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Synthesis and spectroscopic studies of new leucine acid derivative with their metal complexes.

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ABSTRACT

A new ligand N-[(acetyl amino)-thioxo methyl]leucine(ATL) are synthesized by reaction of acetyl-isothio cyanate with leucine acid. The ligand is characterized by elemental analysis, FT-IR and NMR spectra, some transition metal complex of this ligand were prepared and characterized by FT-IR, UV-visible spectra, conductively measurements, magnatic suscpility, atomic absorption and determination of molar ration(M:L). from results obtained, the following formaula [M(ATL)2] where M+2 =(Mn, Fe, Co, Ni, Cu, Zn, Cd and Hg) and the proposed molecular structure for these complexes as tetrahedral geometry.

Introduction

Complexes of amino acids play an essential role for exploring various bio chemical processes or to remove metal toxicity from biological systems[1] Nasser and coworkers[2] reported the synthesis and characterization of Schiff base complexes derived from [2.acetyl pyridine] and leucine with Cu(II), Co(II), Ni(II), Cr(III) and Fe(III). Shaesta and coworkers[3] study the determination of the formation constant of Cu(II), Zn(II), Cd(II), Hg(II) and Pb(II) with N-acetylcysteine by using potentialmetric method. the molar[4] enthalpies of formation of the crystalline form of bis(glycinate)lead(II), bis(DL-alaninate)lead(II), bis(DL-valinate)lead(II), bis(DL-valinate)zinc(II) and bis(DL-valinate)cadmium(II) were determind. Safael and coworkers[5] were reported the synthesis and characterizion of glycine derivative of bis(phenol) amine ligand and its complexes with iron(III) and also[6] new β-aminoacrylic acid Ni(II) complex has been developed and used for the synthesis of α-alkyl-β amino acids via alkylation with alkyl halides under operation ally convenient conditions. We have invstigated in this paper the preparation and properties of some new metal ion complexes with new ligand N-[(acetylamino)-thioxmethyl]leucine(ATL).

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Experimental

Chemicals

Metal salts (MnCl2.4H2O, FeCl2, CoCl2.6H2O, NiCl2.6H2O, CuCl2.2H2O, CdCl2.H2O and HgCl2) were obtained from fluka, Mercke, leucine acid, acetyl chloride and ammoniumthiocyanate(Fluka).

Instrumentations

1H NMR was recorded using Ultra Shield 300 MHz Switzerland,at university of Al al-Bayt, Jordan, melting point was recorded by using stuat-Melting point apparatus, FTIR spectra were recorded as KBr discs using 3800 shimadzu in the range of 4000-400cm-1. Electronic spectra were obtained using uv-160 shimadzu spectrophotometer at 25℃ in 10-3M DMSO. Conductivity were measured by using Philips pw.Digital.Elemental analyses C.H.N.S were performed using acarlo Erba 1106 elemental analyzer.Magnetic susceptibility measurements were obtained by Balance magnetic suscepitiblity by model MSB-MKI. Metal contents of the complexes were determined by atomic absorption technique by using Shimadzu (AA680G).

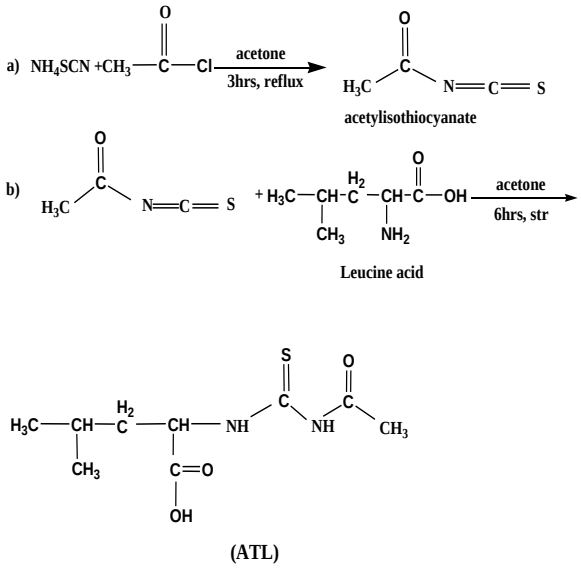
preparation of the ligand(ATL)

a)preparation of the acetyl isothiocyanate[7]

Mixture of acetyl Chloride(2ml,1mmole) and ammoniumthiocyanate(2gm,1mmole) in 25ml acetone was refluxed with stirring for 3hours and then filtered, the filtrate was used for further reaction.

b)preparation of[N-(acetyl amino)-thioxo methyl] leucine(ATL) (3.41gm , 1mmole) of leucine acid in

20ml acetone were rapidly added to the solution to the solution was refluxed for 6 hours, The resulting solid was collected, washed with acetone and recystalized from ethanol(m.p=150-152)℃, yield=80% scheme(1) %C (46.97) while calc 46.55, %H found (6.94) while calculate 6.89, %N found (12.65) while calculate 12.06 and %S found (14.22) while calculate 13.79.



Scheme(1) synthesis route for the preparation ligand(ATL) [N-acetyl amino - thioxo methyl] Leucine

General method for preparation of the complexes

(0.464g,2mmole) of the ligand(ATL) was dissolved in (25ml) of ethanol containing (0.112g,2mmole) of KOH. a solution(5ml) of (1mmole) metal salte (MnCl2.4H2O, FeCl2, CoCl2.6H2O, NiCl2.6H2O, CuCl2.2H2O, CdCl2.H2O and HgCl2) (0.2g, 0.126g, 0.236g, 0.236g, 0.17g, 0.2g and 0.270g) respectively. In ethanol(10ml) was added dropwise to the mixture, and the precipitate formed immediately, after stirring the mixtur at room temperature for 3hours, the precipitate was collected by filtration, washed with ethanol and dried.

Results and Discussion

The physical properties of the ligand(ATL)with their metal complexes are given in table (1) the lower value of molar conductivity in DMSO, indicates the non electrolyte behavior of these complexes.

Spectral studies

1H NMR spectrum for the ligand(ATL) fig(1)showed the following signals:doublet(d) at δ(0.9)ppm for (6H,2CH3), triplet(t) at δ(1.3)ppm for (2H,CH2), multiplet(m) at δ(1.4-2)ppm for (1H,CH(CH3)2), singlet(s) at δ(2.1)ppm for (3H,CH3CO), quartet(q) at δ(2.3-2.5)ppm for (1H,CHCOOH), doublet(d) at δ(4.2)ppm for (1H,NHamine), singlet(s) at δ(7.27)ppm for impurity of solvent(CDCl3), singlet(s) at δ(8.9)ppm for(1H,NH sec.amide), singlet(s) at δ(10.7)ppm for (1H,COOH).

Infrared spectra

The characteristic vibrations and assignments of ligand(ATL)and their complexes as KBr disc are described in table(2). The spectrum of free ligand(ATL) fig(2) exhibited astrong band at(3332)cm-1 this could be attributed to υ(N-H) overlap with υ(OH). While the strong band at(1701)cm-1, which belong to υ(COO)asym and the other bands ν(OCO)sym and υ(C=S)were found at(1385)cm-1 and (1165)cm-1 respectively [8][9]. The FT-IR spectra of the prepared complexes fig(3)exhibited υ(N-H)in the range of (3527-3360)cm-1 which shows ashifted to the higher frequencies by (195-28)cm-1 in compared with free ligand suggested. The possibility of the coordination of ligand through the nitrogen atom at the amine group[10][11]. Absorption assigned for υ(OCO)sym was noticed at the range (1473-1408)cm-1 shifted to higher frequencies by(88-23)cm-1. While the band caused by υ(OCO)asym appeared between (1627-1583)cm-1 Shifted to lower frequencies by(74-118)cm-1 which indicates the carboxylic group to the central metal ion[12][13]. The stretching vibration bands υ(C=S) and υ(C=O)carbonyl group either show no change or very litile in their frequencies therefore indicating do not coordinate to the metal ion[14]. Metal-nitrogen and metal-oxygen bands were confirmed by the presence of the stretching vibration of υ(M-O) and υ(M-N) in the range (415-445)cm-1 and (474-441)cm-1 respectively.

The electronic spectra

The spectrum of free ligand(ATL) fig(4) show bands at (288nm) and (329nm) which are attributed to π→π* and n→π* respectively [15].

-[Mn(ATL)2] complex

The yellow complex of Mn(II) shows band at (35714)cm-1, which belongs to charge transfer and another band at (30211)cm-1 which is caused by the electronic transition 6A1→4T2(p)[16].

[Fe(ATL)2] complex

The spectrum of the yellow complex of Fe(II) fig(5) show bands at (35714)cm-1 and (30211)cm-1 due to chanrge transfer (C.T) and another band at(12406)cm-1, which is caused by the electronic transition 5E→5T2 [17].

-[Co((ATL)2] complex

The brown complex of Co(II) shows three bands at (30864)cm-1, (16051)cm-1 and (12195)cm-1 which attributed to 4A2(f) $\xrightarrow{v_3}$ 4T1(p) mixed with(C.T), 4A2(F) $\xrightarrow{v_2}$ 4T1(F) and 4A2→4T2(F) transition recpectively and the rach interelectronic repulsion parameter B- was found to be (688.66)cm-1 from the relation(β=B⁄BO), β was found to be equal(0.71). These parameters are accepted to Co(II) tetrahedral complex[18].

-[Ni(ATL)2] complex

The electronic spectra of deep-green complex of Ni(II) has revealed the following electronic transition 3T1(F)→3T1(P) whith C.T, 3T1(F)→3A2(F) and 3T1(F)→3T2(F) transition at (30959)cm-1, (12195)cm-1 and (10214)cm-1 respectively. The B-value found to be (834)cm-1 while β was equal to 0.80 , These are the characteristics for tetra hedral complexes of Ni(II)[19].

-[Cu(ATL)2] complex

The spectrum of deep-brown complex of Cu(II) shows two bands at (30769)cm-1 and (27624)cm-1 which belongs to the charge transfer. The band found in the visible region at(14347)cm-1 was attributed to the electronic transition 2T2→2E[20].

[Cd(ATL)2],[Hg(ATL)2]complexes

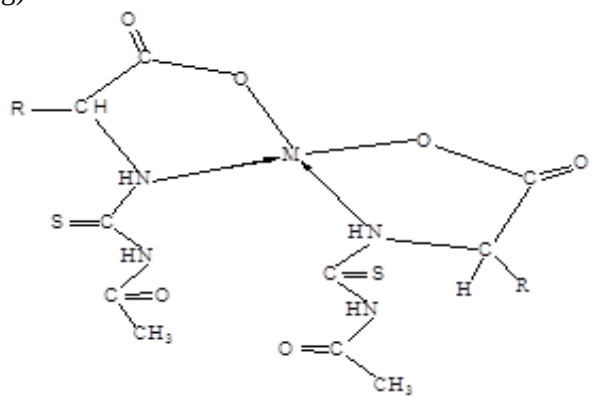
The spectra showed absorptions bands at(31055)cm-1 and (35460)cm-1 (30864)cm-1 respectively attributed to charge transfer(C.T)[21]. All transitions with their assignments are summarized in table(3).

Study of complexes formation in solution:

Complexes of ligand(ATL) with metal ions were studied in solution using ethanol as solvent in order to determine [M ⁄ L] ratio in complexes follow molar ratio method[22] , Aseries of solutions were prepared having a constant concentration(10-3M) 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.

Magnetic properties

The magnetic moment μeff for complexes of Mn+2(d5), Fe+2(d6) and Co+2(d7)were found to be (5.69)B.M, (5.16)B.M and (4.82)B.M respectiviely, which within the expected spin-only values [23]. The higher value of μeff of the Ni+2(d8) complex (3.47)B.M may be due to the orbital contribution[24][25]. The magnetic moment μeff of the Cu+2(d9) complex was found to be 1.75B.M which within the expected value for one electron[26], All the data and remarks are found in table(4). 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(ATL)2] where M+2=(Mn, Fe, Co, Ni, Cu, Cd and Hg).



R=$(CH_3)_2$ CH-CH_2

Fig(6)suggested structure of the complexes $[M(ATL)_2]$ where M^{+2}=(Mn,Fe,Co,Ni,Cu,Cd and Hg).

References

1. Dalia Nayak,Devdeep.M:Aparn A.B and Jhumpa. M;"Studies on complexation of cobalt with bio ligand" J.Radioonal,Nucl.Chem, (2010), 283, 477-480.

2. Nasser M.Hosny and Farid I.El-Dosoki;"Schiff base complexes derived from 2-acedy pyridine,Leucine and some metal chlorides:Their preparation, characterization,and physical properties" J. Chem.Enj.Data, (2008), 53(11) pp 2567-2572.
3. Shaesta Quyoom and Badr-din khan;"poteniometric and Uv spectral studies of Binary and Ternary complexes of some metal ions with N-acetyl cysteine and amino acids";E-Journal of Chemistry, (2009), 6(51),5117-5122.
4. Manuel A.V.Rieiro Dasilva,Luis M.B.F.Santos,Ana C.P.Faria and Filipa .A.Sistelo; "Energetics of Lead(Π), Cadmium(Π) and zinc(Π) complexes with amino acids": J. of Thermal Analysis and Calorimetry", (2010), 100(2), 475-482.
5. Safael,E ,Shexkhi,H, Wojtczak,A and aglicic j;"Synthesis and characterization of an iron(III) complex of glycine derivative of bis(phenol)amine ligand inredevance to catechol dioxygenase active site"Journal polyhedron;(2011), 30(7) 1219-1224.
6. Daizong Lin, Lilv, Jian wang.Xiao Ding, Hualiang Jiang and Hong Liu; "Preparation of α-Alkyl-β-amino acids via β-Alanine Ni(Π) complex; J.Org.Chem (2011), 76(16)pp 6649-6656.
7. kabbani A.T, H.Ramadan, Hammud H.H, hanuoum A.M.G and Mouneimne.Y ;"Synthesis of some metal complexes of N-(benzoyl amino)-[thioxo methyl]-amino acid(HL);Journal of the University of Chemical Technology and Metallurgjy" (2005),40(4) 339-344.
8. Silverstein, Bassler R.M.G.C and Movrll T.C;(1981),"Spectroscopic Identification of organic compound", 4th ed,Wiley, NewYork.
9. Dyer R.G,"Application of absorption spectroscopy of organic compounds" prentice Hall.Inc.Engl Wood Cliffs, N.J.London, (1965).
10. Nakamoto K;"Infrared spectra of Inorganic and coordination compounds"4th ed. John wiley and sons.NewYork, (1996).
11. Nakamoto K and kleft J;"Infrared spectra of some platinum(II)glycine complexes "J.Inor.Nucl.Chem;(1967), 29, 2561-2567.
12. Sadiaa.M. Al Hashimi, Sarhan B.M and Salman A.W;(2002),"Synthesis and characterization of complexes of N-acetyl-Dl Tryptophane with some metal ions Iraq.J.Chem.28 pp 1-11.
13. Jackovitz J.F, Durkin J.A and Lwalter J;"Infrared absorption spectraof meta-amino acid complexes "Spectra Chem.Acta,(1967),23A pp67-80.
14. Dhafir M.H.A- Mudhaffa, Dawoods. Al-Ednai and Suma M.Dawood;"Synthesis characterization and Biological activity of some complexes of some new amino acid derivatives N-[(Benzoyl amino)Thioxo methyl]amino acid(HL); Journal of the karean Chemical Sociely;(2010) 54(5)pp (506-514).
15. Nichllis D;"complexes and first-row transition elements" Macmilolan Chemistry, Text pp73-79(1979).
16. Heidt L.I, Koster G.F. and Johnson A.M;"Absorption spectrum of manganese(II) di ethylene tri amine complexes"J. Am.Chem. Soc; (1958),80 pp 6471.
17. Lever A.B.P;"Inorganic electronic spectroscopy"Elsevier publishing company. Amsterdian, London, NewYork,(1968).
18. Hanna,W.A.and Moaead M.M;"Synthyesis and characterization and anti microbialo activity of Co(II),Ni(II)and Cu(II) complexes with new asymmetrical Schicff base ligand"Transition metal Chemistry;(2002),7 pp 140-144.
19. Al Hashimi S.M, Sarhan B.M and A.j jarad;"Synthesis and Identification of complexes of N-acetyl glycine with some metal salts"(2004), Ibn-Al-Haitham.J.for Pure and App.Sci, 17(2).
20. Musa F.H, AL-Rawi A. and Sarhan B.M;"Synthesis, Biological, Activites studies of prolinyl phenyl isothio cyanato"cysteninyl phenyl isothiocyanate and their complexes "Iraq.J. Chem (2000), 26(4) pp 722-732.
21.Huheey,J.E;(1983)"Inorganic chemistry, principle of structure and reactivity,3rd Edition,Haper,International SI. Edition;Maryland.
22. Doglas, S; Donald W. Holler F, and Grouchs; "Fundamentals of Analytical Chemistry" 8thed saunders College, New York(2004).
23. Nicholls,D;(1984)"complexes and first Row transition elements"
24. Day M.C. and selbin,(1983)"Theoretical Inorganic chemistry Transition elements"
25. Cotton F.A.and G.wllkinson, (1998)"Advanced Inorganic chemistry" wiley-Inter science, NewYork.

26. Sanja O. Podunavac-Kuzmanovic sinisa L.Markov and Ljilianas.Vojinovi; (2004), "Physico Chemical characterization and antimicrobial activity of copper(II) complexes with 2-amino and 2- methyl benzimidazole Derivatives" 35 pp 280.

Complexes	$\upsilon(COO)_{asym}$	$\upsilon(COO)_{sym}$	(N-H)υ	(M-N)υ	(M-O)υ
Ligand (ATL)	1701(s)	1385(m)	3332(s)	—	—
[Mn(ATL)2]	1624(s)	1417(m)	3372(s)	445(w)	474(w)
[Fe(ATL)2]	1625(s)	1408(m)	3441(b)	410(w)	472(w)
[Co(ATL)2]	1627(s)	1446(s)	3396(b)	420(w)	472(w)
[Ni(ATL)2]	1625(s)	1411(s)	3360(s)	425(w)	466(w)
[Cu(ATL)2]	1622(s)	1473(m)	3446(b)	415(w)	460(w)
[Cd(ATL)2]	1583(s)	1408(s)	3452(b)	441(w)	459(w)
[Hg(ATL)2]	1612(m)	1408(s)	3527(m)	426(w)	441(m)

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

Table(1): Physical properties of the ligand and its complexes.

Compound	Coluor	m.p°C or dec.	%M Calac(found)	Molar conductivity $Oh^{-1}.cm^2.mol^{-1}$
Ligand (ATL)	Yellow	150-152	—	—
[Mn(ATL)2]	Yellow	120	10.63 (9.87)	20.00
[Fe(ATL)2]	Drake-green	141	10.78 (11.02)	12.00
[Co(ATL)2]	Brown	142 d	11.31 (11.34)	10.00
[Ni(ATL)2]	Deep-green	183 d	11.27 (10.52)	16.00
[Cu(ATL)2]	Deep-brown	180 d	12.09 (13.03)	13.00
[Cd(ATL)2]	White	202 d	19.57 (19.05)	11.00
[Hg(ATL)2]	White	190 d	30.27 (29.72)	18.00

d= decompose

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

Table(3): Uv- visble spectra of free ligand and their complexes in 10-3M in DMSO.

Complexes	λ max(nm)	ABS	Wav number cm^{-1}	ϵ_{max} $L.m^{-1}.cm^{-1}$	Remarks
Ligand (ATL)	288 329	0.408 0.852	34722 30395	408 852	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$
[Mn(ATL)2]	280 331	0.724 0.995	35714 30211	724 995	C.T $^6A_1 \rightarrow {}^4T_{2(P)}$
[Fe(ATL)2]	280 331 806	0.625 0.539 0.021	35714 30211 12406	625 539 21	C.T C.T $^5E \rightarrow {}^5T_2$
[Co(ATL)2]	324 623 820	1.685 0.031 0.015	30864 16051 12195	1685 31 15	$^4A_2 \rightarrow {}^4T_{2(P)}$ mix with C.T $^4A_2 \rightarrow {}^4T_{1(F)}$ $^4A_2 \rightarrow {}^4T_{2(F)}$
[Ni(ATL)2]	323 820 979	1.672 0.042 0.034	30959 12195 10214	1672 42 34	$^3T_{1(F)} \rightarrow {}^3T_{1(P)}$ $^3T_{1(F)} \rightarrow {}^3A_2$ $^3T_{1(F)} \rightarrow {}^4T_{2(F)}$
[Cu(ATL)2]	325 362 697	1.646 0.819 0.010	30769 27624 14347	1646 819 10	C.T C.T $^2T_2 \rightarrow {}^2E$
[Cd(ATL)2]	322	1.916	31055	1916	C.T
[Hg(ATL)2]	282 324	0.992 1.753	35460 30864	992 1753	C.T C.T

Table(4):The magnetic properties of the complexes at 25°C

complexes	No.of electron	No. of un parier d electron	Electron configure	Term symbol	Term symbol ground stat of Td	Orbital contrib.	μeff
$[Mn(ATL)_2]$	d^5	5	$^2e\ ^3t_2$	^6S	$^6A_1$	NO	5.62
$[Fe(ATL)_2]$	d^6	4	$^3e\ ^3t$	^5D	^5E	NO	5.16
$[Co(ATL)_2]$	d^7	3	$^4e\ ^3t_2$	^4F	$^4A_2$	NO	4.82
$[Ni(ATL)_2]$	d^8	2	$^4e\ ^4t_2$	^3F	$^3T_1$	Yes	3.47
$[Cu(ATL)_2]$	d^9	1	$^4e\ ^5t_2$	^2D	$^2T_2$	Yes	1.79

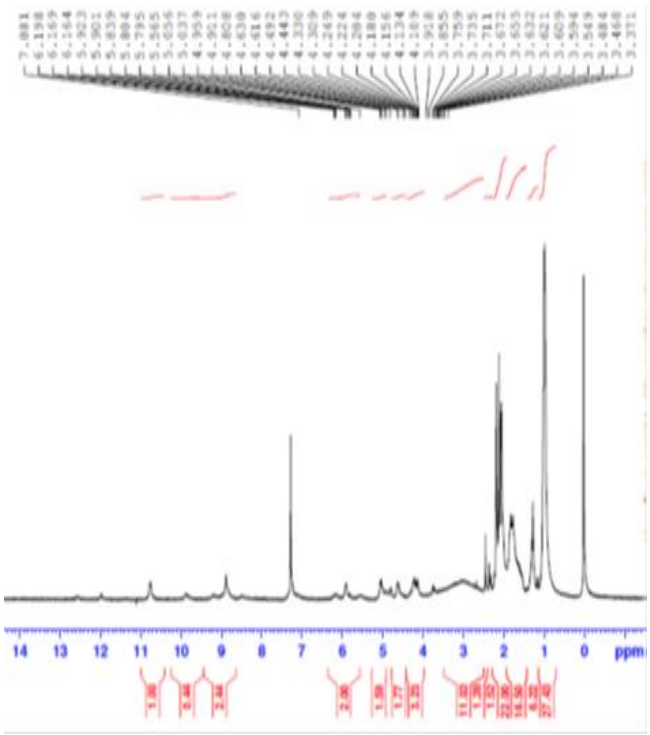


Fig (1) 1H NMR Spectrum for ligand leucine (ATL).

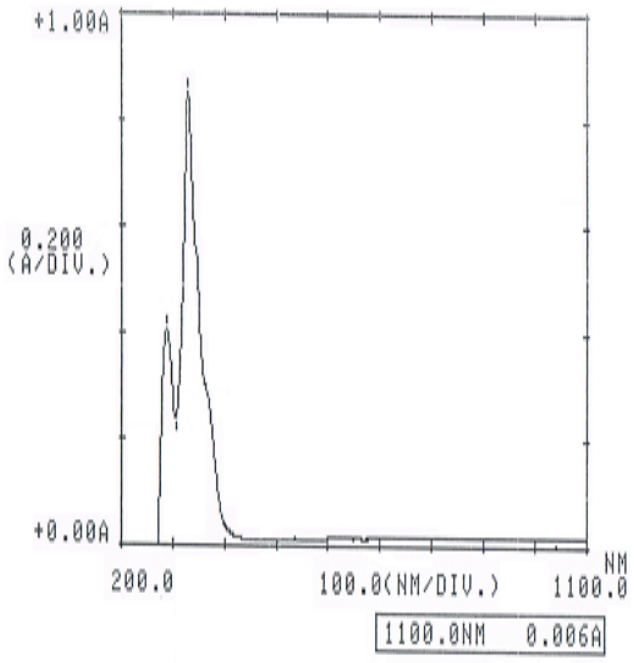


Fig (4) Uv-visble spectrum . of ligand (ATL).

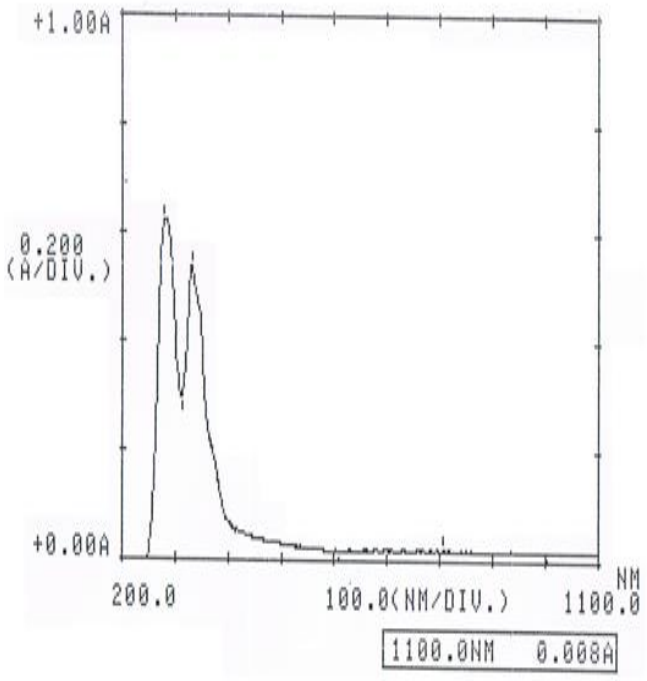
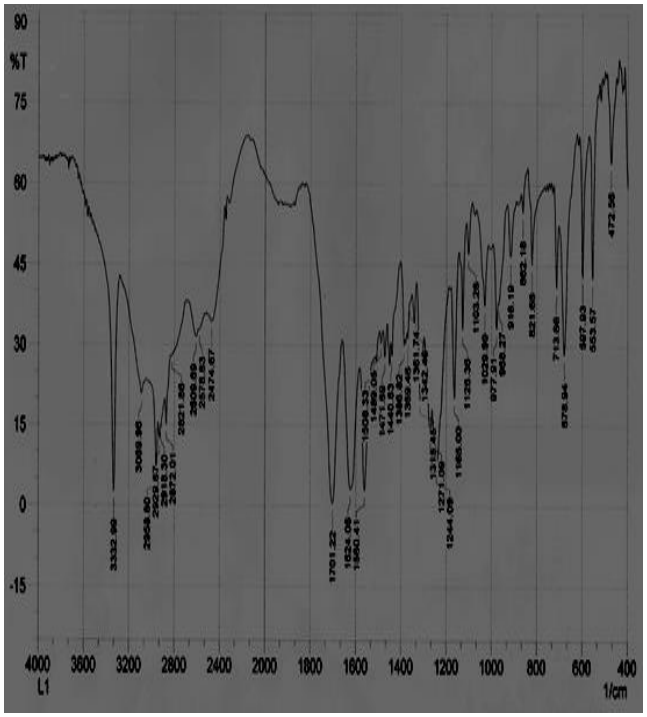


Fig (5) Uv-visble spectrum of complex[Fe(ATL)2].



Fig(2) FT-IR Spectrum for ligand (ATL).

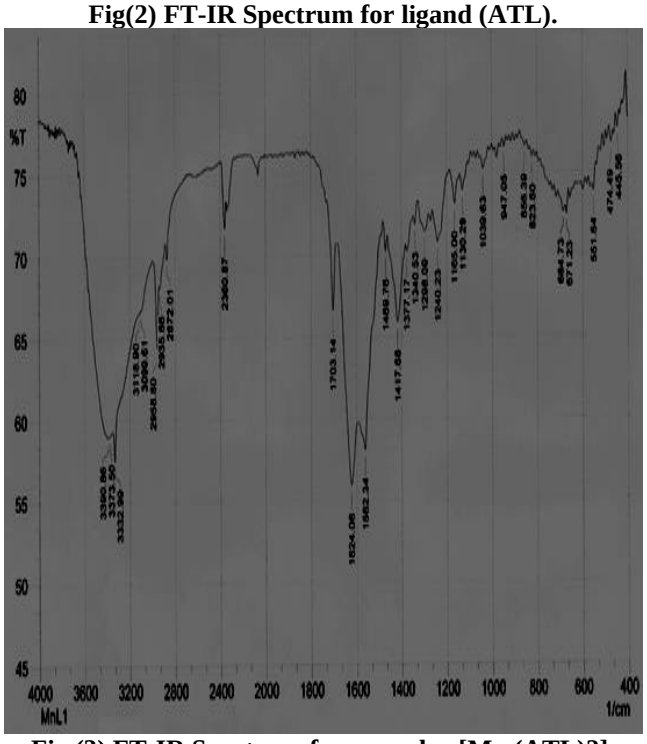


Fig (3) FT-IR Spectrum for complex [Mn (ATL)2].

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تحضير ودراسة طيفيه لمشتق حامض الليوسين الجديد مع معقداته الفلزيه

محمد احمد عواد باسمه محسن سرحان عبدالستار زيدان خلف

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الخلاصة:

حضر الليكاند الجديد N–أستيل أمينو(ثايوكسومثيل) ليوسين ومختصره (ATL) وذلك من خلال مفاعلة استيل آيزوثايوسيانات مع الحامض الاميني (الليوسين) وشخص الليكاند بالطرق الطيفيه ومنها طيف الرنين النووي المغناطيسي 1H NMR، تحاليل C.H.N.S, طيف الاشعه تحت الحمراءIR وطيف الاشعه فوق البنفسجيه–المرئيهUV. كما حضرت بعض المعقدات الفلزية الجديده لأيونات (المنغنيز , الحديد, الكوبلت, النيكل, النحاس, الكادميوم والزئبق) الثنائية التكافؤ مع الليكاند(ATL) وشخصت هذه المعقدات المحضره بالطرق الطيفية المتوفره ومنها طيف الاشعه تحت الحمراءIR, طيف الاشعه فوق البنفسجيه– المرئيهUV إضافةً الى تعيين نسبة الفلز في المعقدات بواسطة طيف الامتصاص الذري، قياس التوصيليه المولاريه لمحاليل المعقدات في مذيب ثنائي مثيل سلفوكسايد(DMSO), إضافة الى تحديد النسبه الموليه الى الليكاند: فلز ، فضلا عن قياس الحساسية المغناطيسية للمعقدات المحضره، ومن نتائج هذه الدراسات أعطاء الصيغه العامة لهذه المعقدات وكالاتي [M(ALT)2] حيث M تمثل,Co+2, Fe+2, Mn+2 M+2 (Ni+2, Cu+2, Cd+2and Hg+2) و ATL تمثل : N–أستيل أمينو(ثايوكسومثيل) ليوسين.