Synthesis and Spectroscopic of Some new Metal Ions Complexes's with [N-(4-Methoxy Benzoyl Amino)-Thioxo Methyl] Leucine

Basima M. Sarhan
Hassan A. Hassan
Bushra M. Fayyadh
Dept. of Chemistry/ College of Education For Pure Science(Ibn-Al Haitham)/ University of Baghdad

Received in :10 June 2013, Accepted in : 24 July 2013

Abstract

A new ligand [N-(4-methoxy benzoyl amino)-thioxo methyl] leucine (MBL) was prepared from the reaction of (4-methoxy benzoyl isothiocyanate with leucine acid in molar ratio (l:l), it was characterized by elemental analysis (C.H.N.S), FT-IR, UV-Vis, ^{1}H and ^{13}C-NMR. The complexes of the bivalent ions (Mn, Fe, Co, Ni, Cu, Zn, Cd and Hg) have been prepared and characterized too.

The structural was established by elemental analysis (C.H.N.S), FT-IR, UV-Vis spectra, conductivity measurements atomic absorption and magnetic susceptibility and determination of molar ration (M:L). The complexes showed characteristic behavior of tetrahedral geometry around the metal ions except with (Cu) complex showed square planer.

Key words: 4-Methoxy benzoyl isothiocyanate, leucine, complexes.

Introduction

Amino acids and their derivatives have been used for different purposes[1-3] and some amino acid derivatives and some of their metal complexes have been prepared[4], other derivatives have potential biological activity and had been evaluated as having anti bacterial, antifungal properties[5]. Safael and coworkers[6] were reported the synthesis and characterization of glycine derivative of bis(phenol) amine ligand and its complexes with iron(III), and new metal complexes derived from the reaction of N-benzoyl-N-glythiourea with Cu(II), Co(II), Ni(II), Zn(II) and Fe(II) ions have been synthesized[7].

Recently a new series of potential ligands [N-(sebacoyl amino)-thioxo methyl] amino acid (HL) where HL = histidine, L-glutamic acid, L-tryptophan, and L-lysine with Cu(II), Co(II) and Ni(II) ions were synthesized and characterized[8]. This work includes preparation of some new transition metals complexes of [N-(4-methoxy benzoyl amino)-thioxo methyl] leucine.

Experimental

Chemicals: All reagents were Analar or chemical pure grade by BDH, Merck and Fluka. Materials: (4- Methoxy benzoyl chloride, luciene acid) (Fluka). Mangesis chloride tetrahydrate ($MnCl_2.4H_2O$), Ferous chloride ($FeCl_2$), Cobalt chloride hexahydrate ($CoCl_2.6H_2O$), Nickel chloride hexahydrate ($NiCl_2.6H_2O$), Copper chloride dihydrate ($CuCl_2.2H_2O$), Zinc chloride ($ZnCl_2$), Cadmium chloride hydrate ($CdCl_2.H_2O$) and Mercury chloride ($HgCl_2$).

Instruments

^{1}H and ^{13}C-NMR was recorded using Ultra Shield 300 MH$_Z$ Switzerland at University of Al al-Bayt, Jordan. Melting point was recorded by using Stuart-melting point apparatus. FT-IR spectra were recorded as KBr disc using 3800 Shimadzu in the range of 4000-400 cm^{-1}. Electronic spectra were obtained using UV-160 Shimadzu spectra photometer at 25 °C in 10^{-3}M DMSO. Conductivity was measured by using Philips PW. Digital. Elemental analyses (C.H.N.S) were performed using acrlo Erba 1106 elemental analyzer. Magnetic susceptibility measurements were obtained by Balance magnetic susceptibility by model MSB-MKI. Metal contents of the complexes were determined by atomic absorption technique by using shimadzu (AA680G).

Preparation of the ligand (MBL)

1- Preparation of the (4-methoxy benzoyl isothiocyanate)[4]

Mixture of 4-methoxy benzoyl chloride (3.55ml, 1mmole) and ammonium thiocyanate (2g, 1mmole) in 25ml acetone was refluxed with stirring for 3 hours and then filtered; the filtrate was used for further reaction.

2- Preparation of [N-(4-methoxy benzoyl amino)-thioxo methyl] leucine (MBL)

(3.44g, 1mmole) of leucine acid in 20ml acetone were rapidly added to the solution (20 ml) to the solution was refluxed for 6 hours. The resulting solid was collected, washed with acetone and recrystallized from ethanol (m.p. = 190-192 °C), yield 72%, %C found (56.00) while calculate (55.55), %H found (6.11) while calculate (6.17), %N found (9.85) while calculate (8.64) and %S found (10.00) while calculate (9.87).

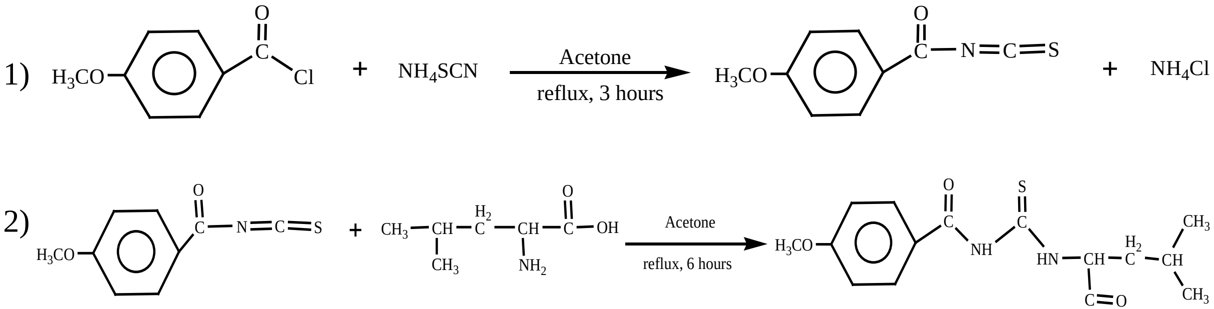
Synthesis of the metal complexes

(0.648g, 2mmole) of ligand (MBL) was dissolved in 25ml of ethanol containing (0.12g, 2mmole) of KOH, then the solution of following metal salts $MnCl_2.4H_2O$ (0.2g, 1mmole), $FeCl_2$ (0.13g, 1mmole), $CoCl_2.6H_2O$ (0.24g,1mmole), $NiCl_2.6H_2O$ (0.24g, 1mmole), $CuCl_2.2H_2O$ (0.2g,1mmole), $ZnCl_2$ (0.14g, 1mmole), $CdCl_2.H_2O$ (0.2g, 1mmole) and $HgCl_2$ (0.3g, 1mmole) in ethanol, were added dropwise to the solution of the ligand (MBL^-K^+). The precipitate formed immediately after stirring the mixture at room temperature for 2 hours. The precipitate was collected by filtration, washed with distilled water and ethanol and dried under vacuum. Physical properties were given in Table (1).

Results and Discussion

Synthesis and physical properties of the ligand [N-(4-methoxy benzoyl amino)-thioxo methyl leucine (MBL).

The ligand was obtained by the reaction of one mole of (4-methoxy benzoyl isothiocyanate) with one mole of leucine acid scheme (1).



Scheme (1): Preparation of the ligand [N-4-methoxy benzoyl amino)-thioxo methyl] leucine (MBL)

Elemental analysis (C.H.N.S) confirmed the purity of the ligand (MBL) with the formula ($C_{15}H_{20}N_2O_4S$).

The ^{1}H and ^{13}C-NMR spectrum of new ligand

The ^{1}H-NMR spectrum (in $CDCl_3$ as a solvent) of ligand (MBL), Fig. (1) showed the following signals: doublet at δ(0.97-1.01) ppm for (6H, $2CH_3$), Multiplet at δ(1.18-1.71) ppm for (1H, CH($CH_3)_2$), triplet at δ(1.85-1.87) ppm for (2H, CH_2), doublet at δ(2.17-2.19) ppm for (1H, NH sec.amine), singlet at δ(3.84) ppm for (3H, OCH_3), quartet at δ(5.08-5.10) ppm for (1H, CHCOOH), two doublet pairs at δ(6.90-8.02) ppm for (4H, aromatic), singlet at δ(9.35) ppm for (1H, NH sec. amide) and singlet at δ(11.20) ppm for (1H, COOH).

The ^{13}C NMR spectrum (in $CDCl_3$ as a solvent) of ligand (MBL), Fig. (2) showed the following signals: signals at δ(19.62-20.26) ppm for ($2CH_3$), signal at δ(22.09-24.55) ppm for ($CH(CH)_3$), signal at δ(38.06)ppm for (CH_2), signal at δ(51.23-53.10) ppm for (OCH_3), signal at δ(54.42) ppm for (CHCOOH), signals at δ(74.20-75.04) ppm for the solvent ($CDCl_3$), signals at δ(103.13-161.42) ppm for (C) aromatic, signal at δ(164.22) ppm for (C=O sec. amide), signal at δ(173.76) ppm for (COOH) and signal at δ(178.12) ppm for (C=S).

FT-IR spectrum of the ligand

FT-IR spectrum of the free ligand (MBL), Fig. (3) showed bands due to υ(OH), υ(NH) amide, υ(C=O) and υ(C=S) which were observed at (3346) cm^{-1}, (3238) cm^{-1}, (1685) cm^{-1} and (1257) cm^{-1} respectively while another absorption band appeared at (1728) cm^{-1} could be explained as $υ(COO)_{asym}$ were the $υ(COO)_{sym}$ was noticed at (1309) cm^{-1}[9-10].

The FT-IR spectra of complexes

These spectra exhibited a marked difference between bands belonging to the stretching vibration of υ(NH) of the amine group in the range between (3423-3332) cm^{-1} shifted to higher frequencies by (185-94) cm^{-1} suggesting the possibility of the coordination of ligand through the nitrogen atom at the amine group[11] absorption assigned for $υ(COO)_{sym}$ was noticed at the range (1473-1354) cm^{-1} shifted to higher frequencies by (164-45) cm^{-1} while the band caused by $\upsilon(COO)_{asym}$ appeared between (1629-1535) cm^{-1} shifted to lower frequencies by (193-99) cm^{-1} which indicates to the coordination of the carboxylic group to the central ion[12].

The stretching vibration band $\upsilon(C{=}O)$ and $\upsilon(C{=}S)$ either show no change or very little in their frequencies (1653-1604) cm^{-1} and (1263-1253) cm^{-1} respectively, therefore indicating to do not coordinate to the metal ions[13].

Metal-nitrogen and metal-oxygen bands were confirmed by the presence of the stretching vibration of υ(M-O) and υ(M-N) around (559-430) cm^{-1} and (514-414) cm^{-1} respectively. Table (2) describes the important bands and assignments for free ligand (MBL) and its complexes. Fig. (4) showed the FTIR spectrum of [Ni(MBL)].

Electronic spectral

The UV-Visible spectrum of the ligand (MBL), Fig. (5) in DMSO solution exhibited absorption band at (300nm, 33333cm^{-1}) which is due to $n \longrightarrow \pi^*$ transition[14].

The UV-Visible spectrum of Mn^{+2} complex showed two bands at (288nm, 34722cm^{-1}) and (796nm, 12562 cm^{-1}) are due to the C.T ligand filed and $^6A_1 \longrightarrow {}^4T_{2(D)}$ respectively[15]. The UV-Visible spectrum of Fe^{+2} complex, Fig. (6) shows bands at (264nm, 37878 cm^{-1}) and (628nm, 15923cm^{-1}) due to charge transfer (C.T) and $^5E \longrightarrow {}^5T_2$[16].

The UV-Visible spectrum of Co^{+2} complex gave four bands at (275nm, 36363cm^{-1}), (450nm, 22222cm^{-1}), (657nm, 15220cm^{-1}) and (1009nm, 9910cm^{-1}) attributed to (C.T), $^4A_2 \xrightarrow{V3} {}^4T_{1(P)}$, $^4A_2 \xrightarrow{V2} {}^4T_{1(F)}$, $^4A_2 \xrightarrow{V1} {}^4T_{2(F)}$ respectively and the rach interelectronic repulsion parameter (B^-) was found to be (514.13) cm^{-1}, from the relation $\beta = B^- / B_o$ was found to be equal (0.51). These parameters are accepted to Co(II) tetrahedral complex[17].

The UV-Visible spectrum of N^{+2} has revealed the following electronic transitions, C.T, $^3T_{1(F)} \xrightarrow{V3} {}^3T_{1(P)}$, $^3T_{1(F)} \xrightarrow{V2} {}^3A_2$ and $^3T_{1(F)} \xrightarrow{V1} {}^3T_{2(F)}$ transition at(291nm, 34364cm^{-1}) (400nm, 25000 cm^{-1}), (723nm, 13831cm^{-1}) and (971nm, 10298cm^{-1}) respectively, the B^- value found to be (529.13) cm^{-1} while (β) was equal to (0.51). These are characteristic for tetrahedral complexes of Ni (II)[18]. Cu^{+2} complex appeared bands at (278nm, 35971cm^{-1}), (663nm, 15082cm^{-1}) and (811nm, 12330cm^{-1}) are due to C.T, $^2B_{1g} \longrightarrow {}^2A_{1g}$ and $^2B_{1g} \longrightarrow {}^2B_{2g}$ transitions respectively[19]. The UV-Visible spectra of Zn^{+2}, Cd^{+2} and Hg^{+2} complexes showed shifted bands compared[20] with free ligand (MBL) are due to charge transfer Table (3).

The molar conductance of all complexes in DMSO was found to be low which indicates the non-electrolyte behavior of these complexes. The μ_{eff} value of Mn, Fe, Co, Ni and Cu complexes are in the range (5.91, 5.11, 4.76, 2.82 and 1.73) B.M. respectively, the physical properties of the ligand (MBL) with their metal complexes are given in Table (1).

Study of complexes formations in solution

Complexes of ligand (MBL) with metal ions were studied in the solution using ethanol as a solvent in order to determine [M/L] ratio in complexes follow molar ratio method[21], A series of solutions were prepared having a constant concentration (10^{-3}M) of metal ion and ligand. The [M/L] ratio determined from the relationship between the absorption of the absorbed light and the mole ratio of [M/L].

The results of complexes in ethanol suggest that the metal to ligand ratio was [1:2] for all complexes which were similar to that obtained from solid state study.

According to spectral data as well as those obtained from elemental analyses the chemical structure of the complexes may be suggested as tetrahedral for $[M(MBL)_2]$ where M^{+2} = Mn, Fe, Co , Ni, Zn, Cd and Hg), Fig. (7) while copper complex has square planer.

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Table (1): Physical properties for free ligand and its complexes

Complex	M. w t	Color	M.p˚C or dec.	M% Calculate (Found)	Molar conductivity ohm^{-1} cm^{2} mole^{-1}	μ_{eff} (B.M.)
Ligand (MBL)	324	Yellow	190 -192˚C	-	4	-
$[Mn(MBL)_2]$	702.94	Deep-yellow	238(dec.)	7.83 (8.01)	7	5.90
$[Fe(MBL)_2]$	703.85	Brown	162(dec.)	7.95 (8.01)	13	5.10
$[Co(MBL)_2]$	706.93	Deep-Brown	170(dec.)	8.35 (8.33)	20	4.75
$[Ni(MBL)_2]$	706.71	Deep-Green	164(dec.)	8.33 (9.01)	13	2.82
$[Cu(MBL)_2]$	711.54	Green	166˚C	8.95 (9.41)	14	1.73
$[Zn(MBL)_2]$	713.37	Yellow	160˚C	9.18 (9.13)	12	0
$[Cd(MBL)_2]$	760.4	Yellow	170˚C	14.82 (14.37)	20	0
$[Hg(MBL)_2]$	848.6	Yellow	150˚C	23.69 (23.12)	21	0

Table (2): the characteristic infrared band for the ligand and its complexes

Complex	$\upsilon(COO)_{asym}$	$\upsilon(COO)_{sym}$	υ(N-H)	υ(M-N)	υ(M-O)
Ligand (MBL)	$1728_{(m)}$	$1309_{(s)}$	$3238_{(m)}$	-	-
$[Mn(MBL)_2]$	$1629_{(m)}$	$1398_{(m)}$	$3423_{(b)}$	$416_{(w)}$	$478_{(m)}$
$[Fe(MBL)_2]$	$1628_{(m)}$	$1400_{(s)}$	$3361_{(b)}$	$416_{(w)}$	$441_{(w)}$
$[Co(MBL)_2]$	$1535_{(m)}$	$1458_{(s)}$	$3429_{(b)}$	$418_{(w)}$	$443_{(w)}$
$[Ni(MBL)_2]$	$1604_{(s)}$	$1455_{(s)}$	$3363_{(b)}$	$424_{(w)}$	$489_{(w)}$
$[Cu(MBL)_2]$	$1610_{(m)}$	$1473_{(m)}$	$3332_{(b)}$	$414_{(w)}$	$439_{(w)}$
$[Zn(MBL)_2]$	$1575_{(m)}$	$1465_{(m)}$	$3405_{(b)}$	$418_{(w)}$	$513_{(m)}$
$[Cd(MBL)_2]$	$1604_{(m)}$	$1413_{(s)}$	$3387_{(m)}$	$514_{(w)}$	$559_{(w)}$
$[Hg(MBL)_2]$	$1602_{(m)}$	$1354_{(s)}$	$3410_{(b)}$	$416_{(w)}$	$430_{(w)}$

Where: s = strong, m = medium, w = weak, b = broad

Table (3): UV-Visible absorption for the ligand (MBL) and its complexes in DMSO

10^{-3}M

Complex	λ (nm)	υ (cm^{-1})	Є max ($L.mol^{-1} cm^{-1}$)	Assignment
Ligand (MBL)	300	33333	2397	$n \longrightarrow \pi^*$
$[Mn(MBL)_2]$	288 796	34722 12562	2057 10	C.T ${}^6A_1 \longrightarrow {}^4T_{2(D)}$
$[Fe(MBL)_2]$	264 628	37878 15923	409 20	C.T ${}^5E \longrightarrow {}^5T_2$
$[Co(MBL)_2]$	275 450 657 1009	36363 22222 15220 9910	1559 60 22 10	C.T ${}^4A_2 \xrightarrow{V3} {}^4T_{1(P)}$ ${}^4A_2 \xrightarrow{V2} {}^4T_{1(F)}$ ${}^4A_2 \xrightarrow{V1} {}^4T_{2(F)}$
$[Ni(MBL)_2]$ V_1 V_2	291 400 723 971	34364 25000 13831 10298	1968 75 16 10	C.T (ligand filed) ${}^3T_1 \xrightarrow{V3} T_{1(P)}$ ${}^3T_1 \xrightarrow[\text{Mixed C.T.}]{V2} {}^3A_2$ ${}^3T_1 \xrightarrow{V1} {}^3T_{2(F)}$
$[Cu(MBL)_2]$	278 663 811	35971 15082 12330	1950 44 24	C.T ${}^2B_{1g} \longrightarrow {}^2A_{1g}$ ${}^2B_{1g} \longrightarrow {}^2B_{2g}$
$[Zn(MBL)_2]$	291	34364	2072	C.T
$[Cd(MBL)_2]$	291	34364	2076	C.T
$[Hg(MBL)_2]$	289	34602	2122	C.T

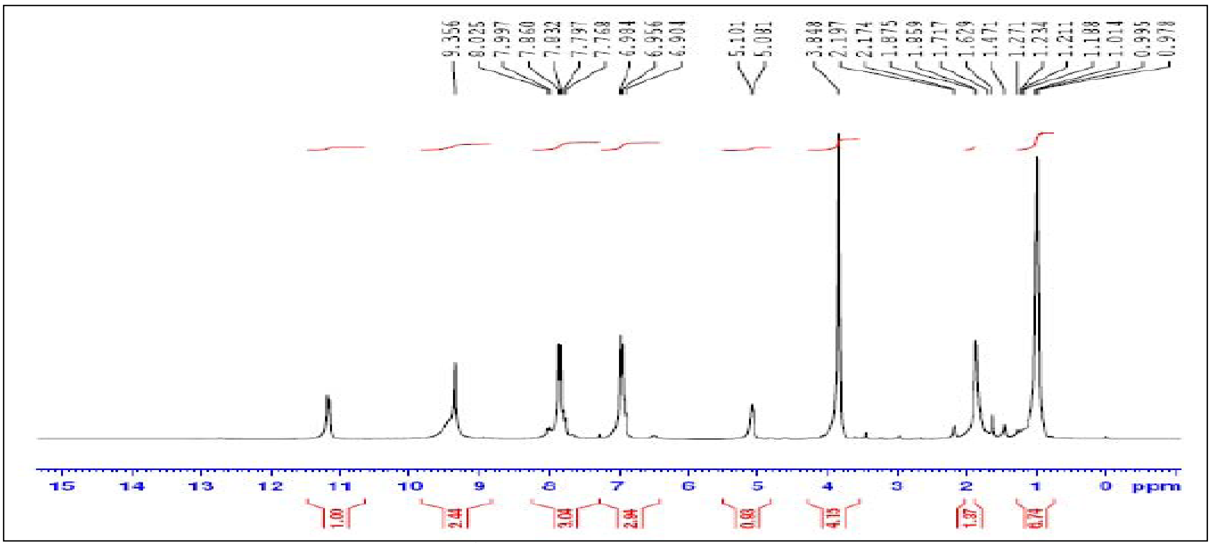

Figure No. (1): ^{1}HNMR spectrum of ligand (MBL)

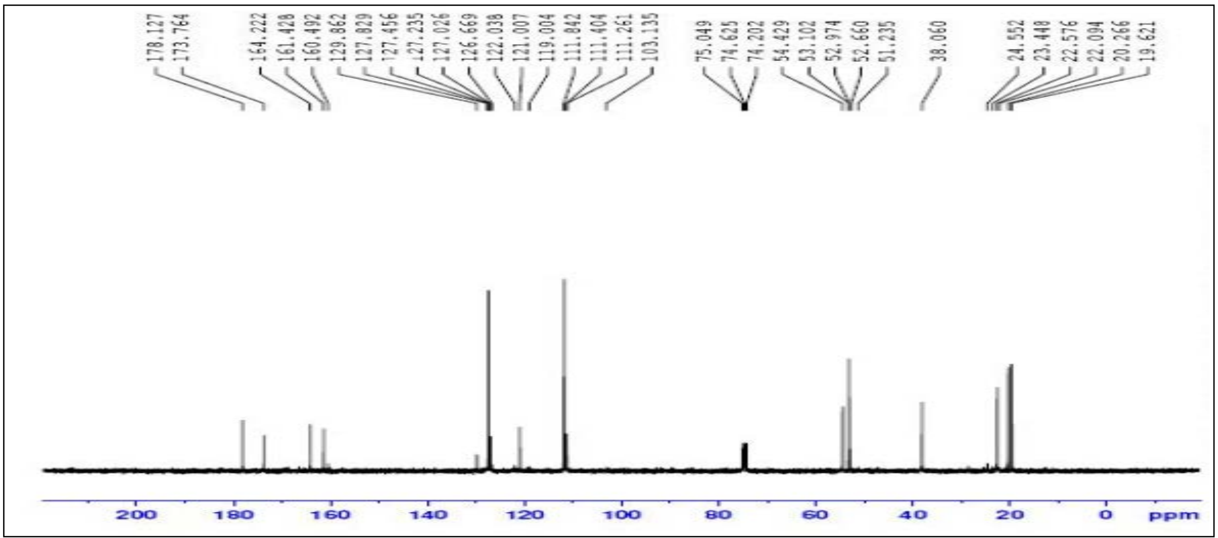

Figure No. (2): ^{13}CNMR spectrum of ligand (MBL)

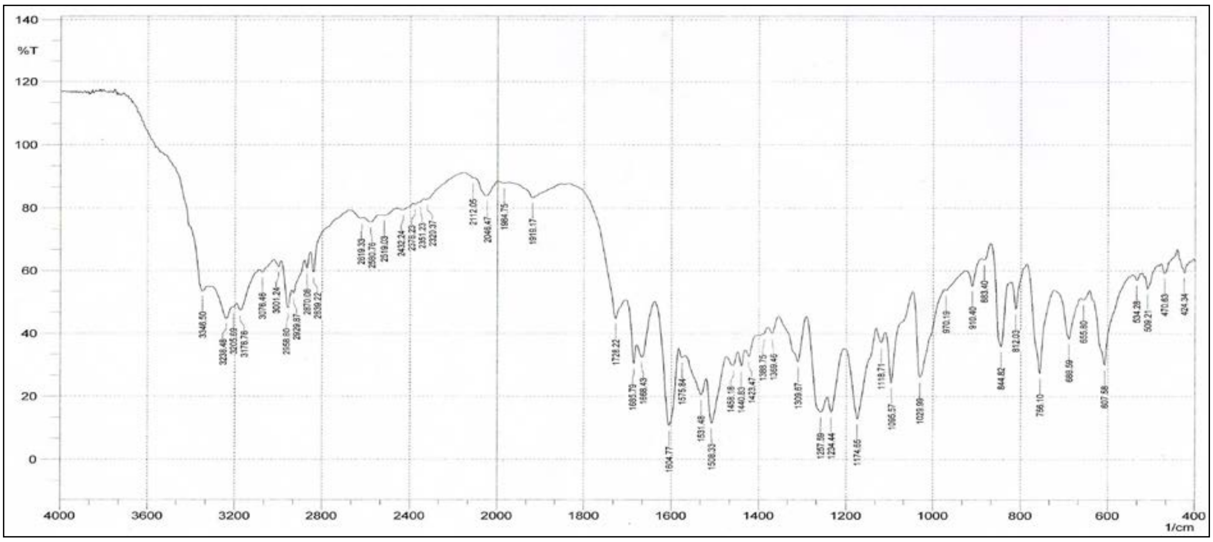

Figure No. (3): FTIR spectrum of ligand (MBL)

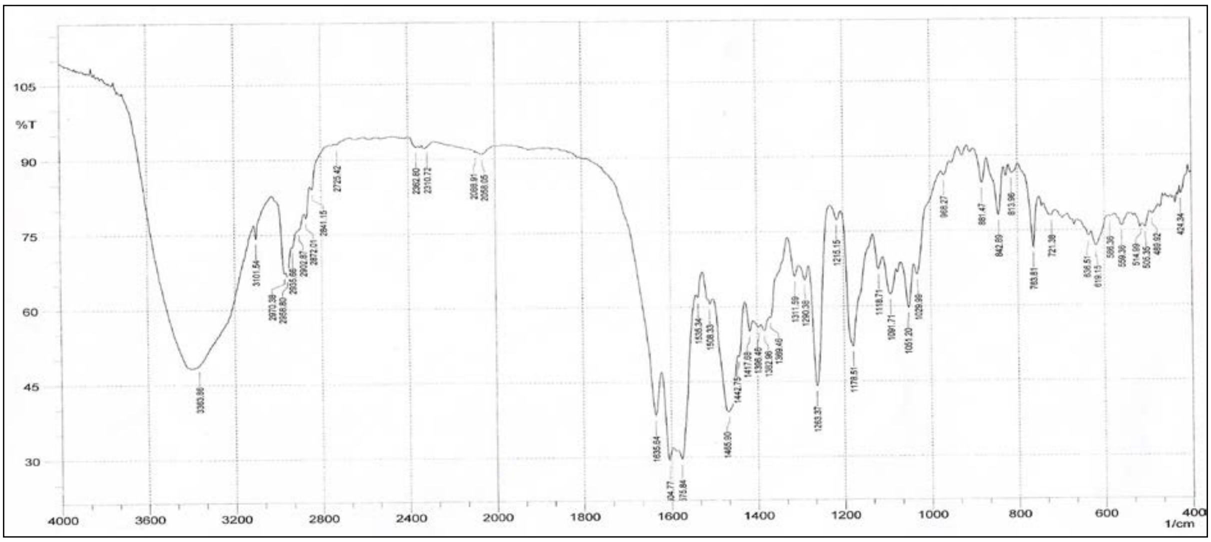

Figure No. (4): FTIR spectrum of $[Ni(MBL)_2]$

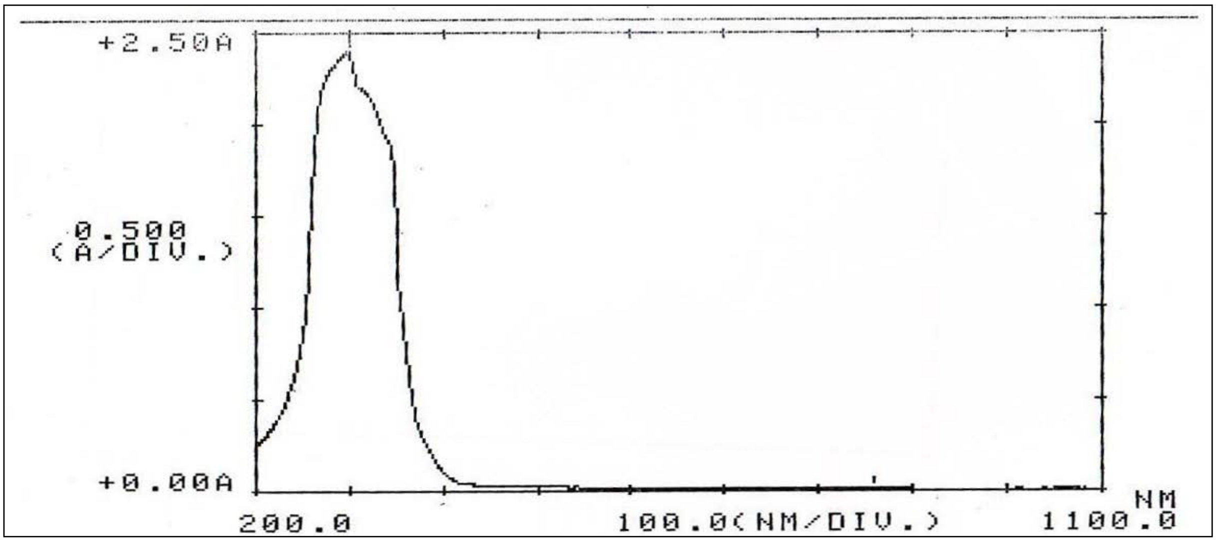

Figure No. (5): Electronic spectrum of ligand (MBL)

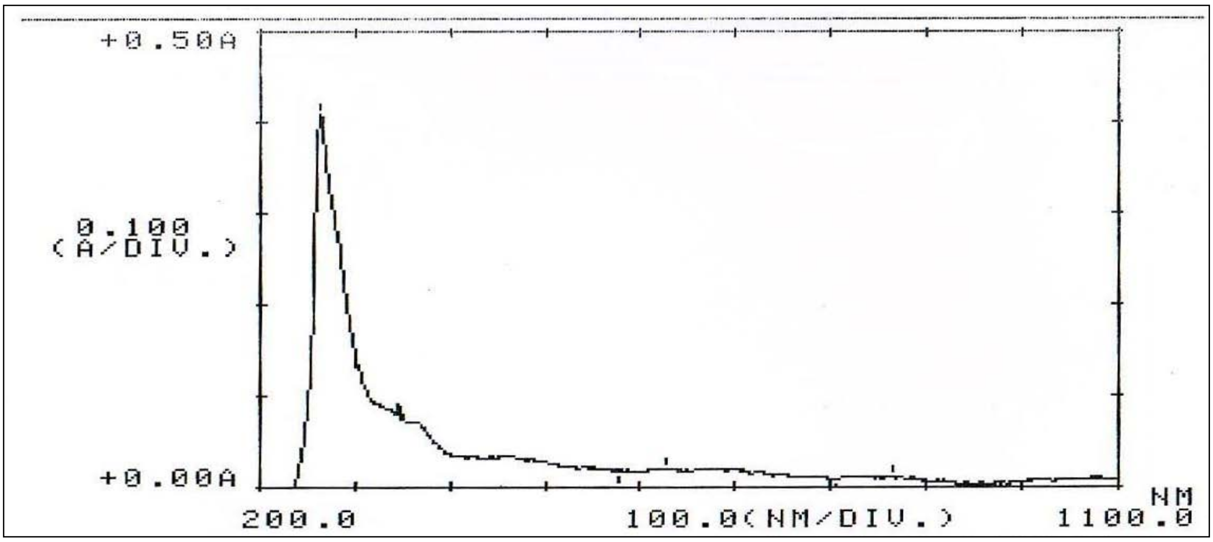

Figure No. (6): Electronic spectrum of $[Fe(MBL)_2]$

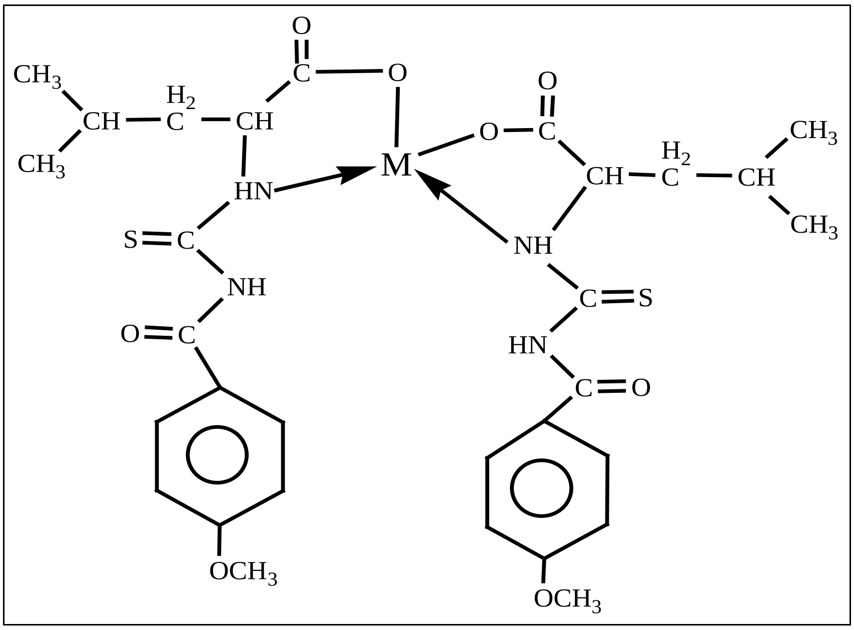

Figure No. (7): Suggested structure of complexes [M(MBL)$_2$] where M^{+2} = [Mn, Fe, Co, Ni, Zn, Cd, Hg]

تحضير ودراسة طيفية لبعض المعقدات الفلزية الجديدة مع [N– (4 - ميثوكسي بنزويل أمينو– ثايواوكسو مثيل)] ليوسين

باسمة محسن سرحان
حسن احمد حسن
بشرى مخلف فياض
قسم الكيمياء / كلية التربية للعلوم الصرفة (ابن الهيثم) / جامعة بغداد

استلم البحث في : 10 حزيران 2013 ، قبل البحث في : 24 تموز 2013

الخلاصة

حضر الليكاند الجديد (MBL) (N-(4- ميثوكسي بنزويل أمينو- ثايواوكسو مثيل) ليوسين وذلك من مفاعلة (4- ميثوكسي بنزويل ايزوثايوسيانات) مع الحامض الاميني الليوسين وبنسبة (1:1) وشخص بوساطة التحليل الدقيق للعناصر (C.H.N.S) والأشعة تحت الحمراء والأشعة فوق البنفسجية - المرئية وطيف الرنين النووي المغناطيسي. كما حضرت وشخصت معقدات أملاح بعض ايونات العناصر الانتقالية الثنائية التكافؤ (Mn, Fe, Co, Ni, Cu, Zn, Cd, Hg) مع الليكاند (MBL) وشخصت المعقدات المحضرة باستخدام الأشعة تحت الحمراء والأشعة فوق البنفسجية - المرئية والتوصيلة المولارية والحساسية المغناطيسية والامتصاص الذري وتحليل النسبة المولية واستنتج من التحاليل إن المعقدات لها شكل رباعي السطوح حول الايون الفلزي مع الليكاند (MBL) ثنائي السن ما عدا (Cu) معطيا الشكل المربع المستوي.

الكلمات المفتاحية: 4- ميثوكسي ايزوثايوسيانات، المعقدات الفلزية، ليوسين