

Synthesis and Characterization of the Complexes of Some Transition Metals with 2-methyl-4-iso propylidene oxazol-5-one.

**تحضير وتشخيص معقدات بعض العناصر الأنتقالية مع 2- مثيل – 4- ازو بروبايلدين
او كسازول – 5- اون**

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Abstract

Complexes of Cr(III), Mn(II), Fe(III), Co(II) and Cu(II) with 2-methyl-4-aceto-5-oxazolone have been synthesized and characterized by Metal content, molar conductance, magnetic susceptibility, and FT-IR, UV-vis spectroscopic techniques. The complexes of Mn(II) and Co(II) exhibit the composition $[M L_2 X_2]$, where some complexes exhibit the composition $[M L_2(H_2O)_2 X_2]$ $M = Cr(III), Fe(III) \text{ and } Cu(II)$, $L = 2\text{-methyl-4-aceto-5-oxazolone}$ and $X = Cl$. The metal coordinate with nitrogen atom C=N group of the ligand. The N donor ligand acts as a monodentate ligand in all complexes. The spectral analysis indicate tetrahedral geometry for Mn(II), Co(II), complexes while octahedral geometry for the Cr(III), Fe(III) and Cu(II) complexes. The Structure geometries of these compounds were also suggested in gas phase by using theoretical treatment, using Hyper chem.-6 program through the molecular mechanics and semi-empirical calculations. The heat of formation (ΔH_f°) and binding energy (ΔE_b) for the free ligands and its metal complexes were calculated by PM3 method.

Key word. Azlactone, complexes of Azlactone.

الخلاصة

معقدات الكروم الثلاثي، المنغنيز الثنائي، الحديد الثلاثي، الكوبلت الثنائي والنحاس الثنائي مع 2-methyl-4-aceto-5-oxazolone حضرت وشخصت بقياس نسبة الفلز، التوصيلية المولارية، الحساسية المغناطيسية واطياف الاشعة تحت الحمراء وفوق البنفسجية - المرئية، اظهرت معقدات الكوبلت الثنائي والمنغنيز الثنائي الصيغة $[ML_2X_2]$ ، بينما اظهرت معقدات الكروم الثلاثي، الحديد الثلاثي والنحاس الثنائي الصيغة التالية $[M L_2(H_2O)_2 X_2]$ حيث $M = Cr(III), Fe(III) \text{ و } Cu(II)$ ، $L = 2\text{-methyl-4-aceto-5-oxazolone}$ و $X = Cl$. ان تناسق الفلز حدث مع مجموعة C=N من خلال ذرة النتروجين الواهبة حيث اظهر الليكاند سلوك احادي السن في جميع المركبات. أظهر التحليل الطيفي ان الكوبلت الثنائي والمنغنيز الثنائي ذات شكل رباعي السطوح، بينما اظهر شكل ثماني السطوح لكل من معقدات الكروم، الحديد والنحاس. اقترح الشكل الهندسي لهذه المعقدات في الحالة الغازية باستخدام المعالجة النظرية وذلك باستخدام برنامج Hyper Chem-6 من خلال حسابات الميكانيك الجزيئي والشبة التجريبية. تم حساب حرارة التكوين القياسية وطاقة الترابط لليكاند والمعقدات المحضرة باستخدام طريقة ال-PM3.

Introduction

azlactone-functionalized materials can serve as convenient 'reactive' platforms for the post-synthesis or post-fabrication introduction of a broad range of chemical functionality to soluble polymers, insoluble supports, and surfaces interfaces. Azlactones have been used to synthesize a broad range of functional materials the broader reactivity and general characterization of azlactone-functionalized polymers has been reviewed comprehensively [1] of particular relevance demonstrated the use of azlactone-functionalized polymers to design reactive interface and tailor the physicochemical properties of surfaces [2] for example azlactone functional polymers have been used in various ways to fabricate polymeric monoliths [3], Polymer brushes [4] polymer layers [5,6] bulk thin films [7] and reactive polymer multilayer [8,9] useful for the immobilization of proteins [7,8] and other molecules [2,7-9]. The last decade has seen an increase in both the number and the variety of reports that exploit the properties and the reactivities of azlactone-functionalized

polymers. Here, we highlight recent work from several different laboratories, including our own, toward the design and characterization of azlactone-functionalized polymers, with a particular emphasis on: (i) new synthetic approaches for the preparation of well-defined azlactone-functionalized polymers using living/controlled methods of polymerization, (ii) the design and modular synthesis of side-chain functionalized polymers and block copolymers *via* post-polymerization modification of azlactone-functionalized polymers, (iii) the development of reactive polymeric supports useful in the contexts of separations and catalysis, and (iv) methods for the fabrication of reactive thin films and other approaches to the immobilization of azlactone functionality on surfaces and interfaces[9].

Experimental :

A-Materials, physical measurements and analysis :

The chemicals used in this work were obtained from BDH. and Fluka, they were pure grade reagents .

A Flame emission spectrophotometer type Perkin Elemer 5000 was used for metal content determination, FTIR spectra were recorded using Shimadzo-8000 spectrophotometer using KBr discs in the rang (4000-400) cm^{-1} .

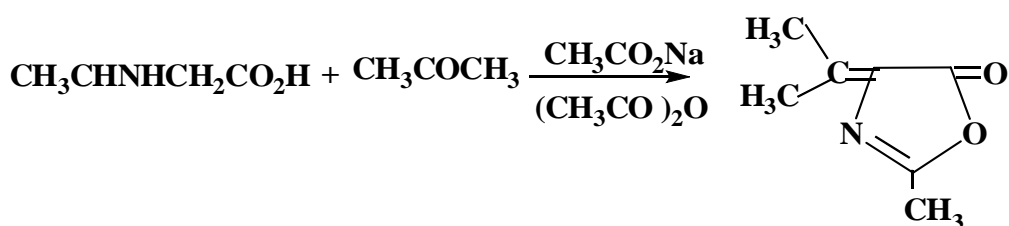
Electronic spectra were recorded using Shimadza UV-Visible (160A) ultra violate spectrophotometer at wave length in the rang (200-1100) nm .

Electrical conductivity was measured using Coring conductometer and magnetic susceptibility was measured by Johnson Matting Catalytic System Division and melting point was measured using Gallen camp M.F.B 600.01 .

Metal contents of the complexes were determined using a Shimadzu A.A680G atomic absorption Spectrophotometer. The chlorine content was determined gravimetrically.

B-Preparation of the ligand [10]:

A mixture of (5.8g,0.04 mol.)of acetyl glycine, (3.0g ,0.036 mol.) of anhydrous sodium acetate ,(7.9g7.5mL) of acetone and(13.0g,12 mol.)of acetic an hydrate. Put that mixture in flask is warmed on the steam bath with occasional stirring until solution is boiled for 1 hour under reflux cooled and placed in refrigerator overnight .The solid mass of crystals is treated with (125mL) of cold water and after that crystallized from carbon tetra chloride CCl_4 ,M.P. =110C^o-112C^o,Yield =89%



C-Preparation of Mn(II),Cr(III),Fe(III), Co(II), and Cu(II) complexes:

Ethanol solution of the selected metal ion salts (2.66,1.98,3.24,2.38,1.71,0.01mol.) of $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{FeCl}_3 \cdot 9\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ respectively was added to ethanolic solution (2.54,0.02 mol.) of ligand. The mixture was refluxed with stirring for one hour. The produced complexes were filtered and washed with hot ethanol .The physical properties of these complexes are listed in table (1).

Table 1: Physical Characteristics and analytical data for Ligand and its metal complexes

Compounds	Colour	m.p(C°)	Yield(%)	metal content(%)		Chloride content(%)		Suggested structure
				Cal.	Found	Cal.	Found	
C ₇ H ₉ NO ₂	Light - brown	110-112	89	-	-			-
[Cr L ₂ Cl ₂ (H ₂ O) ₂]Cl	Dark Brown	320*	78	11.03	11.69	22.5	21.9	Oh
[Mn L ₂ Cl ₂]	Brown	214-216	75	13.64	14.22	17.3	18.0	Td
[FeL ₂ Cl ₂ (H ₂ O) ₂]Cl	Brown	198-200	68	11.73	11.23	22.3	21.6	Oh
[CoL ₂ Cl ₂]	Dark-green	106-108	80	13.74	14.28	17.2	18.1	Td
[CuL ₂ Cl ₂ (H ₂ O) ₂]	Brown-Reddish	178-180	73	14.18	13.99	15.6	16.3	Oh

*:-decomposed

Theoretical treatment

Computational Chemistry

Today, advances in software have produced programs that are easily used by any chemist. Hyper Chem-6 program is known for its quality, flexibility and ease of use, it offers ten semi-empirical methods. Some of them have been devised specifically for the description of inorganic chemistry as well, and generally good for predicting molecular geometry and energetic. They can be used for predicting vibration modes and transition structures [11].

In the present work, parameterization method 3(PM3) was used for the calculation of heat of formation and binding energy for all metal complexes. PM3 is more popular than other Semi empirical methods due to the availability of algorithms and more accurate than with other methods. PM3/TM is an extension of the PM3 method to include d orbitals for use with transition metals[11]. It has been parameterized primarily for organic molecules and certain transition metals listed below: Ti, Cr, Mn, Co, Ni, Cu, Zn, Zr, Mo, Ru, Rh, Pd, Cd, Hf, Ta, W, H.

Parameterisation Model, Version 3 (PM3):- Is a recently developed semi-empirical method that may contain as yet undiscovered defects [11], The parameters for PM3 were derived by comparing a much larger number and wider variety of experimental versus computed molecular properties. PM3 is primarily used for organic molecules, but is also parameterized for many main group and transition metal elements.

Results and Discussion:

1-Metal Analysis:

The physical and analytical data of the metal complexes are given in table(1). The results obtained from metal analysis are in a satisfactory agreement with the calculated values. The suggested molecular formula was also supported by spectral as well as magnetic moments measurements.

Infrared Spectra

The infrared spectra of the free ligands and the metal complexes were obtained over a spectral range of 4000–400 cm⁻¹. The bands at 1579 cm⁻¹ was assigned to the stretching vibration of the C=N group of the ligand. This band is shifted in the complexes toward frequencies in the spectra of all the complexes (1589–1540 cm⁻¹) [12 - 14] Accordingly. Indicating the involvement the double bond character of the C=N bond, which is caused by the coordination of nitrogen into the metal center. The strong band observed at 1631 cm⁻¹ region in the free ligand was assigned to the stretching vibration of the C=O group. Practically no effect on this frequencies after complexation. In conclusion, the ligands acts as a monodentate chelating agent, bonded to the metal ion for the all complexes. Assignment of the proposed coordination sites is further supported by the appearance of

medium bands at 460–432 cm^{-1} which could be attributed to $\nu\text{M-O}$ and 586–501 $\text{cm}^{-1}\nu\text{M-N}$ respectively for complexes with ligand [13-15,] .

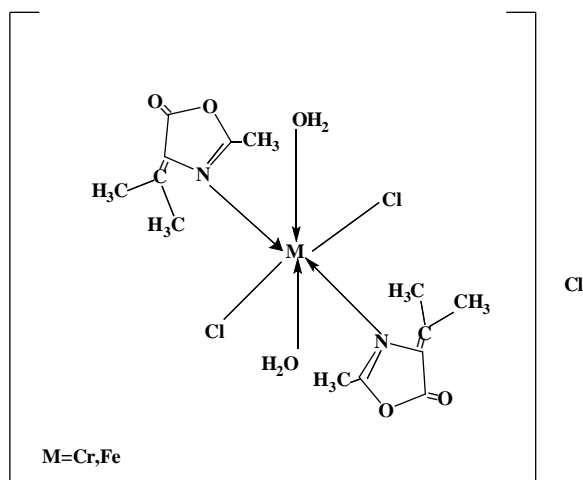
Table 2. Characteristic IR bands (cm^{-1}) of the compounds studied

Compound	$\nu\text{C=N}$	$\nu\text{M-O}$	$\nu\text{M-N}$	Other bands
L	1579	-	-	-
$[\text{Cr L}_2\text{Cl}_2(\text{H}_2\text{O})_2]\text{Cl}$	1565	439	516	$\delta_{\text{H}_2\text{O}}=848$ $\nu_{(\text{H}_2\text{O})}=3387$
$[\text{Mn L}_2\text{Cl}_2]$	1589	432	509	-
$[\text{FeL}_2\text{Cl}_2(\text{H}_2\text{O})_2]\text{Cl}$	1558	433	586	$\delta_{\text{H}_2\text{O}}=830$ $\nu_{(\text{H}_2\text{O})}=3313$
$[\text{CoL}_2\text{Cl}_2]$	1592	456	497	
$[\text{CuL}_2\text{Cl}_2(\text{H}_2\text{O})_2]$	1540	460	501	$\delta_{\text{H}_2\text{O}}=822$ $\nu_{(\text{H}_2\text{O})}=3306$

Electronic spectra, Magnetic susceptibility and Conductivity measurements

Chromium Complex

The dark brown chromium (III) complex with the ligand showed a magnetic moment of (4.8)BM, which indicates a high-spin type octahedral[16]. Electronic spectrum in DMSO solution exhibited two bands attributed at (16474) cm^{-1} and (22222) cm^{-1} , the splitting band is typical octahedral type and can be assigned to ${}^4\text{A}_2\text{g} \rightarrow {}^4\text{T}_{2\text{g}(\text{F})}$, ${}^4\text{A}_2\text{g} \rightarrow {}^4\text{T}_{1\text{g}(\text{F})}$ respectively[16,17]. The molar conductance showed that the complex is ionic[18].



Manganese Complex

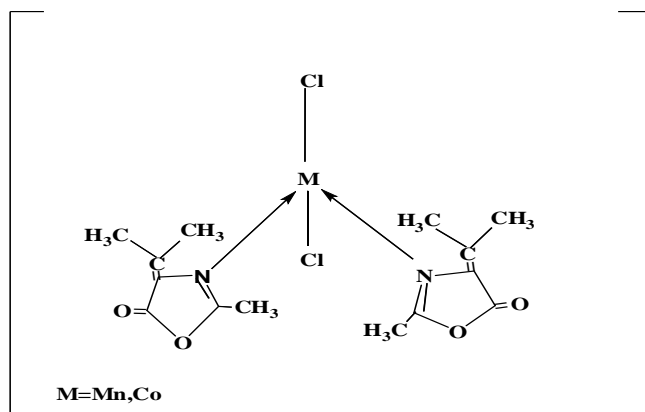
The brown manganese (II) complex with the ligand showed a magnetic moment of (4.72) BM [17,20], which indicates a high-spin type tetrahedral. Electronic spectrum in DMSO solution exhibited one band at (37878) cm^{-1} , this band is typical tetrahedral type and can be assigned to (C.T)[20,21,22]. The molar conductance showed that the complex is non ionic [23].

Iron Complex

The brown iron (III) complex with the ligand showed a magnetic moment of (1.74)BM, which indicates a high-spin type octahedral[16,17]. The electronic spectrum of Fe(III) complex shows two bands at (27322 and 12391) cm^{-1} assignable to (C.T) and ${}^6\text{A}_1\text{g} \rightarrow {}^4\text{T}_1\text{g}(\text{G})$ [23]. The molar conductance showed that the complex is ionic[18] .

Cobalt Complex

The dark green cobalt(II) complex with the ligand showed a magnetic moment of (4.73)BM, which indicates a high-spin type tetrahedral [17,20]. Electronic spectrum in DMSO solution exhibited splitted bands in the 16393, the band is typical tetrahedral type and can be assigned to ${}^4A_2 \rightarrow {}^4T_1(p)$ (ν_3), in addition there is band at $(33940)cm^{-1}$ in the inferred spectrum can be assigned to ${}^4A_2 \rightarrow {}^4T_{2(F)}$ (ν_1) transition [17,22]. The molar conductance showed that the complex is non ionic [23].



Copper Complex

The brown -Reddish copper (II) complex with the ligand showed a magnetic moment of (1.75)BM, which indicates a high-spin type octahedral [16,20]. Electronic spectrum in DMSO solution exhibited one band at $(13755) cm^{-1}$, the splitting band is typical octahedral type and can be assigned to ${}^2T_{2g} \rightarrow {}^2E_g$. [16-17,20]. The molar conductance showed that the complex is non ionic [16,24].

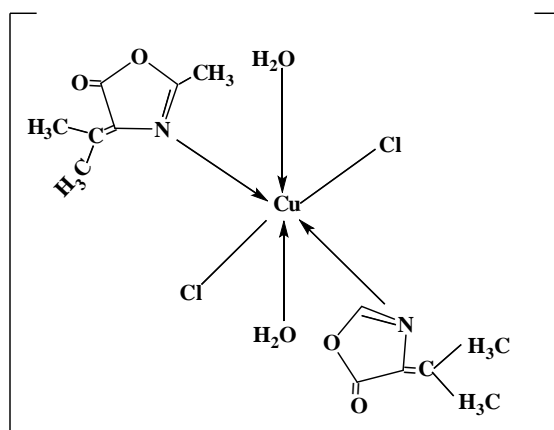


Table3: U v-Visible spectra of free ligand and their complexes in 10^{-3} M in DMF, magnetic moments and molar conductance in DMSO

Comp.	$\lambda_{\max}(\text{nm})$	Wave number (cm^{-1})	(d-d) transitions	Molar conductance $\Delta m(\Omega^{-1} \text{cm}^2 \text{mol}^{-1})$	M_{eff} (BM)
L	267 330	37453 30303	-----	----	---
[Cr L ₂ Cl ₂ (H ₂ O) ₂]Cl	607 450	16474 22222	${}^4A_{2g} \rightarrow {}^4T_{2g}$ ${}^4A_{2g} \rightarrow {}^4T_{1g}$	38.69	4.80
[Mn L ₂ Cl ₂]	264	37878	C.T	18.89	4.72
[FeL ₂ Cl ₂ (H ₂ O) ₂]Cl	366 807	27322 12391	C.T ${}^6A_{1g} \rightarrow {}^4T_{1g(G)}$	36.80	1.74
[CoL ₂ Cl ₂]	610 295	16393 33940	${}^4A_2 \rightarrow {}^4T_{1(p)(v3)}$ ${}^4A_2 \rightarrow {}^4T_{2(F)(v1)}$	16.70	4.73
[CuL ₂ Cl ₂ (H ₂ O) ₂]	727	13755	${}^2T_{2g} \rightarrow {}^2E_g$	14.78	1.75

Electrostatic potential (E.P):

The electrostatic potential has been used to give a simple representation of more important features of molecular [25] reactivity. Therefore, it has been calculated and plotted as 2D and 3D contour for molecule of free ligand, Fig (1) illustrated its contour map.

Optimized geometries, energies and vibrational for ligand and their metal complexes

All theoretically probable structures of metal complexes with ligand have been calculated to search for the most probable model building stable structure Fig (2).

The result of PM3 method of calculation in gas phase for the binding energies and heat of formation of ligand and their metal complexes were calculated to comparison stability free ligand with the metal complexes, are shown in table (4). The vibrational spectra of the free ligand has been calculated in table (5), Fig (3). The theoretically calculated wave number for ligand showed that some deviation from the experimental value, the deviation is generally acceptable in theoretical calculation.

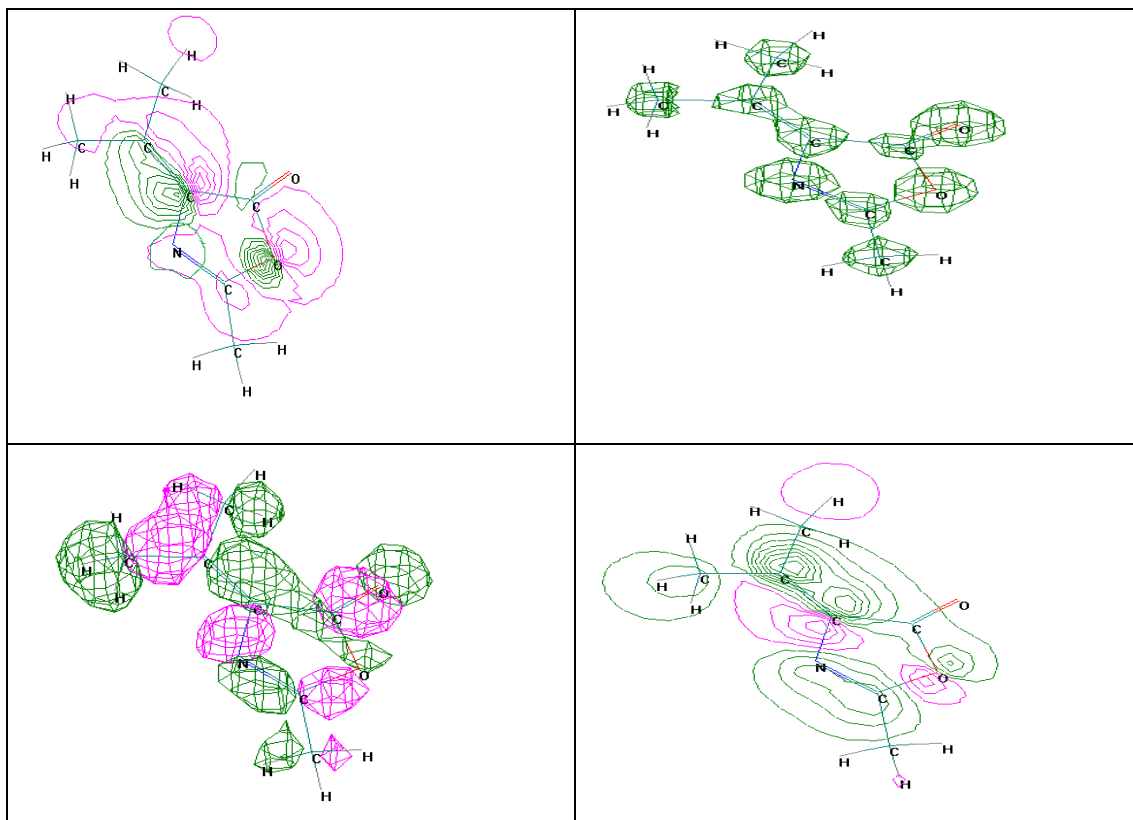
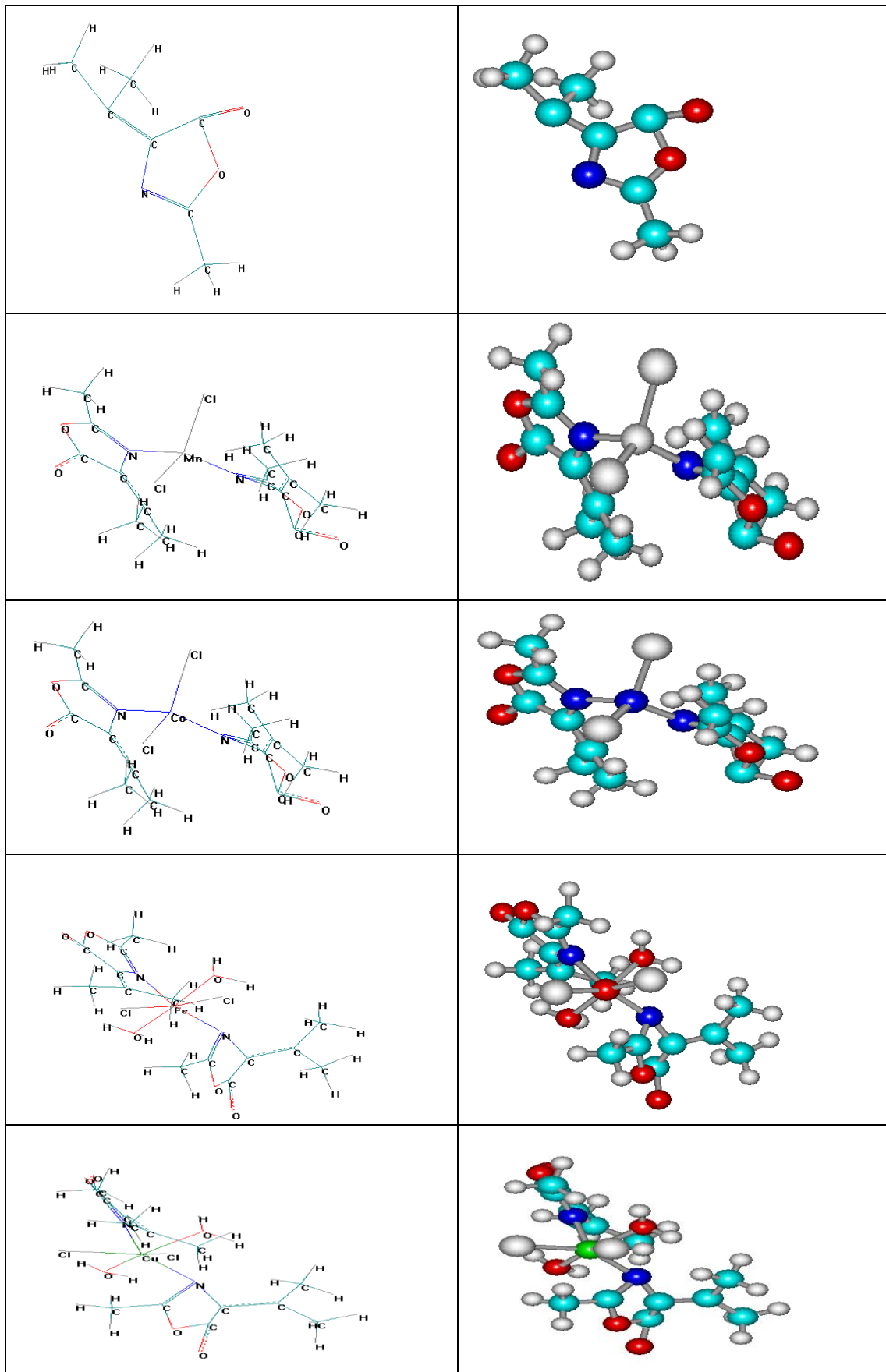


Fig (1): HOMO & Electrostatic potential as 2D and 3D Contours for ligand



Fig(2): conformation structure of L and its complexes

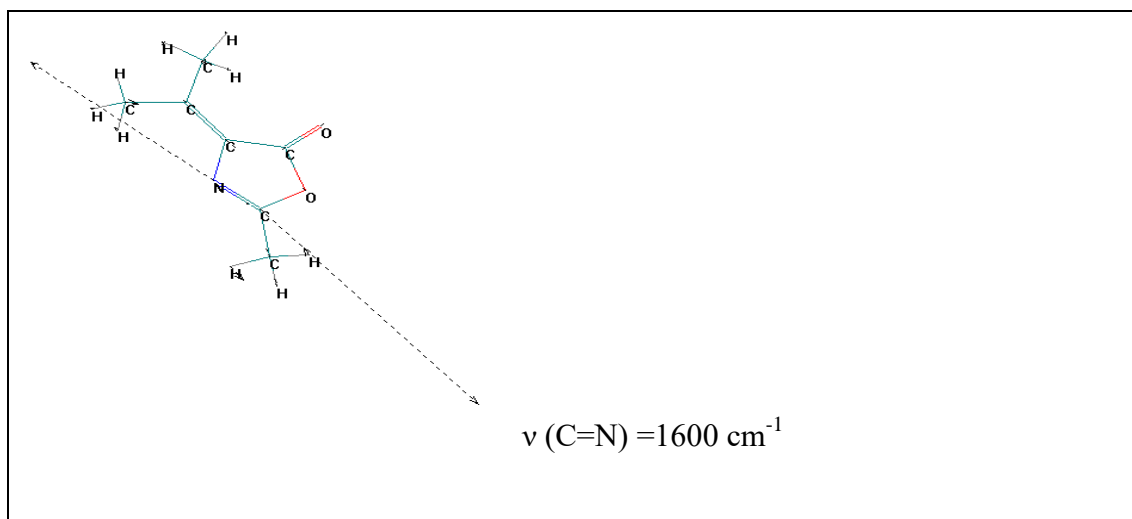


Fig (3): Calculated vibrational frequencies of L

Table (4): Conformation energetic (in $\text{kJ}\cdot\text{mol}^{-1}$) for (L) and their metal complexes.

Conformation	PM3	
	ΔH_f°	ΔE_b
L	-64.0319059	-1961.2979059
[Cr L ₂ Cl ₂ (H ₂ O) ₂]Cl	-345.2133370	-4568.1493370
[Mn L ₂ Cl ₂]	-222.6018287	-4871.6458287
[FeL ₂ Cl ₂ (H ₂ O)]Cl	-399.4087415	-5658.8527415
[CoL ₂ Cl ₂]	-474.5727319	-7589.7712681
[CuL ₂ Cl ₂ (H ₂ O) ₂]	-311.2602399	-4519.8962399

Table (5): Comparison of experimental and theoretical vibrational frequencies(cm^{-1}) for Ligand

COMP.	$\nu \text{ C}=\text{N}$
L	(1579)* (1600)** (-1.32)***

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

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