Synthesis and Characterization of Transition Metals Ions Complexes with 2-Thioxoimidazolidin-4-One Schiff Base as Ligand

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Abstract

Mn(II), Co(II), Ni(II), Cu(II), and Cr(III) metal complexes with the ligand (L) [3-(2-nitro benzylidene) amino-2-thioxoimidazolidin-4-one] have been prepared and characterized in their solid state using the elemental micro analysis (C.H.N.S), flame atomic absorption, UV-Vis spectroscopy, FT-IR, magnetic susceptibility measurements, and electrical molar conductivity. The ratio of metal to ligand [M:L] was got for all complexes in the ethanol by using the molar ratio method, which produced comparable results with those results obtained for the solid complexes. From the data of all techniques, octahedral geometry was proposed for Cr(III), Mn(II), and Co(II) complexes, while tetrahedral structure was proposed for Ni(II), Cu(II) complexes.

Keywords: Synthesis, Characterization, Bidentate Schiff Base, Transition Metal Complexes.

Introduction

Many Schiff base compounds of thiosemicarbazones and their complexes have been widely used and applied in biological, analytical, and pharmaceutical activities [1-3]. Studies of many Imidazol derivatives and their important heterocyclic complexes have been examined for their important biological activities like antibacterial, antifungal, anti-inflammatory, and analgesic [4]. However, these compounds have been variously used in the spectrophotometric determination of the metal ions. Therefore, many of those reagents give intense colors when react with the ions of transition metal [5]; providing probes that some of them can coordinate to rare earth ions also, forming the metal complexes whose interesting structures [6].

In the present paper, the preparation of Schiff base derivative [3-(2-niro benzylidene) amino -2-thioxoimidazolidin-4-one] (L) was used as ligand that provides two sites “potential donor” to produce some transition metal ions. (L) ligand and its complexes have been completely characterized.

Experimental

All the used chemicals were analytical annular and were highly pure.

The Physical Measurements and Analysis

The melting points were measured using Gallen Kamp melting point instrument and were uncorrected. While, FT-IR spectrum was measured using Shimadzu-8300 spectrophotometer at the range (4000-400 cm^{-1}). UV-Vis. Spectrum was recorded on UV-1650-PC-Shimadzu spectrophotometer at room temperature. Furthermore, all these measurements were measured on a concentration of 10^{-3}M of the complex in absolute ethanol as a solvent. The elemental (C.H.N.S) analysis was performed on an EM-017 mth instrument. The atomic absorption of the prepared complexes was measured using “Shimadzu Atomic Absorption 680 Flame” spectrophotometer. Moreover, the conductivity measurements were recorded on W.T.W. conductivity meter. All these measurements were got in “DMF” as a solvent using the concentration of (10^{-3}M) at 25°C. The measurements of magnetic susceptibility were got at 25°C in solid state using Faraday’s method at “Bruker BM6” instrument.

Synthesis

1- Synthesis of 2-nitro benzylidene thiosemicarbazone (1)

A mixture of compound 2-nitro benzaldehyde (1.51 g, 0.01 mole) with thiosemicarbazide (0.91 g, 0.01 mole) was refluxed for 4 hrs. in the absolute ethanol (20 ml), the solvent was segregated, the solid product was collected and crystalized [7].

2- Synthesis of [3-(2-nitrobenzylidene) amino-2- thioxoimidaz-olidin-4-one] (2)

Mixture of the compound (1) (2.24 g, 0.01 mole) and (1.22 g, 0.01 mol) of ethylchloroacetate in (30 ml) of absolute ethanol and then sodium acetate (0.03 mole) was added. Afterwards, the mixture refluxed for 20 hrs. and cooled down to room temperature. The resulting solid recrystallized, and the prepared ligand physical properties are described in (Table 1). The structure of the proposed ligand is shown in scheme (1).

3- Synthesis of Complexes (C_1-C_5):

Ethanol solution of each one of the following quantities of the metal ion salts (1mmol) (0.266, 0.198, 0.238, 0.237, 0.170) g of [$CrCl_3.6H_2O$, $MnCl_2.4H_2O$, $CoCl_2.6H_2O$, $NiCl_2.6H_2O$, and $CuCl_2.2H_2O$] was respectively added to ethanol solution (1mmole, 0.264 g) of (L) with continuous stirring. The mixture then heated with reflux for 2 hrs. Over this time, a precipitate starts forming, which was filtered, washed with water, recrystallized from the ethanol, and then dried using the oven at 50°C for one hour. The prepared complexes physical data are shown in (Table 1).

Results and Discussion

Characterization of ligand (L) along its complexes was achieved by:

(A) The Elemental Micro Analysis

(L) and its metal complexes physical and analytical data are shown in (Table 1), which came in satisfactory agreement with the calculated values. The suggested molecular (formulas) are also supported with the subsequent spectra and the molar ratio, besides the magnetic moment.

(B) Studying the Formation of Complex in Solution

(L) complexes with the metal ions were thoroughly studied in the solution using the ethanol as a solvent to determine the ratio of [M:L] in the complex by depending the molar ratio method [8, 9]. A number of solutions were prepared whose a constant concentration (10^{-3}M) for metal ion and (L). The ratio of [M:L] was set depending on the relationship between the light absorption and the [M:L] mole ratio. The complexes results of formation in solution suggested [1:1] metal to ligand for [C_1-C_5] that were comparable to those got in the study of solid state, (Table 1).

(C) ^{1}H-NMR Spectra

The spectrum data of the free ligand (L) in DMSO-d^6 solution was reported along with the possible assignments in experiment. The NMR spectrum of the proton showed peaks at (8.8) ppm (s, 1*H*, N=CH), (7.9-8.2) ppm (S, 4*H*, phenyl-NO_2), (4.1-4.2) ppm (m, -CH_2), and (12.3) ppm (1*H*, bs, NH) [11]. The number of protons calculated from integration curves and the recorded chemical shifts in (Figure 1) reveal the proposed structure of the formed ligand (L).

(D) Infrared Spectroscopic Study

FT-IR spectra provided good information about complex behavior of the ligand with varied metal ions. The distinctive frequencies of the ligand and its metal complexes have been assigned in comparison to the values found in literature [10]. The structure of the ligand was affirmed by υ(C=O, C=S) imidazole stretching vibrations presence at (1728, 1201) cm^{-1} besides the band that appeared at (1631) cm^{-1} due to the azomethine group υ(C=N) [11], (Table 2), (Figure 2). With all complexes (C_1-C_5), the ligand (L) behaves as bidentate that coordinate to metal ion throw carbonyl imidazole oxygen and the azomethine group nitrogen; so the bands of ($\upsilon_{C=O}$, and $\upsilon_{C=N}$) were consequently shifted to lower frequencies [12], but the band at (1201) cm^{-1} of $\upsilon_{C=S}$ mode remained without change in all complexes, (Table 2).

Moreover, these observations were indicated by (υ_{M-N}, υ_{M-O} and υ_{M-Cl}) appearance at (543-536) cm^{-1}, (470-455) cm^{-1} and (316-324) cm^{-1} respectively [12], (Table 2). Also, there is a broad band observed nearly at (3464-3406)cm^{-1} and weak band range at (952-

940) cm^{-1} in the complexes spectra that assigned to a ($\upsilon_{O\text{-}H}$) suggested water molecules presence in the complexes [11], (Figure 3).

(E) Studying of Electronic Spectra, Magnetic Moment, Conductance:

The ligand (L) UV spectrum mostly showed two intense absorption peaks at $48543 cm^{-1}$ and $34482 cm^{-1}$, which belong to $\pi \to \pi^*$, and $n \to \pi^*$ respectively [11], (Table 3), (Figure 4). The ligand metal complexes electronic spectra were measured for their solution in the absolute ethanol at the range (200-1100) nm, whereas the molar conductance was measured in dimethyl formamide (DMF) as a solvent.

$[Cr(L)(H_2O)_2Cl_2]Cl$: The electronic spectrum of Chromium (III) complex showed three absorption peaks in the region (15408, 21691, and 28571) cm^{-1}, respectively, which attributed to ($^4A_2g \to {}^4T_2g_{(F)}$, $^4A_2g \to {}^4T_1g_{(F)}$, and $^4A_2g \to {}^4T_1g_{(P)}$) transitions. These peaks positions are in a good agreement with octahedral geometry that are reported [13]. Additionally, the magnetic moment μeff., which is measured at room temperature was (3.82 B.M) that reveals high-spin inner-orbital octahedral stereo chemistry for the ligand around Cr(III) metal ion [14], (Figure 6). Furthermore, the conductivity in (DMF) demonstrated that the complex is ionic [1:1], (Table 3).

$[Mn(L)(H_2O)_2Cl_2]$: The electronic spectrum of Mn(II) complex showed absorption bands at (16891, 27173) cm^{-1} due to the transitions $^6A_1g \to {}^4T_1g_{(G)}$, $^6A_1g \to {}^4T_2g_{(D)}$, respectively, indicating octahedral geometry [15]. The measured magnetic moment μeff. of Mn(II) complex is (5.18 B.M) which corresponds to five unpaired electronic indicates high-spin octahedral environment [16], (Table 3). Measuring the conductivity in (DMF) demonstrated that this complex has non-conductive behavior, (Figure 7).

$[Co(L)(H_2O)_2Cl_2]$: The electronic spectrum of Co(II) complex showed three peaks at (14858, 16528, and 30303) cm^{-1} assignable to $^4T_1g \to {}^4A_2g_{(F)}$, $^4T_1g \to {}^4T_1g_{(P)}$, and C.T transitions, respectively, (Table 3), (Figure 5) for an octahedral geometry [17]. Moreover, the magnetic moment μeff. of this complex in the sold state (4.50 B.M) suggests a high-spin octahedral geometry [18]. Furthermore, measuring the conductivity in (DMF) demonstrated that this complex has a non-conductive behavior, (Figure 7).

$[Ni(L)(H_2O)Cl]$: The electronic spectra of Ni(II) complex appears at (32786) cm^{-1} and this attributed to the charge transfer transition (C.T). in addition, the other peak which appears at (27397 cm^{-1}) can be attributed to to ($^3T_1 \to {}^1T_2$) electronic transition, what suggests a tetrahedral geometry [19] around Ni ion. The magnetic measurement μeff. of the solid complex (3.21 B.M) demonstrated two unpaired electrons for Ni(II) ion which again suggests a tetrahedral geometry for Ni(II) complex [20]. Measuring the conductivity in (DMF) shows that this complex is ionic [1:1], (Table 3), (Figure 8).

$[Cu(L)(H_2O)Cl]Cl$: The electronic spectra of Co(II) complex demonstrated a peak at (3205) cm^{-1} which refers to (C.T) transition, while the peak that appears at (12658) cm^{-1} is attributed to ($^2T \to {}^2E$) electronic transition. However, these transitions indicate that the complex has a tetrahedral geometry [21, 22]. Moreover, the value of measuring the magnetic moment is (1.87 B.M), what corresponds to one unpaired electron. Furthermore, measuring the conductivity in (DMF) demonstrated that the complex has electrolyte behavior [1:1], (Table 3), (Figure 8).

Suggested Structure for the Complexes [C_1-C_5]

According to the obtained results from the elemental and spectral analyses, besides measuring the magnetic moment and conductivity, the above mentioned compounds suggested structures can be explained as follows: Figure(6), Figure(7) and Figure(8).

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Table (1): Ligand (L) and its Metal Complexes Physical Data

Compound No.	Color	M. p. °C	M.Wt g/mol	M:L in EtOH	%Elemental Analysis Found (Calc.)				Metal M% Found (Calc.)	Suggest Formula
					C	H	N	S		
(L)	Light Brown	197	264	-	45.15 (45.45)	3.40 (3.03)	21.45 (21.21)	12.38 (12.12)	-	$C_{10}H_8N_4O_3S$
C_1	Green	247d*	458.5	1:1	26.51 (26.17)	2.33 (2.61)	12.00 (12.21)	6.68 (6.98)	11.97 (11.34)	$[Cr(L)(H_2O)_2Cl_2]Cl$
C_2	Pale Brown	280d*	426	1:1	28.62 (28.16)	2.57 (2.81)	13.48 (13.14)	7.59 (7.51)	12.40 (12.91)	$[Mn(L)(H_2O)_2Cl_2]$
C_3	Dark Green	275d*	430	1:1	27.46 (27.90)	2.35 (2.79)	13.41 (13.02)	7.64 (7.44)	13.23 (13.72)	$[Co(L)(H_2O)_2Cl_2]$
C_4	Yellow	202d*	411.7	1:1	29.40 (29.14)	2.69 (2.42)	13.28 (13.60)	7.39 (7.77)	14.02 (14.25)	$[Ni(L)(H_2O)Cl]Cl$
C_5	Green	270d*	416.5	1:1	28.53 (28.81)	2.48 (2.40)	13.09 (13.44)	7.46 (7.68)	15.66 (15.24)	$[Cu(L)(H_2O)Cl]Cl$

d*= decomposition.

Table (2): Ligand (L) and its Metal Complexes Characteristic Stretching Vibration Frequencies (cm^{-1}) Located in the FT-IR

Compound No.	$\upsilon_{C=O}$	$\upsilon_{C=N}$	$\upsilon_{C=S}$	M-O	M-N	M-Cl
(L)	1728	1631	1201	-	-	-
C_1	1627	1562	1201	543	470	320
C_2	1627	1566	1207	543	474	324
C_3	1643	1566	1203	536	462	316
C_4	1647	1570	1203	540	455	320
C_5	1627	1566	1203	543	455	316

Table (3): Ligand (L) and its Metal Complexes (C_1-C_3) Electronic Spectra, Conductance in (DMF) and Magnetic Moment (B.M)

Compound No.	Bands Cm^{-1}	Assignment	Molar Cond. $ohm^{-1}.cm^{2}.mol^{-1}$	μeff. B.M	Suggested Structure
(L)	48543 34482	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$	-	-	-
C_1	15408 21691 28571	${}^4A_2g \longrightarrow {}^4T_2g_{(F)}$ ${}^4A_2g \longrightarrow {}^4T_1g_{(F)}$ ${}^4A_2g \longrightarrow {}^4T_1g_{(P)}$	70.62	3.82	Octahedral
C_2	16891 27173	${}^6A_1g \longrightarrow {}^4T_1g_{(G)}$ ${}^6A_1g \longrightarrow {}^4T_2g_{(D)}$	19.35	5.18	Octahedral
C_3	14858 16528 30303	${}^4T_1g \longrightarrow {}^4A_2g_{(F)}$ ${}^4T_1g \longrightarrow {}^4T_1g_{(P)}$ C.T	16.48	4.50	Octahedral
C_4	27397 32786	${}^3T_1 \longrightarrow {}^1T_2$ C.T	87.94	3.21	Tetrahedral
C_5	12658 32051	${}^2T \longrightarrow {}^2E$ C.T	76.25	1.87	Tetrahedral

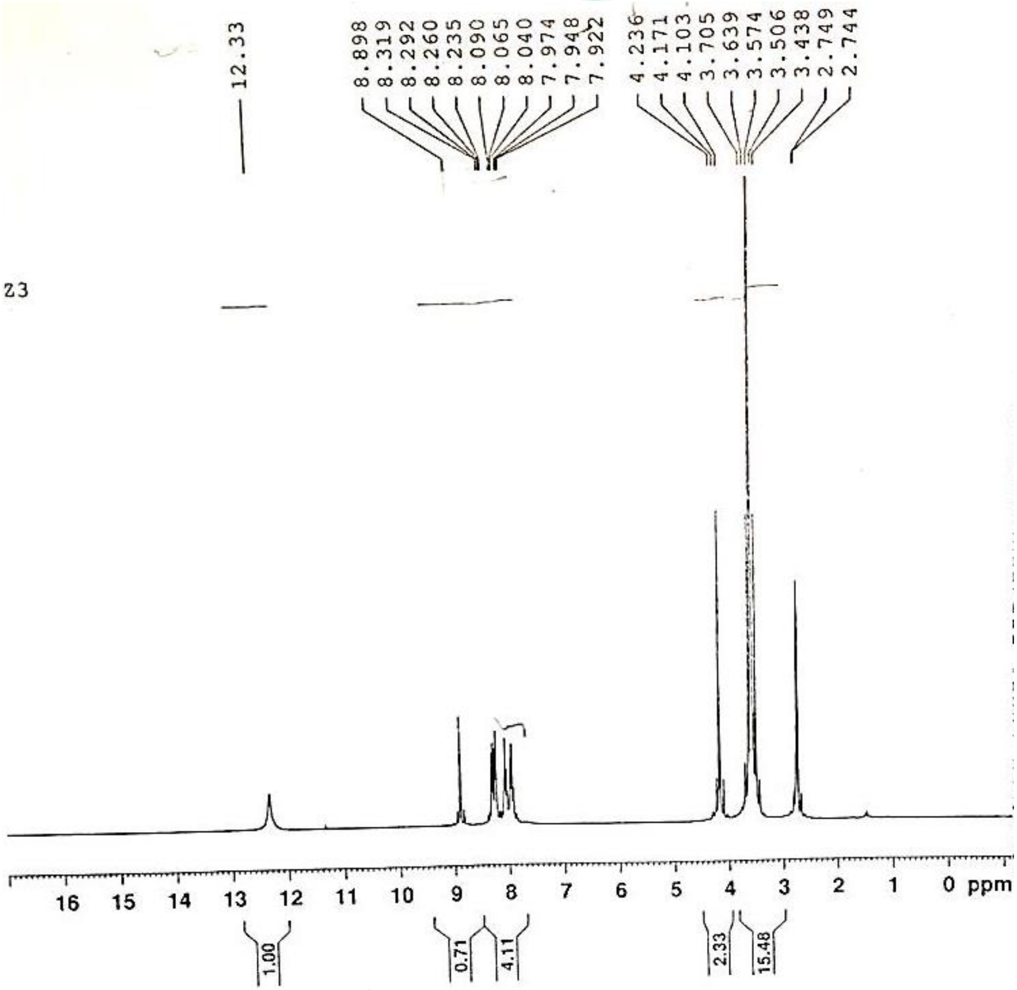


Figure (1): The ^{1}H-NMR Spectrum of the Ligand (L)

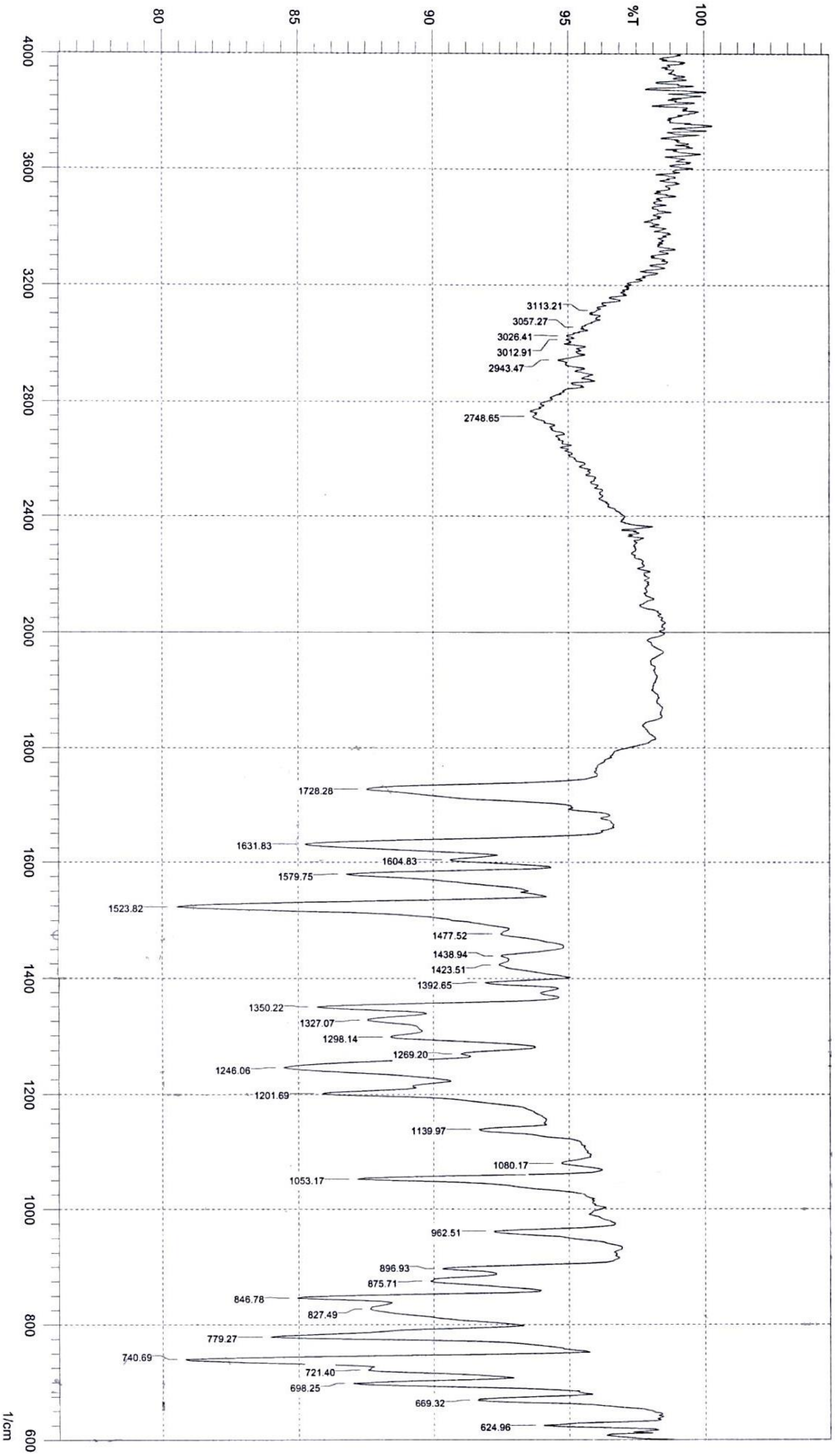


Figure (2): Ligand (L) FT-IR Spectra

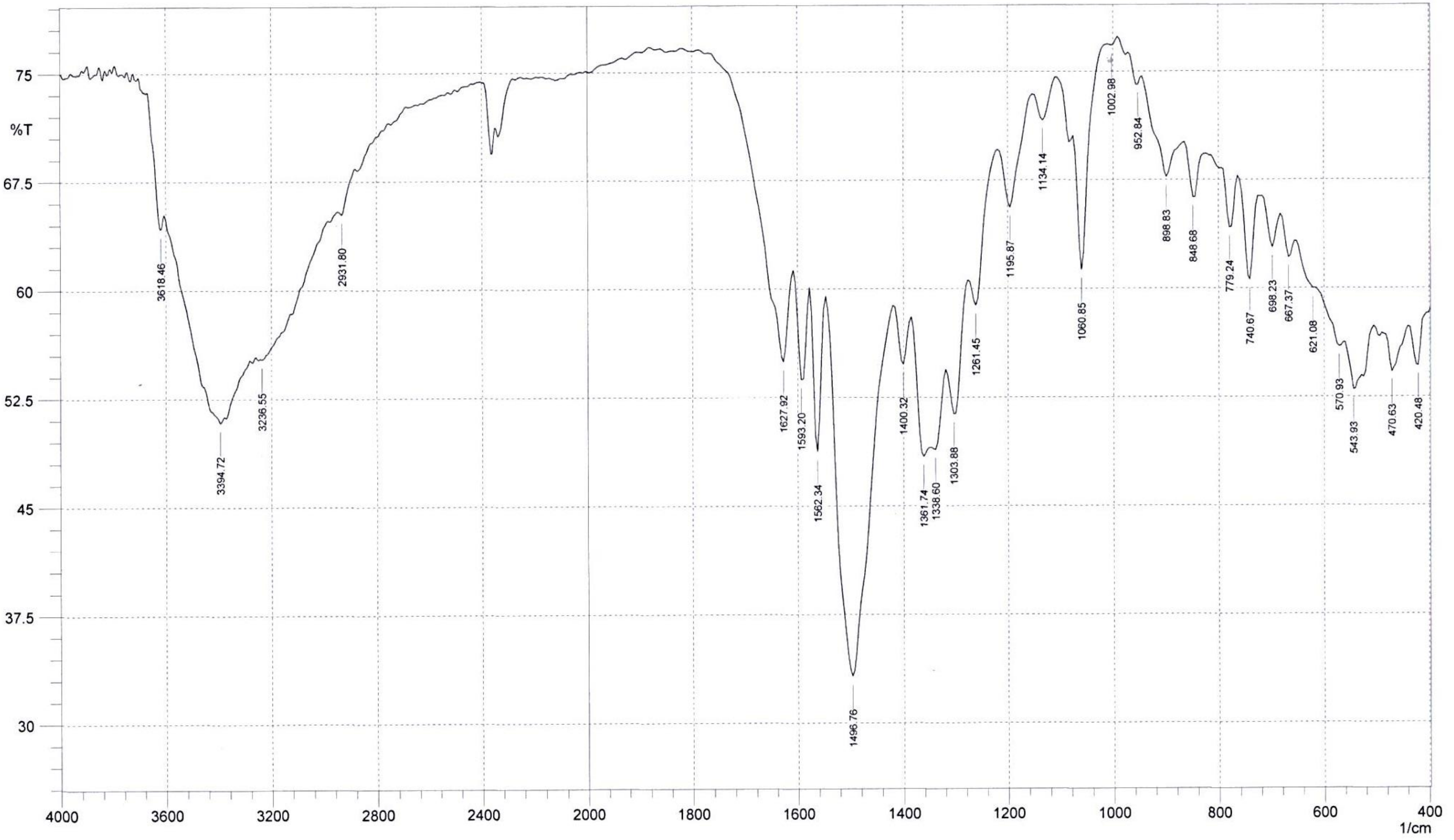


Figure (3): Cr Complex FT-IR Spectra

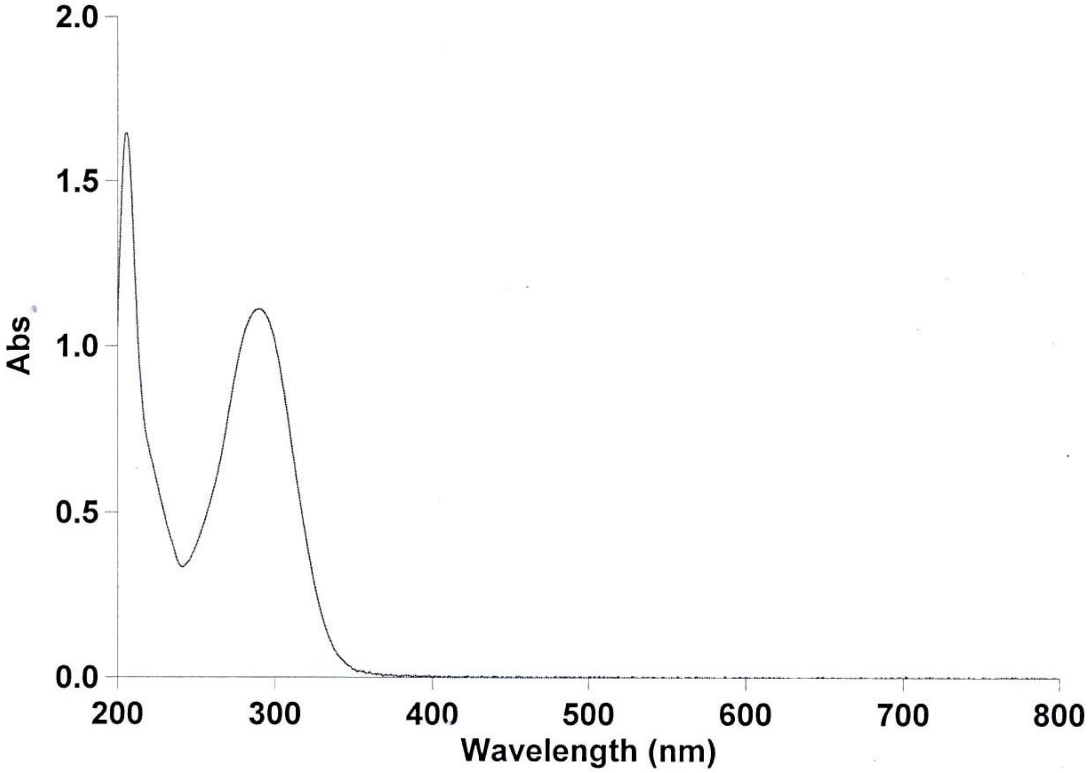


Figure (4): Ligand (L) Electronic Spectrum

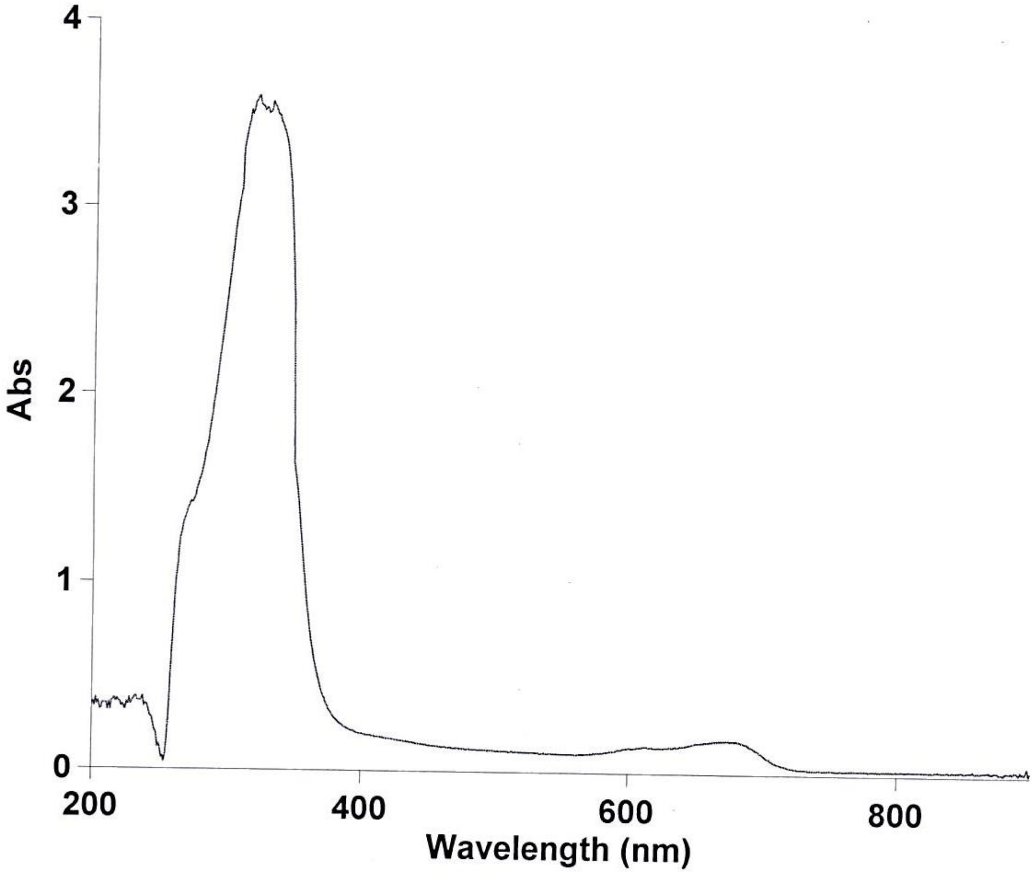


Figure (5): Co Complex Electronic Spectrum

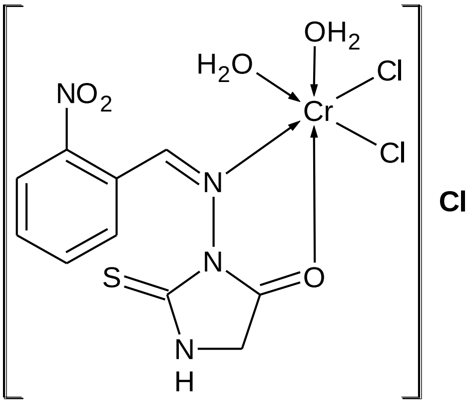


Figure (6): Octahedral Stereo Chemical Structure Suggested for Cr(III) Complex $[Cr(C_{10}H_8N_4O_3S)(H_2O)_2Cl_2]Cl$

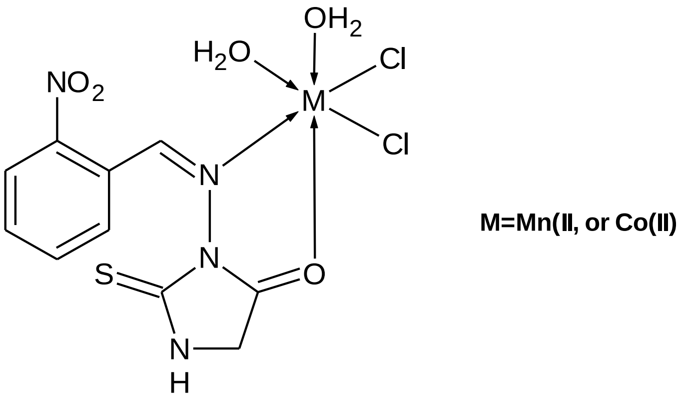


Figure (7): Octahedral Stereo Chemical Structure Suggested for M(II) Complex $[M(C_{10}H_8N_4O_3S)(H_2O)_2Cl_2]$

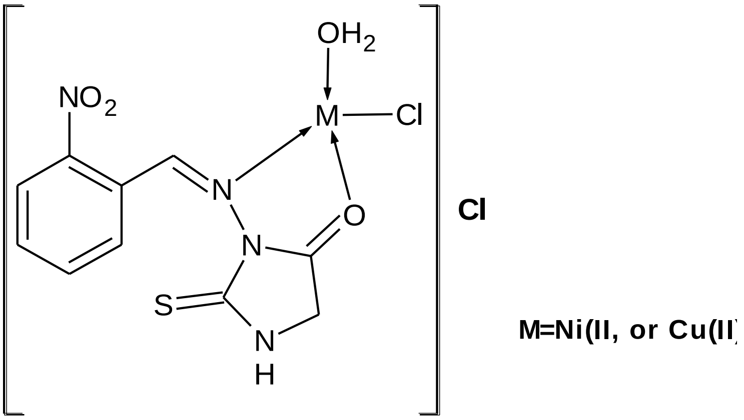
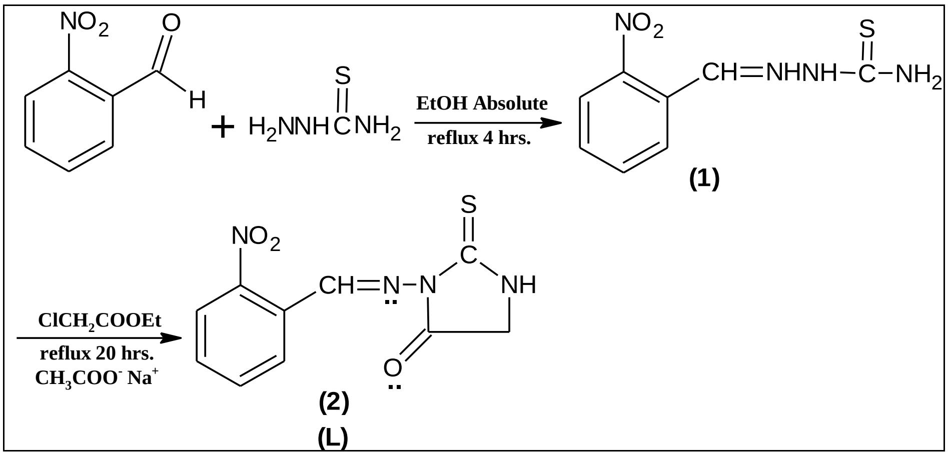


Figure (8): Tetrahedral Stereo Chemical Structure Suggested for M(II) Complex $[M(C_{10}H_8N_4O_3S)(H_2O)\ Cl\ ]Cl$



Scheme (1): General Steps of Preparation of Ligand (L)

تحضير وتشخيص معقدات بعض المعقدات لأيونات العناصر ألانتقاليه لليكند 2-ثايوأوكسوإمادازولدين-4-أون كقواعد شف

سنان مدحت البياتي
أنعام مجيد رشيد
إيناس زهير محمد
زينة خضير حسن
أمجاد غالي
أمل محمد حسين
قسم الكيمياء/ كلية العلوم/ الجامعة المستنصرية

استلم في:21/كانون الأول/2015، قبل في:30/اذار/2016

الخلاصــة

حضر وشخص الليكاند
[3-(2-nitrobenzylidene)amino-2-thioxoimidazolidin-4-one]
ومعقداته مع بعض أيونات عناصر الكروم (III)، المنغنيز (II)، الكوبالت (II)، النيكل (II) والنحاس (II) باستعمال الطرائق الفيزيائية المناسبة مثل تقنية الامتصاص الذري اللهبي والتحليل الدقيق للعناصر (C.H.N.S) وطيف الأشعة تحت الحمراء والأشعة فوق البنفسجية-المرئية إضافةً إلى قياسات التوصيلية الكهربائية والحساسية المغناطيسية. وعينت النسبة المولية بين الليكاند والفلز باستعمال طريقة النسب المولية ووجد أنها مستقرة عند النسب المولية [1:1]. من التحاليل السابقة أقترح الشكل ثماني السطوح لمعقدات الكروم والمنغنيز والكوبالت، أما معقدي النيكل والنحاس فقد اقترح الشكل رباعي السطوح.

الكلمات المفتاحية: تخليق تشخيص قواعد شف ثنائية ألسن معقدات العناصر الانتقالية.