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Synthesis, characterization, theoretical studies and biological activities of naringin metal complexes

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ABSTRACT

The new metal complexes of Cr (III), Mn (II), Fe (III), Co (II), Ni (II) and Zn (II) with naringin(L)were synthesized and were characterized by elemental and thermal analyses as well as FT-IR and UV-Vis Spectra. The magnetic properties and electrical conductivities of metal complexes were also determined. Study of the nature of the complexes formed in ethanol following the mole ratio method. The work also include a theoretical treatment of the formed complexes in the gas phase, this was done using the (hyperchem-8) program for the molecular mechanics and semi-empirical calculations. The heat of formation (ΔHf°), binding energy (ΔE_b)and total energy (ΔET) for ligand and their complexes were calculated by (PM3) method at 298 K°. The electrostatic potential of the free ligand (L) was calculated to investigate the reactive sites of the molecules. PM3 were used to evaluate the bond length, vibrational and electronic spectra for the ligand (L) and their metal complexes then comparing with the experimental values. The theoretical results agreed with those found experimentally. The antibacterial activity for the (L) and its metal complexes were studied against two types of pathogenic bacteriamicro-organisms *(Escherichia coli)* and *(staphylococcus aureus)*. Furthermore the antifungal activity against two micro-organism *(Candida albicans)* and *(Aspergillusflavus)* were studied for (L) ligand and their metal complexes.

KEYWORDS

Flavonoid;
Naringin;
Metal complexes;
Theoretical study and antimicrobial.

INTRODUCTION

Plant sources are abundant in the common polyphenolic compounds known as flavonoids that are known to possess various types of pharmacological effects including antioxidant, anti-microbial, anti-inflammatory, anti-allergic and anti-cancer activity[1-5]. The importance of the antioxidant activity of these compounds lies in their ability to scavenge free radicals[6] that are responsible for DNA damage. Naringina, Figure (1), major bioflavonoid in grapefruit has been shown to reduce radiation-induced damage to DNA[7]. It also acts as the inhibitor of VEGF release, which causes angiogenesis[8] and has been proven to be effective against ethanol injury in rats[9]. The chemopreventive role of naringin

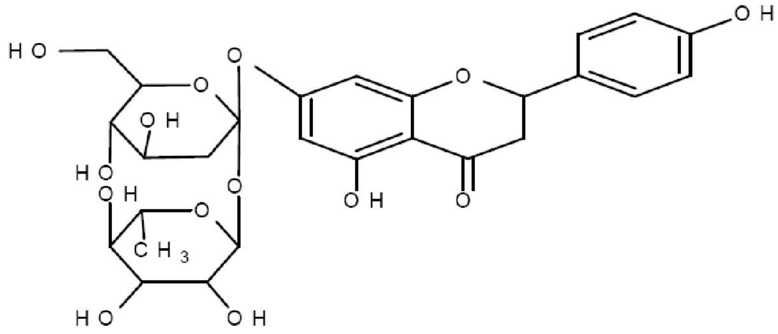

Figure 1 : Structure of naringin

against protoxicants, its action as anti-atherogenic agents in rabbits and its ability to significantly reduce the level of total cholesterol have also been established[10-12]. The oralbioavailability of quinine in rats has been shown to increase after pretreatment with naringin[13]. Naringin and hespe-ridin are the main citrus flavonoids with physiological properties present in grapefruit and orange juice[10,12]. These flavonoids have been detected in human plasma after orange and grapefruit diets[3]. There are numerous reports of HPLC analysis of the composition of commercial juices, con-centrates, fresh oranges, and grapefruit[3-5]. This paper describes the synthesis of Cr (III), Mn (II), Fe (III), Co (II), Ni (II) and Zn (II) transition metals complexes bearing a naringin ligand, and its characterization by (FT-IR and Uv-Vis) Spectroscopy, (elemental analysis and flame atomic absorption) techniques as well as (magnetic susceptibility and conductivity) measurements. The antimicrobial activity for naringin (L) and their metal complexes were studied and compared with the corresponding free flavonoid, naringin. The theoretical studies of the naringin (L) and their metal complexes were also studied and compare with experimental results.

EXPERIMENTAL

Instrumentation

Melting points were recorded on a GallenkampMF B600 melting point apparatus. Elemental analyses (C.H.N.) were obtained using EA-034.mth. for metal complexes of naringin (L). Metal contents of complexes were estimated Spectrophotometrically using Flame atomic absorption Shimadzu-670 AA Spectrophotometer. Infrared spectra were recorded using FT-IR-8300 Shimadzu in the range of (4000-350)cm^{-1}, samples were measured as (CsI) disc. Magnetic susceptibilities of samples in the solid state were measured by using a Bruker BM6 magnetic balance. The molar conductivity was measured by using Electrolytic Conductivity Measuring set Model MC-1-Mark V by using platinum electrode (EDC 304) with cell constant (1cm^{-1}), concentration (10^{-3} M) in dimethylformmide as a solvent at room temperature. Electronic spectra were obtained using UV-1650PC-Shimadzu Spectrophotometer at room temperature, the measurement were recorded using a concentration of (10^{-3}M) of the metal complexes in dichloro-methane as a solvent.

MATERIALS AND METHODS

All chemical were of highest purity and were used as received.

Preparation of metal complexes (1-6) of (L)

An Ethanolic solution of each of the following metal ions salts(0.69mmole) [$CrCl_3.6H_2O$, $FeCl_3.9H_2O$,$MnCl_2.5H_2O$, $CoCl_2.6H_2O$, $NiCl_2.6H_2O$ and $ZnCl_2.H_2O$]was added to an ethanolic solution (0.69mmole)of (L) except in the case of [Mn(II), Cr(III) and Fe(III)](1.38mmole) of (L), with stirring. The resultant pH 6.5 [for Cr(III) and Fe(III)], pH6.2 [for(Mn(II), Co(II) and Ni(II)] and pH5.8 [for Zn(II)] were maintained by adding of sodium acetate. The reaction mixture was heated under reflux for (2-3)hours, during this time a precipitate was formed. The product was filtered off,washed with hot ethanol,followed by cold water and then dried under vacuum. All complexes were identified by elemental analysis (C.H.N),flame atomic absorption, FT-IR and Uv-Vis spectrophotometers,magnetic and conductivity measurements.

Study of complexes formation in the solution

The (1-5) complexes of the (L) ligand with the selected metal ions [Cr(III), Fe(III), Mn(II), Co(II) and Ni(II)], were studied in solution using ethanol as a solvent, in order to determine [M:L] ratio in the prepared complexes, following molar ratio method[14]. A series of solutions were prepared having a constant concentration (10^{-3}M) of the hydrated metal chlorides and the (L) ligand. The [M:(L)] ratio was determined from the relationship between the absorbance of the absorbed and the mole ratio of [M:(L)].

Programs used in theoretical calculation

Materials and methods

Hyperchem is a sophisticated molecular modeler, editor and powerful computational package, that is known for its' quality, flexibility and ease of use[15,16]. It can plot orbital wave functions resulting from semi-empirical quantum mechanical calculations, as well as the electrostatic potential, the total charge density or the total spin density can also be determined during semi-empirical calculation, this information is useful in determining reactivity and correlating calculation results with experimental data.

Computational methods

Semi-empirical quantum mechanical,Molecular mechanics andMopac 2000

Types of calculations

The typesof prediction possible of Molecules are[17,18]:

[1] Geometry optimization calculations employ energy minimization algorithms to locate stable structures.
[2] Bond distances
[3] Molecular dynamics which provide the thermodymemic calculations and dynamic behavior of molecules
[4] Plot the electrostatic potential field (HOMO and LUMO).
[5] Vibrational spectrum (I.R and Raman spectra).

Study of biological activities for (L) ligand and (1 –6) their metal complexes

The biological activities of the ligand(L) and their respective complexes(1-6) were studied against selected types of bacteria which include *(Escherichia coli)* and *(staphylococcus aureus)*cultivated in Nutrient agar medium, DMSO was used as a solvent and as a control, the concentration of the compounds in this solvent were (10^{-3}M).

The new metal complexes(1-6) were tested for their *in vitro* growth inhibitory activity against further pathogenic fungi, i.e., [*Candida albicans*and*Aspergillusflavus*] on potato dextrose agar medium and incubated at 30°C for 72 hours. DMSO was used as a solvent and as a control for both techniques. The concentrations of the compounds in this solvent were (10^{-3}M). The inhibition of fun-

TABLE 1 : Physical data for complexes (1-6)

Comp. No.	Color	Melting point	Molar ratio (in ethanol)	Yield %	Metal analysis Found Calc.			Suggested formula
					C%	H%	M%	
(1)	Dark green	225	1:2	88	50.78 50.64	5.11 5.00	4.13 4.06	$[Cr(C_{27}H_{30}O_{14})_2(H_2O)_2]Cl$
(2)	Yellowish brown	232	1:2	79	52.02 51.97	5.18 5.13	4.50 4.41	$[Mn(C_{27}H_{30}O_{14})_2(H_2O)_2]$
(3)	Dark brown	238	1:2	80	51.07 50.49	5.01 4.99	4.42 4.35	$[Fe(C_{27}H_{30}O_{14})_2(H_2O)_2]Cl$
(4)	Blueishgreen	204	1:1	86	46.99 46.93	4.63 3.88	9.03 8.54	$[Co(C_{27}H_{30}O_{14})H_2O\,Cl]$
(5)	Dark green	222	1:1	84	45.89 45.75	5.00 4.80	8.37 8.29	$[Ni(C_{27}H_{30}O_{14})(H_2O)_2]Cl$
(6)	White	218	1:1	90	46.55 46.49	4.80 4.59	9.44 9.38	$[Zn(C_{27}H_{30}O_{14})H_2O\,Cl]$

gal growth expressed in percentage terms, were determined on the growth in test plates compared to the respective control plates, as given by the Vincent equation[19]. Furthermore the antifungal activity against two micro-organism

Inhibition % = 100 (C – T) / C

Where: C = Diameter of fungal growth on the control plate, T = Diameter of fungal growth on the test plate

RESULTS AND DISCUSSION

Part (I) study complexes in solid stat

Elemental analyses

The physical and analytical data of the (L) ligand and (1-6) metal complexes are given in TABLE (1). The results obtained from elemental analysis are in satisfactory agreement with the calculated value. The suggested molecular formula was also supported by spectral measurement as well as magnetic moment. The new (1-6) complexes colored crystalline solid were soluble in (CH_2Cl_2, $CHCl_3$, DMF and DMSO). They are thermally stable and unaffected by atmospheric oxygen and moisture.

Infrared spectroscopic study

The characteristic vibrations of important groups are described in TABLE (2). The strong band at 1710cm^{-1} is attributed to [$\upsilon_{-C=O}$] group[20], was shifted to a lower frequency by (15-8)cm^{-1} in the all complexes as compared to its ligand (L),TABLE(2). A broad band observed at 3700cm^{-1} in IR spectra of ligand (L) assigned to υ(OH),which were found to have disappeared in all the respective complexes (1-6) that means its bonding with metal ions through deprotonation[20,21]. Another important ligand band occurring at 1275cm^{-1} due to phenolic υ(C-O) shifts to a lower frequency by (22-10)cm^{-1} in the all complexes, TABLE(2). Ligand behaved as bi dentate with one metal ion, through two– donor atoms of oxygen of carbonyl group and oxygen of the hydroxyl group. These observations were further indicated by the appearance of (υM-O and υM-Cl) respectively[22]. All the complexes show additional bands at 840-830cm^{-1} indicating the presence of coordinated water[22,23].

Electronic absorption spectra, magnetic susceptibility and conductivity measurement

The (L) ligand exhibited two high intensity bands in ethanol. The first bands appeared at (36359) and (38613)cm^{-1} respectively and the second bands appeared at (32998) and (31655) cm^{-1}. The two first bands were attributed to $\pi\rightarrow\pi^*$ transitions of the carbonyl group and to conjugated ring system respectively, while bands related to $n\rightarrow\pi^*$ transition may be masked by the extended of the second band[23].

Complexation of (L) with metal ions caused bathochromic shift with the appearance of new bands in the visible and near I.Rregions. These bands were attributed to M-L charge transfer and to ligand field transitions[24]. TABLE (3) describes bands of maximum absorption of (1-6) complexes in dichloromethane with their assignments.

The spectra of Cr (III)complex(1) exhibits three absorption bands at (12364, 16493 and 29881) cm^{-1}. The spectrum was typical of octahedral Cr (III) complexes[25-27]. The (υ_2/υ_1) ratio is (1.33) which is very close to the value of obtained for pure octahe-

TABLE 2 : Stretching vibrational frequencies (cm^{-1}) located in the FT-IRspectra of (L) and itś complexes

Comp. No.	$\upsilon_{C=O}$	υ_{OH}	υ_{C-O}	υ_{M-Cl}	υ_{M-O}	ρ_{O-H} of H_2O
(L)	1710	3700	1275	-	-	-
(1)	1702	-	1255	-	522	840
(2)	1700	-	1253	-	516	838
(3)	1695	-	1260	-	508	830
(4)	1699	-	1265	399	513	833
(5)	1700	-	1257	-	505	838
(6)	1697	-	1261	400	511	830

TABLE 3 : Electronic spectra (CH_2Cl_2), Magnetic moment (B.M) and Conductance in (DMF) for (1-6) complexes

No.	Maximum absorption $\upsilon_{max}(cm^{-1})$	Band assignment	B`	β	10Dq	Molar Cond. $S.cm^2.mol^{-1}$	μeff. B.M	Suggested geometry
(1)	12364 16493 29881	$^4A_2g \rightarrow {}^4T_2g$ $^4A_2g \rightarrow {}^4T_1g$ $^4A_2g \rightarrow {}^4T_1g$ (P)	-	-	-	70.94	3.89	O.h
(2)	11816 (Cal.) 20294 29674 36765	$^6A_1g \rightarrow {}^4T_1g(G)$ $^6A_1g(S) \rightarrow {}^4T_2g(G)$ $^6A_1g(S) \rightarrow {}^4A_1g+{}^4Eg(G)$ C.T	844	0.98	12238	11.36	5.02	O.h
(3)	15018 17803 33214	$^6A_1g \rightarrow {}^4T_1g(G)$ $^6A_1g(S) \rightarrow {}^4T_2g(G)$ C.T	611	0.5	6818	78.68	5.86	O.h
(4)	3749 6310 (Cal.) 16994	$^4A_2 \rightarrow {}^4A_2(F)$ $^4A_2 \rightarrow {}^4T_2$ (F) $^4A_2 \rightarrow {}^4T_1$ (P)	698	0.62	3769.2	18.05	4.62	T.h
(5)	16129 23310	$^1A_1g \rightarrow {}^1A_2g$ $^1A_1g \rightarrow {}^1Eg$	-	-	-	68.33	0.08	S.p
(6)	-	-	-	-	-	13.44	0.0	T.h

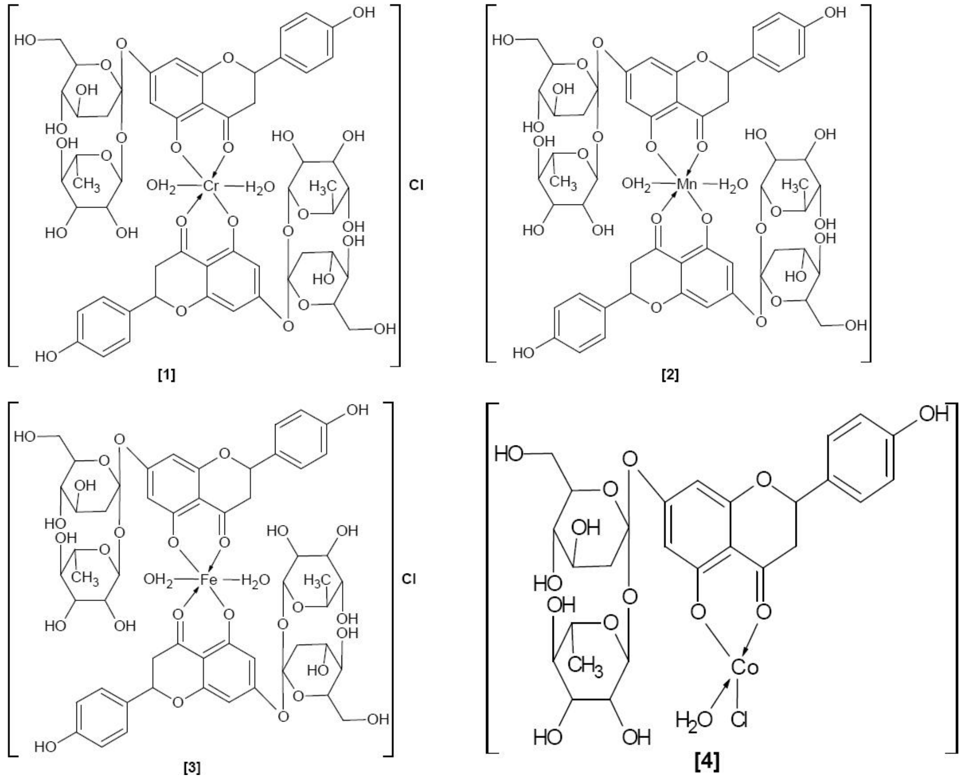

Figure 2 : The suggested structure of complexes (1-6)

dral Cr (III) complexes[26,27]. Magnetic moment of solid complex was found to be (3.89B.M) and conductivity in DMF showed that the complex was ionic, (TABLE (3)).

The Uv-Vis spectrum of the yellowish brown manganese complex(2) show two main absorption bands at(20294 and 29674)cm^{-1},which indicate an octahedral geometry[25]. The value of racahparameters (10Dq, B', β and υ1) have been calculated to be (12238,844,0.98and 11816)cm^{-1},respectively. The effective magnetic moment at room temperature was found to be (5.02B.M),which agree well for low-spin manganese in octahedral coordination[27]. Conductivity measurement showed that the

TABLE 4 : Antibacterial and antifungal activities for ligand (L) and their metal complexes (1-6) (10^{-3} mgm.ml^{-1})

Comp. No.	*E. coli*	*Staph. Aureus*	*Asp. Flavus*	*Penci. SPP.*
Control DMSO	-	-	-	-
(L)	-	-	44	36
(1)	8	6	22	30
(2)	6	10	17	19
(3)	6	-	28	30
(4)	6	6	28	30
(5)	-	6	26	20
(6)	10	6	18	15
		Where:- (+) 6-8 (++) 8-10 (+++)10<		Where:- (+++)30-40 (++++) 20-30 (+++++) 10-20

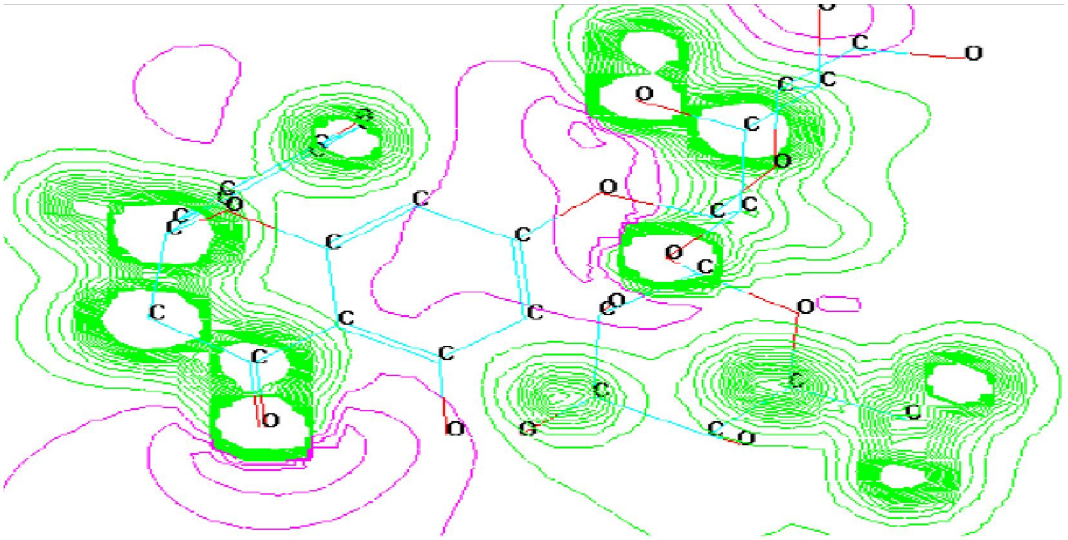

Figure 3 : Electrostatic potential (HOMO and LUMO) as 2D contoursfor(L)

amount of covalent character in metal to nitrogen and oxygen bonds. While the value of (10Dq) to be (3769.2)cm^{-1},one should expect a band due the transition $^4A_2 \rightarrow ^4T_2(F)$ in the infrared region at (3749)cm^{-1}, which couldn't to be observed in the spectrum of the cobalt (II) complex[27]. Conductivity in DMF showed that the complex was not ionic, TABLE(3).

The electronic spectrum of Nickel(II) complex(5) exhibits two main absorption band, TABLE(3) which are assigned to the two transition $^1A_1g \rightarrow ^1A_2g$ and $^1A_1g \rightarrow ^1Eg$ respectively in the a square-planer geometry[25,28,32]. Magnetic moment of the complex (0.08B.M) is higher than spin value of the Nickel metal only, this result indicate orbital contribution[30,31]. Conductivity measurement showed that the complex was ionic, TABLE(3).

The complex(6) of Zinc(II) are colorless and was diamagnetic as expected for (d^{10}) ion, since the UV-Vis spectra of the band position was compared with that of the ligand only. The conductivity measurements indicate a non-ionic behavior, TABLE(3). Thus from the data obtained from FT-IR spectrum and flame atomic absorption, a tetrahedral geometry a round Zn(II) ion[24,29].

Stereo chemistry structure of metal complexes(1-6)

According to the results obtained from elemental and spectral analysis as well as magnetic momentandconductivitymeasurements, the structure of the above mentioned compounds can be illustrated as follows,Figure(2).

Biological studies

The free ligand (L) and its complexes (1-6) were screened *in vitro* for their ability to inhibit the growth of representative [(*E.coli*)as gram negative] and [(*Staph. aureus*) as gram positive] are shown in TABLE (4). Also the study was done against (*Aspergillusflaveus*and*penicillumSpp.*) fungus, in DMSO as a solvent, TABLE(4).

As a result from the above mentioned studies, the following points were concluded:-

A. (L) was not active against *Staph*. And *E.coli*TABLE(4).

B. All complexes (1-6) showed highly active against two types of bacteria compared the ligand(L) active prepared them,TABLE(4).

C. Results of the antifungal activity of the new compounds, TABLE (4) showed that the metal ion chelates (1-6) were more toxic compared with their parent ligand (L) toward the same microorganism and under the identical experimental conditions. The increase in the antifungal activity of metal chelates may be due to the effect of the metal ion on the normal cell process. These activities may be explained by Tweedy's Chelation theory[33], according to which chelation reduces the polarity of the metal atom mainly, because of the partial sharing of its positive charge with the donor groups of the ligand, which favours permeation of the complexes through the lipid layer of cell membrane[34].

Part (II) study complexes in gas stat (theoretical studies)

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;

TABLE 5 : Conformation energetic (in KJ. mol^{-1}) for Naringin and its metal complexes

Com.No.	ΔE_{tot}	ΔH^o_f	ΔE_b
L	-80673.95	35.07	-5200.37
(1)	-185054.96	-84.88	-10681.47
(2)	-113605.75	-266.77	-5662.60
(3)	-119290.09	-85.25	-5481.49
(4)	-122833.58	-98.94	-5607.85
(5)	-96003.98	-36.79	-5361.40
(6)	-137008.36	-15.17	-8153.68

TABLE 6 : Comparison between the experimental and theoretical vibational frequencies (cm^{-1}) for free ligand (L) metal complexes

Com. No.	$\upsilon_{C=O}$	υ_{C-O}	υ_{OH}	υ_{M-O}	υ_{M-Cl}	ρ_{O-H} of $_{H2O}$
L	1715* 1710**	1270* 1275**	3706* 3700**	-	-	-
(1)	1699* 1700**	1260* 1255**	-	545* 522**	-	844* 840**
(2)	1699* 1700**	1250* 1253**	-	515* 516**	-	840* 838**
(3)	1700* 1695**	1258* 1260**	-	505* 508**	-	844* 830**
(4)	1705* 1699**	1260* 1265**	-	512* 513**	379* 399**	828* 833**
(5)	1665* 1700**	1255* 1257**	-	554* 505**	-	829* 838**
(6)	1700* 1697**	1259* 1261**	-	554* 511**	395* 400**	828* 830**

Where:- *Theoretical frequency.Experimental frequency.**

positively charged species tend to attack a molecule where the electro static potential is strongly negative (electrophonic attack) [35]. The (E.P) of the free ligand (L)was calculated and plotted as 2D contour to investigate the reactive sites of the molecules, Figure (3). 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 transition metal ions prefer to react with the HOMO of two-donor atoms of oxygen of carbonyl and oxygen of the hydroxyl group for Naringin free ligand (L).

Optimized energies

The program Hyperchem-8 was used for the semi-empirical and molecular mechanics calculations. The heat of formation (ΔH_f^o) and binding energy (ΔE_b) for free ligand (L) and their metal complexes(1-6) were calculated, TABLE (5).

Optimized vibrational spectra for ligand(L)

The vibrational spectra of the free ligand (L)and their metal complexes (1-6) have been calculated, TABLE (6). The theoretically calculated wave numbers for this ligand showed that some deviations from the experimental values, these deviations are generally acceptable in theoretical calculations[36]. The most diagnostic calculated vibrational frequencies were chosen for the assignment of ligand (L) and metal complexes (1-6) which are included in TABLE (6) and their respective experimental vibrational modes are shown in the same table.

The results obtained for the theoretical calculations of the frequencies agreed well with those obtained for the experimental values, TABLES (2).

Bond length measurements for the (L) and their metal complexes

TABLE 7 : Selected bond lengths (A°) for (E) ligand and their metal complexes[1-6]

Com. No.	*C=O*	*C-O*	*M-O*	*M-Cl*
L	1.62	1.50	-	-
(1)	1.67	1.55	2.28	-
(2)	1.71	1.58	2.25	-
(3)	1.69	1.55	2.22	-
(4)	1.65	1.53	2.28	1.92
(5)	1.70	1.56	2.14	-
(6)	1.63	1.54	2.19	1.89

TABLE 8 : Comparison between experimental and theoretical of the electronic spectra for (1-5) complexes

Symb.	**Maximum absorption υ_{max}(nm)**	**Band assignment**	**Suggested geometry**
(1)	810*,808**	$^4A_2g \rightarrow {}^4T_2g$	O.h
	628*,606**	$^4A_2g \rightarrow {}^4T_1g$	
	350*,334**	$^4A_2g \rightarrow {}^4T_1g$ (P)	
(2)	866*,846**	$^6A_1g \rightarrow {}^4T_1g$(G)	O.h
	498*,492**	^6A_1g(S) $\rightarrow {}^4T_2g$(G)	
	340*,336**	^6A_1g(S) $\rightarrow {}^4A_1g + {}^4Eg$(G)	
	290*,271**	C.T	
(3)	688*,665**	$^6A_1g \rightarrow {}^4T_1g$(G)	O.h
	548*,561**	^6A_1g(S) $\rightarrow {}^4T_2g$(G)	
	311*,301**	C.T	
(4)	2682*,2667**	$^4A_2 \rightarrow {}^4A_2$(F)	T.h
	1590*, 1584**	$^4A_2 \rightarrow {}^4T_2$ (F)	
	592*,588**	$^4A_2 \rightarrow {}^4T_1$ (P)	
(5)	630*,620**	$^1A_1g \rightarrow {}^1A_2g$	S.p
	443*,429**	$^1A_1g \rightarrow {}^1Eg$	

Where:- *Theoretical frequency, **Experimental frequency.

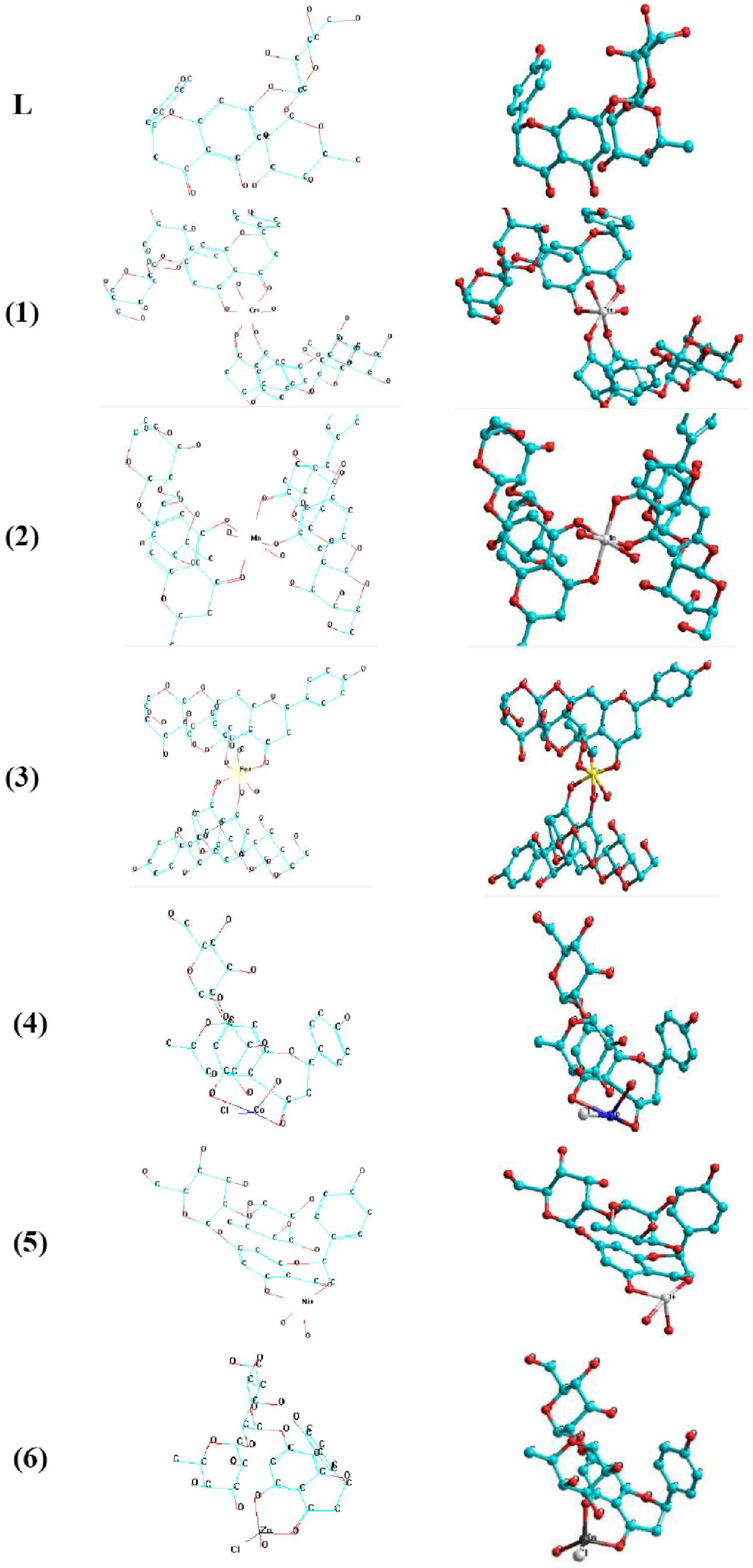

Figure 4 : Conformational Structure of(L) and their metal complexes (1-6)

Calculation of parameters has been optimized bond lengths of the free ligand (L) and their metal complexes by applying the Semi-empirical (PM3) at Geometry Optimization (0.001 K.Cal.mol^{-1}), which to give excellent agreement with the experimental data[37,38] as shown in TABLE (7).

Theoretical electronic spectra for the metal complexes (1-5)

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 (8). 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[39,40]. The most diagnostic calculated electronic spectra were chosen for the assignment of the metal complexes[1-5]. 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[1-5] metal complexes in TABLE (8).

Optimized geometries of (L) and their complexes (1-6)

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

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