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Synthesis and Characterisation of Some mixed-Ligand Complexes Contaning N-acetyl Glycine and Pyridine with some Metal Ions

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Abstract

Some metal ions (Mn^{+2} , Fe^{+2}, Co^{+2} , Ni^{+2} , Cu^{+2} , Zn^{+2} , cd^{+2} , Hg^{+2}) complexes of N-acetyl glycine (NAGH) and (pyridine) have been synthesized and then characterized on the basis of their (C.H.N) analysis, IR,UV-Visble spectroscopy and conductive measurements and Magneticsuseptibity. From the results obtained, the following general formula has been given for the prepared complexes:

$[M^{+n}(NAG)_2\,(Py)_2]\,XC_2H_5OH$.

where M=Mn^{+2}, Fe^{+2} , Co^{+2} , Ni^{+2} , Cu^{+2} , Zn^{+2} , Cd^{+2} , Hg^{+2})

n =2 , X= 0.1

$(NAG)^{-}$ =Ligand ion (N-acetylglycinato)

py = pyridine

Introduction

First row transition metal (II) complexes of amino acids have been investigated in consideable details and if there are no complicating donor side chains .The acids coordinate solely through the amino and carboxylato groups forming stable five or six- membered chelate rings with the metal ion .In the peptide complexes, the N(peptide) atom binds a metal only by the dissociation of the peptide proton and the formation of metal-N(peptide) bonds are limited to the d^6-d^9 first row transition metal (1).A third type of coordination was evidentiated in the metal complexes of simple amino acids containing a peptide group,asN-acetyl,N-benzoyl-glycine,β,α-N-benzoyl-Dl- and N-acetyl-L-alanine in which the coordination occurs toward the carboxylato group(2-5) while the peptide

-group is only involved in hydrogen bonding interactions in the crystal packing (6-8).

We have investigated In this paper, the preparation and properties of some metal ion complexes with N-acetyl glycine and amine adduct pyridine.

Experimental

Materials and measurements

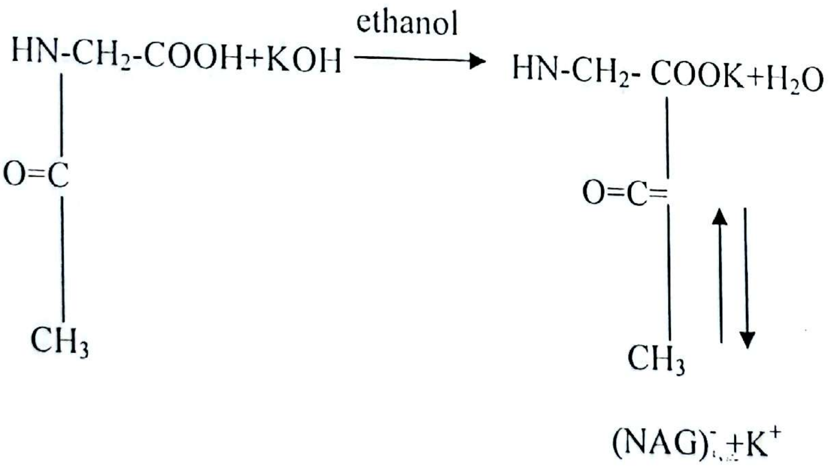
Metal salts($MnCl_2.4H_2O$,$FeSO_4.2H_2O$,$CoCl_2.6H_2O$,$NiCl_2.6H_2O$, $CuCl_2.2H_2O$,$ZnCl_2$,$CdCl_2.H_2O$,$HgCl_2$)were obtained from Fluka,Merk in high purity.Ligand (N-acetyl glycine)(BDH)and (pyridine)(Merck).

Conductivity measurements were carried out using Philips pw.Digital-meter.

The IR spectra in the region(4000-400)Cm^{-1} were recorded using(py-unicam sp_3-300).Infrared spectrophotometer as potassium bromide disc. The Uv –vis spectra were recorded using (Hitachi -4-2000),Uv-vis spectrophotometer in absolute ethanol solution(10^{-3}M).Elemental analysis of the complexes were carried out on a(C.H.N) analyzer at the Department of chemistry.College of Science,University of Mosul.Melting points were determined using(stuart-melting point apparatus).

General Method for the synthesis :

a) N-acetyl glycine (NAGH)was deprotenated according to the following reaction



$$\underset{\underset{CH_3}{|}}{\underset{O=C}{|}}HN-CH_2-COOH+KOH \xrightarrow{\text{ethanol}} \underset{\underset{CH_3}{|}}{\underset{O=C=}{|}}HN-CH_2-COOK+H_2O \rightleftharpoons (NAG)^-+K^+$$

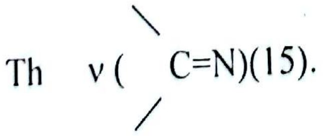
b) synthesis of complexes: Ethanolic solution of the metal salt was added to the solution of the ligand ((NAG)$^-$ in ethanol using stoichiometric amounts(1:2) (Metal:Ligand) the mixture was stirred for half an hour at room temperature.Complexes were separated by adding an excess of pyridine(2mM) (4.5-1 ml) and by treating the solution with diethyl ether until complete precipitation.The precipitates were crystallized from ethanol and dried at 50 C$^\circ$.

Results and Discussion

The isolated complexes were crystalline solids,soluble in some of common solvents such as distilled water ,ethanol and methanol. They are relatively thermally stable.The conductivity measurements in ethanol indicated the non electrolyte behavior. The elemental analysis (C.H.N)were found to be in agreement with the calculated values, table (1) includes the physical properties and elemental analyses.The analytical data confirmed the (1:2:2)(metal):(NAG)$^-$:(pyridine)composition of the complexes. The magnetic measurements (μ_{eff} B.M) for the complexes are also listed in table(1).

Spectral Studies :

Infrared spectra: In order to get further information about the coordination behavior of the ligand (NAGH)and (pyridine)with metal ions,comparisons of the infrared spectra of the free ligands and their complexes have been made and table(2) describes the important absorptions and assignments .The strong band at (3380)cm^{-1} in the spectrum of the free ligand (NAGH)assigned to the ν(N-H)+ ν (OH),while another strong absorption band at (1740)cm^{-1} appeared could be explained as (ν (OCO)$_{asym}$ where the ν (OCO)$_{sym}$ was noticed at (1300) cm^{-1} (9-14) .The spectrum of free pyridine showed bands at (705)cm^{-1}and(748)cm^{-1} the assigned as (CH-out of plane def) and (out of- plane ring def) respectively but the band observed at (1620)cm^{-1} was assingned to



Th ν($>$C=N)(15).

The spectra of complexes exhibited a marked difference .

The absorption band belonging to the stretching vibration of ν (N-H)of the amine group have been found in the range between (3300-3200)cm^{-1} shifted to lower frequencies by (180-80)cm^{-1} suggesting the possibility of the coordination of ligand $(NAG)^-$ through the nitrogen atom at the amine group(16-18) absorption assigned for ν $(OCO)_{sym}$ was noticed at the range(1430-1350)cm^{-1} shifted to higher position by (130-50)cm^{-1} while the band caused by ν $(OCO)_{asym}$ appeared between (1680-1550)cm^{-1} shifted to lower frequencies by (190-60) cm^{-1} which indicates the coordination of the carboxylic group to the central metal ion (17-18).

The stretching vibration band ν (C------N) has been found in the range (1580-1410)cm^{-1}shifted to lower frequency by (200-30)cm^{-1} .Which means that the nitrogen atom of pyridine was involved in the coordination (15).Metal-nitrogen and metal-oxygen bands were further confirmed by the presence of the stretching vibrations of ν(M-N)and ν(M-O)around(650-550)cm^{-1} and (590-420)cm^{-1}, respectively.

Electronic Spectra

The absorptions and assigements related to the ligand and their complexes are listed in table (3).The ligand exhibited an absorption band in (u.v) region at wave number (46728.9)cm^{-1} which may be attributed to (n→ *6) transition ,other two bands of low intensity appeared at (39840.6)cm^{-1} and at (28818.4)cm^{-1} were explained as (∏→∏*) and (n→∏*). respectively .Free pyridine showed absorption band in the (u.v)region at (31250)cm^{-1}which was expressed as the (n→∏*) (19)

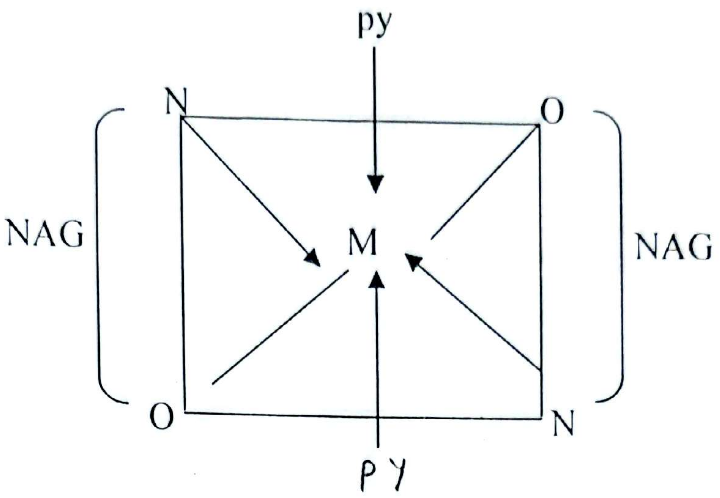
The Spectra of Complexes :

- $[Mn(NAG)_2(Py)_2]$. $C_2H_5OH(d^5)$:-
  The white complex spectrum showed two absorptions at (46948)cm^{-1} and(40322) cm^{-1} and (39525)cm^{-1} attributed to(C.T). The octahedral complex $[Mn(H_2O)_6]^{+2}$spectrum gave similar absorptions at (40000)cm^{-1} and (32960)cm^{-1} related to the same transition (20-21).
- $[Fe(NAG)_2(py)_2](d^6)$: In the spectrum, the yellow complex three absorptions have been noticed at (49504)cm^{-1},(46728)cm^{-1} and (37317)cm^{-1} explanined as (C.T).The band found at (23333)cm^{-1}

was caused by the electronic transition. $^5Eg \leftarrow {}^5T_2g$(22).

- $[Co(NAG)_2(py)_2](d^7)$: The spectrum of the violet complex exhibited the following bands:at (36363)cm^{-1},(21739)cm^{-1} and (16393)cm^{-1}which have been assigned as(C.T),$^4T_1g_{(F)} \xrightarrow{v_3} {}^4T_1g_{(p)}$ and $^4T_1g_{(F)} \xrightarrow{v_2} {}^4A_2g$ respectively ,the calculated value (22) of the other transition $^4T_1g_{(F)} \xrightarrow{v_1} {}^4T_2g$ found to be (8707.8) cm^{-1} (10Dq),the racach inter electronic repulsion parameter (B)found to be (800)cm^{-1} the ratio β=B/ B$_o$ comes out to be (0.824),these parameters are accepted for cobalt (II)octahedral complexes (23- 24).
- $[Ni(NAG)_2(py)_2](d^8)$: The spectrum of green complex exhibited the following absorptions at (36900)cm^{-1} ,(12970)cm^{-1} and (12690)cm^{-1}: these bands are characteristic of octahedral nickel (II)(25)complex and were assigned to the transitions $^3A_2g \xrightarrow{v_3} {}^3T_1g(p)$ Mixed with (C.T),$^3A_2g \xrightarrow{v_2} {}^3T_1g$ and $^3A_2g \xrightarrow{v_1} {}^3T_2g$ respectively ,and the (B) found to be (786.6)cm^{-1} and $\beta = B / B_o$ comes out to be (0.754).
- $[Cu(NAG)_2(py)_2](d^9)$: The blue complex of Cu (II) gave two bands at (39060)cm^{-1} and (34364)cm^{-1} caused by (C.T) transitions and only one absorption band was observed in the visible region at (16077)cm^{-1} which originated to (d $\longrightarrow$ d) transition,similarly the electronic spectra for octahedral complexes of $[Cu(A\text{-}ala)_2(py)_2]$(A-ala)=N-acetyl-alanine) and $[Cu(A\text{-}trp)_2]$(A-trp)=(N-acetyl-Tryptophane)exhibited absorptions at (15750)cm^{-1} and (15400)cm^{-1} respectively (26-27).
- The white complexes $[Zn(NAG)_2(py)_2]$,$[Cd(NAG)_2(py)_2]$ and $[Hg(NAG)_2(py)_2]$. Where the electronic configuration of the metal is (d^{10})confirms the absence of any (d $\longrightarrow$ d) transition (25), the transition with their assignments are summarized in table(3). According to spectral data as well as those obtained from elemental analyses ,the chemical structure of the complexes may be suggested as octahedral for

$[M(NAG)_2(py)_2]$
M^{+2}=(Mn,Fe,Co.Ni,Cu,Zn,Cd,Hg)
$(NAG)^-$= (N- acetyl glycinato)
(py)= (pyridine)



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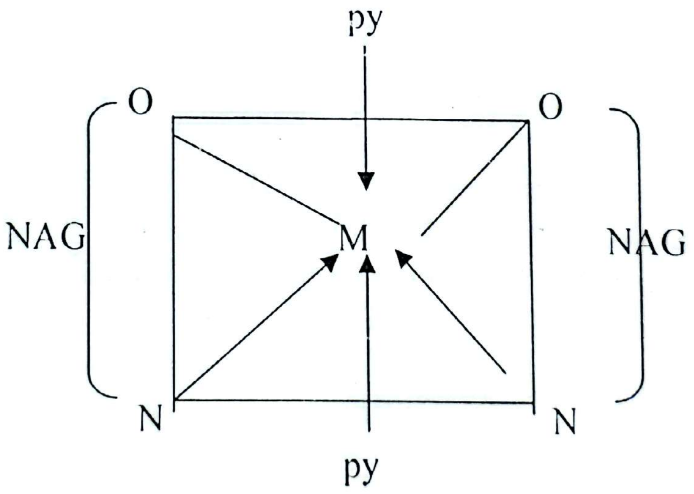

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Table (1) Physical properties and elemental analysis of the complexes

Complexes	Color	M.P.˚C	Dec. .˚C	Analysis calc(found)			Molar conductivity A m (ohm^{-1}.cm^{2}. mol^{-1})in absoult ethanol 10^{-3} M	μ eff (B.M)
				%C	%H	%N		
(NAGH)Ligand	White	209-207	-	-	-	-	2.76	-
[Mn(NAG)$_2$(py)$_2$]C$_2$H$_5$OH	White	202	218	48.87 (48.80)	5.7 (4.42)	11.4 (12.60)	18.50	5.3
[Fe(NAG)$_2$(py)$_2$]	Yellow	-	237	48.43 (48.22)	4.93 (5.02)	12.55 (12.42)	3.39	3.98
[Co(NAG)$_2$(py)$_2$]	Violet	-	186	48.10 (47.24)	4.89 (4.79)	12.47 (12.09)	25.7	4.7
[Ni(NAG)$_2$(py)$_2$]	Grecn	260	272	48.10 (47.78)	4.89 (4.69)	12.47 (12.30)	29.2	3.5
[Cu(NAG)$_2$(py)$_2$]	Blue	156	177	47.6 (47.3)	4.85 (5.00)	12.34 (12.17)	17.36	1.7
[Zn(NAG)$_2$(py)$_2$]	White	212	237	47.47 (46.94)	4.83 (4.79)	12.30 (12.11)	27.7	Di
[Cd(NAG)$_2$(py)$_2$]	White	-	360	43.02 (42.76)	4.38 (4.29)	11.15 (10.98)	15.70	Di
[Hg(NAG)$_2$(py)$_2$]	White	-	187	36.61 (35.98)	3.72 (3.63)	9.48 (9.30)	12.12	Di

***Table (2)* The characteristic infrared of(NAGH),pyridine and its metal complexes**

Complexes	>C=N Pyridine	ν(N-H)	ν $(OCO)_{asym}$	ν $(OCO)_{sym}$	ν (M-N)	ν (M-O)
Ligand (NAGH)	-	3380 sh	1740 s	1300 s	-	-
pyridine	1610	-	-	-	-	-
$[Mn(NAG)_2(py)_2]C_2H_5OH$	1550 w	3250 w	1630 b	1350 w	650 w	450 w
$[Fe(NAG)_2(py)_2]$	1500 w	3200 b	1680 b	1390w	600	440
$[Co(NAG)_2(py)_2]$	1410 w	3240	1650	1390	640	590
$[Ni(NAG)_2(py)_2]$	1410 w	3300	1550 b	1430	600	570
$[Cu(NAG)_2(py)_2]$	1580 w	3240	1630	1390	550	420
$[Zn(NAG)_2(py)_2]$	1550 w	3300	1640 s	1395 m	650 w	560
$[Cd(NAG)_2(py)_2]$	1530 w	3320 w	1595	1430	560	430
$[Hg(NAG)_2(py)_2]$	1550 w	3300 wb	1650	1395	600	560

S = strong , sh =sholder , w =weak

M= middle , b = brode , wb = weak brode

Table (3) The electronic spectra for the free ligand(NAGH),pyridine and its complexes in ethanol(10 M)

Complexes	λ_{max} (nm)	ABS	Wave number cm^{-1}	ϵ_{Max} $LM^{-1}cm^{-1}$	Remarks
(NAGH) $_{Ligand}$	214	0.272	46728.9	272	$n\rightarrow{}^{*}6$
	251	0.161	39840.6	161	$n\rightarrow\Pi^{*}$
	347	0.188	28818.4	188	$\Pi\rightarrow\Pi^{*}$
pyridine	320	109	31250	3800	$n\rightarrow\Pi^{*}$
$[Mn(NAG)_2(py)_2]C_2H_5OH$	213	1.9299	46948	1929.9	(C.T)
	248	2.7545	40322	2754.5	-
	253	2.6830	39525	2683	-
$[Fe(NAG)_2(py)_2]$	202	0.09	49504	90	(C.T)
	214	0.22	46728	220	(C.T)
	268	0.20	37317	200	(C.T) ,(23333)cm^{-1} tail
$[Co(NAG)_2(py)_2]$	275	0.140	36363	140	(C.T) chargetrans fer
	460	-0.011	21739	11	${}^{4}T_1g(f)\xrightarrow{v_1}{}^{4}T_{1g(p)}$
	610	0.009	16393	9	${}^{4}T1g(f)\xrightarrow{v_2}{}^{4}A_2g$
$[Ni(NAG)_2(py)_2]$	271	0.207	36900	207	${}^{3}A_{2g}\xrightarrow{v_1}{}^{3}T_{1g}$ (p),Mixed with (C.T)
	771	0.014	12970	14	${}^{3}A_{2g}\xrightarrow{v_2}{}^{3}T_{1g}$
	788	0.017	12690	17	${}^{3}A_{2g}\xrightarrow{v_1}{}^{3}T_{2g}$
$[Cu(NAG)_2(py)_2]$	256	1.144	39062	1144	(C.T)
	273	0.116	36630	116	(C.T)
	291	0.367	34.364	367	(C.T)
	622	0.040	16077	40	(d→d)
$[Zn(NAG)_2(py)_2]$	211	1.9461	47393	1946.1	Blue shift
	251	2.6698	39840	2669.8	Blue shift
	256	2.6430	39060	2643	Blue shift
$[Cd(NAG)_2(py)_2]$	206	1.1745	48543	1174.5	Blue shift
	251	2.7380	39840	2738	Blue shift
	255	2.6728	39215	2672.8	Blue shift
$[Hg(NAG)_2(py)_2]$	229	2.6813	43668	2681.3	Red shift
	245	2.3484	40816	2836.3	Blue shift
	256	2.3709	39062	3906.2	Blue shift

مجلة ابن الهيثم للعلوم الصرفة والتطبيقية المجلد 18 (4) 2005

تحضير وتشخيص بعض المعقدات الفلزية مع ليكاندات مختلفة من N- استيل كلاسين والبردين

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الخلاصة

يتضمن هذا البحث تحضير وتشخيص بعض المعقدات الفلزية التي تحوي على ليكاندات مختلطة للمشتق (NAGH)(N-acetyl glycine) والبردين (py) وقد تم دراسة هذه المعقدات بالطرائق الطيفية (الاشعة تحت الحمراء والاشعة المرئية –فوق البنفسجية) كما تم اجراء تحليل نسبة العناصر (الكاربون-هيدروجين –نتروجين) والتوصيلية المولارية والحساسية المغناطيسية ، ومن نتاج هذه الدراسات التشخيصية امكن اعطاء الصيغة العامة لهذه المعقدات وكالاتي:

$$[M^{+n}(NAG)_2(py)_2].XC_2H_5OH$$

حيث M= الايون الفلزي

$(Hg^{+2},Cd^{+2},Zn^{+2},Cu^{+2},Ni^{+2},Co^{+2},Fe^{+2},Mn^{+2})$

$n = 2+$ و $x = 0$ و 1

Py= pyridine

$(NAG)^-$= الليكاند الايوني (N-acetyl glycinato)