Synthesis And Characterization Of New Metals Complexes Of [N-(acetyl amino) Thioxomethyl] Valine

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Abstract

A new ligand [N-(acetyl amino) thioxomethyl] valine was prepared from the reaction of acetyl iso thiocyanate with valine.

The ligand was characterized by FT-IR, UV- vis and ^{1}HNMR spectrum, The complexes with some metal ions (M^{+2} =Co,Ni,Cu,Zn,Cd,Hg) have been prepared and characterized. The structural diagnosis were established by IR,UV-Vis spectrum, flame atomic absorption spectroscopy conductivity and magnetic susceptibility ,the complexes showed tetrahedral geometry around the metal l.

Keywords : valine, acetylisothiocynate complexes

Introduction

Metal complexes of amino acids posses considerable potential in many application including biological,clinical,antibiotics and tumor inhibitors [1-4] ,metal complexes of Cu(II),Ni(II),Cr(III),and Fe(II) chloride with Schiff base ligand[5] derived from reaction between leucine and 2 – acetyl pyridine were prepared and
Brij [6], used paper electro phoretic technique (PET) to calculate the stability constants of (Be(II)) –proline and Co-proline Complexes, also Dhafir and co-work[7] had synthesis, characterization and biological activity of some complexes of some new amino acid derivatives with transition metals .

This work includes preparation of some transition metals complexes of [N-(acetyl amino) thioxomethyl] valine .

Experimental

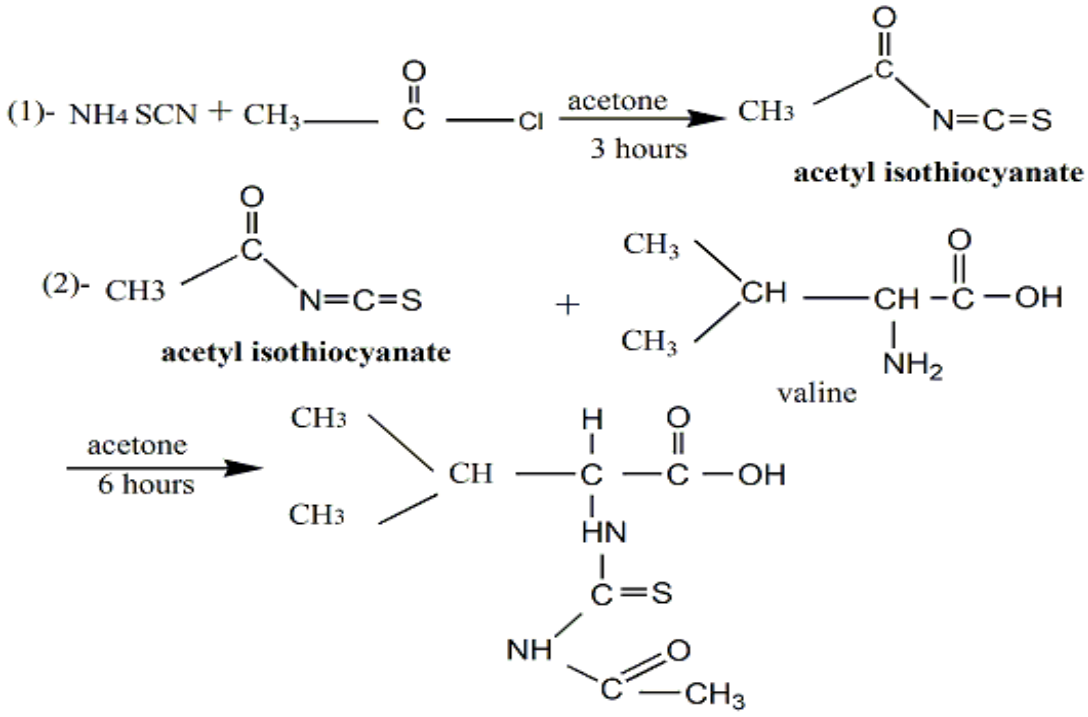
All reagents used were analar or chemically pure grade by British drug house(BDH) ,Merk and Fluka.
Metal salts (CoCl2.6H2O, NiCl2.6H2O, CuCl2.2H2O , ZnCl2, CdCl2.H2O, HgCl2), valine, ammoniumthiocyanate, acetyl chloride (CH3COCl) acetone 99% dimethyl formaminde 99.5% (DMF), ethanol 99% .

Instruments

HNMR were recorded using ultra shield 300MHz Switzerland, at university of AL-Al-bayt, Jordan. conductivity measurements were carried out using Philips pw digital meters conductivity in DMF at 10^{-3}M .FT-IR spectra were recorded as KBr discs in the range (4000-400) cm $^{-1}$ using shimadzu FT-IR. UV-visible spectra were recorded by shimadzu UV-8300 vis-160 A , ultra violet spectra photometer, at the range of (200-1100) nm at 10^{-3} M in DMF. metal contents of the complexes were determined by atomic absorption using (shimadzu aa 6806) atomic absorption spectra photometer. magnetic susceptibility (μeff B.M) were recorded by farada method using balance magnetic susceptibility) model MsB –MKI). melting points were determined by using (shtutart –melting point apparatus).

Synthesis of the ligand

1- Preparation of the acetyl -isothiocyanate : mixture of acetyl chloride (1.9 ml) (1mmole) and ammonium thiocynate (2gm)(1mmol) in 25 ml acetone was stirred under refluxed for 3 hours and then filtered , the filtrate was used for further reaction[8]
2- Preparation of [N-(acetyl- amino) thioxomethyl] valine [ATV].
3.08 gm (1mmol) of valine in 20 ml acetone was rapidly added to the above solution to maintain vigoross reflux. After refluxing for 6 hours , the resulting solid was collected , washed with acetone and recrystallized from ethanol . Scheme (1)
(yield 80%), (M.P. 135^{0} C).



[N-(acetyl amino)- thioxmethyl] valine (ATV)

Scheme (1) :preparation [N-(acetyl amino)- thioxo methyl] valine(ATV).

Synthesis of the complexes

0.2 g (2mmol) of the ligand (ATV) was dissolved in 25 ml of ethanol containing 0.05g (2mmol) of KOH, Then the solution of (1mmol)metal salt (CoCl2.6H2O, ,NiCl2.6H2O, CuCl2.2H2O ,ZnCl2,CdCl2.H2O and HgCl2) (0.11g,0.11g,0.08g,0.06g,0.09g and 0.120g) respectively in ethanol was added drop-wise to the solution of the ligand(ATV), the precipitate formed immediately, after stirring the mixture at room temperature for 2 hours , the precipitate was collected by filtration, washed with ethanol and dried .

Results and discussion

The solid complexes,soluble in some commen solvents such as dimethylformamide , dimethylsulphoxide , and relatively thermally stable . The molar conductivity of all complexes in DMF was found to be non electrolyt . Table (1) includes the physical properties for the ligand and its complexes

Spectral studies

H^{1}NMR spectrum for the ligand (ATV)

The H^{1}NMR (CDCL3) spectrum of (ATV) Fig.(1) showed the following signals : doublet (d) at δ(0.8-1.2)ppm for (6H,2CH3) , singlet(s) at δ(2.1)ppm for(3H,CH3CO), multiplet(m) at δ(2.32-3.10) ppm for (1H,CH(CH3)2) , triplet (t) at δ(4.43-4.53) ppm for (1H,CHCOOH) , doublet (d) at δ (6.12- 6.15) ppm for (1H,NH) , singlet (s) at δ(7.27) ppm for impurit of solvent (CDCl3) , singlet(s) at δ(9.12) ppm for (1H,NHsec.amide) , singlet(s) at δ(12.6) ppm for (1H,COOH).

Infrared spectra

FT-IR spectrum of the free ligand (ATV) Fig.(2) showed bands due to amide υ(NH) υ(C=0) and υ(C=S) which were observed at (3369) cm^{-1} (1602) cm^{-1} and (1217) cm^{-1} respectively While another absorption band appeared at (1728) cm^{-1} could be explained as υ(COO)asym [9-10] were the υ(OCO)sym was noticed at(1315) cm^{-1}.

The FT-IR spectra of complexes

These spectra exhibited a marked difference between bands Fig.(3) belonged to the stretching vibration of υ(N-H) of the amine group in the range between(3426-3383) cm^{-1} shifted to higher frequencies by (93-14) cm^{-1} suggesting the possibility of the coordination of ligand[11-13] through the nitrogen atom at the amine group ,absorption assigned for υ(OCO)sym was noticed at the range (1388-1438) sym cm^{-1} shifted to higher frequencies by (123-73) cm^{-1} while the band caused by υ(COO)asym appeared between (1506-1629) cm^{-1} shifted to lower frequencies by (89-222) cm^{-1} which indicates to the coordination of the carboxylic group to the central ion [12-14] .

The stretching vibration band υ(C=O) and υ(C=S) carbonyl group either show no change or very little in their frequencies(1610-1600)cm^{-1} and (1220-1203)cm^{-1} respectively therefor indicating do not coordinate to the metal ions[15]

Metal nitrogen and metal-oxygen bands were confirmed by the presence of the stretching vibration of υ(M-O) and υ(M-N) around(425-570)cm^{-1} and (401-426) cm^{-1} respectively .

Table (2) describes the important bands and assignments for free ligand (ATV) and its complexes

Electronic spectral

The UV- visible of the ligand (ATV) and its complexes are recorded in table(3) . the solution of the ligand (ATV) in 10^{-3} M (DMF) exhibited two peaks Fig.(4) at (36496) cm^{-1} and (30487) cm^{-1} which are attributed to $\Pi \longrightarrow \Pi^*$ and $n \longrightarrow \Pi^*$ transition respectively [16].

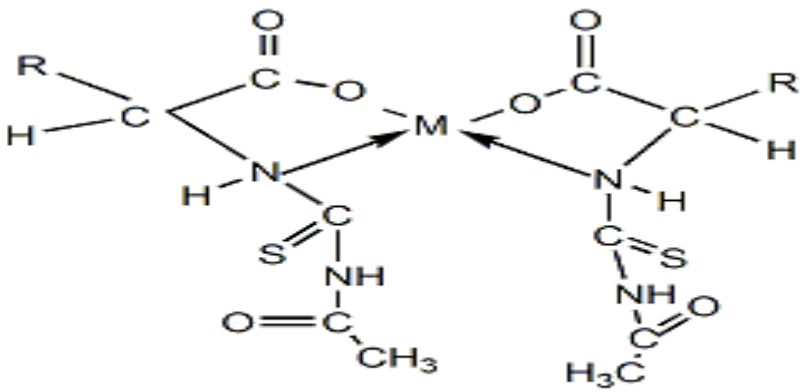
The spectra of complexes

- [Co(ATV) 2] d^7 : the spectrum of the deep-blue exhibited the following bands at (35211) cm^{-1} and (18656) cm^{-1} attributed to (C.T) and $^4A_2 \longrightarrow {}^4T_{1(p)}$ respectively [17-18]
- [Ni(ATV)2](d^8) : the spectrum of green complex , gave two bands at (42016) cm^{-1} and (26881) cm^{-1} caused to (C.T) and $^3T1(F) \longrightarrow {}^3T1(p)$ transition respectively .[19]
- [Cu(ATV)2) d^9 the deep green complex spectrum Fig. [5] showed two absorptions at (36363) cm^{-1} and (12062) cm^{-1} attributed to (C.T) and $^2T2 \longrightarrow {}^2E$ transitions receptively [20].
- the yellow complexes of [Zn(ATV)2)] , [Cd(ATV)2], [Hg(ATV)2] showed only charge transfer of (M ⟶ L) in the range (38461-27322) cm^{-1} respectively [21]

According to spectra data as well as those abtained from elemental analysis the chemical structure of the complexes may be suggested as [M(ATV)2] Were

M= Co^{+2} , Ni^{+2}, Cu^{+2}, Zn^{+2} ,Cd^{+2} and Hg^{+2}

ATV=[N-(methyl amino)-thioxomethyl] valine



R= $(CH_3)_2CH_2$

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

Complexes	M.wt	Color	m.p or D.	M% Calculate (Found)	Molar conductivity ($ohm^{-1}m^2.mol^{-1}$ In(DMF) 10^{-3} M	μ eff (B.M)
Ligand(ATV)	218	Yellow	135^0 C		17	
[Co(ATV)2]	492.93	Deep-blue	250 ^{0} d	11.96 (12.1)	23	4.60
[Ni(ATV)2]	492.71	Green	230 ^{0} d	11.92 (10.9)	27	3.26
[Cu(ATV)2]	497.5	Deep-green	188 ^{0} d	12.77 (12.1)	22	1.74
[Zn(ATV)2]	499.4	Yellow	225 ^{0} d	13.1 (12.08)	25	0.00
[Cd(ATV)2]	546.4	Yellow	210 ^{0} d	20.57 (20.1)	32	0.00
[Hg(ATV)2]	635	Yellow	225^0 d	31.59 (32,2)	23	0.00

d= decomposition

Table (2) : The characteristic infrared of ligand (ATV) and its complexes

complexes	υ(N-H)	υ(COO)asym	υ(OCO)sym	υ (M-N)	υ (M-O)
ligand (ATV)	$3369_{(s)}$	$1728_{(s)}$	$1315_{(m)}$	___	___
$(Co (ATV)_2)$	$3396_{(b)}$	$1629_{(b)}$	$1388_{(m)}$	402	570
$(Ni (ATV)_2)$	$3383_{(m)}$	$1635_{(m)}$	$1400_{(s)}$	401	450
$(Cu (ATV)_2)$	$3421_{(m)}$	$1583_{(S)}$	$1438_{(s)}$	418	499
$(Zn (ATV)_2)$	$3462_{(b)}$	1622	$1435_{(s)}$	418	425
$(Cd (ATV)_2)$	$3421_{(m)}$	$1597_{(S)}$	$1417_{(m)}$	426	472
$(Hg (ATV)_2)$	$3442_{(b)}$	$1506_{(S)}$	1417	426	472

Table (3):UV–visible absorption for the ligand (ATV) and its complexes in DMF(10^{-3} M)

complexes	λ (nm)	υ cm^{-1}	Єmax. L. mol^{-1} cm^{-1}	Assignment
Ligand(ATV)	274 329	36496 30487	848 35 3	Π →Π* n → Π*
$\{Co (ATV)_2\}$	284 536	35211 18656	3991 151	C.T. $^4A_2 \rightarrow {}^4Tg(p)$
$\{Ni (ATV)_2\}$	238 272	42016 26881	2329 65	C.T. $^3T_{1(F)} \rightarrow {}^3T_{1\ (p)}$
$\{Cu (ATV)_2\}$	270 829	36363 12062	827 11	C.T $^2T_2 \rightarrow {}^2E$
$\{Zn (ATV)_2$	260 329	38461 30395	2235 292	C.T. C.T
$Cd (ATV)_2$	279 327	35842 30581	1707 1586	C.T C.T
$Hg (ATV)_2$	328 366	30487 27322	713 249	C.T C.T

C.T = charge transfer

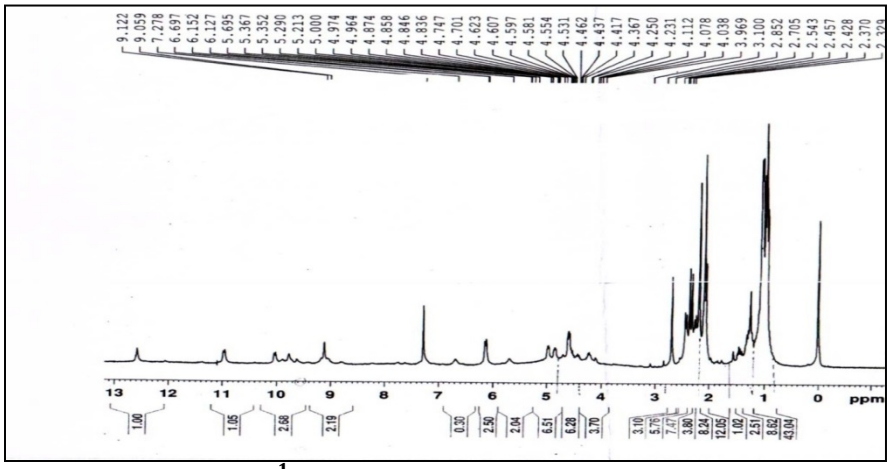

Fig. (1) : H[1]NMR spectrum of the ligand ATV.

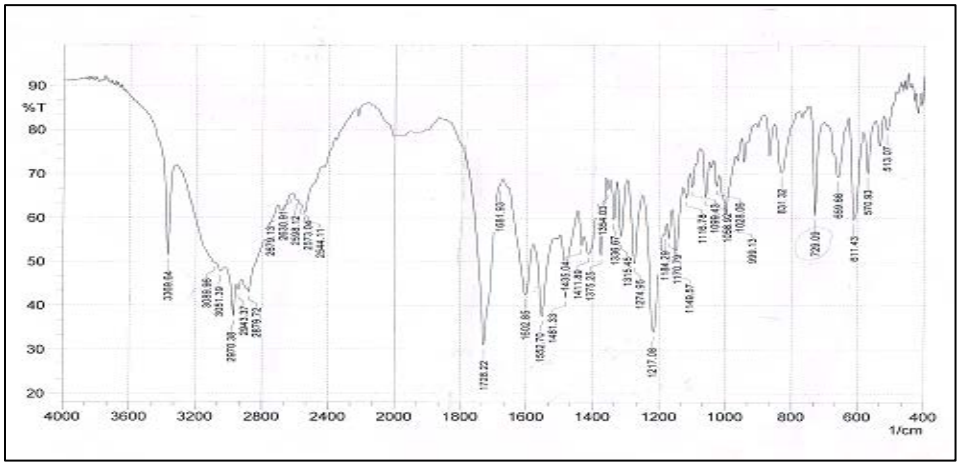

Fig. (2) : FT-IR spectrum of the ligand ATV

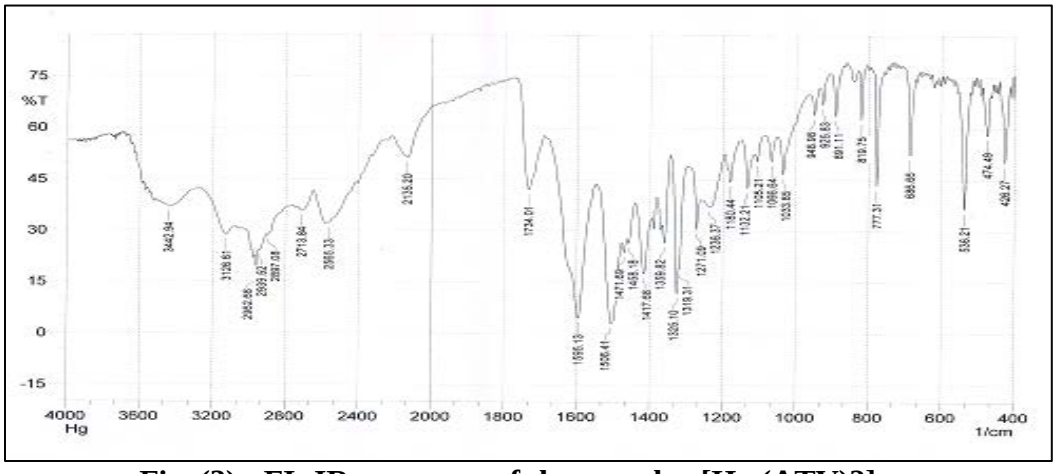

Fig. (3) : FI- IR spectrum of the complex [Hg (ATV)2]

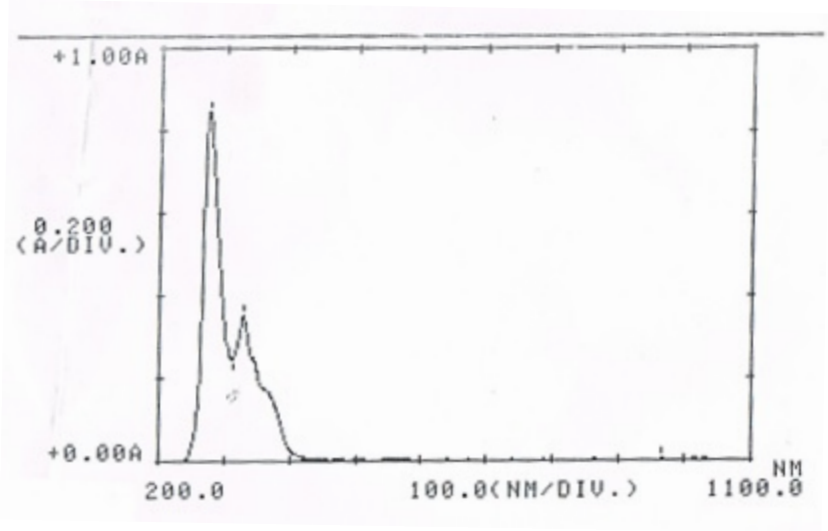

Fig. (4) : UV – Visible spectrum of the ligand ATV

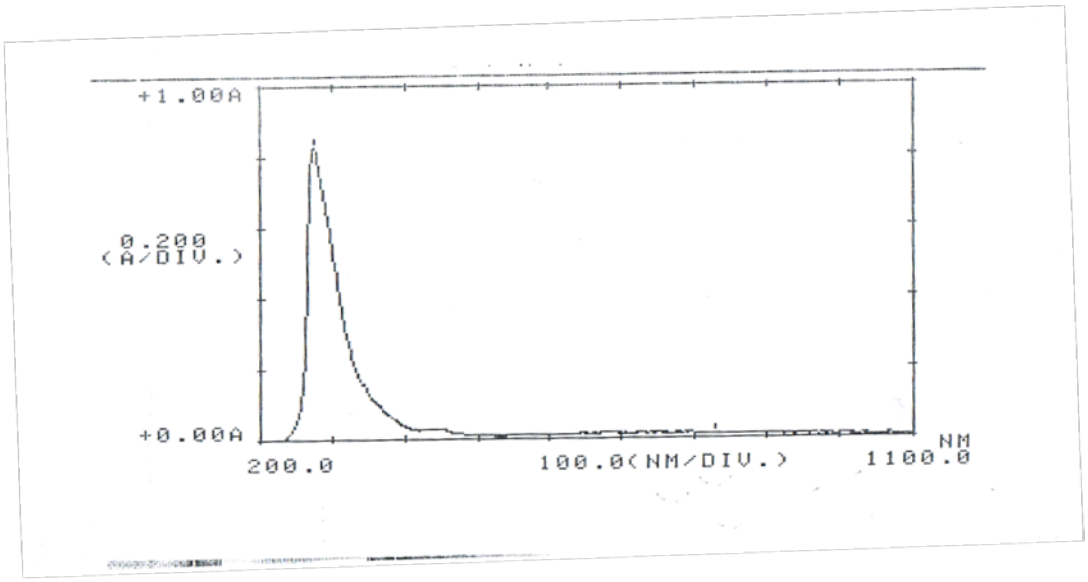

Fig. (5) : UV – Visible spectrum of the complex Cu (ATV)2

تحضير وتشخيص بعض المعقدات الفلزية لليكاند [N- (استيل آمينو) ثايوكسو مثيل] فالين

عالية سلمان قنديل
قسم الكيمياء / كلية التربية للعلوم الصرفة (ابن الهيثم) / جامعة بغداد

استلم البحث في : 6 آيار 2012 قبل البحث في:22 تشرين الأول 2012

الخلاصة

حضر الليكاند الجديد (N-(مثيل امينو)ثايوكسو مثيل) فالين بوساطة تفاعل استيل ايزوثايو- سيانات مع الحامض الاميني فالين (ATV) ، وقد شخص الليكاند مع معقداته المحضرة بالطرائق الطيفية المتوفرة وهي (طيف الرنين النووي المغناطيسي (H^1NMR) ، الاشعة فوق البنفسجية والمرئية والاشعة تحت الحمراء ، وقياس نسبة الفلز بوساطة طيف الامتصاص الذري اللهبي A.A.S فضلا عن قياس التوصيلية المولارية ، الحساسية المغناطيسية . من نتائج هذه الدراسات اعطت الصيغة المقترحة العامة لهذه المعقدات : ($M(ATV)_2$) ، التي اقترح لها الشكل الهندسي رباعي السطوح
إذ $M = Co^{+2}, Ni^{+2}, Cu^{+2}, Zn^{+2}, Cd^{+2}, Hg^{+2}$
ATV= الليكاند الايوني (N- (استيل امينو) ثايوكسو مثيل) فالين

الكلمات المفتاحية : فالين ، استيل ايزوثايو سينات ، المعقدات