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Preparation, Spectral, Thermal and Bio Activity Studies of Azo Dyes Complexes.

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ABSTRACT

Monomeric complexes of this ligand, of general formulae $[M(L)(H_2O)_3]nCl$ with ($M = Cr^{(III)}$ $n=1$, $Fe^{(III)}$ $n=1$, $Pt^{(IV)}$ $n=2$ and $Re^{(V)}$ $n=3$ and $[(VO)(L)(H_2O)]$ were reported. The compounds were isolated and characterized in solid state by using ^1H-NMR , FT-IR, UV-Vis and mass spectral studies, TGA, elemental microanalysis, metal content, magnetic moment measurements, molar conductance, chloride containing and thermal analysis. These studies revealed octahedral geometries for all complexes except $V^{(IV)}$ complex is Square pyramidal. The study of complexes formation via molar ratio of (M: L) as (1:1). Theoretical studies of these ligand and their complexes in gas phase using Hyper chem.-8. Studies of these compounds are prepared for the bacterial activity.

Keywords: Thermal analysis, Bio Activity, Azo dye Complexes

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INTRODUCTION

Azo colors described by the near nest of at least one azo gathering (-N=N-) in molecular structure [1, 2]. Include the biggest gathering of organic reagent utilized as a part of spectrophotometric examination. They are found in an assortment of modern applications due to their shading quickness. These colors are described by chromophoric azo gathering (-N=N-) offering a wide range of hues [1]. They are generally firmly hued mixes, which can be intensity yellow, red, orange, blued or even green, contingent upon the correct structure of the particle. Inlight of their shading, azo mixes are enormous significance as colors as shades for quite a while [2,3]. They additionally utilizes for shading shopper products, for example, calfskin, cololthes, sustenance, toys, plastic and beauty care products [1]. In fact, about half of the colors in modern utilized today are azo dyes, which are for the most part arranged from diazonium salts [4,5].The azo gathering has magnificent contributor properties and vital in coordination science [6]. Azo mixes are vital class of substance mixes getting consideration in logical research [7]. The point of this paper is incorporation, portrayed.

EXPERIMENTAL

Instrumentation

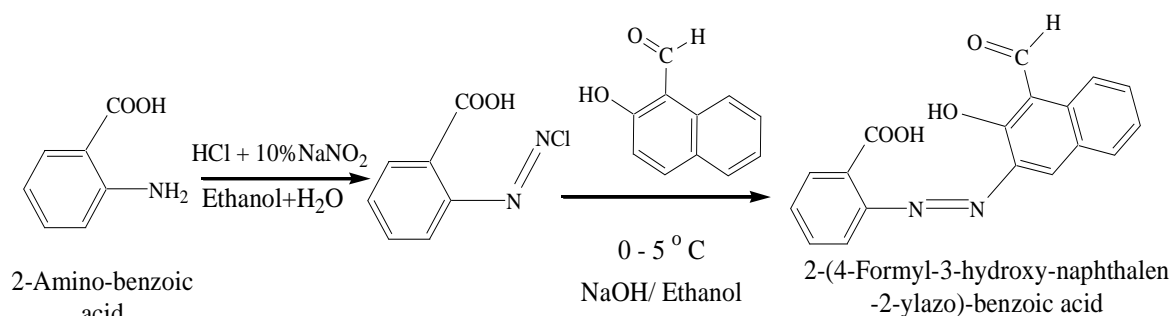
NMR spectra were acquired in DMSO -d₆ solution using Brucker AMX 300 MHz spectrometer with tetramethylsilane (TMS) as an internal standard for ¹H-NMR analysis. IR spectra were obtained using Perkin – Elmer FT-IR spectrometer. Elemental microanalyses (C.H.N.) were performed by using a flash E A 1112 Series elemental microanalyses. UV-Visible spectra were recorded using (Shimadzu 160) spectrophotometer. Thermal analysis studies of the compounds were performed on Perkin – Elmer pyris Diamond DTA / TG. Chloride was determined using a 686-Titro processor –665 Dosimat Metrohm Swiss. Conductivity measurements were made with using a Jenway 4071 digital. Magnetic moments were measured with a magnetic susceptibility balance (Jonson Matthey Catalytic system Division). Mass spectra were obtained by LC-Mass 100 P Shimadzu. Metals were determined using a Shimadzu (A. A) 680 G. Melting points were obtained on a Buchi SMP -20 capillary.

Materials

All chemicals were purchased from commercial sources and were used without further purifications VOSO₄.H₂O, CrCl₃.6H₂O, FeCl₃.2H₂O and ReCl₅ from Sigma-Aldrich, H₂PtCl₆.6H₂O, 2-hydroxy-1-naphthaldehyde, 2-aminobenzoic acid, NaNO₂, NaOH, HCl, DMSO, CH₃OH and C₂H₅OH from Merck

Synthesis of Azo dye Ligand: 2-((4-Formyl-3-Hydroxynaphthalen-2-yl) Diazenyl) Benzoic Acid (H₂L) [8]

(1g, 0.007mol) of 2-aminobenzoic acid was dissolved in a mixture of (2 ml) hydrochloric acid, (20 ml) ethanolic solution, and diazotized at (0 to -5) °C with NaNO₂ solution. The diazonium salt solution was added drop wise with stirring to a cooled ethanolic solution of (1.255g, 0.007mole) of 2-hydroxy-1-naphthaldehyde. (25 ml) of (1 M) NaOH solution was added to the light yellow colored mixture. The precipitate was filtered off and washed several times with (1:1) ethanol: water, mixture then left to dry. After that, the product precipitated yield (84.88%), m. p. (88-90°C), see scheme 1. ¹H-NMR(DMSO-d₆,ppm): 5.623(s, O-H phenol), 7.838- 8.135 (m, arom-CH), 9.130 (s, C-H aldehyd), 10.13 (s, O-H carboxylic, figure 1.



Scheme 1: synthesis of the ligand

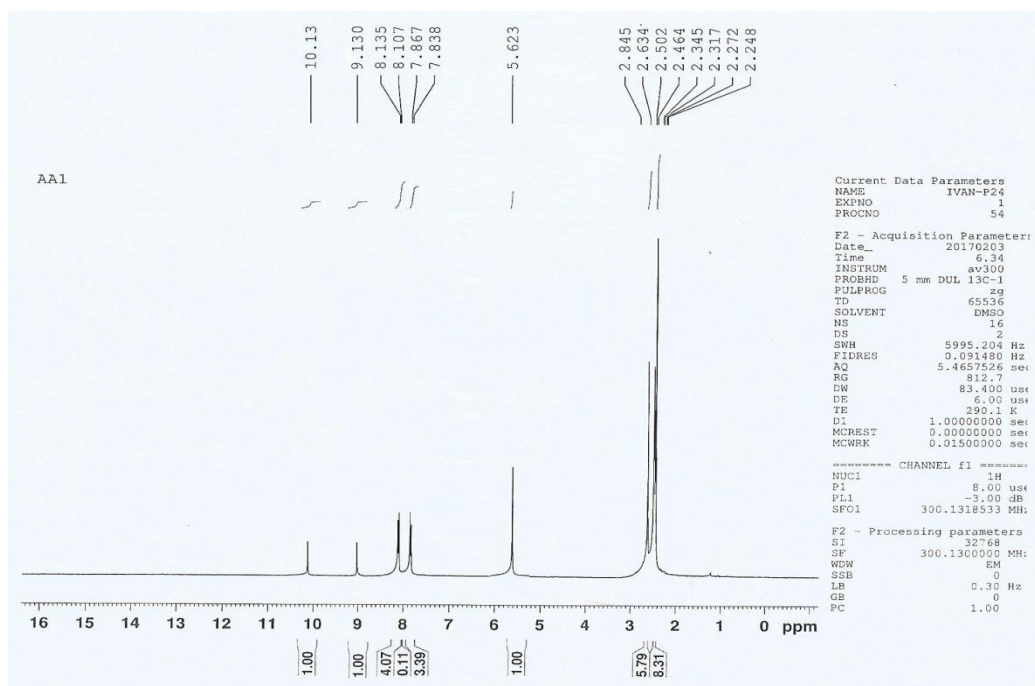
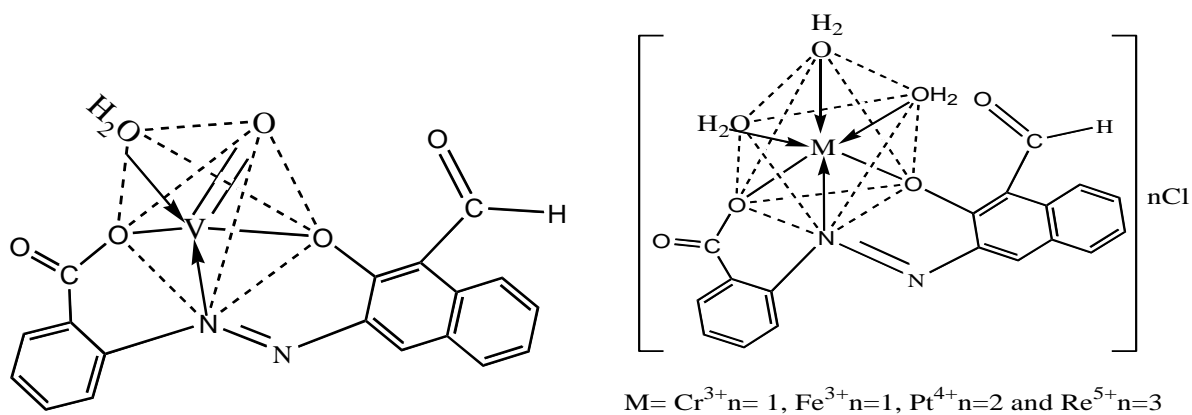


Figure 1. ^1H -NMR spectrum for ligand

Synthesis of Complexes

The preparation of all complexes is essentially the same and so a generic description will be presented. To a solution of (H_2L) (0.006 mole) in ethanol was added slowly to a solution of metal salt ($\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{FeCl}_3 \cdot 2\text{H}_2\text{O}$, $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ ReCl_5 and $\text{VO}(\text{SO}_4) \cdot \text{H}_2\text{O}$ in (ethanol and water) ratio (1:1) with stirring the mixture was refluxed for (3hrs). Elemental micro analysis data, color and yield for the complexes are given in table 1, see scheme 2.



Scheme 2. proposed structures of its metal ions complexes

Microbiological investigations

For these investigations the filter paper disc method was applied according to [9]. The investigated isolates of bacteria were seeded in tubes with nutrient broth (NB). The seeded NB (1 cm^3) was homogenized in tubes with (9 cm^3) of melted (37°C) nutrient agar (NA). The homogeneous suspensions were poured into Petri dishes. The discs of filter paper (diameter 4 mm) were ranged on the cool medium. After cooling on the formed solid medium ($2 \times 10^{-5} \text{ dm}^3$) of the investigated compounds were applied using a micropipette. After incubation for (24 hours) in a thermostat at ($25\text{--}27^\circ \text{C}$), the inhibition (sterile) zone diameters (including disc) were measured and expressed in mm. An inhibition zone diameter over 7 mm indicates that the tested compound is active against the bacteria under investigation.

RESULTS AND DISCUSSION

The new (ONO) dentate ligand H₂L was obtained in good yield by the reaction of 2-aminobenzoic acid and 2-hydroxy-1-naphthaldehyde, scheme 1. In general the ligand was characterized by elemental microanalysis and physical properties table 1, FT-IR table 2, UV-Vis table 3, mass spectroscopy. Monomeric complexes of the ligand with metal ions were synthesized by heating (1mmol) of each ligand with (1 mmol) of metal salt, using ethanolic and water. However, in ethanolic, deprotonation of the ligand occur facilitating the formation of the complexes [M(L) (H₂O)₃]nCl with (M = Cr^(III) n=1, Fe^(III) n=1, Pt^(IV) n=2 and Re^(V) n=3 were reported and [(VO)(L) (H₂O)] are reported. The analytical data table 1 agrees well with the suggested formulae.

Table 1. Analytical and physical data of the ligand and its complexes

Compounds	Formula M. wt	color	m.p °C	Yield %	Elemental micro analysis, found (Calc.)%				
					C	H	N	M	Cl
H ₂ L	C ₁₈ H ₁₂ N ₂ O ₄ 320.08	Light yellow	88-90	85	67.16 (67.50)	3.42 (3.78)	8.77 (8.75)	-	-
[VOL(H ₂ O)]	C ₁₈ H ₁₂ N ₂ O ₆ V 403.24	Light green	222d	78	55.02 (53.61)	3.92 (3.00)	7.41 (6.95)	12.41 (12.63)	-
[CrL(H ₂ O) ₃]Cl	C ₁₈ H ₁₆ N ₂ O ₇ CrCl 459.78	Yellow greenish	188 d	77	45.11 (47.02)	3.31 (3.51)	7.00 (6.09)	14.43 (11.31)	8.09 (7.71)
[FeL(H ₂ O) ₃]Cl	C ₁₈ H ₁₆ N ₂ O ₇ FeCl 463.63	Yellow greenish	168 d	81	45.09 (46.63)	3.32 (3.48)	7.45 (6.04)	11.51 (12.05)	7.90 (7.65)
[PtL(H ₂ O) ₃]2Cl	C ₁₈ H ₁₆ N ₂ O ₇ PtCl ₂ 638.31	Brown reddish	200 d	64	34.00 (33.87)	3.32 (2.53)	5.53 (4.39)	31.56 (30.56)	12.09 (11.11)
[ReL(H ₂ O) ₃]3Cl	C ₁₈ H ₁₆ N ₂ O ₇ ReCl ₃ 664.89	Brown reddish	224d	80	34.00 (32.52)	3.32 (2.43)	5.53 (4.21)		14.99 (16.00)

IR spectra

The IR spectra bands of the ligand (H₂L) and its complexes were characterized at 3076, 2889, 3341, 1605 and 1569 cm⁻¹ due to the ν(CH) aromatic, ν(CH) aldehyde, ν(O-H) phenol, υ(COOH) carbonyl and υ(N=N) azo, functional groups, respectively, for the ligand [10, 11]. The IR spectra of the complexes exhibited ligand bands with the appropriate shifts due complexes formation [11]. On complex formation the bands of ν(N=N) and ν(COO) are shifted to lower frequencies by (11 to 77) and (19 to 41) cm⁻¹ respectively; these shifts confirm the coordination of the ligand through the nitrogen of the azo group and the carboxylate ion with the metal ions. The presence of coordination water in the spectra of all complexes were suggested by the very broad absorption around (3522 to 3389) and (900 to 878) cm⁻¹. This indicates that the ligand was coordinated with the metal ions through the (O) carbonyl group, (O) phenol group and (N) azo group atoms. At lower frequency the complexes exhibited new bands around (588-480), and (450-412) cm⁻¹ assigned to the υ(M-N) and υ(M-O), respectively [12,13].

Mass Spectra

Ligand H₂L

The electron impact spectrum of [H₂L] confirms the probable formula by showing a peak at 320.08 m/z, corresponding to complex moiety [(C₁₈H₁₂N₂O₄), calculated atomic mass 320]. The series of peaks in the range of 319, 302, 288, 261, 196 and 143 m/z may be assigned to various fragments.

Complex of [VOL(H₂O)]

The electron impact spectrum of [VOL(H₂O)] confirms the probable formula by showing a peak at 403 m/z, corresponding to complex moiety [(C₁₈H₁₂N₂O₆V), calculated atomic mass 403.24]. The series of peaks in the range of 385, 251 and 250 m/z may be assigned to various fragments.

Complex of [CrL(H₂O)₃]Cl

The electron impact spectrum of [CrL(H₂O)₃]Cl confirms the probable formula by showing a peak at 536.9 m/z, corresponding to complex moiety [(C₁₈H₁₆N₂O₇CrCl), calculated atomic mass 536.87]. The series of peaks in the range of 518.9, 398.8, 216.6, 184.2 and 122 m/z may be assigned to various fragments.

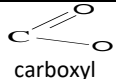
Complex of [FeL(H₂O)₃]Cl

The electron impact spectrum of [FeL(H₂O)₃]Cl confirms the probable formula by showing a peak at 459.2 m/z, corresponding to complex moiety [(C₁₈H₁₆N₂O₇FeCl), calculated atomic mass 459.78]. The series of peaks in the range of 385.4, 205.2, 204.2 and 79.4 m/z may be assigned to various fragments, see figure 2.

Complex of [PtL(H₂O)₃]2Cl

The electron impact spectrum of [PtL(H₂O)₃]2Cl confirms the probable formula by showing a peak at 638.5 m/z, corresponding to complex moiety [(C₁₈H₁₆N₂O₇PtCl₂), calculated atomic mass 638.31]. The series of peaks in the range of 430.3, 429.3, 79.4 and 36 m/z may be assigned to various fragments, see figure 3.

Table 2. FT-IR spectral data (wave number ν) cm⁻¹ for the ligand and its complexes

Compounds	C-H arom C-H ald	 carboxyl	N=N	M-N	M-O	Other bands
H ₂ L	3076 2889		1569	-	-	ν (O-H) phenol = 3341 ν (O-H)carboxyl =3402 ν (C=O)carboxyl =1605
[VOL(H ₂ O)]	3056 2888	1576 1340	1491	480	438 418	ν (H ₂ O)= 3487, 890
[CrL(H ₂ O) ₃]Cl	3029 2789	1576 1325	1542	590 518	444 410	ν (H ₂ O)= 3522, 900
[FeL(H ₂ O) ₃]Cl	3081 2835	1581 1332	1512	497 588	450 443	ν (H ₂ O)= 3389, 899
[PtL(H ₂ O) ₃]2Cl	3118 2795	1580 1330	1559	554	425 413	ν (H ₂ O)= 3464, 896
[ReL(H ₂ O) ₃]3Cl	3101 2778	1576 1333	1499	534	442 412	ν (H ₂ O)= 3465, 878

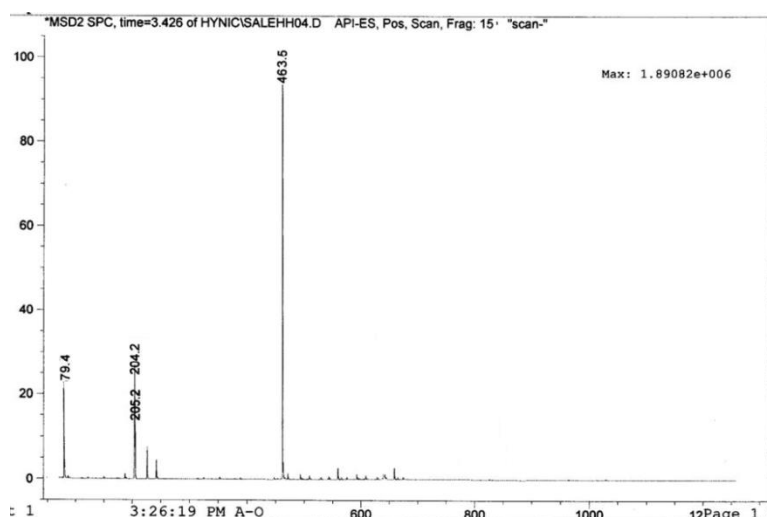


Figure 2. Mass spectrum for [FeL(H₂O)₃]Cl

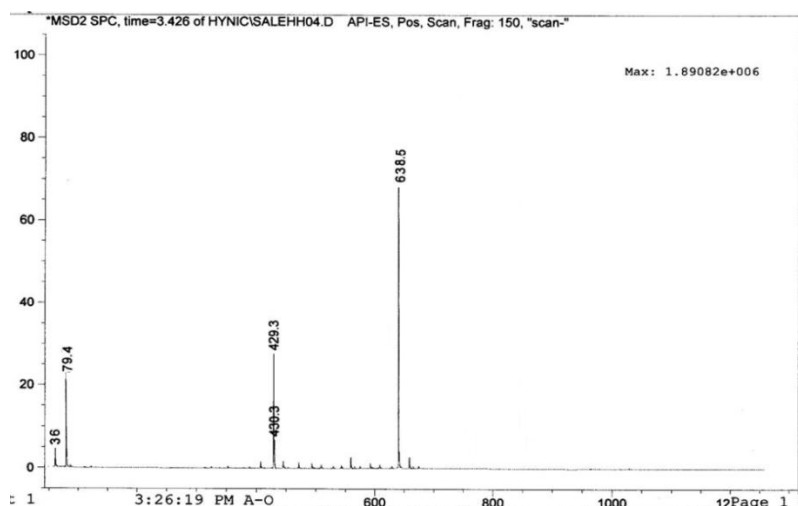


Figure 3. Mass spectrum for $[\text{PtL}(\text{H}_2\text{O})_3]2\text{Cl}$

Electronic spectral, magnetic moments

The electronic spectrum of the ligand exhibit intense absorption at 273, 278 and 315 nm attributed to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ respectively. The electronic spectrum of $\text{V}(\text{IV})$ complex showed two broad peaks at 815 and 915 nm assigned to ${}^2\text{B}_{2g} \rightarrow {}^2\text{B}_{1g}$ and ${}^2\text{B}_{2g} \rightarrow {}^2\text{E}_g$ respectively, suggesting an square pyramidal geometry figure 4. The electronic spectrum of $\text{Cr}(\text{III})$ complex showed three broad peaks at 601, 736 and 864 nm assigned to ${}^4\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{P})$, ${}^4\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{F})$ and ${}^4\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}(\text{F})$, suggesting an octahedral geometry figure 5, the electronic spectrum of $\text{Fe}(\text{III})$ complex showed one broad peak at 615 nm assigned to ${}^5\text{T}_{2g} \rightarrow {}^5\text{E}_g(\text{D})$ suggesting an octahedral geometry [14, 15]. The $\text{Re}(\text{V})$ complex, there are three absorption bands at 450, 540 and 909 nm which are attributed to the ${}^3\text{T}_{1g} \rightarrow {}^3\text{A}_{2g}$, ${}^3\text{T}_{1g} \rightarrow {}^3\text{T}_{1g}(\text{P})$ and ${}^3\text{T}_{1g} \rightarrow {}^3\text{T}_{2g}(\text{F})$ respectively, suggesting an octahedral geometry. The brown reddish of the $\text{Pt}(\text{IV})$ complex show two bands in the visible region of the 597 and 690 nm lower energy was attributed to ${}^1\text{A}_{1g} \rightarrow {}^1\text{T}_{2g}$ and ${}^1\text{A}_{1g} \rightarrow {}^1\text{T}_{1g}$ respectively, suggesting an octahedral geometry [16]. In this case the magnetic moment for $\text{Cr}(\text{III})$, $\text{Fe}(\text{III})$, $\text{Re}(\text{V})$ and $\text{Pt}(\text{VI})$ complexes are 3.77, 5.77, 2.95 B.M and diamagnetic respectively which confirmed the octahedral geometry for the $[\text{CrL}(\text{H}_2\text{O})_3]\text{Cl}$, $[\text{FeL}(\text{H}_2\text{O})_3]\text{Cl}$, $[\text{ReL}(\text{H}_2\text{O})_3]3\text{Cl}$ and $[\text{PtL}(\text{H}_2\text{O})_3]2\text{Cl}$ complexes, in this case the magnetic moment for $\text{V}(\text{IV})$ complex is 1.86 B.M which confirmed the square pyramidal geometry for $[\text{VOL}(\text{H}_2\text{O})]$ complex [16]. All the absorption bands were fully assigned in table 3.

Table 3. Electronic data magnetic moment and molar conductivity for the metal complexes

Complexes	Molar Conductive S. $\text{cm}^2 \text{mole}^{-1}$ in DMSO	μ_{eff} M. B.	λ_{max} nm	ν cm^{-1}	Assignment
$[\text{VOL}(\text{H}_2\text{O})]$	11.48	1.86	815 915	12269.9 10928.9	${}^2\text{B}_{2g} \rightarrow {}^2\text{B}_{1g}$ ${}^2\text{B}_{2g} \rightarrow {}^2\text{E}_g$
$[\text{CrL}(\text{H}_2\text{O})_3]\text{Cl}$	38.6	3.77	601 736 864	16638.9 13586.9 11574	${}^4\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{P})$ ${}^4\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{F})$ ${}^4\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}(\text{F})$
$[\text{FeL}(\text{H}_2\text{O})_3]\text{Cl}$	42.3	5.77	615	16260.1	${}^5\text{T}_{2g} \rightarrow {}^5\text{E}_g(\text{D})$
$[\text{PtL}(\text{H}_2\text{O})_3]2\text{Cl}$	148	Diamagnetic	597 690	16750.4 14492.7	${}^1\text{A}_{1g} \rightarrow {}^1\text{T}_{2g}$ ${}^1\text{A}_{1g} \rightarrow {}^1\text{T}_{1g}$
$[\text{ReL}(\text{H}_2\text{O})_3]3\text{Cl}$	209	2.95	450 540 909	22222.2 18518.5 11001.1	${}^3\text{T}_{1g} \rightarrow {}^3\text{A}_{2g}$ ${}^3\text{T}_{1g} \rightarrow {}^3\text{T}_{1g}(\text{P})$ ${}^3\text{T}_{1g} \rightarrow {}^3\text{T}_{2g}(\text{F})$

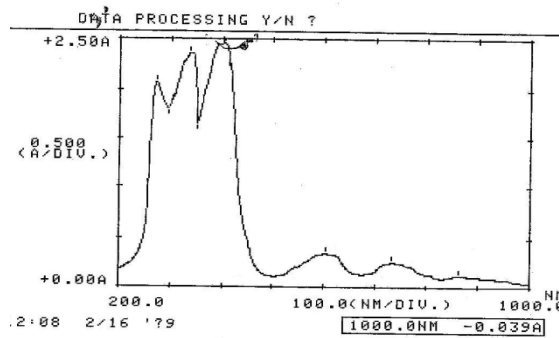
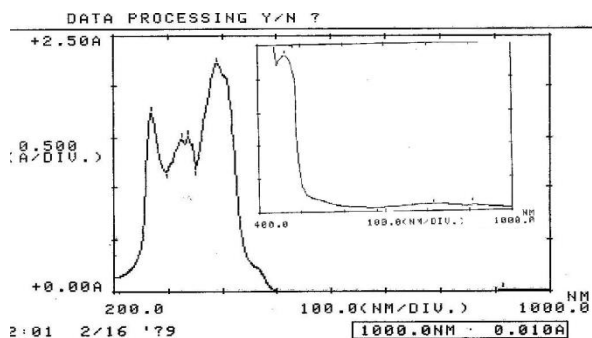


Figure 4. Electronic spectrum for [VOL(H₂O)] Figure 5. Electronic spectrum for [CrL(H₂O)₃]Cl

Thermal analyses TGA

The results of thermo gravimetric analyses of complexes are given in table 4. The thermograms have been carried out in the range of (25–350 °C) at a heating rate of 10 °C/min in nitrogen atmosphere, they showed an agreement in weight loss between their results obtained from the thermal decomposition and the calculated value, which supports the results of elemental analysis and confirms the suggested formulae, figure 6.

Table 5. Thermal analysis data of the complexes

Complexes.	Step	TGA				Reaction	Total mass loss%
		T _i /°C	T _f /°C	T _{DTG max}	Weight mass loss (calc) found%		
[PtL(H ₂ O) ₃]2Cl	1	35	128	94	(19.426) 20.09	3H ₂ O+2Cl	(64.231) 65.518
	2	128	226	188.13	(30.392) 29.568	C ₁₂ H ₆ N ₂ O	
	3	226	295	262.6	(14.413) 15.86	C ₆ H ₄ NO ₂	
						PtO ₂	
[CrL(H ₂ O) ₃]Cl	1	50	143	113.1	(19.465) 20.547	3H ₂ O+Cl	(85.148) 86.507
	2	143	344	147.6	(65.683) 65.96	C ₁₈ H ₁₀ N ₂ O ₃	
						CrO ⁺	
[ReL(H ₂ O) ₃]3Cl	1	54	126	99	(23.989) 24.068	3H ₂ O+3Cl	(67.002) 68.119
	2	126	244	188	(23.161) 23.98	C ₁₀ H ₆ N ₂	
	3	244	349	297	(19.852) 20.071	C ₈ H ₄ O ₂	
						ReO ₂ ⁺	

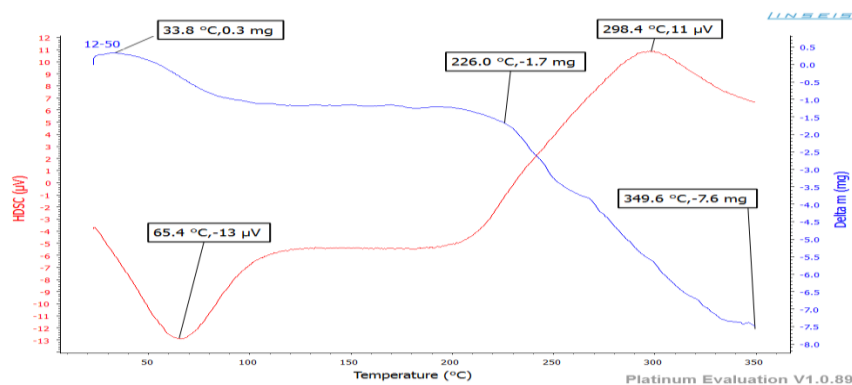


Figure 6. The curve of (TGA) for [CrL(H₂O)₃]Cl complex

Theoretical studies in Gas Stat

Electrostatic Potentials:

Electron distribution governs the electrostatic potential of the molecules. The electrostatic potential (E.P) describes the interaction of energy of the molecular system with a positive point charge. (E.P) is useful for finding sites of reaction in a molecule; positively charged species tend to attack a molecule where the electrostatic potential is strongly negative (electrophonic attack) [16]. The (E.P) of the free ligand (H_2L) was calculated and plotted as 2D contour to investigate the reactive sites of the molecules, figure 6. Also one can interpret the stereochemistry and rates of many reactions involving “soft” electrophiles and nucleophiles in terms of the properties of frontier orbital (HOMO, highest occupied molecular orbital) and (LUMO, lowest unoccupied molecules). The results of calculations show that the LUMO of metal ions prefer to react with the HOMO of two-donor atoms with nitrogen of azomethane and oxygen of the hydroxyl group for free ligand (H_2L).

Optimized energies:

The program Hyperchem-8 was used for the semi-empirical and molecular mechanics calculations. The heat of formation (ΔH_f°) and binding energy (ΔE_b) for free ligand and their metal complexes were calculated, table 4.

Optimized vibrational spectra for ligand (H_2L):

The vibrational spectra of the free ligand and their metal complexes have been calculated, table 5. The theoretically calculated wave numbers for this ligand showed that some deviations from the experimental values, these deviations are generally acceptable in theoretical calculations [17]. The most diagnostic calculated vibrational frequencies were chosen for the assignment of ligand (H_2L) and metal complexes which are included in table 5 and their respective experimental vibrational modes are shown in the same table 2. The results obtained for the theoretical calculations of the frequencies agreed well with those obtained for the experimental values, tables 2.

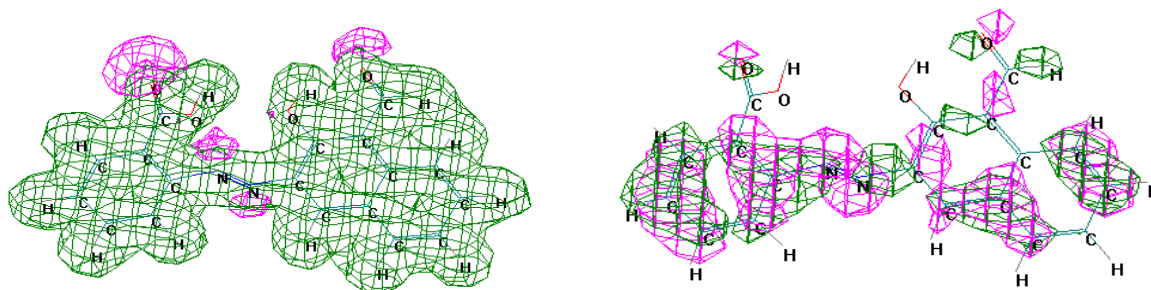


Figure 5. Electrostatic potential (HOMO and LUMO) as 2D contours for (H_2L)

Bond length measurements for the (H_2L) and their metal complexes:

Calculation of parameters has been optimized bond lengths of the free ligand (H_2L) and their metal complexes by applying the Semi-empirical (PM3) at Geometry Optimization ($0.001 \text{ K.Cal.mol}^{-1}$), which to give excellent agreement with the experimental data [18,19] as shown in table 5.

Table 4. Conformation energetic (in KJ. mol^{-1}) for naringin and its metal complexes

Compounds	ΔE_{tot}	ΔH_f°	ΔE_b	Dipole (Debyes)
H_2L	-87967.755158	-53.6708260	-4219.1508260	4.955
$[\text{VOL}(\text{H}_2\text{O})]$	-112992.15433	-311.453788	-4638.8927885	3.778
$[\text{CrL}(\text{H}_2\text{O})_3]\text{Cl}$	-118832.84153	-286.290938	-4614.1299383	4.478
$[\text{FeL}(\text{H}_2\text{O})_3]\text{Cl}$	-122087.37381	-152.547237	-4458.2862378	4.174
$[\text{PtL}(\text{H}_2\text{O})_3]2\text{Cl}$	-14526.463316 (AMBER)			6.309
$[\text{ReL}(\text{H}_2\text{O})_3]3\text{Cl}$	-25357.82801 (AMBER)			5.04

Table 5. Comparison between the experimental and theoretical vibrational frequencies (cm⁻¹) for free ligand (H₂L) metal complexes

Compounds	ν N=N		ν M-N		ν M-O		H ₂ O raking	
H ₂ L	1577*	1569**	-	-	-	-	-	-
[VOL(H ₂ O)]	1455*	1491**	503*	480**	445*	438** 418**	880*	890**
[CrL(H ₂ O) ₃]Cl	1550*	1542**	586*	590** 518**	501*	444** 410**	896*	900**
[FeL(H ₂ O) ₃]Cl	1555*	1512**	535*	497** 588**	455*	450** 443**	885*	899**
[PtL(H ₂ O) ₃]2Cl	1540*	1559**	519*	554**	418*	425** 413**	885*	896**
[ReL(H ₂ O) ₃]3Cl	1544*	1499**	557*	534**	438*	442** 412**	883*	878**

Where: *Theoretical frequency; **Experimental frequency.

Table 6. Selected bond lengths (Å) for (E) ligand and their metal complexes

Compounds	N=N	C-O	M-N	M-O
H ₂ L	1.248	1.3608		
[VOL(H ₂ O)]	3.1734	2.133	3.458	3.005
[CrL(H ₂ O) ₃]Cl	3.1734	2.138	3.429	3.037
[FeL(H ₂ O) ₃]Cl	3.1734	2.142	3.335	3.111
[PtL(H ₂ O) ₃]2Cl	3.1734	2.137	3.435	2.9853
[ReL(H ₂ O) ₃]3Cl	3.1734	2.116	3.564	2.899

Theoretical electronic spectra for the metal complexes

The electronic spectra of the metal complexes have been calculated and the wave number for these compounds showed some deviations from the experimental values as shown in table 7. These deviations in theoretical calculation are generally acceptable due to couplings between the electronic spectra modes and the approximation that each normal mode of the electronic spectra inter acts independently electronic spectra beam [20-22]. The most diagnostic calculated electronic spectra were chosen for the assignment of the metal complexes. Experimental electronic modes are shown in table 3. All the theoretical electronic spectra of all compounds were calculated by using the semi-empirical (PM3) method at geometry optimization (0.01 K.Cal. Mol⁻¹) was used, and the comparison between of the experimental data and theoretical data of the electronic spectra for metal complexes in table 7.

Table 7. Comparison between experimental and theoretical of the electronic spectra for complexes

Complexes	Maximum absorption (nm)		Band assignment	Suggested geometry
[VOL(H ₂ O)]	788*	815**	² B _{2g} → ² B _{1g}	Square pyramidal
	901*	915**	² B _{2g} → ² E _g	
[CrL(H ₂ O) ₃]Cl	587*	601**	⁴ A _{2g} → ³ T _{1g} (p)	Octahedral
	777*	736**	⁴ A _{2g} → ³ T _{1g} (F)	
	953*	864**	⁴ A _{2g} → ³ T _{2g} (F)	
[FeL(H ₂ O) ₃]Cl	585*	615**	⁵ T _{2g} → ⁵ E _g (D)	Octahedral
[PtL(H ₂ O) ₃]2Cl	587*	597**	¹ A _{1g} → ¹ T _{2g}	Octahedral
	702*	690**	⁴ A _{2g} → ¹ T _{1g}	
[ReL(H ₂ O) ₃]3Cl	498*	450**	³ T _{1g} → ³ A _{2g}	Octahedral
	592*	540**	³ T _{1g} → ³ T _{1g} (p)	
	990*	909**	³ T _{1g} → ³ T _{2g} (F)	

Where: *Theoretical frequency; **Experimental frequency

Optimized geometries of (H₂L) and their complexes:

All theoretically probable structures of free ligand and their complexes have been calculated by (PM3) method in gas phase to search for the most probable model building stable structure, figure 4.

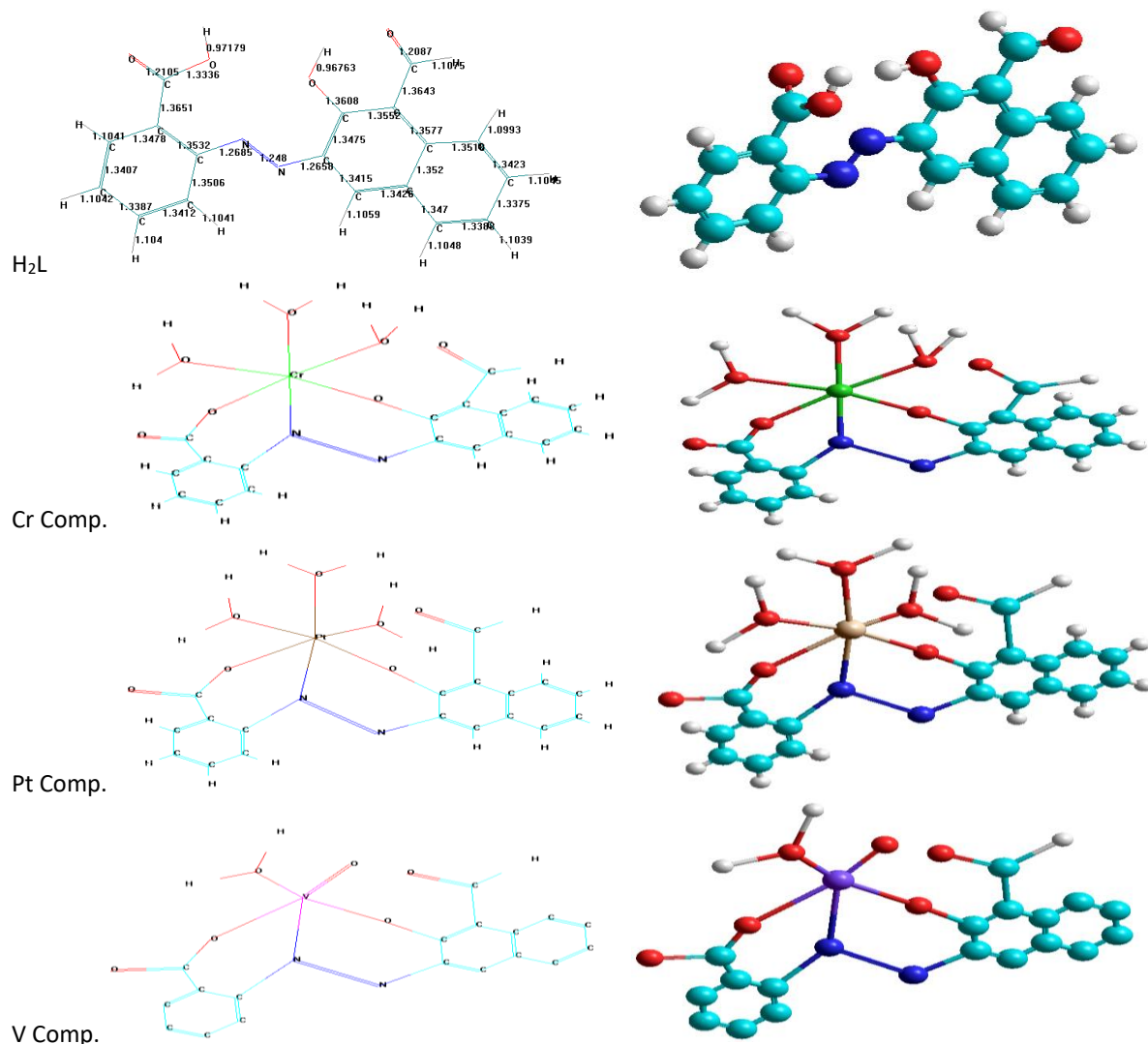


Figure 6. Conformational structure of (H_2L) and their metal complexes

Microbiological investigation

The biological activity of ligand and their metal complexes was tested against bacteria; we used more than one test organism to increase the chance of detecting antibiotic principles in tested materials. The organisms used in the present investigation included Gram positive bacteria (*S. aureus*) and Gram negative bacteria (*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 ligand and their complexes as inhibition zone (mm).

Compound	<i>Staphylococcus aureus</i> G+	<i>Pseudomonas aeruginosa</i> G ⁻
H_2L	16	18
[VOL(H_2O)]	21	16
[CrL(H_2O) ₃]Cl	21	21
[FeL(H_2O) ₃]Cl	23	22
[PtL(H_2O) ₃]2Cl	23	20
[ReL(H_2O) ₃]3Cl	22	26

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

CONCLUSION

In this paper synthesis and characterization of new complexes with general formulae $[M(L)(H_2O)_3]nCl$ with ($M = Cr^{(III)} n=1, Fe^{(III)} n=1, Pt^{(IV)} n=2$ and $Re^{(V)} n=3$ and $[(VO)(L)(H_2O)]$ are reported. The molar conductivity of the complexes in DMSO solution was electrolyte for all complexes, except $VO^{(IV)}$ complex was non-electrolyte, and the configurations were performed to coordinate the azo through the nitrogen and oxygen atoms. Therefore, from the presented results the complexes have octahedral for all complexes except VO^{2+} is Square pyramidal. Theoretically probable structures of metal complexes with azo have been calculated, these shapes shows the calculated optima geometries for H_2L and its metal complexes.

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