L2 was added to the salt in a ratio of 2:2 and a dark blue precipitate was obtained, which was filtered and recrystallized using ethanol and weighed and the resulting complex was 55%, then the reaction was confirmed by thin layer chromatography (TLC). The rest of the complexes were prepared by dissolving Mn (II), Fe (III), Cr (III), Ni (II), Zn (II) and Cd (II) ions in the same way. **Table 1** shows the amount of metal salt used in the preparation of the complexes, the molecular formulas of the prepared complexes, their weights, the percentage of the resulting complex and its colour.

Table 1: Amount of metal salt used in complex preparation, molecular formulas of the prepared complexes, their weights, proportion and colour of the resulting complex.

NO	Metal salt	Wight(g)	Complex	Color	Yield	M.P.℃
1	$CdCl_2.H_2O$	0.402	$[Cd_2(L_2)_2Cl_4]$	White	89%	198-199
2	$CoCl_2.6H_2O$	0.474	$[Co_2(L_2)_2Cl_4]$	Dark blue	55%	206-209
3	$CrCl_3.6H_2O$	0.532	$[Cr_2(L_2)_2Cl_4]\ Cl_2$	Green	61%	196-199
4	$CuCl_2.2H_2O$	0.340	$[Cu_2(L_2)_2Cl_4]$	White	66%	250-253
5	$FeCl_3.6H_2O$	0.324	$[Fe_2(L_2)_2Cl_4]\ Cl_2$	Acrylic yellow	44%	200-204
6	$MnCl_2.4H_2O$	0.394	$[Mn_2(L_2)_2Cl_4]$	Light yellow	43%	210-214
7	$NiCl_2.6H_2O$	0.474	$[Ni_2(L_2)_2Cl_4]$	Green squar	58%	200-203
8	ZnCl2	0.272	$[Zn_2(L_2)_2Cl_4]$	Yellow to brown	79%	198-201



Scheme 2: Preparation of metal complexes

Solubility of the prepared metal complexes The solubility of the prepared ligand and complexes was tested in various solvents and it was observed that most of them were soluble in THF (DMSO) and insoluble in ethyl acetate, water and cyclohexane as shown in **Table 2**.

Table 2: Solubility test of ligand and its solvents

NO	Complexes	C_2H_5OH	C_6H_{12}	$C_4H_8O_2$	CH_3OH	DMSO	H_2O	DMF	THF
1	**L2**	+	-	-	+	+	-	+	+
2	$C_{20}H_{36}Cr_2N_8S_4Cl_4$	-	-	-	-	+	-	-	+
3	$C_{20}H_{36}Mn_2N_8S_4Cl_4$	-	-	-	-	+	-	+	+
4	$C_{20}H_{36}Fe_2N_8S_4Cl_4$	-	-	-	-	+	-	-	+
5	$C_{20}H_{36}Co_2N_8S_4Cl_4$	-	-	-	+	+	-	+	+
6	$C_{20}H_{36}Ni_2N_8S_4Cl_4$	-	-	-	-	+	-	-	+
7	$C_{20}H_{36}Cu_2N_8S_4Cl_4$	-	-	-	-	+	-	-	+
8	$C_{20}H_{36}Zn_2N_8S_4Cl_4$	-	-	-	+	+	-	-	+
9	$C_{20}H_{36}Cd_2N_8S_4Cl_4$	-	-	-	+	+	-	+	+

(+) Soluble) (-) in Soluble) (÷) Sparingly Soluble)

3. Results and discussion.

Infrared spectroscopy (IR):

The prepared ligand was characterised by the appearance of stretching vibration absorption bands for the C=N group at the frequency of 1614 cm^{-1} of the ligand. [13,14] as well as the C=S group, which is located at the frequency of 1083 cm^{-1}. This indicates the presence of a thio group within the ligand [15,16]. Where the appearance of beams for the effective groups in the ligand structure is evidence of its composition and the correctness of its diagnosis and analogy for the rest of the prepared complexes as shown in table 3, where the absorption bands appeared the absorption of the vibration of the elongation of the group C=N whose frequencies appeared within the range of 1624 - 1609 cm^{-1} for ligand and complexes together. [17,18] as well as the NH_2-NH group, respectively, which showed frequencies in the range 3996 - 33331 cm^{-1}. [19] as well as the C=S group, which indicates the presence of a thio group within the ligand in the range of 1080-1116 cm^{-1}. [20] and absorption bands of the (N - M) group, which showed frequencies within 704 - 538 cm^{-1}, which confirms the binding of ligand by these atoms to the metal and the occurrence of coordination. [21] Also, the appearance of absorption bands for the M-Cl group, which showed frequencies within the range 503 – 447 cm^{-1}, which indicates that the ligand is coordinated with the metal.

Table 3: shows the FT-IR absorption band values for ligand and complexes

NO	Complexes	v-NH	NH_2	C=N	C=S	M-N	M-Cl
1	L2	3381 Sh	3275 sh	1614 sh	1083 sh	----	-----

2	$C_{20}H_{36}Cr_2N_8S_4Cl_6$	3385 S	3300 s	1616 s- sh	1085 sh	704 s	472 s
3	$C_{20}H_{36}Mn_2N_8S_4Cl_4$	3381 m-sh	3277 m-sh	1612 s	1080 m-sh	624 m-sh	447 w
4	$C_{20}H_{36}Fe_2N_8S_4Cl_6$	3996 W	3442 w	1617 w	1085 w	603 w	464 s
5	$C_{20}H_{36}Co_2N_8S_4Cl_4$	3388 Sh	3296 sh	1624 sh	1085 s	559 sh	503 s
6	$C_{20}H_{36}Ni_2N_8S_4Cl_4$	3383 Sh	3294 s-sh	1618 m-sh	1088 s	542 sh	482 w
7	$C_{20}H_{36}Cu_2N_8S_4Cl_4$	3331 W	3290 s	1609 m-sh	1085 s	601 sh	476 sh
8	$C_{20}H_{36}Zn_2N_8S_4Cl_4$	3371 Sh	3286 sh	1622 s-w	1087 sh	560 sh	480 s
9	$C_{20}H_{36}Cd_2N_8S_4Cl_4$	3388 Sh	3248 sh	1618 sh	1088 sh	538 sh	S

S=Small , Sh=sharb, W=weak , B=broad, m=middle

Ultra violet - visible spectroscopy of dimedon and prepared ligands

The UV-visible spectrum of dimedon showed a broad absorption peak at a certain wavelength. A broad absorption peak at a wavelength of (271) nm , (36900cm^{-1}) is indicative of the π→π* electronic transition. The prepared ligand also has an absorption peak at (267) nm, (37453 cm^{-1})which is due to the π→π* electronic transition.] 23,24]. It was also measured for the prepared complexes] and gave the results shown in Table (4)

Chromium complex [$Cr_2(L_2)_2Cl_4$]Cl_2

The UV-visible spectrum showed absorption peaks at 891nm (11223 cm^{-1}) due to the $4A_2g_f \rightarrow 4T_2g_f$ d-d electron transfer, at(726) nm (13774 cm^{-1}) due to the $4A_2g \rightarrow 4T_1g_p$ electron transfer, at 629nm (15898 cm^{-1}) due to the $4A_1g \rightarrow 4T_1g_G$ electron transfer, and at 629nm (15898 cm^{-1}) due to the $4A_1g \rightarrow 4T_1g_G$ electron transfer, as well as at (629)nm (15898 cm^{-1}), as well as absorption peaks at (542) nm (18450 cm^{-1}) for the LCT→M transition, absorption peaks at (396) nm (2552 cm^{-1}) for the n→π* transition, and at (263)nm (38022 cm^{-1}) for the π→π* transition. This is consistent with the octahedral geometry of chromium complexes. [25]

Manganese $[Mn_2(L_2)_2Cl_4]$

Absorption peaks appeared at a wavelength of (882)nm, (1337cm^{-1}) due to the $6A_1g\rightarrow 4T_2g$ electronic transition, as well as at (702) nm, (11210 cm^{-1}) due to the $6A_1g\rightarrow 4T_2g$ electronic transition, and (702) nm (11210 cm^{-1}) due to the $6A_1g\rightarrow 4T_2g$ electronic transition. As well as at (542) nm , (18450 cm^{-1}) (6A1g→ 4A1g, 4Eg) and (410)nm, (24390 cm^{-1}) (n→π*, LCT →M) as well as at (266) nm, (37593 cm^{-1}) which is due to the π→π* transition. This is consistent with the octahedral geometry [26]

Iron complex $[Fe_2(L_2)_2Cl_4]Cl_2$

The UV-visible spectrum showed absorption peaks at (670) nm, (14925 cm^{-1}) due to the $6A_1g\rightarrow 4T_2g_G$ electronic transition as well as at (470) nm, (21276 cm^{-1}) due to the $6A_1g\rightarrow 4A_1g\ 4Eg_G$,electronic transition and at (266) nm, (37593 cm^{-1}) due to the n→π* transition. As well as at (236) nm, (42372 cm^{-1}) which is due to the π→π* transition. This is consistent with the octahedral geometry [27].

Cobalt complex $[Co_2(L_2)_2Cl_4]$

Absorption peaks appeared at wavelength (681) nm, (14684 cm^{-1}) due to the $4A_2g_f\rightarrow 4T_1g_f$ transition, as well as at (542) nm, (18450 cm^{-1}) due to the 4T1gf→4T1gp transition, and at (371) nm (26954 cm^{-1}) due to the n→π*, LCT→M transition, as well as at (371) nm, (26954 cm-1) due to the n→π*, LCT→M transition. As well as at (268) nm, (37313 cm^{-1}) which is due to the π→π* electronic transition. This is consistent with the octahedral geometry. [28]

Nickel complex $[Ni_2(L_2)_2Cl_4]$

Absorption peaks appeared at wavelength (880) nm, (11363 cm^{-1}) due to the $3A_2g_f\rightarrow 3T_2g_f$ electron transition. As well as at (851) nm, (11750 cm^{-1}), which is due to the $3A_2g_f\rightarrow 3T_1g_f$ electron transition. Also at (812)nm, (12315 cm^{-1}) which is due to the $3A_2g_f\rightarrow 3T_1g_p$ transition and at (745)nm, (13422 cm^{-1}) which is due to the $3A_1g\rightarrow 3T_1g_G$ transition. Also at (375)nm, (266666 cm^{-1}) which is due to the n→π*, LCT→M transition as well as at (281) nm, (235578cm^{-1}) which is due to the π→π* transition, this is consistent with the octahedral geometry. [29]

Copper complex $[Cu_2(L_2)_2Cl_4]$

Absorption peaks appeared at (883)nm,(11325 cm^{-1}) which is due to the $2Eg\rightarrow 2T_2g$ electronic transition as well as at (822)nm, (12165 cm^{-1}) which is due to the $2Eg\rightarrow 2T_1g$ electronic transition. As well as (542)nm, (18450 cm^{-1}) (Intra - ligand) and (265) nm, (37735 cm^{-1}) (n→π*). As well as at (225) nm, (44444 cm^{-1}), which belongs to the π→π* electronic transition. This is consistent with the deformed octahedral geometry of the copper complex. [22]

Zinc complex $[Zn_2(L_2)_2Cl_4]$

Two absorption peaks appeared at (263)nm, (25575cm^{-1}) (391nm) (38022cm-1) which are due to the intra-electronic transition. No peak appeared after (391)nm because the orbital (d) in Zn is saturated $3d^{10}$, so an octahedral shape of the Zn complex was proposed based on elemental analysis and molar conductivity. Measurement of metal content and measurement of chlorine content. 30]]

5.8 Cadmium complex. [$Cd_2(L_2)_2Cl_4$]

Two absorption peaks appeared at a wavelength of (542)nm, (1845 cm^{-1}), which is due to the intra-ligand transition. As well as an absorption peak at (291)nm,(34129 cm^{-1}) which is due to the Intra - ligand transition as well. No absorption peak appeared after wavelength (542) nm. Because orbital d is cadmium filled ($3d^{10}$), an octahedral shape for the cadmium complex was proposed based on elemental microanalysis, molar conductivity, metallometry, and chlorine content measurements. This is consistent with the octahedral geometry. as published in the literature [31].

Table (4) shows the UV spectral data of the prepared ligand and complexes

NO	**Compound**	**ʎmax**	**Abs**	***γcm^{-1}***	**Emax $Mol^{-1}cm^{-1}$**	**Electronic Transition type**	**Shape**
1	Dimedon	271		36900	3311	$\pi \rightarrow \pi *$	
2	$C_{20}H_{36}Cr_2N_8S_4Cl_6$	891	0.031	11223	31	$^{4}A_{2}g_{f}\rightarrow{}^{4}T_{2}g_{f}$	Octaheadral
		726	0.025	13773	25	$^{4}A_{2}g_{f}\rightarrow{}^{4}T_{1}g_{p}$	
		629	0.020	15898	200	$^{4}A_{2}g\rightarrow{}^{4}T_{1}g_{G}$	
		542	0.020	18450	200	M→LCT	
		396	0.253	25252	2530	$n \rightarrow \pi *$	
		263	1.315	38022	1315	$\pi \rightarrow \pi *$	
3	$C_{20}H_{36}Mn_2N_8S_4Cl_4$	882	0.010	1137	10	$^{6}A_{1}g\rightarrow{}^{4}T_{1}g$	Octaheadral
		702	0.030	11210	30	$^{6}A_{1}g\rightarrow{}^{4}T_{2}g$	
		542	0.030	18450	30	$^{6}A_{1}g\rightarrow{}^{4}A_{1}g\ ,{}^{4}Eg$	
		410	2.167	24390	2167	M→LCT	
		266	0.171	37593	7710	$\pi \rightarrow \pi *$	
4	$C_{20}H_{36}Fe_2N_8S_4Cl_6$	670	0.030	14925	30	$^{6}A_{1}g\rightarrow{}^{4}T_{2}g_{G}$	Octaheadral
		470	0.021	21276	210	$^{6}A_{1}g\rightarrow{}^{4}A_{1}g,E^{4}.g_{G}$	
		266	2.402	37593	2402	$n \rightarrow \pi *$	
		236	0.319	42372	3190	$\pi \rightarrow \pi *$	
5	$C_{20}H_{36}Co_2N_8S_4Cl_4$	681	0.020	14684	20	$^{4}T_{1}g_{f}\rightarrow{}^{4}A_{2}g_{f}$	Octaheadral
		542	0.007	18450	70	$^{4}T_{1}g_{f}\rightarrow{}^{4}T_{1}g_{p}$	
		371	0.372	26954	3720	M →LCT,$n \rightarrow$	
		268	1.492	37313	1492	$\pi \rightarrow \pi *$	

6	$C_{20}H_{36}Ni_{2}N_{8}S_{4}Cl_{4}$	880	0.037	11363	370	$^{3}A_{2}g_{f}\rightarrow{}^{3}T_{2}g_{f}$	Octaheadral
		851	0.050	11750	50	$^{3}A_{2}g_{f}\rightarrow{}^{3}T_{1}g_{f}$	
		812	0.060	12315	60	$^{3}A_{2}g\rightarrow{}^{3}T_{1}g$	
		745	0.070	13422	70	$^{3}A_{1}g\rightarrow{}^{3}T_{1}g_{G}$	
		35	0.020	26666	200	M →LCT,$n \rightarrow$	
		281	0.644	35587	6440	$\pi \rightarrow \pi *$	
7	$C_{20}H_{36}Cu_{2}N_{8}S_{4}Cl_{4}$	883	0.017	11325	170	$^{2}Eg\rightarrow{}^{2}T_{2}g$	Octaheadral
		822	0.016	12165	160	$^{2}Eg\rightarrow{}^{2}T_{1}g$	
		542	0.030	18450	300	Intra-Ligand	
		265	1.610	37735	1610	$n \rightarrow \pi *$	
		225	0.244	44444	2440	$\pi \rightarrow \pi *$	
8	$C_{20}H_{36}Zn_{2}N_{8}S_{4}Cl_{4}$	391	0.318	25575	3180	Intra-Ligand	Octaheadral
		263	2.201	38022	2201	Intra-Ligand	
9	$C_{20}H_{36}Cd_{2}N_{8}S_{4}Cl_{4}$	542	0.069	18450	6	Intra-Ligand	Octaheadral
		293	1.449	34129	1449	Intra-Ligand	

6. Elemental Analysis

The results of these analyses were listed in Table (5), and the values obtained in practice were compared with those calculated theoretically, showing clearly the degree of convergence between them. This proves the validity of the elemental ratios in the complexes [32].

Table (5) Quantitative analysis of the elements of complexes.

Compound		**C%**	**H%**	**N%**	**Cl%**	**M%**	**S%**
$C_{20}H_{36}Cr_{2}N_{8}S_{4}Cl_{6}$	Practical	29.67	5.43	14.55	17.74	12.41	15.33
	Theory	31.62	4.74	14.75	18.44	13.57	16.86
$C_{20}H_{36}Mn_{2}N_{8}S_{4}Cl_{4}$	Practical	29.66	3.97	14.87	17.08	19.09	14.09
	Theory	28.95	4.34	13.51	16.88	20.86	15.44
$C_{20}H_{36}Fe_{2}N_{8}S_{4}Cl_{6}$	Practical	29.75	3.97	14.08	17.99	14.08	15.99
	Theory	31.03	4.69	14.62	18.27	14.36	16.71
$C_{20}H_{36}Co_{2}N_{8}S_{4}Cl_{4}$	Practical	29.22	3.87	14.33	17.91	14.88	15.99
	Theory	31.03	4.65	14.48	18.11	15.13	16.55
$C_{20}H_{36}Ni_{2}N_{8}S_{4}Cl_{4}$	Practical	29.33	5.42	13.94	16.94	14.83	15.32

	Theory	31.08	4.66	14.50	18.13	15.02	16.58
$C_{20}H_{36}Cu_2N_8S_4Cl_4$	Practical	31.27	3.67	15.67	17.66	15.29	16.03
	Theory	30.69	4.60	14.32	17.90	16.11	16.36
$C_{20}H_{36}Zn_2N_8S_4Cl_4$	Practical	29.73	4.69	15.39	17.67	16.01	16.90
	Theory	30.53	4.58	14.23	17.81	16.53	16.28
$C_{20}H_{36}Cd_2N_8O_4Cl_4$	Practical	28.49	4.67	13.55	15.67	24.97	15.88
	Theory	27.27	4.09	12.72	15.90	25.45	14.54

4.Magnetic sensitivity:

Magnetic measurements have been used in the characterization and study of transition metal complexes, as well as the calculation of the correction factor value to correct the magnetic susceptibility values [33,34,35]. From the results in Table (6), all measured complexes were octahedral in shape.

Table (6) Results of magnetic measurements of complexes

NO	Complexes	Magnetic moment is effective Practically (B.M μeff)	Expected shape	Hybridization
1	$C_{20}H_{36}Cr_2N_8S_4Cl_6$	6.85	Octaheadral	SP^3d^2
2	$C_{20}H_{36}Mn_2N_8S_4Cl_4$	7.88	Octaheadral	SP^3d^2
3	$C_{20}H_{36}Fe_2N_8S_4Cl_6$	5.705	Octaheadral	SP^3d^2
4	$C_{20}H_{36}Co_2N_8S_4Cl_4$	4.66	Octaheadral	SP^3d^2
5	$C_{20}H_{36}Ni_2N_8S_4Cl_4$	2.95	Octaheadral	SP^3d^2
6	$C_{20}H_{36}Cu_2N_8S_4Cl_4$	2.18	Octaheadral	SP^3d^2
7	$C_{20}H_{36}Zn_2N_8S_4Cl_4$	Dia Megnatic	Octaheadral	SP^3d^2
8	$C_{20}H_{36}Cd_2N_8S_4Cl_4$	Dia Megnatic	Octaheadral	SP^3d^2

7. Molar Conductivity Measurement

It was found from the measured electrical conductivity values of the prepared complexes. All the prepared complexes were found to be non-electrolytic except for Fe and Cr complexes which were found to be electrolytic [36,37,38]. As shown in Table (7)

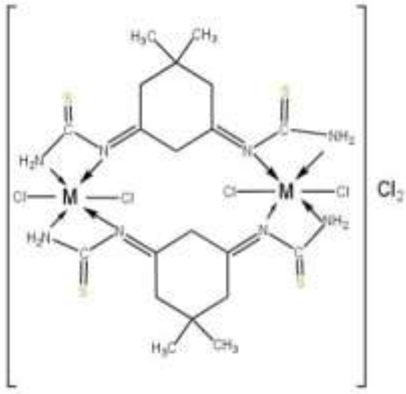
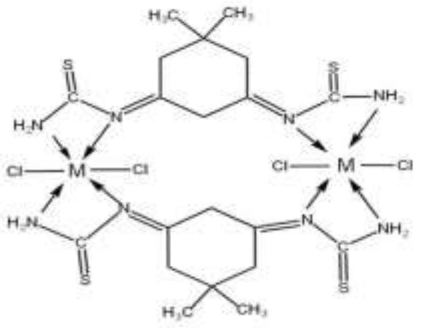
Table (7) Molar electrical conductivity values for Compounds

No	Compounds	Λ_m (S.cm^2.Mol^{-1})
1.	$C_{20}H_{36}Cr_2N_8S_4Cl_6$	44
2.	$C_{20}H_{36}Mn_2N_8S_4Cl_4$	20
3.	$C_{20}H_{36}Fe_2N_8S_4Cl_6$	48
4.	$C_{20}H_{36}Co_2N_8S_4Cl_4$	11
5.	$C_{20}H_{36}Ni_2N_8S_4Cl_4$	21
6.	$C_{20}H_{36}Cu_2N_8S_4Cl_4$	19
7.	$C_{20}H_{36}Zn_2N_8S_4Cl_4$	9
8.	$C_{20}H_{36}Cd_2N_8S_4Cl_4$	17

8.Proposed shapes of the complexes

The shapes of the nodes were suggested by the results obtained

Table (8) Proposed shapes of the complexes

 **M(III)=Fe, Cr**	 **M(II) =Co, Zn, Cu, Cd, Ni, Mn**

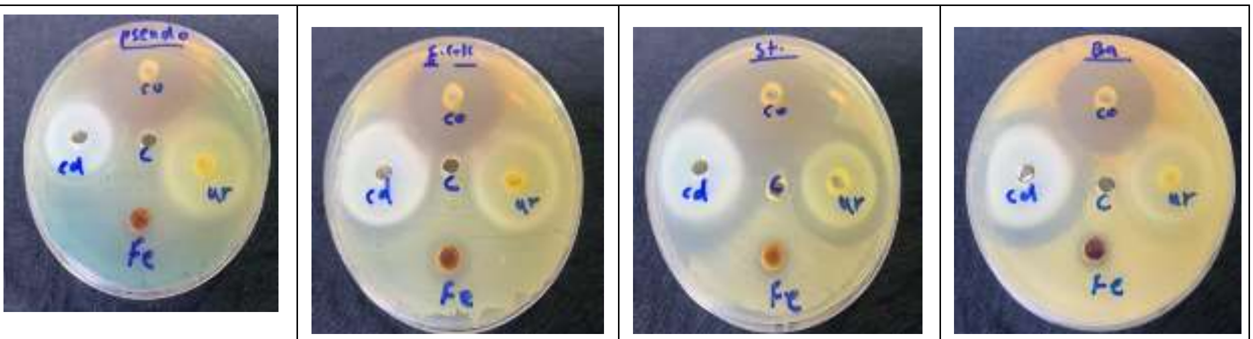
9.Antimicrobial study of metal complexes.

In this research, four types of bacteria were used, two of which are positively sensitive to chromium dye (***Staphylococcus aureus***.), ***Bacillus*** inhibition, and two of the other bacteria are negatively sensitive to chromium dye (*E.Coli*) inhibition, where the antimicrobial test was carried out in vitro for metal complexes is zinc cobalt. [39-41]

The following was concluded: Prepared complexes cadmium and iron showed clear inhibition against gram-negative and gram-positive bacteria of four species, although ***bacillus*** and ***staphylococcus*** bacteria are characterized by resistance to antibiotics and also because they contain genetic factors of resistance and the effectiveness of solutions of these compounds is attributed to the ability to dissolve the outer cell wall, which leads to the exudation of the fluids of this cell and its death, so compounds that affect the cell wall are among the most selective agents with a very effective therapeutic index. Due to the difference in structure between the cell wall of the host and microbial cells [41,42].

Table (9) Inhibition values of the prepared complexes against Gram-negative and Gram-positive bacteria

No	Sample	Mg\ml	Gramposative		Gramnegative	
			Staphy zone(cm)	Bacillus zone(cm)	Spuedo zone(cm)	E.coli zone(cm)
1.	$C_{20}H_{36}Fe_2N_8S_4Cl_6$	0.5	1	1.1	1.4	1.2
2.	$C_{20}H_{36}Cd_2N_8S_4Cl_4$	0.25	5.5	4	3	3.9



$[Cd_2(L_2)_2Cl_4]$
$[Fe_2(L_2)_2Cl_4]Cl_2$

$[Cd_2(L_2)_2Cl_4]$
$[Fe_2(L_2)_2Cl_4]Cl_2$

$[Cd_2(L_2)_2Cl_4]$
$[Fe_2(L_2)_2Cl_4]Cl_2$

$[Cd_2(L_2)_2Cl_4]$
$[Fe_2(L_2)_2Cl_4]Cl_2$

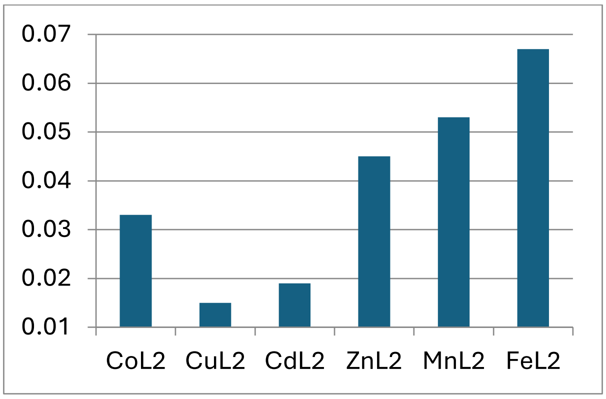
Figure (1) Inhibition zones of group I and II complexes against bacteria (***Bacillus, Spuedo, E.coli, Staphylococcus***)

Antioxidant activity of complexes

Inhibition of metal complexes was measured Mn(II), Cr(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II). They were evaluated against reactive oxygen species using (II)Cd radical (DPPH) scavenging. This combination contributes to changing the color of DPPH from purple to yellow. This is due to the transfer of hydrogen from the complex to the DPPH molecule. The color shift was detected by UV-spectrophotometer at 517nm in the following order: FeL2>MnL2>ZnL2>CoL2>CdL2>CuL2. As shown in the following chart, the inhibition of complexes towards reactive oxygen species is measured at (30 minutes) where (MnL2, FeL2) shows higher antioxidant activity [43].

Table (9) Antioxidant activity values

Compound	**Concentration**	**PI%**	**RSA%**	**IC_{50} mg/Ml**
$[Co_2(L_2)_2Cl_4]$	0.066	11.63	88.37	0.031
	0.033	38.72	61.28	
	0.015	62.78	37.22	
	0.008	80.33	19.67	
$[Cu_2(L_2)_2Cl_4]$	0.068	32.36	67.64	0.013
	0.034	65.09	34.91	
	0.017	82.62	17.38	
	0.009	90.72	9.28	
$[Cd_2(L_2)_2Cl_4]$	0.056	33.39	66.61	0.019
	0.028	66.19	33.81	
	0.014	83.11	16.89	
	0.007	91.06	8.94	
$[Zn_2(L_2)_2Cl_4]$	0.050	8.95	91.05	0.045
	0.025	23.49	76.51	
	0.012	42.49	57.51	
	0.006	72.45	27.55	
$[Mn_2(L_2)_2Cl_4]$	0.048	19.45	80.55	0.053
	0.024	29.36	70.64	
	0.012	38.48	61.52	
	0.006	50.38	49.62	
$[Fe_2(L_2)_2Cl_4]Cl_2$	0.040	29.47	70.53	0.064
	0.020	40.12	59.88	
	0.010	49.76	50.24	
	0.005	61.03	38.97	



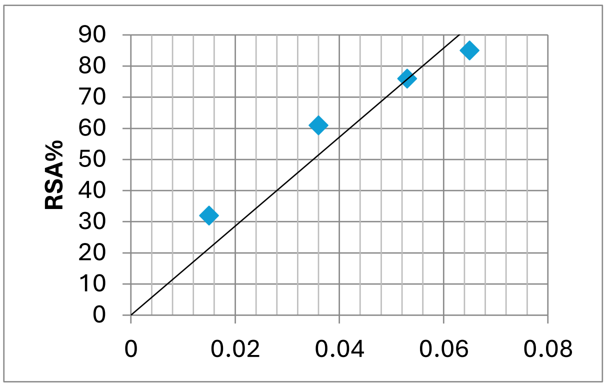
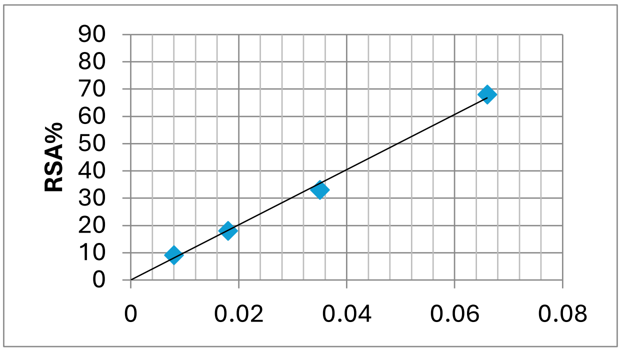
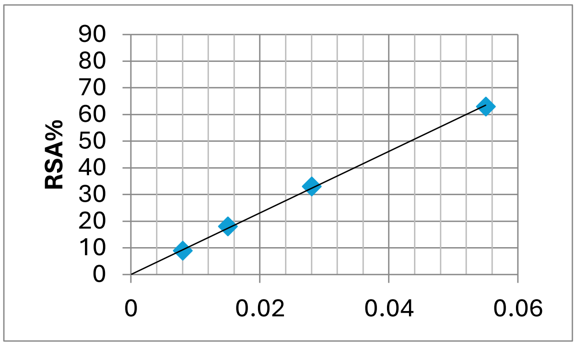


Chart (1) shows the difference between the IC50 Scheme (2) Inhibition efficacy of the complex
$[Co_2(L_2)_2Cl_4]$

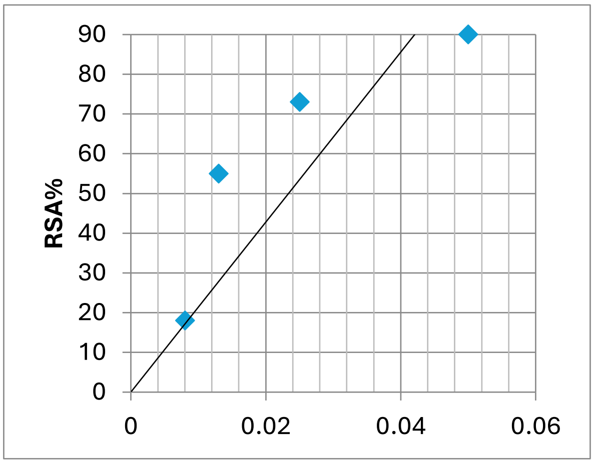
values of the complexes

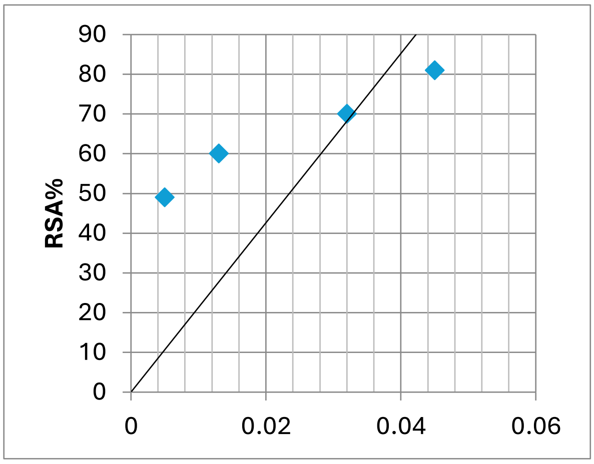




Scheme (3) Inhibition efficacy of the complexes Scheme (4) Inhibition efficacy of the complex $[Cd_2(L_2)_2Cl_4]$

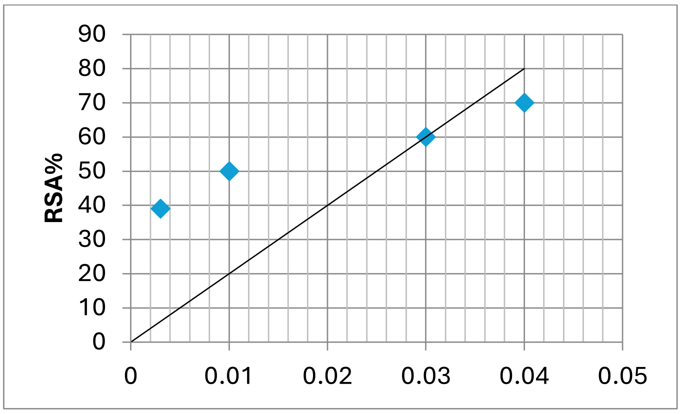
$[Cu_2(L_2)_2Cl_4]$



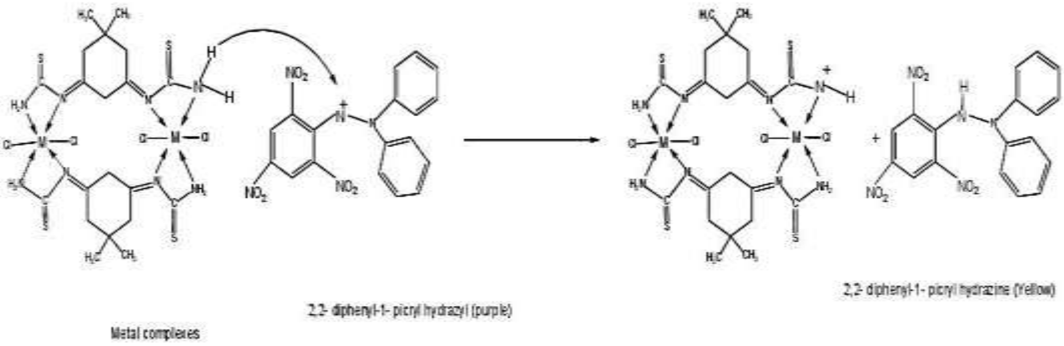


Scheme (5) Inhibition efficacy of the complex Scheme (6) Effectiveness of complex inhibition $[Mn_2(L_2)_2Cl_4]$

$[Zn_2(L_2)_2Cl_4]$



Scheme (7) Effectiveness of complex inhibition [$Fe_2(L_1)_2Cl_4$]



Scheme (8) shows the conversion of purple DPPH to the corresponding hydrazine (yellow) by adding a metal complex to DPPH due to proton transfer

3. Conclusion

The molecular structures of the prepared ligands have been established. All the molecular structures of the prepared complexes were stabilized. The theoretical study was fairly close to the practical results. Prepared complexes showed clear antibacterial activity. Prepared complexes showed antioxidant activity. Infrared spectra showed new bands indicating the correctness of the method used to prepare the complexes. Prepared complexes showed absorption bands (C=N) different from their location in the ligand, which is evidence that the reaction occurred. The complexes showed different (M-N) absorption bands, indicating that the metal ion is bonded to the ligand through the electron pair of the nitrogen atom. The UV spectra also showed the d-d absorption section of the complexes, which helped to determine the final complex shape. The complexes showed Mn, Co, Fe electron transitions with LL attributed to the octahedral shape and the other part of the group showed Cu, Zn, Cd electron transitions attributed to the octahedral .

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