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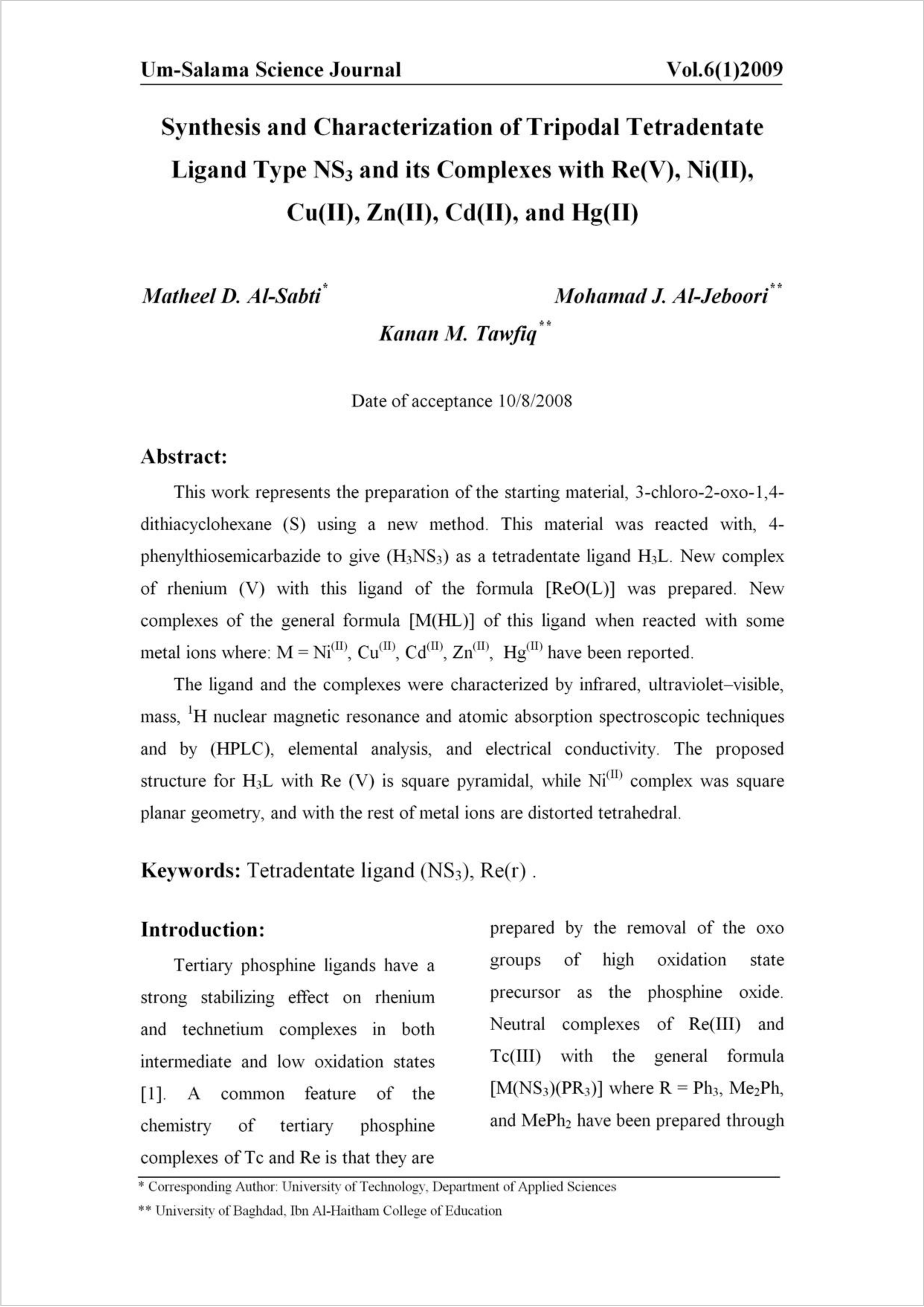

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Synthesis and Characterization of Tripodal Tetradentate Ligand Type NS_3 and its Complexes with Re(V), Ni(II), Cu(II), Zn(II), Cd(II), and Hg(II)

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Abstract:

This work represents the preparation of the starting material, 3-chloro-2-oxo-1,4-dithiacyclohexane (S) using a new method. This material was reacted with, 4-phenylthiosemicarbazide to give (H_3NS_3) as a tetradentate ligand H_3L. New complex of rhenium (V) with this ligand of the formula [ReO(L)] was prepared. New complexes of the general formula [M(HL)] of this ligand when reacted with some metal ions where: M = $Ni^{(II)}$, $Cu^{(II)}$, $Cd^{(II)}$, $Zn^{(II)}$, $Hg^{(II)}$ have been reported.

The ligand and the complexes were characterized by infrared, ultraviolet–visible, mass, ^1H nuclear magnetic resonance and atomic absorption spectroscopic techniques and by (HPLC), elemental analysis, and electrical conductivity. The proposed structure for H_3L with Re (V) is square pyramidal, while $Ni^{(II)}$ complex was square planar geometry, and with the rest of metal ions are distorted tetrahedral.

Keywords: Tetradentate ligand (NS_3), Re(r) .

Introduction:

Tertiary phosphine ligands have a strong stabilizing effect on rhenium and technetium complexes in both intermediate and low oxidation states [1]. A common feature of the chemistry of tertiary phosphine complexes of Tc and Re is that they are prepared by the removal of the oxo groups of high oxidation state precursor as the phosphine oxide. Neutral complexes of Re(III) and Tc(III) with the general formula $[M(NS_3)(PR_3)]$ where R = Ph_3, Me_2Ph, and $MePh_2$ have been prepared through

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the reaction of some ligands type

H_3NS_3 with $[MO_4^-]$ in presence of triphenyl phosphine as a reducing agent and as a unidentate ligand where H_3NS_3=N $(CH_2CH_2SH)_3$ = 2,2′,2″-nitritotris (ethanethiol) [2].

New tetradentate ligands having three negative charges of the type (H_3NS_3) containing amide and amine groups have been prepared in basic medium by loosing three protons [3]. These ligands were used to prepare new complexes of Tc(IV) and Re(V) with the general formula: $[TcO(NS_3)]^-$, $[ReO(NS_3)]$ using $[MOCl_4]^-$ and $[ReOCl_3(PPh_3)_2]$ or $[ReO_2(Py)_4]Cl$ as starting materials in the reaction where [M= Tc, Re]. Some complexes of the oxo-Re(V) with new tetradentate ligands of the type (H_3NS_3); N(phenylthiocarbamido)-N'-(1-mercapto-2- thiapentanoyl) hydrazine & N(phenylthiocarbamido)-N'-(1-mercapto-3-methyl-2-thiapentanoyl) hydrazine were prepared [4]. These ligands were reacted with the complex $[ReO_2\ (Py)_4]Cl$ using THF as a medium for the reaction in the presence of triethylamine as a base. The proposed structure for the complex is square pyramidal.

Some complexes of Ni(II) were prepared using tetradentate ligands with the general formula $K[Ni(NS_3)]$ [5]. Comba and coworkers[6] prepared the square planar complex [(6-methyl-6- nitro-1, 11-dithia-4, 8-diazacyclotetradacane) Copper(II)] [perchlorate]. Some complexes with the general formula $[MLX_2]$ of Zn(II), Cd(II), and Hg(II) were prepared from different metal ions with tetramethyl dithiooxamide and tetraethyl dithiooxamide, where X= Cl, Br, I [7].

Material and Methods:

All the chemicals used were of high purity from Fluka, Readel-deTaeu, Merck, and Aldrich.

Instruments:

Stuart Melting Point Apparatus; Pye-Unicam SP3-300; Shimadzu UV-160A Ultraviolet Visible Spectrophotometer; Shimadzu GC-Mass 1000 P; Hitachi Perkin Elmer R-24B 60 MHZ NMR Spectrometer; Perkin Elmer 240B Elemental Analyzer; Shimadzu AA 680G; Titroprocessor–665 Dosimat-Metrohm Swiss; Phillips PW9 526 Conductivity Meter; HPLC Shimadzu LC-6A (koyota-Tapan); Computer programs SHLXL-93 and 3DSMAX were used for calculating bond lengths and bond angles.

Preparation of Compounds:

1. Preparation of $[ReO_2(py)_4]Cl$: Dioxotetrapyridine rhenium(V) Chloride:

In a round bottom flask (1.2 mmol) of $[ReOCl_3\ (PPh_3)_2]$ was added with stirring to a mixture of (21 mmol) pyridine and (1 ml H_2O in 30 ml acetone). The mixture was refluxed for 90 min., and the color of the mixture was changed from green-yellow to orange. After that the flask was put in an ice bath for half an hour, crystals were formed, then washed with toluene and diethylether and allowed to dry to give an orange precipitate [8]. Yield (90%), m. p. = 105^{o}C (dec.). The IR spectrum shows a band at 815 cm^{-1} which is due to trans $\upsilon(ReO_2)$.

2. Preparation of (S): 3-Chloro-2-oxo-1, 4-dithiacyclohexane:

In a three neck round bottom flask was added (88 mmol) 1, 2-ethanedithiol and (176 mmol) triethylamine under an inert atmosphere (N_2). The mixture was cooled to (- 10^{o}C), then a mixture (100 ml dichloromethane and 88 mmol dichloroacetyl chloride) was added dropwise from a pressure equalized funnel with stirring and the temperature was maintained at (-5^{o}C) for 90 min., the white precipitate of triethylammonium chloride was formed. The mixture was maintained at room temperature with stirring for two hours, and then the solution was filtered, and washed with distilled water. The organic layer was separated and dried with anhydrous $MgSO_4$, then the solvent was evaporated under reduced pressure leaving a white-yellow oily mass (10.4 gm); (69%) yield.

3: Preparation of (H_3L): N (phenylthiocarbamido)-N'(1-mercapto-3-chloro-2-thiapentanoyl) hydrazine:

Under an inert gas the 3-Chloro-2-oxo-1,4-dithiacyclohexane (1.8 mmol) in 25 ml dimethyl formamide (DMF) was added in a two neck round bottom flask. From a pressure equalized funnel was added dropwise with constant stirring (1.8 mmol) of 4-phenylthiosemicarbazide in 25 ml DMF. After the addition has finished, the mixture was maintained at constant stirring for 60 minutes. The solvent was evaporated leaving a yellowish-white oily mass which was solidified after cooling (0.38 gm); (64%) yield, m. p. = 124^{o}C.

Detection of (S-H) group in the ligand using iodine method:

The detection of (S-H) group in the ligand was performed using iodine method as follows:

A small quantity of the ligand (H_3L) was dissolved in (1:1) methanol & dichloromethane in a test tube. In another test tube, same quantity of iodine was dissolved in methanol which gave a brown colored solution. The iodine solution was added to the ligand solution with shaking where the color of iodine was disappeared with the formation of yellowish-white precipitate due to the oxidation of the thiol group as shown in figure (1).

4. Preparation of the complex [ReO(L)]:

The H_3L (0.7 mmol) in 25 ml THF was added to 0.3 ml (2.1 mmol) of triethylamine in a round bottom flask under an inert atmosphere with stirring. To this mixture was added 0.7 mmol of the complex $[ReO_2(Py)_4]Cl$. The mixture was refluxed for (3 hrs) and it was noticed that the color of the reaction mixture was changed to red-brown. The solution was left to cool, filtered and concentrated to 15 ml under reduced pressure. After addition 14 ml of the mixture (1:1) n-hexane and isopropanol, a red-brown precipitate was formed. The solution filtered and the precipitate was recrystallized from (1:1) n-hexane/ CH_2Cl_2. Yield (0.2 gm); (54%), m. p. > 300^oC.

5. General procedure for the preparation of [M(HL)] complex:

In a 100 ml round bottom flask (X mmol) of H_3L in 20 ml (1:1) dichloromethane and methanol was added then, potassium hydroxide solution was added to raise the pH to (8-9). To this mixture dropwise under nitrogen atmosphere with stirring (X mmol) of metal salt in 20 ml methanol was added. The solution was refluxed for 90 minutes until a precipitate was formed. The mixture was cooled, filtered, and the precipitate washed with 5 ml methanol then with 10 ml diethylether and vacuum dried.

Results and Discussion:

Characterization of the compound S:

This compound (S) was prepared in 1993 by Larsen and co-workers into two steps [9]. In this work it was prepared by a new method in one step through the direct reaction between 1,2-ethanedithiol and dichloroacetyl chloride using dichloromethane and triethylamine as a reaction medium. The new method takes less time with the same yield and less expensive. It was characterized by HPLC, mass spectrometry (table 1), (UV-Vis.) table (2), IR (table 3), (C.H.N.S) table (4), and ^{1}HNMR.

The HPLC chromatogram shows one absorption band at (254 nm) with retention time (R_t=4.8 min.) an indication that this compound is pure and occurs as one isomer in solution. The electron impact mass gave the fragments as shown in (table 1) which are inconsistent with the mentioned compound. The ultra violet-visible spectrum (table 2) show one absorption band at (279.5 nm) which is due to ($n - \pi^*$) and ($\pi - \pi^*$) transitions. Table (3) shows the IR bands and their characterization. The ^{1}HNMR spectrum of this compound show two chemical shifts. The first triplet at (δ = 2.4 – 2.7 p.p.m.) due to the protons of the CH_2 group, while the second singlet at (δ = 3.28 – 3.1 p.p.m.) which is due to the proton of (Cl-CH) group.

Characterization of the ligand H_3L:

This tetradentate ligand of the type (H_3NS_3) was prepared as mentioned in the experimental section. Different spectral techniques were used to characterize this ligand and some of the data are reported in tables (2), (3), & (4). The H_3L ligand occurs in two isomer forms (A) and (B) in the solid state due to tautomerism phenomenon because of the transfer of the proton between nitrogen and sulfur atoms forming thion (keto) and enol forms as in figure (2).

The UV-visible spectrum for the ligand (H_3L) show one absorption band at (287 nm) which is due to ($n- \pi^*$) and ($\pi - \pi^*$) transitions.

The ultra violet visible spectra for complexes:

The electronic absorption bands for the complexes are due to:

1. Absorption bands due to the ligand.
2. Charge transfer between M and L.
3. d – d transitions at low energy due to the ligand field.
4. Ion pair.

The d – d transitions are forbidden due to (Laporte law Forbidden), which is appeared at lower energy with low intensity, and appeared in the visible region.

Table (2) show the (UV–Vis) bands for the ligands (H_3L) and its complexes. **[H_3L]** ligand gave a band at 287 nm due to ($n-\pi^*$) and ($\pi-\pi^*$) transitions. **[ReO(L)]** compound show three absorption bands. The first at 299 nm are at longer wavelength than that for the ligand by 12 nm due to (M–L) coordination. The second band at 347 nm may be due to (d–d) electronic transition and this peak withdrawn to shorter wavelength due to (intensity stealing) and its origin is due to ($^1e \rightarrow {}^1b_2$) transition. The third absorption band appeared at 557 nm is due to d – d transition and its origin ($^1e \rightarrow {}^1a_1$) transition [10]. **[Ni(HL)]** show three absorption bands: The band at 300 nm is due to (M–L) coordination (shift 13 nm to longer wavelength than that of the ligand). The band at 344 nm is due to d–d transition assigned ($^1a_{1g} \rightarrow {}^1b_{1g}$). The band at 536 nm is due to ($^1b_{2g} \rightarrow {}^1b_{1g}$) transition [11,12]. **[Cu(HL)]** show two bands: The band at 282 nm is due to (M–L) coordination (shift 5 nm to shorter wavelength than that of the ligand). The band at 726 nm is due to ($^2B_2 \rightarrow {}^2E$) (broad due to Jan-Teller distortion) [13-15]. **[Zn(HL)]** show two absorption bands. The first band at 277 nm is due to (M – L) coordination (shift 10 nm to shorter wavelength than that of the ligand). The band appeared at 346 nm may be due to (charge transfer). **[Cd(HL)]** show one band at 281 nm (which it's origin for the ligand) is shifted to shorter wavelength by 6 nm due to coordination to the metal. **[Hg(HL)]** show one band at 293 nm (which it's origin for the ligand) is shifted to longer wavelength by 6 nm due to coordination to mercury ion.

The IR spectra for the ligands H_3L and its complexes:

Tables (3) show the IR bands for the H_3L ligand and its complexes. The IR spectrum of the ligand H_3L show two bands at 3250 cm^{-1} & 3350 cm^{-1} which are due to the stretching frequencies of υ(N-H) bond. The weak band which appeared at 2580 cm^{-1} is due to υ(S-H) stretching frequency. On the formation of the complex [ReO(L)] these bands were merged and appeared at 3313 cm^{-1}. Also the band which appeared at 1610 cm^{-1} is due to the shift of υ(C=O) from that of the ligand (1660 cm^{-1}) to high frequency by 50 cm^{-1} which indicates coordination of the ligand to rhenium metal. The band for the ligand which appeared at 1070 cm^{-1} due to the stretching of υ(C-S) bond was disappeared on the formation of complex. The strong band which appeared at 890 cm^{-1} is due to υ(Re=O)$^{(3)}$. The band appeared at 470 cm^{-1} is due to υ(Re-N) [16] bond. The band at 340 cm^{-1} is due to υ(Re-S) [17] bond. For the rest of complexes, the absorption bands are listed in the above table.

Molar Conductivity:

The molar conductivity for coordinating compounds in general is used to characterize the behavior of compounds in solution (molecules or ions) [18,19]. Because of the insolubility of the majority of organic compounds in water, it can't be used as a medium for conductivity measurements. Dimethyl formamide and dimethyl sulfoxide were used as solvents for these compounds in which the concentration of the solution was (10^{-3} M) at room temperature. These studies show that all the complexes in solution are neutral (table 5).

HPLC study:

In order to identify the number of components formed during the reaction, the number of isomers, and the purity of the complexes, HPLC technique was adopted using (ODS–C_{18}) column by isocratic elution method with a flow rate (1 ml/min) at wavelength 254 nm. **[ReO(L)]** complex show two absorption peaks at retention times (R_t = 1.5 & 1.11 min.) respectively which show that the complex occurs in two isomer forms in solution (syn and anti) with (2:1) percent respectively. This behavior has been noticed in previous studies for rhenium(V) complexes with five coordination of the type N_2S_2 which has the molecular structure of square pyramidal [20]. **[Ni(HL)]** complex show one absorption peak at (R_t = 1.53 min.) an indication of pure compound with one isomer in solution.

Conclusions and the proposed molecular structure for the complexes:

The molecular structure of Rhenium(V) complexes with H_3L ligand:

According to the results found from the characterization of [ReO(L)] complex, the following notes are given:

1. The IR spectra for [ReO(L)] show strong absorption band at 890 cm^{-1} which is due to υ(Re=O) stretching frequency. The absorption bands due to the stretching frequencies for υ(N-H) and υ(S-H) for the ligand are either shifted or disappeared on the formation of complex.
2. The (UV–Vis) spectra for the complex show absorption bands at (299, 347, & 357 nm) which is in consistent with the previous studies for five coordination rhenium complexes containing oxo center on the top of the pyramid [21,22].

3. The (C.H.N) for the complex (tables 4) show compatible results with the calculated data which gave good proof for the expected molecular structure.

From above the proposed molecular structure for the complex is square pyramidal where rhenium has (+5) oxidation state. Figure (1) show the expected molecular structure for [ReO(L)] complex where rhenium metal coordinate to the H_3L ligand (after loosing three protons) through three negatively charged atoms (two sulfur and one nitrogen) and one lone pair belong to another sulfur atom (thio-ether) where the oxo-group on the top of the pyramid. Table (6) show the bond lengths and bond angles for the complex [3,23].

The proposed molecular structure for [Ni(HL)] complex:

According to all the data collected on those complexes from this study, the proposed molecular structures was square planar depending on the bond lengths and bond angles for comparable systems as shown in table (7) [23,24]. The proposed structure for the complex is shown in figure (2) where nickel is coordinated to H_3L ligand (after loosing two protons) through two negatively charged sulfur atoms and two lone pairs for nitrogen and the third sulfur atom (thio-ether).

The proposed molecular structure for [Cu(HL)] complex:

From the measured data collected on these complexes, the proposed molecular structures are distorted tetrahedral depending on bond lengths for comparable systems as shown in table (8) [24-26]. Figure (3) show the coordination of copper to H_3L ligand (after loosing two protons) through two negatively charged sulfur atoms and one lone pair from nitrogen atom and one lone pair from the third sulfur.

The proposed molecular structure for [Zn(HL)], [Cd(HL)], and [Hg(HL)] complexes:

The proposed structures for all the above complexes are distorted tetrahedral according to the spectral data collected for these complexes and the coordination of the ligand to metal ions is the same as that in copper.

Figure (1): Detection of (S-H) group in the ligand using iodine method

Figure (2): Keto & Enol forms of H_3L ligand

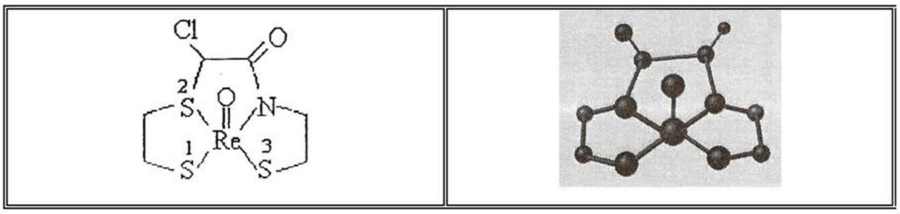

Figure (3)
The proposed structure for [ReO(L)]

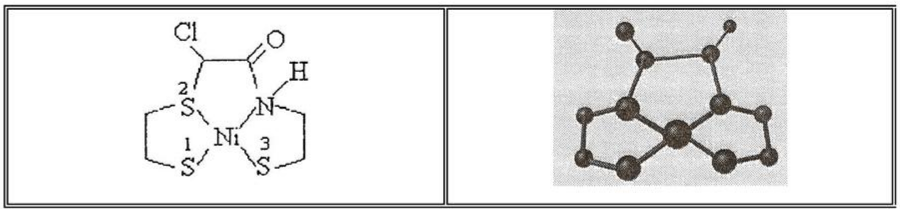

Figure (4)
The Proposed Structure for [Ni(HL)]

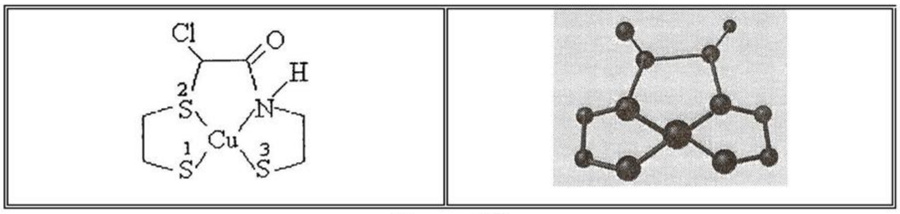

Figure (5)
The Proposed Structure for [Cu(HL)]

Table (1)
The fragments of compound (S)

Fragments	Mass/ charge	Relative abundant
M^+	169	3.77
$[M-(OC-Cl)]^+$	105	100
$[M-(C-OC-Cl)]^+$	93	4.24
$[M-(S-CH_2CH_2-S-H)]^+$	76	5.66
$[M-(CH_2CH_2-S-CHCl)]^+$ or $[M-(CH_2CH_2SCH-Cl)]$	60	35.8
$[M-(CH_2-CH_2-S-OC-Cl)]^+$	45	33.9
$[M-(CH_2-CH_2-S-OC-CH-Cl)]^+$	32	34.9

Table (2): The (UV-Vis) absorption bands and the molar absorptivity for the ligand (H_3L) and its complexes

Compound	λ (nm)	ν (cm^{-1})	ε ($l. mol^{-1}. cm^{-1}$)	Type of Transition
S	279.5	35778	1234	$(\pi - \pi^*)$, $(n- \pi^*)$
H_3L	287	34843	2094	$(\pi - \pi^*)$, $(n- \pi^*)$
[ReO(L)]	299	33444	2474	$(\pi - \pi^*)$, $(n- \pi^*)$
	347	28818	2260	$^1e \rightarrow {}^1b_2$
	557	28011	1930	$^1e \rightarrow {}^1a_1$
[Ni(HL)]	300	33333	2178	$(\pi - \pi^*)$, $(n- \pi^*)$
	344	29069	1833	$^1a_{1g} \rightarrow {}^1b_{1g}$
	440	22727	633	$^1b_{2g} \rightarrow {}^1b_{1g}$
	536	18656	466	$^1a_{1g} \rightarrow {}^1e_g$
[Cu(HL)]	282	35460	2493	$(\pi - \pi^*)$, $(n- \pi^*)$
	726	13774	218	$^2B_2 \rightarrow {}^2E$
[Zn(HL)]	277	36101	790	$(\pi - \pi^*)$, $(n- \pi^*)$
	346	28901	523	**Charge Transfer**
[Cd(HL)]	281	35587	8313	$(\pi - \pi^*)$, $(n- \pi^*)$
[Hg(HL)]	293	34129	2401	$(\pi - \pi^*)$, $(n- \pi^*)$

Table (3): The IR absorption bands for the ligands [S] & [(H_3L) and its complexes] in cm^{-1}, ν(Re=O) = 890 cm^{-1}

Formula	ν(C=N)	ν(C=O)	ν(C-S)	ν(C-N)	δ(N-H)	ν(C=C)	Additional peaks
H_3L	1630 (vs)	1660 (vs)	1050 (m) 1070 (m)	1270 (w)	1520 (w)	1590 (w) 1470 (m)	[3350 (w) & 3250 (w)] ν(N-H), 2960 (m) ν(C-H), 2580 ν(S-H) (w), 740 δ(C-H) o.o.p. arom, 680 δ(N-H) o.o.p, 660 ν(C-Cl)
[ReO(L)]	overlapped	1610 (vs)	1070 (w)	1230 (m)	overlapped	overlapped	3313 ν(N-H), 3090 ν(C-H), 760 δ(C-H) o.o.p. arom, 470 ν(Re-N), 340 ν(Re-S)
[Ni(HL)]	1650 (s)	1660 (s)	1060 (m)	1270	1520 (w)	1570 (w) 1550 (w)	3400 ν(N-H) (br), 2940 ν(C-H) (aliph), 1410 δ(C-H) (aliph)
[Cu(HL)]	1650 (s)	1670 (s)	-	1260 (m)	1530 (w)	1580 (w) 1560 (w)	2940 ν(C-H) (aliph), 1410 δ(C-H), 850 δ(N-H) o.o.p.
[Zn(HL)]	1660 (w)	1740 (s)	1150 (w)	1280 (m)	1530 (w)	1560 (w) 1540 (w)	1030 δ(N-H), 840 δ(C-H) o.o.p. arom, 1460 δ(C-H) aliph.
[Cd(HL)]	1640 (w)	1740 (s)	1150 (m)	1250 (s)	1520 (w)	1560 (w) 1540 (w)	1460 δ(C-H) aliph (m), 2900 ν(C-H) aliph (w)
[Hg(HL)]	1670 (w)	1730 (s)	1170 (m)	1270 (s)	1530 (w)	1590 (w) 1570 (w)	920 δ(N-H) o.o.p, 2940 ν(C-H) aliph, 860 δ(N-H) o.o.p (arom.)

VS: very strong, S: strong, W: week, m: medium, br: broad, o-o-p: out of plane, aliph: aliphatic, arom: aromatic, γ: stretching, δ: bending

Table (4): The Elemental Analysis Data and some Physical Properties for the Ligands and their Complexes

Formula	Solubility	M. P. (°C)	M. Wt.	Micro Analysis				
				% Metal	% C	% H	% N	% S
S	DCM	oily	168.66		(28.48)	(2.98)		(38.02)
					27.7	2.8		37.6
H_3L	DCM	oily	335.9		(39.33)	(4.2)	(12.5)	(28.63)
					40.2	3.9	11.4	29.3
[ReO(L)]	DMF, DMSO, CH_2Cl_2, $C_2H_4Cl_2$	> 300	535.09	(34.69)	(24.69)	(2.07)	(7.85)	
				-	24.52	2.13	8.00	
[Ni(HL)]	DMF, DMSO	260 (dec.)	392.58	(19.40)	(23.82)	(3.33)	(4.63)	
				18.90	23.94	3.28	4.70	
[Cu(HL)]	DMF, DMSO	203	397.43	(20.67)	(23.44)	(3.27)	(4.55)	
				21.32	23.21	3.31	4.60	
[Zn(HL)]	Yellowish-White	204 (dec.)	399.28	(16.37)	(33.09)	(3.02)	(10.52)	
				16.92	33.36	3.14	10.45	
[Cd(HL)]	DMF, DMSO	210 (dec.)	446.30	(25.18)	(29.60)	(2.71)	(9.41)	
				-	29.39	2.82	9.53	
[Hg(HL)]	DMF, DMSO	145 (dec.)	534.48	(37.53)	(24.72)	(2.26)	(7.86)	
				-	24.94	2.31	7.68	

Table (5)
The Molar Conductivity Data for the Complexes in DMF and DMSO as solvents (Concentration = 10^{-3} M at 25°C), Molar Conductivity in ($S.cm^2.mol^{-1}$)

Complex	Molar Conductivity
$[ReO(L^2)]$	34.0
$[Ni(HL^2)]$	11.0
$[Cu(HL^2)]$	17.6
$[Zn(HL^2)]$	14.2
$[Cd(HL^2)]$	23.6
$[Hg(HL^2)]$	15.8

Table (6)
Bond Lengths and Bond Angles For [ReO(L)] Complex

Type of Bond	Length in Angstrom	Type of Angle	Angle in Degree
Re – S1	2.28	**S2 – Re – S3**	152.8
Re – S2	2.36	**O – Re – S1**	114.5
Re – S3	2.29	**O – Re – S2**	100.3
Re – O	1.68	**O – Re – S3**	106.6
Re – N	2.00	**O – Re – N**	119.8
C – Cl	1.7		

Table (7)
Bond Lengths and Bond Angles For [Ni(HL)] Complex

Type of Bond	Length in Angstrom	Type of Angle	Angle in Degree
Ni – S1	2.10	**N1 – Ni – S2**	87.5
Ni – S2	2.20	**N1 – Ni – S3**	86.5
Ni – S3	2.11	**S1 – Ni – S2**	94.0
Ni – N	1.90	**S1 – Ni – S3**	92.0

Table (8)
Bond Lengths and Bond Angles
For [Cu(HL)] Complex

Type of Bond	Length in Angstrom	Type of Angle	Angle in Degree
Cu – S1	2.11	**N1 – Cu – S2**	86.2
Cu – S2	2.23	**N1 – Cu – S3**	123.5
Cu – S3	2.21	**S1 – Cu – S2**	95.3
Cu - N	1.92	**S1 – Cu – S3**	91.2

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تحضير وتشخيص ليكاند رباعي السن نوع NS_3 ومعقداته مع ايونات Re(V)، Ni(II)، Cu(II)، Zn(II)، Cd(II)، و Hg(II)

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الخلاصة:

تضمن البحث تحضير المادة الأولية 3-كلورو-2-اوكسو-4،1-ثنائي ثايا سايكلوهكسان (S) بطريقة جديدة. تم مفاعلة هذه المادة مع 4-فنيل ثايو سميكاربزايد للحصول على ليكاند رباعي السن (H_3L) نوع (H_3NS_3). كذلك تضمن البحث تحضير معقد جديد لهذا الليكاند مع أيون الرينيوم الخماسي بالصيغة [ReO(L)]. كذلك تم تحضير معقدات جديدة بالصيغة العامة [M(HL)] لهذا الليكاند مع أيونات Ni(II)، Cu(II)، Zn(II)، Cd(II)، و Hg(II).

شخص الليكاند والمعقدات بواسطة طيف الأشعة تحت الحمراء، طيف الأشعة فوق البنفسجية والمرئية، طيف الكتلة، طيف الرنين النووي المغناطيسي، طيف الامتصاص الذري، تقنية (HPLC)، التحليل الكمي الدقيق للعناصر، وكذلك قياس التوصيلية الكهربائية. بينت الدراسات ان الشكل الفراغي المتوقع لمعقد الرينيوم الخماسي مع H_3L هو هرم مربع القاعدة، مع Ni(II) والأيونات الأخرى مربع مستو.