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Synthesis and Characterization of New Metal Complexes of [N-acetyl (amino)thioxo methyl] Glycine

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Abstract

A new Ligand (ATG)(N-acetyl amino thioxomethyl) Glycine was prepared by the reaction of acetyl iso thiocyanate with Glycine, The Ligand was characterized by FT-IR, UV-vis and ^{1}HNMR, some complexes of the ligand were synthesized and characterized by FT-IR, UV-vis spectra, move over determination of metal content by Flame atomic absorption spectroscopy, molar conductance in DMSO solution and magnetic moments(μ_{eff}).

Keywords: Glycine derivative, metal complexes.

Introduction

Many simple amino acids have been complexed with a large number of transition metals ions on the assumption that the complexes formed act models for the metal-binding sites of proteins[1], some transition metal complexes of (7-hydroxy-4-methyl-8-coumaryl) glycine and acetyl aceton with glycine have been synthesized and characterized[2-3], clandiac and cowork synthesis and characterization and study vibrational spectra of copper(II) complexes of L-proline[4], mixed ligand complexes of Zn(II) and Cd (II) containing amino acids as glycine, proline and antibiotics and other ligands have been prepared and characterized by elemental analysis, spectral, biological and thermal studies[5], Iron(III) complexes with glycine derivative of bis(phenol)amine ligand (HLGly) was synthesized and characterized by IR, uv-Vis, X-ray and magnetic susceptibility[6].

The aim of this work is to prepar some metal complexes ions with (N-acetyl (amino) thioxo methyl) glycine.

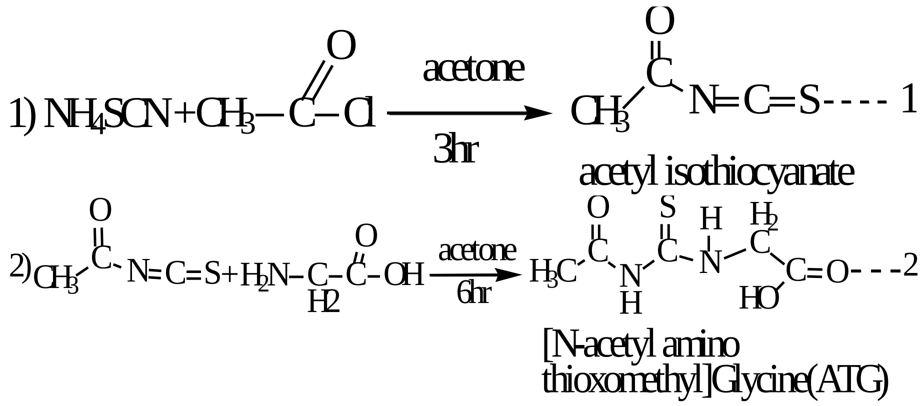
Experimental

Metal salts ($CoCl_2.6H_2O$, $NiCl_2.6H_2O$, $CuCl_2.2H_2O$, $ZnCl_2$ and $CdCl_2.H_2O$) were obtained from Fluka, Merek; Glycine acetyl chloride and ammonium thio cyanate(Fluka) ^{1}HNMR were recorded using ultra shield 300 MHz switzerland, at University of Ahel al-Bayt, Jordan, Conductivity measurements were carried out using Philips Pw. Digtal-meter. The FT-IR spectra in the region (4000-400) cm^{-1} were recorded using shimadzu, FT-IR 3800),Infrared spectra photometer as KBr disc, the uv-vis spectra were recorded using (shimadzu uv-vis160A), uv-vis spectrophotometer in dimethyl sulfoxide solution(10^{-3}M) contents of complexes were determined by Atomic absorption using(shimadzu AA6806) Atomic absorption spectro-photometer, The magnetic moments (μ_{eff}B.M) were calculated by Farady method using (Blance magnetic susceptibility) model(MSB-MKT), melting points were determind using(stuart-melting point apparatus).

Synthesis of the ligand

1) Preparation of the acetyl isothiocyanate: A mixture of acetyl chloride (2ml)(1mmole) and ammonium thio cyanate(2gm,1mmole) in 25ml acetone was refluxed with stirring for 3 hours, and then filtered, the filtrate was used for further reaction(6).
2) Preparation of [N-acetyl amino-thioxo methyl] Glycine(ATG).

(2gm, 1mmole) of Glycine in 20ml acetone were rapidly added to the above solution to maintain vigorous reflux. After refluxing for 6 hours, the resulting solid was collected, washed with acetone and recrystallized from ethanol (M.P = 188ºC) yelid (86%). Scheme (1).



Scheme (1) Preparation[N-acetyl amino thioxo methyl]Glycine (ATG).

Synthesis of the complexes

(0.25 gm) (2mmole) of the ligand (ATG) was dissolved in (25ml) of ethanol containing (0.08gm)(2mmole) of KOH. A solution of (1mmole) metal salt ($CoCl_2.6H_2O$, $NiCl_2.6H_2O$, $CuCl_2.2H_2O$, $ZnCl_2$ and $CdCl_2.H_2O$) (0.17gm, 0.17gm, 0.12g, 0.096g, and 0.143gm) respectively, in ethanol was added drop wise to the mixture and precipitate formed immediately. After stirring the mixture at room temperature for 2hours, the precipitate was crystallize from ethanol and dried.

Results and Discussion

The isolated complexes were crystalline solids, soluble in some of the common solvents such as dimethylsulphoxide, the conductivity measurements in DMSO indicted the non-electrolyte behavior, Table (1) includes the physical propertles for the ligand and its complexes.

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

Complexes	*Color*	*M.W*	*Dec.°C Or M.P.*	*M% Calculate (Found)*	*Molar conductivity ($ohm^{-1}.cm^{-2}mol^{-1}$) In DMF $10^{-3}M$*	*M_{eff} (B.M.)*
Ligand (ATG) ($C_5H_5N_2SO_3$)	yellow	176	188-190	——	-------	——
Co(ATG)$_2$]	pink	408.94	100°d	14.41 (13.64)	10	4.56
Ni(ATG)$_2$]	Green	408.71	176°d	14.36 (14.21)	15	2.21
Cu(ATG)$_2$]	Green	413.54	168°d	15.36 (14.93)	18	1.68
Zn(ATG)$_2$]	Yellow	415.38	180°d	15.74 (14.87)	19	0.00
Cd(ATG)$_2$]	Yellow	462.4	150°d	24.30 (23.95)	20	0.00

Spectral Studies

^{1}HNMR spectrum for the ligand (ATG)

The ^{1}HNMR spectrum for the ligand, Fig.(1) showed the following signls: broad (b) at δ(1)ppm for (2H,2OH), singlet(s) atδ(1.8)ppm for ($3H,CH_3CO$),triplet(t) at δ(2-2.17) ppm for (1H,NH amine), doublet(d) at δ(2.64) ppm for ($2H,CH_2COOH$), singlet(s) at δ(6.46) ppm for (1H,NHsec.amide), singlet(s) at δ(7.27) ppm for impurity of solvent ($CDCL_3$).

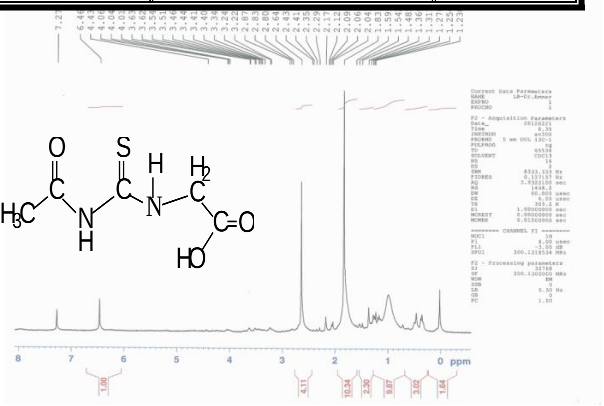


Fig.(1) ^{1}HNMR Spectrum of ligand(ATG).

Infrared spectra

The spectrum of free ligand the infrared spectrum of ligand (ATG) Fig.(2) exhibited astrong band at (3452)cm^{-1}assigned to the υ(N-H), while another strong absorption band at (1718)cm^{-1} appeared could be explained as $(OCO^{-})_{asym}$ were the $(OCO^{-})_{sym}$ was noticed at (1355)cm^{-1}[7-8].

Table (2) exhibited a marked difference between bands of the stretching vibrating of υ(N-H) of(the amino group) in the range between (3105-3352)cm^{-1} shifted to a lower position by (347-100)cm^{-1}[9-10] suggesting the possibility of the coordination of ligandthrough the nitrogen atom at the amine group [11]. Absorption assigned for $\upsilon(OCO^{-})_{sym}$ was noticed at the range (1381-1440)cm^{-1} shifted to higher frequencies by (85-26)cm^{-1} while the band caused by $\upsilon(OCO^{-})_{asym}$ appeared between (1622-1550)cm^{-1} shifted to lower frequencies by (96-168)cm^{-1}which indicates the coordination of the carboxylic group to the central metal ion[12] the stretching vibration bands υ(C=S) and υ(C=O) carbonyl group either show no change or very little in their frequencies therefore indicating do not coordinate to the metal ion [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 υ(560-462)cm^{-1} and υ(425-472) cm^{-1} respectively. Table (2) describes the important absorptions and assignments for the free ligand and its complexes and Fig.(3) showed the FT-IR spectra of cupper complexes $[Cu(ATG)_2]$.

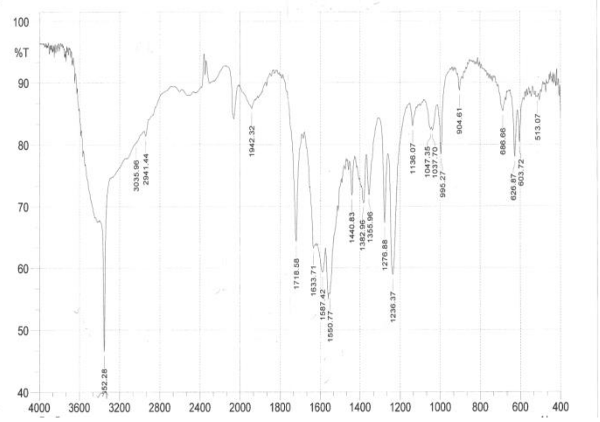


Fig.(2) FT-IR spectum of ligand(ATG).

Table (2)
The characteristic infrared of ligand (ATG) and its complexes.

Complexes	*υ(NH:)*	*$\upsilon(COO^{-})_{asy}$*	*$\upsilon(OCO^{-})_{Sym}$*	*υ(M-N)*	*υ(M-O)*
Ligand(ATG)	**3452(s)**	**1718(S)**	**1355(m)**	——	——
$[Co(ATG)_2]$	**3105(m)**	**1598(m)**	**1408(m)**	**509(w)**	**443(w)**
$[Ni(ATG)_2]$	**3348(s)**	**1585(m)**	**1440 (m)**	**466(w)**	**455(w)**
$[Cu(ATG)_2]$	**3332(m)**	**1622(s)**	**1381(m)**	**560(w)**	**425(w)**
$[Zn(ATG)_2]$	**3352(s)**	**1585(m)**	**1440(m)**	**462(w)**	**451(w)**
$[Cd(ATG)_2]$	**3352(s)**	**1550(m)**	**1440(m)**	**487(w)**	**472(w)**

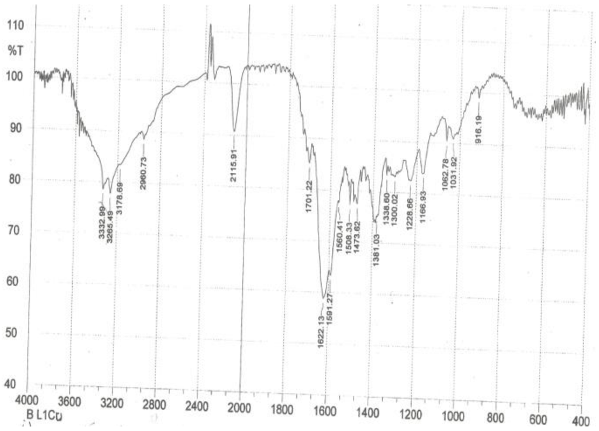


Fig.(3) FT-IR spectrum of $[Cu(ATG)_2]$.

Electronic spectra

The ligand Fig.(4) exhibited an absorption band in (uv) region at wave number (35842)cm^{-1} which may be attributed to $(\pi\rightarrow\pi^{*})$ transition, other band appeared at (30211)cm^{-1} was expressed at the $(n\rightarrow\pi^{*})$ [14].

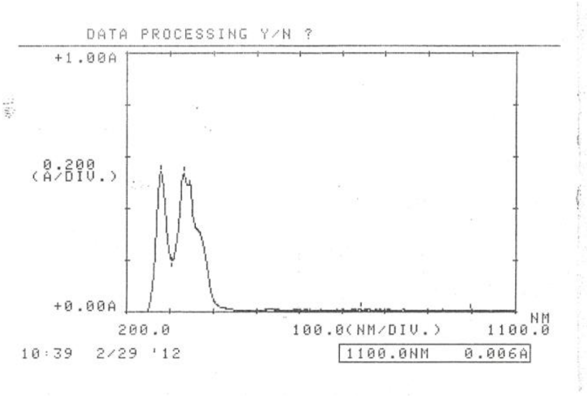


Fig.(4) uv-vis spectrum of ligand.

The spectra of complexes

- [Co $(ATG)_2$] d^7 The spectrum of the pink showed three absorption at(30395) cm^{-1} (29154)cm^{-1} and (18691)cm^{-1} attributed to (C.T.), $^4A_2 \rightarrow {}^4T_{1\ (p)}$ and $^4A_2 \rightarrow {}^4T_{1\ (F)}$ transitions respectively[15-16].
- [Ni $(ATG)_2$]d^8 The green complex spectrum exhibited the following absorptions at (30487)cm^{-1} and (12360)cm^{-1} attributed (C.T.) and $^3A_2 \rightarrow {}^3T_{1(p)}$ transitions respectively [17-18].
- [Cu$(ATG)_2$] d^9 The spectrum of the green showed two absorptions at(30581)$cm^{-1}$and (14450)cm^{-1} attributed to (C.T.)[19-20] and $^2T_2 \rightarrow {}^2E$ transitions respectively.
- The complexes of Zn(II) and Cd(II) showed only charge transfer of M→L in the rang (27932-29069) cm^{-1} respectively [21-22].

The absorptions and assignments related to the ligand and its complexes are listed in Table (3) and Fig.(5) showed the uv-vis spectrum of Nickel complex [Ni $(ATG)_2$].

Table (3)
UV-visble absorptions for the free ligand (ATG) and its complexes in DMSO as solvent in (10^{-3}M).

Complexes	$\lambda_{max(nm)}$	*Wave number (cm^{-1})*	ϵ_{max} $L.mo1^{-1}.cm^{-1}$	*Assignment*
Ligand(ATG)	٢٧٩ ٣٣١	٣٥٨٤٢ ٣٠٢١١	٥٤٤ ٤٣٦	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$
[Co$(ATG)_2$]	٣٢٩ ٣٤٣ ٥٣٥	٣٠٣٩٥ ٢٩١٥٤ ١٨٦٩١	٤٣٦ ٤٣٤ ٤٣٦	**C.T.** $^4A_2 \rightarrow {}^4T_{1\ (P)}$ $^4A_2 \rightarrow {}^4T_{1\ (P)}$
[Ni$(ATG)_2$]	٣٢٨ ٨٠٩	٣٠٤٨٧ ١٢٣٦٠	٩٥١ ١٢	**C.T.** $^3A_2 \rightarrow {}^3T_{1\ (P)}$
[Cu$(ATG)_2$]	٣٢٧ ٦٩٢	٣٠٥٨١ ١٤٤٥٠	٤٠٠ ٧٠	**C.T.** $^2T_2 \rightarrow {}^2E$
[Zn$(ATG)_2$]	٣٥٨	٢٧٩٣٢	٥٩٠	**C.T.**
[Cd$(ATG)_2$]	٣٤٤	٢٩٠٦٩	٦٨٥	**C.T.**

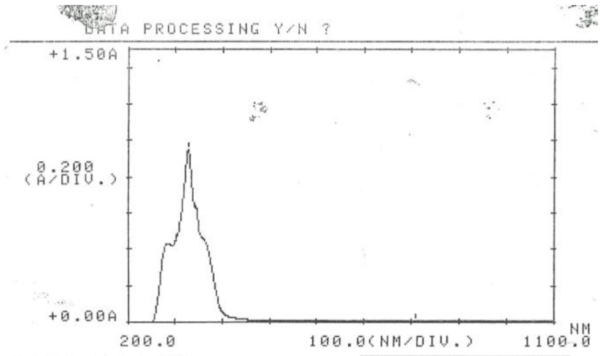


Fig.(5) uv-vis spectrum of complexe [Ni $(ATG)_2$].

Conclusion

According to spectral data as well as those obtained from elemental analyses, the chemical structure of the complexes may be suggested as:
[M$(ATG)_2$]

Where M^{+2} = (Co, Ni, Cu, Zn, and Cd) ATG = [N-(acetyl amino)-thioxo methyl] Glycine also suggested the tetrahedral form of complexes as it show in Fig.(6).

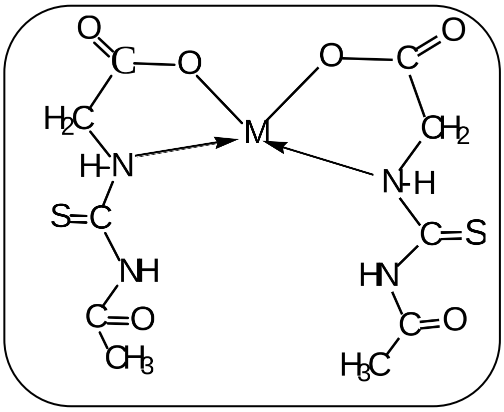


Fig.(6) General structure of complexes.

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الخلاصة

حضر الليكاند الجديد (N–استيل(امينو) ثايوكسو) مثيل كلايسين عن طريق تفاعل استيل ايزو ثايوسيانيت مع الحامض الاميني الكلايسين ومختصره (ATG). وشخص الليكاند مع معقداته المحضرة بالطرق الطيفية ومنها (طيف الرنين النووي المغناطيسي (^{1}HNMR) والاشعة تحت الحمراء (FTIR) وطيف الاشعة فوق البنفسجية والمرئية (UV-VIS) وقياس نسبة الفلز في المعقدات بواسطة طيف الامتصاص الذري فضلا عن قياس التوصيلية الملارية والحساسية المغناطيسية. ومن نتائج هذه الدراسات اقترح الصيغة العامة لهذه المعقدات $[M(ATG)_2]$ اذ ان M تمثل (Co^{+2}, Ni^{+2}, Cu^{+2}, Zn^{+2} و Cd^{+2}) كما اقترح شكل رباعي السطوح لهذه المعقدات.