Open Access
Baghdad Science Journal **Vol.13(3)2016**

DOI: http://dx.doi.org/10.21123/bsj.2016.13.3.0511

Spectroscopic Studies and Thermal Analysis of New Azo Dyes Ligands and their Complexes with some Transition of Metal Ions

Abbas Ali Salih Al-Hamdani ***Zainab Abd Al-Hadi Hasan***

Department of Chemistry, College of Science for Women, University of Baghdad, Iraq

E-mail: - Abbas_alhamadani@yahoo.co.uk

Received 20/4 /2015
Accepted 15/6 /2015

Abstract:

New Azo ligands HL_1 [2-Hydroxy-3-((5-mercapto-1,3,4-thiadiazol-2-yl)diazenyl)-1-naphth aldehyde] and HL_2 [3-((1,5-Dimethyl-3-oxo-2-phenyl-2,3-dihydro-1*H*-pyrazol-4-yl)diazenyl)-2-hydroxy-1-naphthaldehyde] have been synthesized from reaction (2-hydroxy-1-naphthaldehyde) and (5-amino-1,3,4-thiadiazole-2-thiol) for HL_1 and (4-amino-1,5-dimethyl-2-phenyl-1H-pyrazol-3(2H)-one) for HL_2. Then, its metal ions complexes are synthesized with the general formula; $[CrHL_1Cl_3(H_2O)]$, $[VOHL_1(SO_4)]$ $[ML_1Cl(H_2O)]$ where M = Mn(II), Co(II), Ni(II) and Cu(II), and general formula; $[Cr(L_2)_2]Cl$ and $[M(L_2)_2]$ where M = VO(II), Mn(II), Co(II), Ni(II) and Cu(II) are reported. The ligands and their metal complexes are characterized by phisco- chemical spectroscopic techniques (FT.IR, Mass, UV-Vis, ^{1}H and ^{13}C-NMR, TGA, (C.H.N.), molar conductivity, Atomic Absorbance, Chloride containing magnetic susceptibility). The spectral data suggest that the (HL_1) behaves as a bidentate ligand in all complexes, whereas (HL_2) behaves as a tridentate ligand for all complexes; bidentate ligand in Vanadium complex is coordinated with the metal ions through azo nitrogen and oxygen atoms. Theoretical studies of these ligands and their metal complexes in gas phase using Hyper chem.8. Studies of these compounds are prepared for their bacterial activity

Key words: Tri and Bidentate Ligands; Azo Ligand; Thermal Analysis and Kinetics Thermodynamic Parameters.

Introduction:

The coordination chemistry of transition al metals with ligands from the 5-amino-1,3,4-thiadiazole-2-thiol, 2-hydroxy-1-naphthaldehyde and 4-amino-1,5-dimethyl-2-phenyl-1H-pyrazol-3(2H)-one (aromatic heterocyclic components) has been of interest due to different bonding modes shown by these ligands with both electron rich and electron poor metals. Furthermore, they have been studied widely because of their excellent thermal and optical properties in applications such as optical recording medium [1-4], toner [5,6], ink-jet printing [7,8], and oil-soluble lightfast dyes [9]. Several ligands containing 1,2,4-triazole are well known as drugs. For vorozole, letrozole, and anastrozole are non-steroidal drugs used for the treatment of cancer [10], while loreclezole is used as anticonvulsant [11] and fluconazole is used as an antimicrobial drug [12,13]. We report here, in the preparation and spectroscopic studies new ligands HL_1 [2-Hydroxy-3-((5-mercapto-1,3,4-thiadiazol-2-yl)diazenyl)-1-naphth aldehyde] and HL_2 [3-((1,5-Dimethyl-3-oxo-2-phenyl-2,3-dihydro-1*H*-pyrazol-4-yl)diazenyl)-2-hydroxy-1-naphthaldehyde] and their complexes.

Materials and Methods:

All the following chemicals and reagents are of an analytical grade and used as supplied without any further purification (BDH) sigma Aldrich, and (Fluka).

IR spectra are obtained by using KBr discs (4000-400 cm^{-1}) on Perkin –Elmer FT-IR spectrometer. The electronic spectra are carried out using a Cary 50 Conc. UV-Visible spectra are recorded using spectrophotometer. Thermal analysis studies of the compounds are performed on Perkin – Elmer pyris Diamond DTA / TG. Elemental microanalyses (C.H.N.S.) are performed by using a flash E A 1112 Series elemental analyzer. Chloride is determined by using potentiometer titration method on a 686-Titro processor – 665 Dosimat Metrohm Swiss. Conductivity measurements are made with DMSO solution by using a Jenway 4071 digital conductivity meter. The magnetic properties are measured by using (Jonson Mattey Catalytic system Division). Melting points are measured by using a Buchi SMP -20 capillary melting point apparatus, LC-Mass spectra by using (LC-Mass 100 P Shimadzu).NMR spectra (^{1}H-, ^{13}C-NMR) by using Brucker AMX 400 MHz spectrometer. Atomic Absorption technique is used to determine the metal contents by using a Shimadzu (A. A) 680 G atomic absorption spectrophotometer.

Preparation of the Ligand 2-Hydroxy-3-((5-mercapto-1,3,4-thiadiazol-2-yl)diazenyl)-1-Naphth Aldehyde (HL_1):

(1g, 9.17 mmole) of 5-amino-1,3,4-thiadiazole-2-thiol is dissolved in a mixture of (2 ml) hydrochloric acid, (10 ml) ethanol and (10 ml) distilled water, and diazotized at 5^{o}C with sodium nitrite solution. The diazo solution 5-amino-1,3,4-thiadiazole-2-diazonium is added dropwise with stirring to a cooled ethanolic solution of (1.5g, 9.17 mmole) of (2-hydroxy-1-naphthaldehyde (25 ml) of (1 M) NaOH solution is added to the orange colored mixture. The precipitate is filtered off and washed several times with (1:1) ethanol: water, mixture then left to dry. After that, the product is precipitated (1.875 g) yielding (64.88%), m. p. (145ºC). The reaction is shown in Scheme (1).

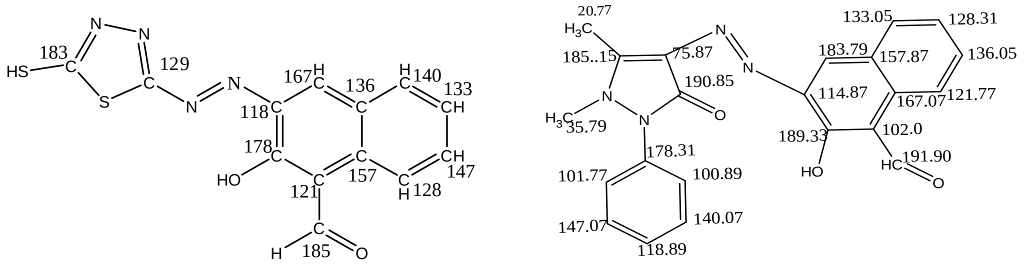
IR (KBr) for HL_1: υ(azo -N=N-) = 1520-1430, υ(O-H) = 3566, υ(C-OH) = 1096, υ(Ar-CH) = 3067, υ(aldehyde C-H) = 2889, υ(aldehyde C=O) = 1645, υ(S-H) = 2597, υ(C-S) = 660-653 and υ(C=N) = 1635 and 1575 cm^{-1}. The GC-Mass for HL1 (316m/z) with ($C_{13}H_8N_4O_2S_2$), (315m/z) with ($C_{13}H_7N_4O_2S_2$), (289m/z) with ($C_{11}H_5N_4O_2S_2$), (253m/z) with ($C_{11}HN_4O_2S$), (237m/z) with ($C_{11}HN_4OS$), (209m/z) with ($C_{11}HN_2OS$), (195m/z) with ($C_{11}HNOS$), (145 m/ z) with ($C_{11}NOS$), (50 m/ z) with (C_7NOS) and (39 m/ z) with (C_6NOS). ^{1}H-NMR for HL1 (DMSO-*d*$_6$, ppm): δ 1.09 (s,6H, CCH_3), 5.273 (1H, s, SH), 3.929 (1H, s, OH), 9.123 (1H, s, O=CH) aldehyde, 6.309-8.515 (5H, m, naphthalene-H) arom.

^{13}C-NMR for HL1 (100.622 MHz, DMSO-d_6): shown in Figure 1- A.

Preparation of the Ligand 3-((1,5-Dimethyl-3-oxo-2-phenyl-2,3-dihydro-1*H*-pyrazol-4-yl) diazenyl)-2-Hydroxy- 1-Naphthaldehyde (HL_2):

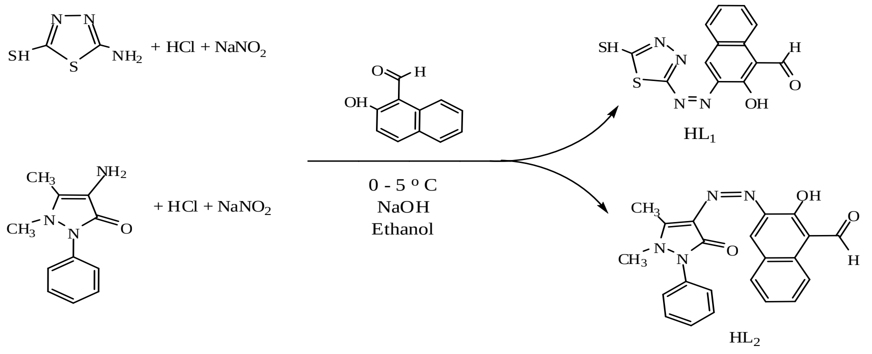
(1g, 4.923 mmole) of 4-amino-1,5-dimethyl-2- phenyl- 1H-pyrazol-3 (2H)-one is dissolved in a mixture of (2 ml) hydrochloric acid, (10 ml) ethanol and (10 ml) distilled water, and diazotized at 5°C with sodium nitrite solution. The diazo solution (1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1H-pyrazole-4-diazonium is added drop wise with stirring to an ethanolic solution of (0.846 g, 4.923 mmole) of (2-hydroxy-1-naphthaldehyde (25 ml) of (1 M) NaOH solution is added to the orange colored mixture. The precipitate is filtered off and washed several times with (1:1) ethanol: water, the mixture then is left to dry. After that, the product is precipitated (1.822 g) yielding (96%), m. p. (153-154ºC). The reaction is shown in Scheme (1).

IR (KBr) for HL_2: υ(azo -N=N-) = 1481 and 1419, υ(O-H) = 3429, υ(C-OH) = 1087, υ(Ar-CH) = 3055, υ(aldehyde C-H) = 2924, υ(aldehyde C=O) = 1636, υ(pyrazol ring C=O)= 1643 and υ(C=C) = 1593 cm^{-1}. The GC-Mass for HL2 (386 m/ z) with ($C_{22}H_{18}N_4O_3$), (289m/ z) with ($C_{14}H_{17}N_4O_3$), (253 m/ z) with ($C_{14}H_{13}N_4O$), (237m/z) with ($C_{14}H_{13}N_4$), (209 m/ z) with ($C_{14}H_{13}N_2$), (195 m/ z) with ($C_{14}H_{13}N$), (145m/z) with ($C_{11}H_{13}$), (96 m/ z) with (C_7H_{12}), (79 m/ z) with (C_6H_7) and (39 m/ z) with (C_3H_3). ^1H-NMR for HL2 (DMSO-d_6, ppm): δ 1.09 (s,6H, CCH_3), 3.632 (3H, s, CH), 1.407 (3H, s, CH), 4.329 (1H, s, OH) phenolic, 9.123 (1H, s, O=CH) aldehyde, 7.059-7.815 (10H, m, aromatic-H). ^{13}C-NMR for HL2 (100.622 MHz, DMSO-d_6): show in Figure 1- B.



HL_1 HL_2

Figure (1): Structure of New Azo Dye Ligands



Scheme (1): Synthesis Route of New Azo Dye

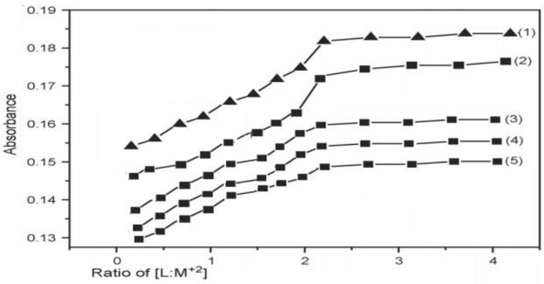
Preparation of Metal Complexes (General Procedure) with Ligands:

An ethanolic solution of the ligand (1g, 3.164 mmole) HL1 and (2g, 5.18 mmol) HL_2 was added gradually with stirring to the 0.235g, 0.421g, 0.313g 0.376g 0.363g and 0.212g (3.164 mmole) and 0.192g, 0.344g, 0.256g 0.307g 0.307g and 0.174g (2.59 mmol) respectively, of $VOSO_4.H_2O$, $CrCl_3.6H_2O$, $MnCl_2.4H_2O$, $CoCl_2.6H_2O$, $NiCl_2.6H_2O$ and $CuCl_2$ respectively dissolved in the buffer solution of the required PH. The solid is collected by filtration recrystallized from methanol dried at room temperature. Elemental micro analysis data color and yield for the compounds are given in Table (1).

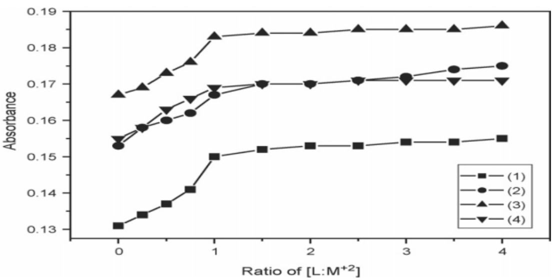
The LC-Mass for CrL_1 (493 m/z) with M= ($C_{13}H_{10}N_4O_3S_2CrCl_3$), (360m/z) with (M- $C_2H_3Cl_3$) and (119 m/z) with (M- $C_9H_9N_2O_2S_2$). The LC-Mass for VOL_1 (479m/z) with M= ($C_{13}H_8N_4O_7S_3V$), (360m/z) with (M-$C_2H_1NSO_3$) and (119m/z) with (M-$C_8H_3NS_2O_4$). The LC-Mass for CoL_2 (829.3m/z) with M= ($C_{44}H_{34}N_8O_6Co$), (430.3m/z) with (M-$C_{21}H_{11}N_4O_5$), (429.3m/z) with (M-H), (205.2m/z) with (M- $C_{18}H_8$), (204.2 m/z) with (M- H), (79.4m/z) with (M-$CH_{10}ON_2Co$) and (36m/z) with (M-CH_3N_2). The LC-Mass for MnL_2 (825.5m/z) with M=($C_{44}H_{34}N_8O_6Mn$), (430m/z) with (M-$C_{22}H_{11}N_4O_4$), (429m/z) with (M-H), (205m/z) with (M-$C_{12}H_8N_4O$), (204m/z) with (M-H), (79.4m/z) with (M-C_4H_6OMn) and (36m/z) with (M-C_3H_7).

Elemental microanalysis and some physical properties of the (HL_1 and HL_2) and their prepared complexes are shown in Table (1),

The composition of the complexes formed in solution has been established by the mole ratio method. In both cases, the result reveals (1:1) metal to ligand for HL_1 but (1:2) metal to ligand for HL_2 respectively (Figure - 2).



For HL_1 complexes (Co^{2+}, Cu^{2+}, Mn^{2+}, Cr^{3+} and Ni^{2+})



For HL_2 complexes (Co^{2+}, Cu^{2+}, Mn^{2+} and Ni^{2+})

Fig. (2) Linear Relation between Molar Concentration and Absorbance

Results and Discussion:

Table (1) Analytical and Physical Data of the Ligands and their Complexes

Compounds	Formula M. wt	Color	M. P. ºC	Yield %	Elemental analysis, Calc. (found) %				
					C	H	N	M	Cl
HL_1	$C_{13}H_8N_4O_2S_2$ 316.36	Orange	145	64.879	49.36 (50.12)	2.55 (3.07)	17.71 (17.67)	-	-
HL_2	$C_{22}H_{18}N_4O_3$ 386.40	Orange	153-154	96	68.38 (67.88)	4.70 (5.02)	14.50 (14.54)	-	-
VOL_1	$C_{13}H_8N_4O_7S_3V$ 479.36	Blue green	220	75	33.21 (32.57)	1.09 (1.68)	10.98 (11.69)	11.00 (10.98)	-
$VO(L_2)_2$	$C_{44}H_{34}N_8O_7V$ 837.73	Green brown	136-137	79	62.89 (63.08)	4.32 (4.09)	14.14 (13.38)	6.66 (6.08)	-
CrL_1	$C_{13}H_{10}N_4O_3S_2CrCl_3$ 492.73	Green yellow	188	80	31.99 (31.69)	2.03 (2.05)	10.98 (11.37)	11.12 (10.55)	22.05 (21.59)
$Cr(L_2)_2$	$C_{44}H_{34}N_8O_6CrCl$ 858.24	Red brown	127-130	71	61.58 (62.01)	3.99 (4.12)	13.06 (13.86)	6.06 (6.34)	4.13 (4.10)
MnL_1	$C_{13}H_9N_4O_3S_2MnCl$ 423.76	Light yellow	190 d	70	37.06 (36.85)	1.78 (2.14)	12.98 (13.22)	13.67 (12.96)	9.02 (8.37)
$Mn(L_2)_2$	$C_{44}H_{34}N_8O_6Mn$ 825.73	Deep yellow	128-130	76	64.43 (64.0)	7.05 (6.65)	4.03 (4.15)	14.04 (13.57)	-
CoL_1	$C_{13}H_9N_4O_3S_2CoCl$ 427.75	Light violet	192 d	74	37.08 (36.50)	2.67 (2.12)	12.78 (13.10)	13.21 (13.78)	7.87 (8.29)
$Co(L_2)_2$	$C_{44}H_{34}N_8O_6Co$ 829.72	Brown yellow	144-146	73	64.12 (63.69)	4.05 (4.13)	14.22 (13.50)	7.11 7.10	-
NiL_1	$C_{13}H_9N_4O_2S_2NiCl$ 427.51	Light green	199 d	75	35.98 (36.52)	3.04 (2.12)	12.87 (13.11)	13.98 (13.73)	8.98 (8.29)
$Ni(L_2)_2$	$C_{44}H_{34}N_8O_6Ni$ 829.48	Deep yellow	201	78	64.03 (63.71)	3.88 (4.13)	12.99 (13.43)	7.23 (7.08)	-
CuL_1	$C_{13}H_9N_4O_3S_2CuCl$ 432.36	Yellow green	229 d	74	37.02 (36.11)	1.96 (2.10)	13.45 (12.96)	13.98 (14.70)	8.76 (8.20)
$Cu(L_2)_2$	$C_{44}H_{34}N_8O_6Cu$ 834.34	Brown	220-222	86	63.64 (63.34)	4.43 (4.11)	12.99 (13.43)	7.24 (7.62)	-

d=decompose

Infrared Spectral Studies of the Complexes

The main vibrational bands of the FTIR spectrum are assigned to the functional groups of the ligands HL_1 and HL_2. The spectrum of the HL_1 shows strong bands at 1520- 1430, 3566 and 1096 cm^{-1} that are assigned to the ν(N=N) and ν(O-H) phenolic and ν(C-OH) respectively [14-15]. On complex formation, the bands of ν(N=N) are shifted to lower frequencies by (56-53 to 16-3); these shifts confirm the coordination of the HL_1 through the oxygen of the phenol group and nitrogen of azo group with the metal ions. The spectrum of the HL_2 shows strong bands at 1481-1419, 3429, 1087 and 1643 cm^{-1} that are assigned to the ν(N=N) and ν(OH) phenolic and ν(C-OH) and ν(C=O) pyrazol ringe respectively [14-15]. On complexes formation, the bands of ν(N=N) and ν(C=O) are shifted to lower frequencies by (12-4 to 39-8) and (11-6); these shifts confirm the coordination of the HL_2 through the (O) of the (C=O) group, (N) of azo group and (O) of (O-H) group with the metal ions but Vanadium ion coordination through the (O) of the (O-H) group, and (N) of azo group ion. Moreover, the spectra of the complexes exhibit weak bands between (505-586) cm^{-1} and (420-505) cm^{-1} which are attributed to ν(M-N) and ν(M-O) respectively [16-18]. The spectra of the Vanadium complexes exhibit weak band between (940-935) cm^{-1} which are attributed to ν(V=O). This indicates that the ligands are coordinated to the metal ions through the N and O atoms. Characteristic vibrations and assignments of the complexes are reported in Table (2).

Table (2) FTIR Spectral Data (Wave Number υ^{-}) cm^{-1} for the Complexes

Compounds	H_2O Roking	S-H	C-S	OH Phen.	C=O ring	C=O ald	C=N Triazol azo	N=N	M-N	M-O
[VO $HL_1(SO_4)$]	-	2590	654	3575	-	1644	1634	1465	534	484 423
[VO$(L_2)_2$]	-	-	-	-	1637	1633	-	1473 1456	586 536	491 474
[Co $L_1Cl(H_2O)$]	3450 864	2570	660 653	-	-	1647	1635	1465 1400	530	480 424
[Co$(L_2)_2$]	-	-	-	-	1632	1629	-	1477 1457	582 536	500 474
[Cu $L_1Cl(H_2O)$]	3451 864	2585	653	-	-	1644	1634	1465 1404	534	484 423
[Cu$(L_2)_2$]	-	-	-	-	1635	1636	-	1469 1411	580 540	490 420
[Ni $L_1Cl(H_2O)$]	3448 864	2573	654	-	-	1647	1637	1467 1403	533	483 423
[Ni$(L_2)_2$]	-	-	-	-	1637	1632	-	1477 1458	582 520	505 474
[Cr $HL_1Cl_3(H_2O)$]	3415 868	2583	660 653	3580	-	1644	1634	1464 1414	534	484 423
[Cr$(L_2)_2$]Cl	-	-	-	-	1637	1633	-	1475 1455	585 505	486 475
[Mn $L_1Cl(H_2O)$]	3448 864	2570	664 653	-	-	1644	1634	1465 1414	534	484 423
[Mn$(L_2)_2$]	-	-	-	-	1638	1638	1632	1477 1458	582 520	488 474

Electronic Spectral, Magnetic Moments, and Conductivity Measurements

The electronic spectra of the ligands HL_1 and HL_2 exhibits intense absorption at (265) and (315, 357, 420) nm for HL_1 and (267), (324, 346, 388) nm for HL_2 attributed to $\pi\rightarrow\pi^*$ and $n\rightarrow\pi^*$ transitions respectively [18,19].

The electronic spectra of the Co(II) complexes with HL_1 and HL_2 ligands exhibit one and three absorption band at 677 nm and (615,678,909) nm which are attributed to $^4A_2\rightarrow{}^4T_{1P}$ and$^4T_{1g}\rightarrow{}^4T_{1g(P)}$, $^4T_{1g}\rightarrow{}^4A_{2g(F)}$ and $^4T_{1g}\rightarrow{}^4A_{2gF}$ respectively. Furthermore, the magnetic moment of the Co(II)(*d7)* complexes was found to be 4.1 and 4.8 B.M., All the above mentioned data correspond to an tetrahedral and octahedral geometry respectively [18-20]. The electronic spectra of the Ni(II) complexes with HL_1 and HL_2 ligands exhibit one and three absorption band at 797 nm and (597, 690, 780) nm which are attributed to $^3T_1 \rightarrow {}^3T_{1P}$ and $^3A_{2g} \rightarrow {}^3T_{1gP}$, $^3A_{1g} \rightarrow {}^3T_{1gF}$ and $^3A_{1g} \rightarrow {}^3T_{2gF}$ respectively.Furthermore , the magnetic moment of the Ni(II) (*d8)* complexes is found to be 3.9 and 2.80 B.M., All the above mentioned data correspond to an tetrahedral and octahedral geometry respectively [18-20]. The electronic spectra of the Cu(II) complexes exhibit one and two absorption band with HL_1 and HL_2 ligands at 953 nm and (450 and 540) nm which attributed to $^2T_2 \rightarrow {}^2E$ and $^2B_{1g} \rightarrow {}^2A_{1g}$ and $^2B_{1g} \rightarrow {}^2B_{2g}$ respectively. Furthermore, the magnetic moment of the Cu(II) (*d9)* complexes is found to be 2.01 and 1.9 B.M., All the above mentioned data correspond to an tetrahedral and octahedral geometry respectively [18]. The electronic spectra of the Cr(III) complexes exhibit three absorption band with HL_1 and HL_2 ligands at (535, 645, 905) nm and (601,736, 864) nm which attributed to $^4A_{2g} \rightarrow {}^3T_{1gP}$, $^4A_{2g} \rightarrow {}^3T_{1gF}$ and $^4A_{2g} \rightarrow {}^3T_{2gF}$ respectively [20-22]. Furthermore, the magnetic moment of the Cr(III)(*d3)* complexes is found to be 3.87 and 3.77 B.M., All the above mentioned data correspond to an octahedral geometry respectively [22]. The electronic spectra of the VO(II) complexes exhibit two absorption band with HL_1 and HL_2 ligands at (515 and 618) nm and (815 and 915) nm which are attributed to $^2B_{2g} \rightarrow {}^2B_{1g}$ and $^2B_{2g} \rightarrow {}^2E_g$ respectively [20-22]. Furthermore, the magnetic moment of the VO(II) (*d1)* complexes is found to be 1.81 and 1.86 B.M., All the above mentioned data correspond to an square pyramidal geometry respectively [22]. The electronic spectra of the Mn(II) complexes exhibits two and three absorption band with HL_1 and HL_2 ligands at (696 and 850) nm and (540, 650, 905) nm which are attributed to ($^6A_1 \rightarrow {}^4A_1 + {}^4E_G$, $^6A_1 \rightarrow {}^4T_{1G}$) and ($^6A_1 \rightarrow {}^4T_2g$, $^6A_1 \rightarrow {}^4T_1g$, $^6A_1 \rightarrow {}^4E_1g$) respectively. Furthermore, the magnetic moment of the Mn(II) (*d5)* complexes is found to be 5.45 and 5.01 B.M., All the above mentioned data correspond to an tetrahedral and octahedral geometry respectively [18].

The molar conductivity value of the complexes is consistent with non-electrolytes for all complexes and 1:1 electrolytes Cr(III) complex with HL_2. See structure for the complexes Figure (3).

Table (3) Electronic Data, μ_{eff} and Molar Conductivity for the Complexes

Complexes	Λ nm	$\bar{\upsilon}$ cm^{-1}	ε L. mol^{-1}cm^{-1}	Assignment	Ω Ohm^{-1} cm^2 mol^{-1}	μ_{eff} B.M	Suggested Formula
[VO $HL_1(SO_4)$]	515 618	19417.4 16181.2	206 121	$^2B_{2g} \rightarrow {}^2B_{1g}$ $^2B_{2g} \rightarrow {}^2E_g$	15.7	1.81	Square Pyramidal
[Cr $HL_1Cl_3(H_2O)$]	535 645 905	18691.5 15503.8 11049.7	64 56 8	$^4A_{2g} \rightarrow {}^3T_{1g(P)}$ $^4A_{2g} \rightarrow {}^3T_{1g(F)}$ $^4A_{2g} \rightarrow {}^3T_{2g}$	18	3.87	Octahedral
[Mn $L_1Cl(H_2O)$]	696 850	14367.8 11764.7	216 68	$^6A_1 \rightarrow {}^4A_1 + {}^4E_{(G)}$ $^6A_1 \rightarrow {}^4T_{1G}$	11.6	5.45	Tetrahedral
[Co $L_1Cl(H_2O)$]	677	14771.0	306	$^4A_2 \rightarrow {}^4T_{1(P)}$	13.76	4.10	Tetrahedral
[Ni $L_1Cl(H_2O)$]	797	12547.0	102	$^3T_1 \rightarrow {}^3T_{1(P)}$	9.21	3.9	Tetrahedral
[Cu $L_1Cl(H_2O)$]	953	10493.1	528	$^2T_2 \rightarrow {}^2E$	14.8	1.63	Tetrahedral
$[VO(L_2)_2]$	815 915	12269.9 10928.9	102 17	$^2B_{2g} \rightarrow {}^2B_{1g}$ $^2B_{2g} \rightarrow {}^2E_g$	11.42	1.86	Square Pyramidal
$[Cr(L_2)_2]Cl$	601 736 864	16638.9 13586.9 11574.0	406 285 154	$^4A_{2g} \rightarrow {}^3T_{1g(P)}$ $^4A_{2g} \rightarrow {}^3T_{1g}$ $^4A_{2g} \rightarrow {}^3T_{2g}$	36.7	3.77	Octahedral
$[Mn(L_2)_2]$	540 650 905	18518.5 15384.6 11049.7	125 102 80	$^6A_1 \rightarrow {}^4T_{2g}$ $^6A_1 \rightarrow {}^4T_{1g}$ $^6A_1 \rightarrow {}^4E_g$	15.08	5.01	Octahedral
$[Co(L_2)_2]$	615 678 909	16260.1 14749.2 11001.1	61 106 9	$^4T_{1g} \rightarrow {}^4T_{1g\ (P)}$ $^4T_{1g} \rightarrow {}^4A_{2g\ (F)}$ $^4T_{1g} \rightarrow {}^4T_{2g\ (F)}$	7.78	4.39	Octahedral
$[Ni(L_2)_2]$	597 690 780	16750.4 14492.7 12820.5	86 146 79	$^3A_{2g} \rightarrow {}^3T_{1g(P)}$ $^3A_{1g} \rightarrow {}^3T_{1g}$ $^3A_{1g} \rightarrow {}^3T_{2g}$	6.9	3.24	Octahedral
$[Cu(L_2)_2]$	450 540 909	22222.2 18518.5 11001.1	630 208 50	$^2B_1g \rightarrow {}^2A_1g$ $^2B_1g \rightarrow {}^2B_2g$ $^2B_1g \rightarrow {}^2Eg$	8.08	1.9	Octahedral

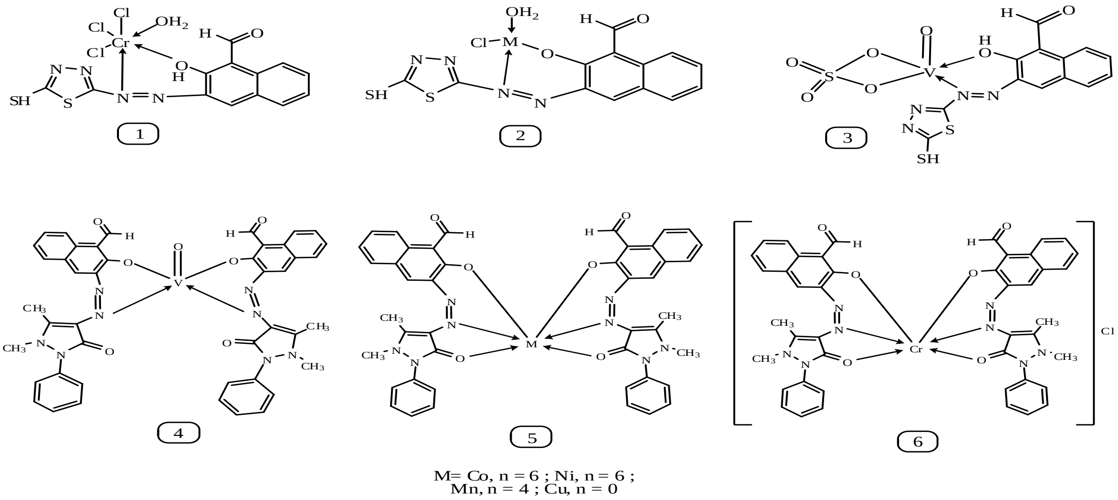


Fig. (3) Structure of the Complexes

Thermal Analyses TGA and Kinetic Studies:-

The results of thermo gravimetric analyses of ligands and complexes are given in Table (4). The thermograms have been carried out in the range of 25–700 °C at a heating rate of 10 °C/min in nitrogen atmosphere. They show an agreement in weight loss between their results obtained from the thermal decomposition and the calculated values, which supports the results of elemental analysis and confirms the suggested formulae. Thus, the ligands and complexes show a common general behavior as show in Scheme (1). Coats–Redfern is the method mentioned in the literature related to decomposition kinetics studies; this method is applied in this study [23,24]. Kinetic parameters are calculated by employing the Coats–Redfern equations which are summarized in Table (5). The Coats–Redfern equation may be written as the following:

$$\log\left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right] = \log\frac{ZR}{qE}\left[1-\frac{2RT}{E}\right] - \frac{E}{2.303RT} \quad n\neq1 \text{ for complex} \qquad (1)$$

$$\log\left[\frac{-\log(1-\alpha)}{T^2}\right] = \log\left[\frac{AR}{\beta E}(1-\frac{2RT}{E}\right]\frac{E}{2.303RT} \quad n\neq1 \text{ for ligands} \qquad (2)$$

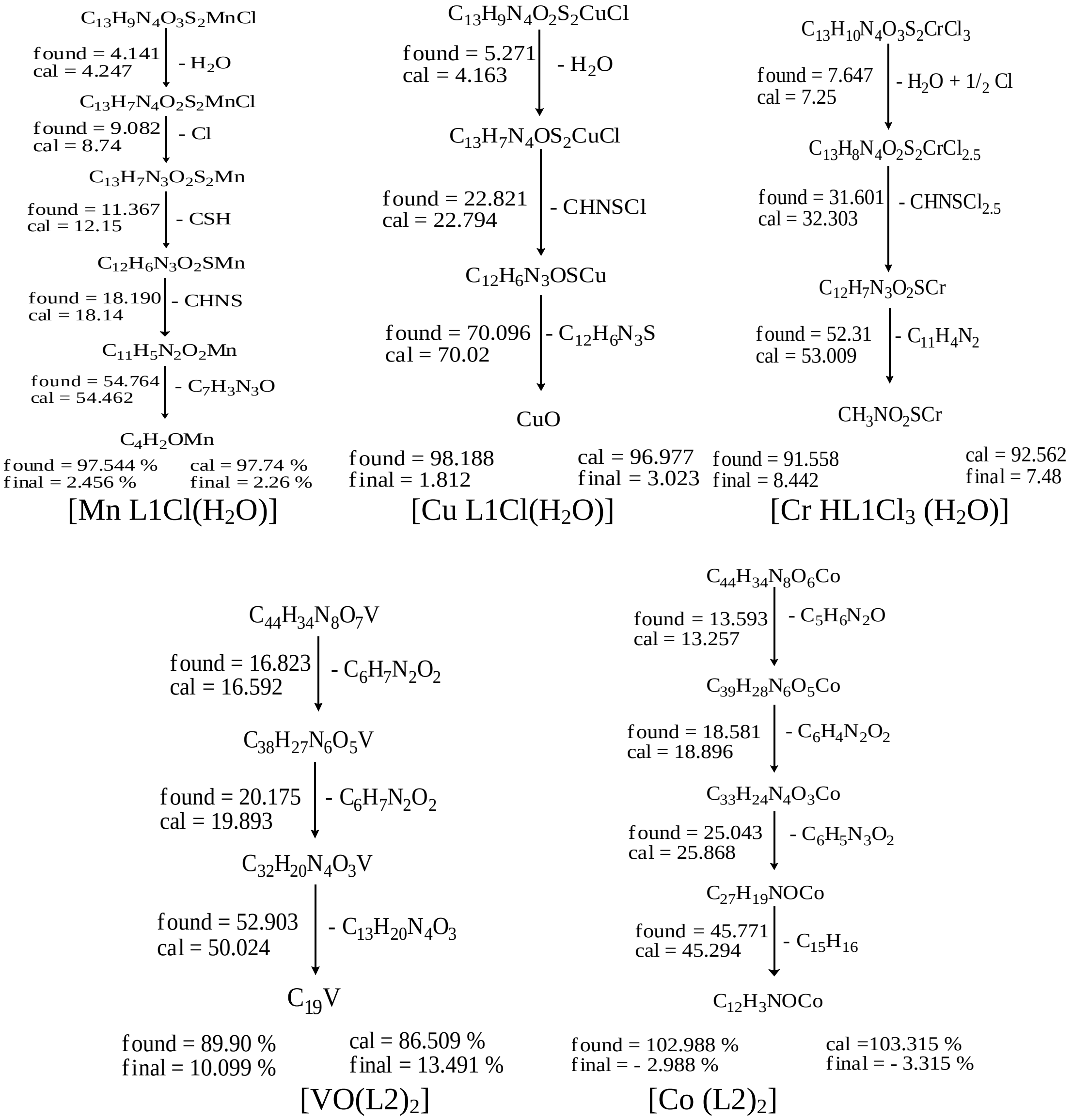
The activation entropy ΔS*, the activation enthalpy ΔH* and the free energy of activation ΔG* were calculated using the following equations:

$$S^* = 2:303(\log Ah/KT)R; H^* = E^* - RT; G^* = H^* - T_S S^* \cdots 3$$

Where K and h are the Boltzmann’s and Planck’s constants, respectively. The calculated values of ΔE*, ΔS*, ΔH* and ΔG* for the dehydration and the decomposition steps are given in table (5).

Table (4) Thermal Analysis Data of the Free Ligands and Metal Complexes

Compounds	TGA					DTA	
	TG range (°C)	DTG max(°C)	% Estimated (calculated)		Assignment	Tdta	Peak
			Mass loss	Total mass lose			
HL_1	164.2-235.5 235.5-599.5	210.1 566.5	28.88(28.47) 68.72(67.33)	97.6 (96.2)	CO_2+H_4N_3 $C_{11}H_4NS_2$	185 503.4	endo endo
HL_2	199.1-313.7 313.7-589.3	287.9 524.4	29.8(29.53) 69.54(70.47)	99.34 (100)	$C_4H_6N_2O_2$ $C_{18}H_{12}N_2O$	267.7 464.7	exo exo
MnL_1	51.6-109.3 178.8-257.9 297-408.9 408.9-519.7 543.8-699.6	95.13 241.5 358.8 467.8 614.3	4.247(4.141) 8.74(9.082) 12.15(11.367) 18.14(18.19) 54.462(54.764)	97.74 (97.544)	-H_2O -Cl -CSH -CHNS -$C_7H_3N_3O$ C_4H_2OMn	105 251 360.7 484.1 635.9	end end end end end
CuL_1	33.5-132.8 133-433.7 462.9-699.4	70.32 319 611.6	4.163(5.271) 22.794(22.821) 70.02(70.096)	96.977 (98.188)	-H_2O -CHNSCl -$C_{12}H_6N_3S$ CuO	69.44 314.3 605.66	endo endo endo
CrL_1	33.6-147.6 305.4-399.7 430.1-699.3	72.03 359 476	7.25(7.647) 32.303(31.601) 53.009(52.31)	92.562 (91.558)	-H_2O + 1/2Cl -$CHNSCl_{2.5}$ -$C_{11}H_4N_2$ CH_3NO_2SCr	63 359 452	endo endo endo
VOL_2	33.7-164.8 195-352 384-699.4	75.35 263 477	16.592(16.823) 19.893(20.175) 50.024(52.903)	86.509 (89.901)	-$C_6H_7N_2O_2$ -$C_6H_7N_2O_2$ -$C_{13}H_{20}N_4O_3$ C_{19}+ V	66 258 489	End End end



Scheme (1) The Tentative Decomposition Reaction of the Complexes

Table (5) Thermodynamic Data of the Thermal Decomposition of Ligands and their Complexes.

Sam (step)	T range ºC	n	R^2	T_{max} ºK	E KJ mol^{-1}	Δ H^* KJ mol^{-1}	Z s^{-1} $x10^5$	Δ S^* J $mol^{-1}K^{-1}$	Δ G^* KJ mol^{-1}	K $x10^{-7}$
HL_1 (1)	164.2-235.5	1	0.99	210.1	7.666994	2.982	425.5	-104.171	61.983	17.958
HL_1 (2)	235.5-599.5	1	0.99	566.5	12.24048	5.6986	830.9	-101.378	85.467	21.189
HL_2 (1)	199.1-313.7	1	0.99	287.9	7.442325	2.56101	505.41	-103.0818	68.4756	8.0847
HL_2 (2)	313.7-589.3	1	0.99	524.4	11.90189	5.49496	794.69	-101.5799	83.77449	20.9573
$CuL_{1=}1$	33.5-132.8	0.9	0.97	70.32	4.57425	1.736	124.3	-117.54	41.86	3.9316
$CuL_{1=}2$	133-433.7	0.9	0.99	319	9.60396	4.509	479.0	-103.878	68.160	15.4668
$CuL_{1=}3$	462.9-699.4	0.9	0.99	611.6	12.68103	7.174	410.0	-107.65	96.022	8.37053
$CrL_{1=}1$	33.6-147.6	0.9	0.99	72.03	5.792853	2.9547	146.04	-108.8958	40.12847	7.2377
$CrL_{1=}2$	305.4-399.7	0.9	0.99	359	12.11535	6.85467	477.78	-104.1716	72.76927	9.8303
$CrL_{1=}3$	430.1-699.3	0.9	0.99	476	12.36905	5050709	977.70	-100.4266	8.8394191	25.44185
VOL_1=1	33.7-164.8	0.9	0.99	75.35	6.609926	3.7215	1087.817	-92.370	35.9035	41.5445
VOL_1=2	195-352	0.9	0.99	263	9.66478	5.19925	359.8129	-105.167	61.6855	10.011818
VOL_1=3	384-699.4	0.9	0.99	477	16.21645	9.97655	646.665	-103.074	87.336	8.3455
MnL_1=1	51.6-109.3	0.9	0.99	95.13	6.289215	2.84248	203.67145	-107.7458	47.510686	10.3174
MnL_1=2	178.8-257.9	0.9	0.99	241.5	7.706092	3.4988	314.8201	-105.7825	57.03	12.9757
MnL_1=3	297-408.9	0.9	0.99	358.8	10.67851	5.239813	534.23834	-103.5197	72.95827	14.9305
MnL_1=4	408.9-699.6	0.9	0.99	467.8	13.42782	6.36765	926.9402	-101.1067	722.6238	21.4988

R^2 =correlation coefficient of the linear plot, *n* = order of reaction, Z = pre-exponential factor

Theoretical Study

The vibration spectra Azo dyes ligands are calculated by using a Hyber chem.8 method. The results obtained for wave numbers are presented in Table (6), and the comparison with the experimental values indicates some deviations. These deviations may be due to the harmonic oscillator approximation and lack of electron correlation. It is reported [25] that frequencies coupled with (HFT) approximation and quantum harmonic oscillator approximations tend to be 10% too high. And structures of ligands are calculated to search for the most probable model building stable structure. These shapes show the calculated optima geometries for compounds prepared as shown in Figure (4). And the ΔE_b and ΔH_f for compounds in table (7).

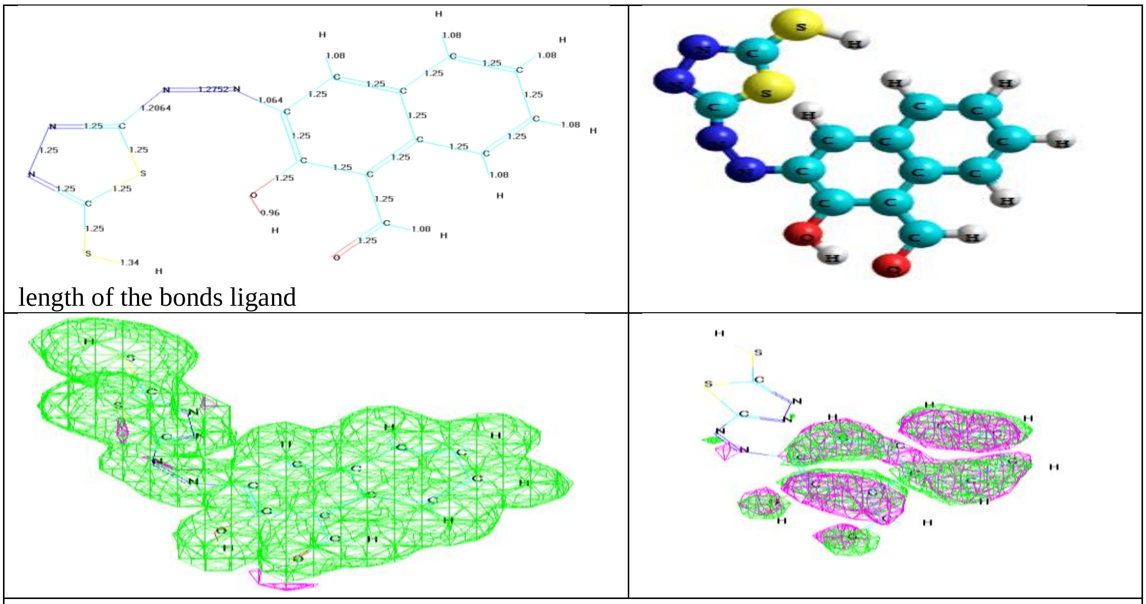
Table (6) Comparison of Experimental and Theoretical Vibration Frequencies for Ligands

Ligand	υ(OH)	υ(CH) aromatic	υ(CH) aleph	υ(C-H) aldehyde	υ (C-S)	υ (C=N)	υ (S-H)	υ(C=O) aldehyde	υ(C=O) ring	υ(N=N)
HL_1	*3566 **3600 ***-0.95	*3076 **3110 ***-1.10	-	*2889 **2800 ***3.17	*660 *653 **680 **621 ***-3.03 ***4.90	*1635 *1575 **1643 **1455 ***-0.4 ***7.61	*2597 **2553 ***1.69	*1645 **1656 ***-0.66	-	*1520 *1430 **1400 **1390 ***7.89 ***2.79
HL_2	*3429 **3488 ***-1.720	*3055 **3090 ***-1.146	*2893 **2888 ***0.173	*2924 **2943 ***-0.650	-	-	-	*1636 **1647 ***-0.672	*1643 **1650 ***-0.426	*1481 *1419 **1470 ***-1.379

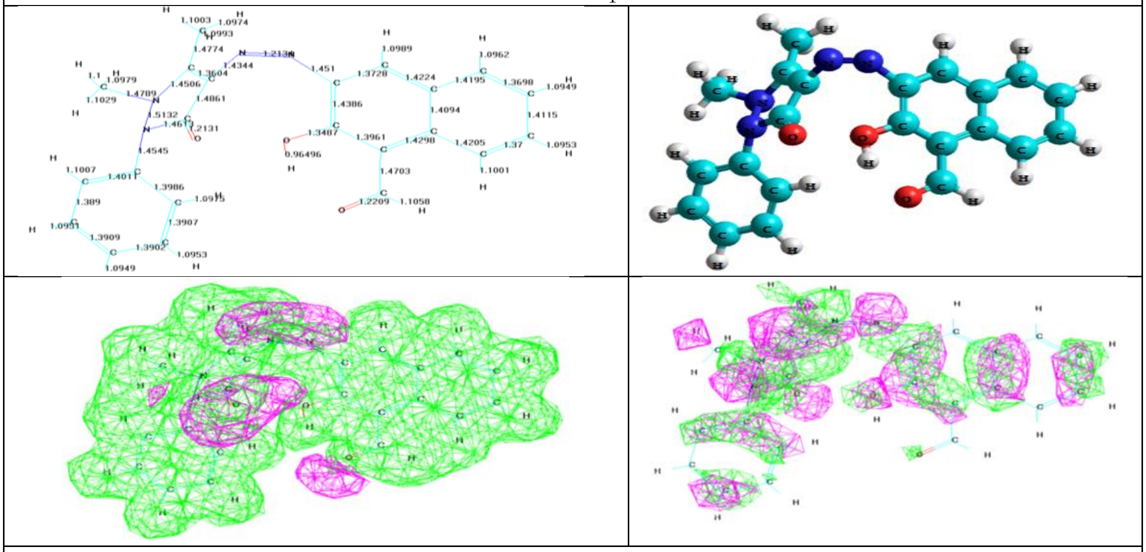
*Experimental frequency. ** Theoretical frequency. *** Error% due to main difference in the experimental measurements and theoretical treatments of vibration spectrum.

Table (7) Conformation Energies in (kJ mol^{-1}) for the Ligands and its Metal Complexes

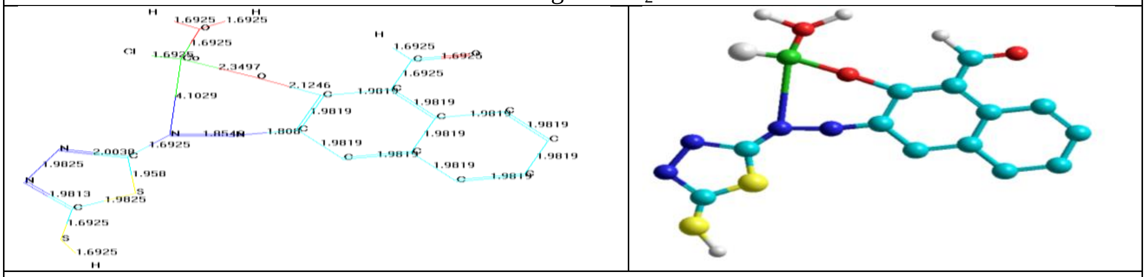
Compounds	PM3		Compounds	PM3	
	ΔH_f°	ΔE_b		ΔH_f°	ΔE_b
HL_1	117.873	-3224.430	HL_2	36.82307	-5291.2765
CrL_1	15.3232	-4321.657	CrL_2	54.873	-6443.3034
MnL_1	88.49704	-997.4150296	MnL_2	210.8897177	-5927.125282
CoL_1	21.4043223	-976.5386777	CoL_2	750.3750690	-7634.2229310
CuL_1	65.543243	-4675.322179	CuL_2	132.76597	-7652.546235
NiL_1	23.314242	-6543.646497	NiL_2	33.76855	-4567.834
VOL_1	43.658	-5256.7683	VOL_2	87.9665	-3445.678



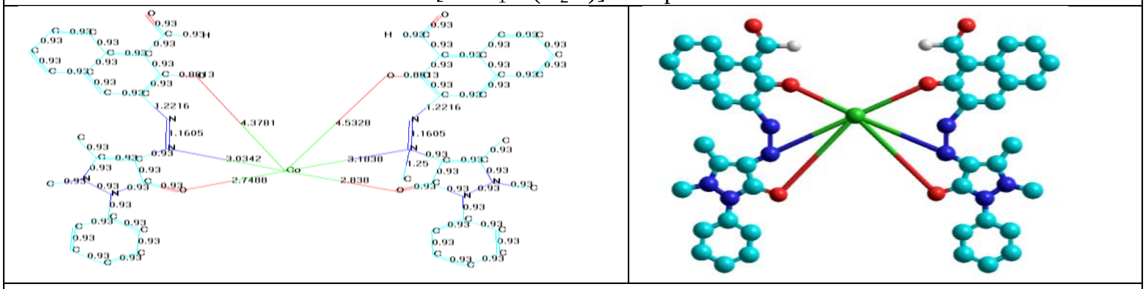
For HL_1



For ligand HL_2



[Co $L_1Cl(H_2O)$] Complex



[$Co(L_2)_2$] Complex

Fig. (4) Conformational Structures of Ligands and Cobalt Complexes.

Microbiological Investigation

The biological activity of ligands and their metal complexes is tested against bacteria; we use more than one test organism to increase the chance of detecting antibiotic principles in tested materials. The organisms used in the present investigation includes two Gram positive bacteria (*B. subtilis and S. aureus*) and two Gram negative bacteria (*E. coli and P. aeruginosa*). The results of the bactericidal screening of the synthesized compounds are recorded in Table (8). An influence of the central ion of the complexes in the antibacterial activity against the tested Gram positive and Gram negative organisms shows that the complexes have an enhanced activity compared to the ligand itself.

Table (8) Antibacterial Activity Data of Ligands and their Complexes as Inhibition Zone (mm).

Compound	*Bacillus subtilis G+*	*Staphylococcus aureus G+*	*Escherichia coli* G^-	*Pseudomonas aeruginosa* G^-
HL_1	18	16	19	18
HL_2	25	19	19	24
VOL_1	18	23	22	20
VOL_2	22	29	22	18
CrL_1	12	10	9	8
CrL_2	12	13	21	7
MnL_1	22	21	23	16
MnL_2	26	15	12	28
CoL_1	20	21	24	21
CoL_2	26	9	23	22
NiL_1	15	23	21	22
NiL_2	17	22	24	17
CuL_1	20	22	19	26
CuL_2	21	22	23	24

Key to interpretation: Less than 10 mm=inactive, 10– 15 mm=weakly active, 15–20 mm=moderately active, more than 20 mm= highly active.

References:

[1]Savic, J. and Vasic, S. 2006. Complex Formation Between Pd(II) and Immobilized Imidazol Azo Chromotropic Acid. *Acta Chim. Slov.*; 53(12): 36-42.

[2]Maradiya, H. R. 2001. Synthesis of Azobenzo (b) Thiophene Derivatives and Their Dyeing Performance on Polyester Fiber. *Turk.J.Chem*; 25 : 441-450.

[3]Jarad, A.J. 2012. Synthesis and Characterization of New Azo Dye Complexes with Selected Metal Ions. J. of Al-Nahrain Uni.; 15(4):74-81.

[4]Karipcin, F. and Kabalcilar, E. 2007. Spectroscopic and Thermal Studies on Solid Complexes of 4-(2-Pyridylazo)-resorcinol with Some Transition Metals. *Acta. Chim.Slov*; 54(6):242-247.

[5]Patel, V. H.; Petal, M. P. and Patel, R. G. 2002. Synthesis and Application of Novel Hetrocyclic Dyes Based on 11-amino-13-H-acenaphtho[1,2-e] Pyridazin[3,2-b]Quinazolin-13-one. *J. Serb. Chem. Soc*; 67 (11): 727-737.

[6]Kupradinun, P.; Rienkijakaru, M.; Tanyakaset, M.; Tepsuwan, A. and Kusamran, W. R. 2002. Carcinogenicity Testing of the Cosmetic Dye:D and C Red No.36. *Asi. Pac. J. of Canc. Pre.*; 3: 55-60.

[7]Maradiya, H. R. and Patel, V. S. 2001. Synthesis and Dyeing Performance of Some Novel Hetrocyclic Azo Disperse Dyes. *J. Braz. Chem. Soc*; 12 (6) : 1-6.

[8]Gregory, P.; Waring, D. R. and Hallos, G. 1990. The Chemistry and Application of Dyes. plenum press, London. : 18-20.

[9]Kutgen, H. K. and Heren, Z. 1998. Thermal Behaviour of Some Azo Dyes Containing Sterically Hindered

and Water Soluble Groups. *Turk. J. Chem.*; 22 : 403-408.

[10] Pal, S. and Sinho, C. 2001. Studies on the Reactivity of cis-RuCl2 Fragment in Ru(pph3) 2(TaiMe) Cl2 with N,N-Chelators (Taime=1-Methyl-2-(p-Tolylazo) Imidazole). Spectral and Electrochemical Characterization of the Products, *Proc. Ind. Acad. Sci*.; 113(3):173-182.

[11] Carballo, R.; Castineiras, A.; Covelo, B.; Niclos, J. and Vazguez-Lopez, E. 2001. Synthesis and Characterization of Potassium Complex of Magneson: [K(HL) (OH2)2] [H2L=4-(4-nitrophenylazo) resorcinol (Magneson)], *Polyhedron.*; 20(3): 2415-2420.

[12] Shujuan, S.; Hongxiang, L.; Gao, Y.; Fan, P.; Ma, B.; Ge, W. and Wang, X. 2004. Liquid chromatography-tandem mass spectrometric method for the analysis of fluconazole and evaluation of the impact of phenolic compounds on the concentration of fluconazole in Candida albicans. *J. Pharm. Biomed. Anal.*; 34 : 1117–1124.

[13] Dixit, B.; Patel, H.; Dixit, R. and Desai, D. 2010. Synthesis, characterization and dyeing assessment of novel acid azo dyes and mordent acid azo dyes on 2-hydroxy-4-methoxybenzophenone on wool and silk fabrics. *J. Serb. Chem. Soc.*; 75 (5): 605-614.

[14] Al-Hamdani, A. A. S. and Shaker Sh. A. 2011. Synthesis, characterization, Stuctural Studies and Biological Activity of a New Schiff Base–Azo Ligand and its Complexation with Selected Metal Ions. *Oriental J. Chem.*; 27 (3): 825-845.

[15] Nakamoto, N. 2009. Infrared and Raman Spectra of Inorganic and Coordination Compounds, 6th Ed, Part 2 John wiley and Sons, Inc., New Jersy.

[16] Shaker, Sh. A.; Yang, F. and Al-Hamdani, A. A. S. 2009. Synthesis and Characterization of Mixed Ligand Complexes of 8-Hydroxyquinoline and o-hydroxybenzylidene-1-phenyl-2,3-dimethyl-4-amino-3-pyrazolin-5-on with Fe(II), Co(II), Ni(II) and Cu(II) ions. European J. Scie. Resea.; 33(4): 702-709.

[17] Sliverstein, R. M. and Webser, X. F. 2005. Spectrometric Identification of Organic Compounds. 7th Ed., Jon Wiley and Son, Inc. USA.

[18] Lever, A. B. P. 1968. Inorganic Electronic Spectroscopy. New York. 6. 121.

[19] Al-Hamdani, A. A. S. 2013. Metal Complexes of Multidentate Schiff Base-Azo Ligand: Synthesis, Characterization and Biological Activity. *Dirasat, Pure Scie*.; 39 (1): 61-72.

[20] Shaker, Sh. A. 2010. Preparation and Spectral Properties of Mixed-Ligand Complexes of VO(II), Ni(II), Zn(II), Pd(II), Cd(II) and Pb(II) with Dimethylglyoxime and N-Acetylglycine. *E-J. Chem.*; 7 (4): 1598-1604.

[21] Al-Hamdani, A. A. S. and Al-Zoubi, W. 2015. New metal complexes N3 tridentate ligand: Synthesis, spectral studies and biological activity. *Spectrochimica Acta Part A: Mole. and Biomol. Spect.*, 137 : 75-89.

[22] Al-Hamdani, A. A. S.; Jarad, A. J. and Al-Atrakchi, S. A. 2009. Synthesis and spectral analysis of VO(II), Cr(II), Zn(II), Cd(II), Hg(II) and UO_2 complexes with mixed ligands of bipyridyl and novel Schiff base. *Diala. J.* 36: 349-361.

[23] Coats, A. W. and Redfern, J. P.1964. Kinetic parameters from thermogravimetric data. Nature, 201: 68-79.

[24] Frost, A. A. and Pearson, R. G.1964. Kinetics and Mechanism 2nd Ed., with permission of john wiley & sons, Inc Wiley, New York.

[25] Baker, Sh. R. 2012. Synthesis, Spectral study and biological activity of some metal ions complexes with bidentate ligands. *J. AL-Nahra. Uni. Sci.*; 15 (3): 30-42.

دراسات طيفية وتحليل حراري لليكاندات أصباغ آزو جديدة و معقداتها مع بعض ايونات الفلزات الانتقالية

عباس علي صالح الحمداني **زينب عبد الهادي حسن**

قسم الكيمياء، كلية العلوم للبنات، جامعة بغداد، العراق

الخلاصة :

حضرت ليكاندات الازو الجديدة 2-هيدروكسي-3-((5-ميركبتو-1،3،4-ثايادايازول-2-يل(دايازينيل)-1-نفثالديهايد (HL_1) و3-((1،5-ثنائي مثيل -3-اوكسو-2-فنيل-3،2-ثنائي هايدرو-1-بيرازول-4-ايل) دايازنيل)-2-هايدروكسي-1-نفثالديهايد (HL_2) من تفاعل 2-هايدروكسي-1-نفثالديهايد مع 5-امينو-1،3،4-ثايادايزول-2-ثايوول (HL_1) أو 4-امينو1،5-ثنائي مثيل -2-فنيل-1-بايرزول-3-اون (HL_2).

حضرت المعقدات بالصيغة العامة [$Cr HL_1Cl_3(H_2O)$] و [$VO HL_1(SO_4)$] و [$M L_1Cl(H_2O)$] حيث M = منغنيز، كوبالت، نيكل ونحاس. شخصت معقدات الليكاندات المحضرة بالطرق (الاشعة تحت الحمراء، فوق البنفسجية – المرئية، الرنين النووي المغناطيسي للبروتون والكاربون، الكتلة ، التحليل الحراري الوزني، التحليل الدقيق للعناصر، الامتصاص الذري، محتوى الكلور، التوصيلية المولارية و الحساسية المغناطيسية)

القيم الطيفية اقترحت ان (HL_1) ثنائي السن لكن (HL_2) ثلاثي السن فقط مع الفناديوم يكون ثنائي السن لهما القابلية على التناسق مع الايونات الفلزية عن طريق ذرة النتروجين و ذرة الاوكسجين. الدراسات بينت ان الاشكال الهندسية ثمانية السطوح لكل معقدات المعادن فقط الفناديل هرم مربع القاعدة لليكاند (HL_2) ورباعي السطوح لمعقدات المعادن مع الليكاند (HL_1) لكن هرم مربع القاعدة مع الفناديل وثماني السطوح لمعقد الكروم. كما درست المركبات المحضرة نظريا باستخدام برنامج الهايبر كيم الثامن بالحالة الغازية. كما درست فعالية المركبات المحضرة ضد البكتريا.

الكلمات المفتاحية: ليكاندات ثنائية وثلاثية، ليكاندات أزو، تحلل حراري والثوابت الحركية والثرموديناميكية