

Synthesis and Identification of Glycineamide Complexes of Divalent Metal Ion

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Abstract :

Complexes of some divalent metal ions with glycineamide (GlyA) were prepared and identified by IR, UV-Visible, atomic absorption , magnetic susceptibility and conductivity measurements .

The ligand (GlyA) and metal ions were brought into reaction using (1:2) metal: ligand molar ratio in ethanolic medium.

The results showed that the ligand (GlyA) was coordinated to Mn^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} and Zn^{2+} ions through the carbonyl oxygene and the amino nitrogen atoms while it was coordinated through the two amino nitrogen atoms with Cd^{2+} and Hg^{2+} ions .

From the results obtained the following general formula has been given for the prepared complexes $[M(GlyA)_2Cl_2].xH_2O$ with an octahedral geometry around the metal ions for all the complexes.

Where:

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

GlyA= Glycineamide ($H_2N - CH_2 - \overset{O}{\parallel} C - NH_2$)

X = two molecules of water in Mn(II) and Cu(II) complexes .

Introduction :

The metal – ion chemistry of amino acid ligand has now become a major subdivision in inorganic chemistry .It showed wide interesting applications in nature⁽¹⁾and biological system^(2,3),such as in the form of different ternary complexes⁽⁴⁾.They are drew attention to the synthesis and remarkable physical properties of glycine and other amino acids⁽⁵⁻¹⁰⁾.

The Knowledge of metal ion interaction with the amide group will provide insight into protein structure and functional pathways in biological system⁽¹¹⁾,therefore we report the synthesis and spectral studies of some metal ion complexes of ligand glycineamide which contents amide group.

Experimental:

a- Materials and measurements :

Metal salts ($MnCl_2.4H_2O$, $CoCl_2.6H_2O$, $NiCl_2.6H_2O$, $CuCl_2.2H_2O$, $ZnCl_2$, $CdCl_2.2.5H_2O$ and $HgCl_2$) were obtained from fluka and merck in high purity , ligand (glycineamide) from B.D.H .

The I.R spectra of the prepared compounds were recorded in the region $(4000-200)cm^{-1}$ using (SHIMADZU FT.IR-84005) Fourier Transform Infrared Spectrophotometer as cesium-iodid disc . The UV- VIS spectra were recorded in ethanol solution ($10^{-3}M$) by using (SHIMADZU UV-VIS-160A) Spectrophotometer , metal contents of the complexes were determined by atomic absorption technigue by using (SHIMADZU AA 680G) Atomic

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Absorption Spectrophotometer . Conductivity measurements of complexes were carried out at room temperature in ethanol solution (10^{-3} M) by (ELEKTRILEITFA HIGKEIT type SIEMENS) Conductimeter . The magnetic moments (μ_{eff} B.M) were calculated on Faraday method by using (Johnson Matthey Catalytic Systems) . Melting points were determined by using (STUART. SCIENTIFIC) melting point SMP₁ .

b-General procedure for the Synthesis :

A solution of the metal salt (1mmol) in ethanol was added to the ethanolic solution of the ligand (Glycineamide) (GlyA) (2mmol) with constant stirring . The mixture was evaporated on water bath to dryness , the product was crysyalized from ethanol and dried at 50C° .

Results and Discussion :

All the complexes are crystalline powder, freely soluble in ethanol and methanol.

The high melting points of the prepared metal complexes indicated the stability behavior of the new complexes.

The results of atomic absorption analysis are given in table(1), along with the corresponding theoretical values. The % age of metal in each complex suggest a 1:2 metal: ligand structure. .

Spectral Studies :

Infrared Spectra

Peak positions in the IR spectra of the complexes are given in table (2).the frequencies corresponding to uncoordinated ligand are also given for comparison.

The IR spectrum of the free ligand showed a strong band at $(3384)\text{cm}^{-1}$ due to $\gamma(\text{NH}_2)$ stretching vibration ⁽¹²⁻¹⁴⁾. This band has been shifted to higher frequency between

$(3438-3390)\text{cm}^{-1}$ in the spectra of the complexes^(15,16).

A strong sharp band was observed at $(1685)\text{cm}^{-1}$ in the free ligand and was attributed to the stretching mode of carbonyl group⁽¹²⁻¹⁴⁾. This band was shifted towards lower frequencies in all complexes except the Cd(II) and Hg(II) complexes where it was shifted to higher frequencies $(1785$ and 1701cm^{-1} respectively)⁽¹⁷⁻¹⁸⁾. This may be attributed to the coordination of carbonyl oxygen atom to all metal ions except Cd(II) and Hg(II) ions.

On the other hand the C-N stretching mode of the free ligand observed at $(1461)\text{cm}^{-1}$ ⁽¹²⁻¹⁴⁾ was shifted to higher frequencies in all complexes except Cd(II) and Hg (II) complexes where it was shifted to lower frequencies $(1326$ and 1319cm^{-1} respectively) ^(15,16) , this indicates that the over lapping of lone pair of electrons on C-N nitrogen with the two ions Cd(II) and Hg(II) was stronger than with the other ions.

Mn(II) and Cu(II) complexes showed broad absorption band in the rang $(3600-3550)\text{cm}^{-1}$ due to the (OH) stretching vibration of latic water⁽¹³⁾ . In addition several new bands appeared at $(3197-3091)\text{cm}^{-1}$ due to the $\delta(\text{NH}_2)$ bending⁽¹²⁾ .

Other weak bands in the rang $(563-536)\text{cm}^{-1}$, $(476-455)\text{cm}^{-1}$ and $(360-250)\text{cm}^{-1}$ attributed to the $\gamma(\text{M-O})$, $\gamma(\text{M-N})$ and $\gamma(\text{M-Cl})$ bands respectively⁽¹⁶⁾ , table (2) .

All these differences indicate the coordination of ligand (GlyA) to metal ions through the nitrogen atoms of the amine group and oxygen of (C=O) group . While in Cd (II) and Hg(II) complexes , the ligand coordinates with metal ions through the two nitrogen atoms of the amine groups .

Electronic Spectra, Magnetic Moments and Electrical Conductivity Measurements:

The absorption peak related to the ligand and metal complexes and their assignments are listed in table (3) along with the magnetic moments and electrical conductivity measurements.

The electronic spectrum of the ligand (GlyA) Fig(1) exhibited an absorption band in (UV) region at wave number $(45454)\text{cm}^{-1}$ which may be attributed to $(\pi \rightarrow \pi^*)$ transition⁽¹²⁾, another band of low intensity appeared at $(28985)\text{cm}^{-1}$ is explained as $(n \rightarrow \pi^*)$ ⁽¹²⁾.

The magnetic moments values $\mu_{\text{eff}}(B.M)$ of the complexes in the solid state were measured at room temperature using Faraday method. Diamagnetic corrections were carried out using Pascal constants⁽¹⁹⁾. These calculations provide information on the nature of bonding between metal ions and ligand atoms as well as help to estimate the geometry of the complexes.

The molar conductance values of all the compounds in ethanol are in the range $(10-18)$ (siemens.mol⁻¹.cm²) This refers to the non electrolytic nature of the complexes.⁽²⁰⁾

The spectra of Complexes .:

$[\text{Mn}(\text{GlyA})_2\text{Cl}_2](\text{d}^5)$.:

The spectrum of white complex showed an absorption at $(28985.5)\text{cm}^{-1}$ related to the charge transfer (C.T) and only one absorption band was observed in the visible region $(15174.5)\text{cm}^{-1}$ which was assigned to ${}^6A_1g \rightarrow {}^4T_2g_{(g)}$ ^(21,22) the magnetic moment $(\mu_{\text{eff}} = 5.2B.M)$ refer to the octahedral geometry around Mn(II) ion⁽¹⁹⁾.

$[\text{Co}(\text{GlyA})_2\text{Cl}_2] 2\text{H}_2\text{O}(\text{d}^7)$.:

The spectrum of the violet complex fig(2) exhibited the following

bands at $(31446.5)\text{cm}^{-1}$, $(15151.5)\text{cm}^{-1}$ and $(10989)\text{cm}^{-1}$ which have been assigned to ${}^4T_1g \xrightarrow{\gamma_1} {}^4T_1g_{(p)}$ mixed with (C.T), ${}^4T_1g_{(p)} \xrightarrow{\gamma_2} {}^4A_2g$ and ${}^4T_1g \xrightarrow{\gamma_3} {}^4T_2g$ respectively⁽²¹⁾. the observed magnetic moment $(\mu_{\text{eff}} = 4.5B.M)$ further illustrated the octahedral geometry around Co(II) ion^(19,21).

$[\text{Ni}(\text{GlyA})_2\text{Cl}_2](\text{d}^8)$.:

The spectrum of green complex fig (3) exhibited the following absorption at $(31250)\text{cm}^{-1}$, $(11001)\text{cm}^{-1}$ and $(9560)\text{cm}^{-1}$ these bands are characteristic to the transition

${}^3A_2g \xrightarrow{\gamma_1} {}^3T_1g_{(p)}$ mixed with (C.T)

${}^3A_2g \xrightarrow{\gamma_2} {}^3T_1g$ and ${}^3A_2g \xrightarrow{\gamma_3} {}^3T_2g$ respectively⁽²²⁾ related to octahedral nickel (II) complex $(\mu_{\text{eff}} = 3.2B.M)$

$[\text{Cu}(\text{GlyA})_2\text{Cl}_2]2\text{H}_2\text{O}(\text{d}^9)$.:

The blue complex of Cu(II) gave two bands at $(34722)\text{cm}^{-1}$ and $(28985)\text{cm}^{-1}$ caused by (C.T) transitions and only one absorption band was observed at $(12853)\text{cm}^{-1}$ which assigned to $(d \rightarrow d)$ transition^(21,22). the magnetic moment $(\mu_{\text{eff}} = 1.7B.M)$ gives another evidence for the octahedral geometry around Cu(II) ion⁽¹⁹⁾.

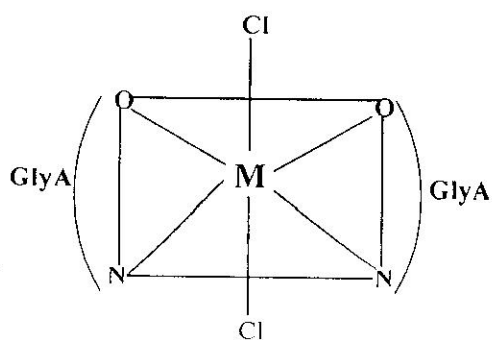
The white complexes $[\text{Zn}(\text{GlyA})_2\text{Cl}_2]$, $[\text{Cd}(\text{GlyA})_2\text{Cl}_2]$ and $[\text{Hg}(\text{GlyA})_2\text{Cl}_2]$ in which the electronic configuration of the metal is (d^{10}) confirm the absence of any $(d \rightarrow d)$ transition⁽²⁰⁾. these complexes were diamagnetic⁽¹⁹⁾.

According to spectral data as well as the magnetic moment and those obtained from metal analyses, the structural formula of the complexes may be suggested as octahedral for $[\text{M}(\text{GlyA})_2\text{Cl}_2] \cdot x\text{H}_2\text{O}$.

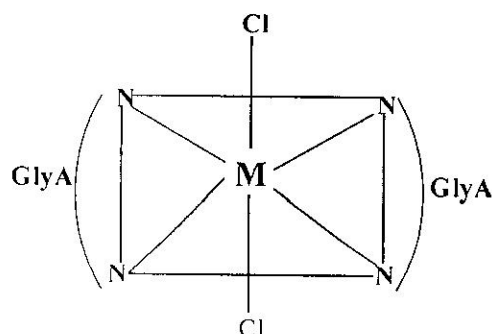
GlyA = Glycineamide ($\text{H}_2\text{N}-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{NH}_2$)

$\text{M}^{+2} = \text{Mn}, \text{Co}, \text{Ni}, \text{Cu}, \text{Zn}, \text{Cd}, \text{Hg}$.

X = two molecules of water in Mn(II) and Cu(II) complexes.



$\text{M} = \text{Mn(II)}, \text{Co(II)},$
 $\text{Ni(II)}, \text{Cu(II)},$
 $\text{Zn(II)}.$



$\text{M} = \text{Cd(II)}, \text{Hg(II)}$

Table (1) : Physical properties and metal analysis of the compounds .

Sl. No.	Compound	Color	Molecular Weight (Calcd)	Weight %	Elemental Analysis (%)
1	[GlyA]	Whit	182	-	-
2	[Mn(GlyA) ₂ Cl ₂].2H ₂ O	Whit	170black (192)	35.6	17.7 (16.8)
3	[Co(GlyA) ₂ Cl ₂]	Violet	(238)	58.9	21.27 (20.7)
4	[Ni(GlyA) ₂ Cl ₂]	Green	(236)	35.01	21.2 (20.81)
5	[Cu(GlyA) ₂ Cl ₂].2H ₂ O	Blue	156 brown (190)	38.62	20 (19.3)
6	[Zn(GlyA) ₂ Cl ₂]	Whit	(224)	46.02	23.06 (22.3)
7	[Cd(GlyA) ₂ Cl ₂]	Whit	(248)	42.59	34.01 (33.4)
8	[Hg(GlyA) ₂ Cl ₂]	Whit	(210)	43.36	47.9 (-)

Table (2) : The characteristic infrared bands (cm^{-1}) for the free ligand (GlyA) and metal complexes .

Sl. No.	Compound	$\nu(\text{NH}_2)$	$\nu(\text{C}=\text{O})$	$\nu(\text{C}-\text{N})$	$\delta(\text{NH}_2)$	$\nu(\text{C}-\text{O})$	$\nu(\text{C}-\text{H})$	$\nu(\text{C}-\text{N})$
1	[GlyA]	3384	1685	1461	-	-	-	-
2	[Mn(GlyA) ₂ Cl ₂].2H ₂ O	3390	1654	1593	3197	474	536	250 w
3	[Co(GlyA) ₂ Cl ₂]	3394	1604	1571	3170	472	559	275 w
4	[Ni(GlyA) ₂ Cl ₂]	3392	1637	1591	3176	476	555	360 w
5	[Cu(GlyA) ₂ Cl ₂].2H ₂ O	3392	1670	1585	3083	470	559	285 w
6	[Zn(GlyA) ₂ Cl ₂]	3394	1593	1556	3155	474	563	300 w
7	[Cd(GlyA) ₂ Cl ₂]	3398	1785	1326	3122	464	-	320 w
8	[Hg(GlyA) ₂ Cl ₂]	3438	1701	1319	3124	455	-	310 w

Table (3) : UV/Visible absorption bands and assignment for the free ligand (GlyA) and metal complexes with magnetic moments and electrical conductivity data.

Ord. No.	Compound	λ_{max} (nm)	ϵ_{max} (L mol ⁻¹ cm ⁻¹)	λ_{max} (nm)	ϵ_{max} (L mol ⁻¹ cm ⁻¹)	Assignment	Molar Conductivity Λ_m (S cm ² mol ⁻¹)	μ_{eff} (BM)
1	[GlyA]	220 345	0.554 0.033	43454 28985	554 33	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$	3	.
2	[Mn(GlyA) ₂ Cl] ₂ H ₂ O	345 659	0.233 0.199	28985 15174.5	233 199	C, T ${}^6A_{1g} \rightarrow {}^2T_{2g}(D)$	10	5.2
3	[Co(GlyA) ₂ Cl]	318 660 910	2.260 0.260 0.200	31446 15151 10999	260 260 200	${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(F)$ ${}^4T_{1g}(F) \rightarrow {}^4A_{1g}$ ${}^4T_{1g} \rightarrow {}^4T_{2g}$	14	4.5
4	[Ni(GlyA) ₂ Cl]	320 909 1046	0.584 0.201 0.199	31250 11001 9560	384 201 199	${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$ ${}^3A_{2g} \rightarrow {}^3T_{1g}$ ${}^3A_{2g} \rightarrow T_{1g}$	12	3.2
5	[Cu(GlyA) ₂ Cl] ₂ H ₂ O	226 345 778	1.216 0.224 0.236	34722 28985 12853	1216 224 236	C, T C, T $d \rightarrow d$	15	1.7
6	[Zn(GlyA) ₂ Cl]	224 340	0.345 0.201	44642 29111	245 201	Red Shift Blue Shift	13	Diamagnetic
7	[Cd(GlyA) ₂ Cl]	224 342	0.359 0.199	44642 29239	359 199	Red Shift Blue Shift	11	Diamagnetic
8	[Hg(GlyA) ₂ Cl]	226	1.335	44247	1335	Red Shift	18	Diamagnetic

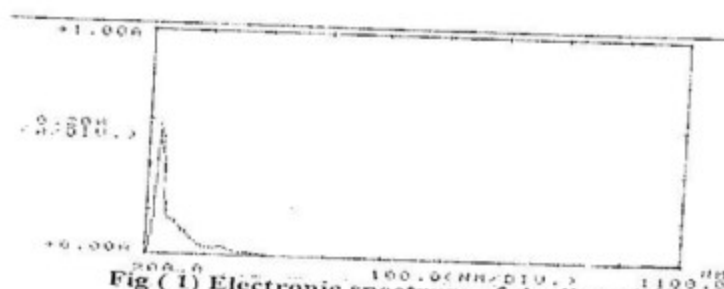


Fig (1) Electronic spectrum of the ligand (GlyA)

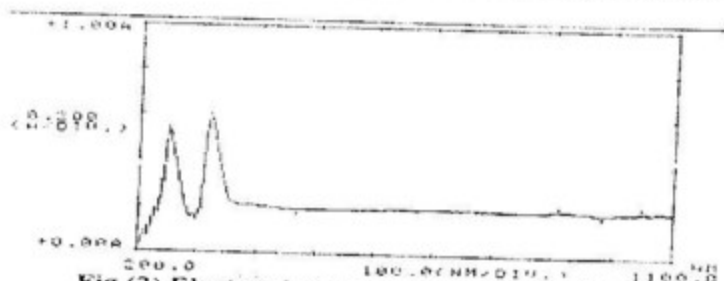


Fig (2) Electronic spectrum of the Co(II) complex

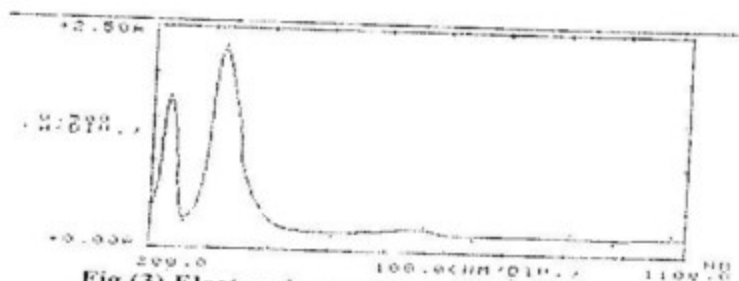


Fig (3) Electronic spectrum of the Ni(II) complex

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تحضير وتشخيص معقدات للكلاليسين أميد مع بعض أيونات الفلزات ثنائية الشحنة

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الخلاصة :-

لقد تم تحضير وتشخيص معقدات لبعض أيونات الفلزات ثنائية الشحنة مع الليكاند (Glycineamide)(GlyA) وذلك من خلال مفاعله مع أيونات المنغنيز ، الكوبلت ، النيكل ، النحاس ، الزنك ، الكاديوم ، والزرنيق الثنائية الشحنة في مذيب الأيثانول بنسبة مولية (٢:١) (فلز : ليكاند) . المعقدات المحضرة مواد صلبة بعضها ملون . وقد تم تشخيصها بالطرائق المعروفة ومنها الأمتصاص الذري وأطياف الأشعة تحت الحمراء والأشعة فوق البنفسجية - المرئية ، والتوصيلية المولارية والحساسية المغناطيسية ومن الدراسات التشخيصية اعلاه . أمكن اعطاء الصيغة العامة لهذه المعقدات وكالاتي
 $[M (GlyA)_2 Cl_2] . xH_2O$

اذ : M = الأيون الفلزي الثنائي الشحنة ($Hg^{+2}, Cd^{+2}, Zn^{+2}, Cu^{+2}, Ni^{+2}, Co^{+2}, Mn^{+2}$) .



X = جزيئين ماء في كل من المعقدين Cu(II) , Mn(II) .

ويسلك الليكاند سلوك ثنائي السن اذ يرتبط بالأيون الفلزي عن طريق الاوكسجين في مجموعة الكربونيل وذرة النتروجين في مجموعة الأمين في معقدات (المنغنيز ، الكوبلت ، النيكل ، النحاس ، الزنك) في حين يرتبط عن طريق ذرتي النتروجين للأمين في معقدات (الكاديوم ، الزرنيق) .