



Research Article

ISSN : 0975-7384
CODEN(USA) : JCPRC5

Synthesis and investigation of complex formation between amino acid (glycine) and various metal ion by using spectroscopic methods

Faliah Hassan Ali Al-Jeboori and Thaera Abdulridha Mussa Al-Shimiesawi

Ministry of Science and Technology, Baghdad, Iraq

ABSTRACT

The solid complexes of $[M(C_2H_4O_2N)_2 \cdot H_2O]$ [where M: Mn^{+2} , Cu^{+2} , Co^{+2} , Ni^{+2} , Zn^{+2} , Cd^{+2} and Pb] were obtained from the reaction of chloride salt of cobalt (II), copper (II), Nickel (II), Manganese (II), Zinc (II), Cd (II), and Pb(II), with the sodium salt of the amino acid glycine. The complexes characterized by mean infrared, microelemental analysis (C.H.N) and atomic absorption analysis (A.A.S). The amino acid act as bidentate ligand with coordination involving the carboxylic oxygen and nitrogen atom of amino group. The $\nu(C=O)$, $\nu_{st}(N-H)$ and $\nu_b(N-H)$ vibration are shifted to higher frequencies for complexes comparable with ligand the atomic absorption spectroscopy and microelemental analysis, confirms the compounds stoichiometry. The compounds show poor solubility in water and in the common organic solvents. This behavior is consistent with a polymeric chain.

Keywords: amino acid, glycine, metal, complex, spectroscopic.

INTRODUCTION

In recent years transition metals amino acid complexes have received much attention because they proved to be useful antibacterial agents applied against *Staphylococcus aureus*, *Escherichia coli*, nutritive supplies for humans and animals [1]. Twenty natural amino acids comprise the building block of proteins, which are chemical species indispensable to perform a large number of biological functions [2]. From these twenty amino acids, eight are essential and cannot be produced by the human body. Complexes of transition metal with amino acids in proteins and peptides are utilized in numerous biological processes, such as oxygen conveyer, electron transfer and oxidation. In these processes the enzymatic active site which is very specific, forms complexes with divalent metal ions [3].

A knowledge of the interaction between biological active molecules and metal is needed when preparing biomaterials or considering certain aspects of biocompatibility. The study of model species such as the simple amino acids can assist in the interpretation of more complex systems. Amino acids have a neutral donor N at one end and a sufficient length to span two adjacent coordinating sites and the resulting complexes are non-electrolyte chelates or inner complex compounds.

Glycine is the simplest amino acid in the body and the only protein amino acid that does not have optical isomers. Glycine consists of a single carbon molecule attached to an amino and a carboxyl group. Its small size helps it to function as a flexible link in proteins and allows for the formation of helices, an extracellular signaling molecule, recognition sites on cell membranes and enzymes, a modifier of molecular activity via conjugation and glycine extension of hormone precursors, and an osmoprotectant. There is substantial experimental evidence that free glycine may have a role in protecting tissue, against insults such as ischemia, hypoxia and reperfusion [4].

Glycine is a necessary building block for all proteins in the body, glycine plays a major role in calcium absorption, building muscle protein, recovering from surgery or sports injuries and the body's production of hormones, enzymes and antibodies. It has been suggested that glycine may be beneficial for those with herpes simplex infection [4].

EXPERIMENTAL SECTION

Chemical :- All common laboratory chemicals and reagents have been used without further purification.

Physical Measurements:- The following measurements were used to characteristic the complexes.

Infrared spectra were performed using [FT- IR] [ABB-MB 3000] spectrophotometer in the range (4000-400) cm^{-1} spectra were recorded as potassium bromide discs .

Elemental microanalysis were performed on a (C.H.N.) analyzer from [Perkin Elmer-2400 CHNSO]

Metal analysis were measured with [Phoenix-986] atomic absorption spectrophotometer.

An electrothermal apparatus start melting point was used to measure the melting points.

Synthesis of metal ions complexes :- The purpose of the study, was, to obtain, neutral, complexes, of [$\text{M}^{+2}(\text{GLY H}_2\text{O})_2$] [where M = metal ion : (Mn , Cu , Co ,Ni , Zn , Cd and Pb) GLY = Glycine. Type at pH= (8-10) , in the presence of a strong basic (NaOH) to obtain the ionization conditions of the amino acid Glycine . The complexes were prepared following procedure described in the literature [5]:

2 mmole of GLY (0.15 g) were dissolved in 20 ml distilled water and deprotonation of the amino acid 0.33 ml 30% NaOH was added , then 1 mmole of metal salt of metal ions was dissolved in 2 ml distilled water and was added to deprotonated amino acid solution under stirring for several minutes. The precipitate was filtered off , washed with water several times and dried in air . Melting point were recorded on an electrothermal analyser working in the temperature range of (20°C and 370°C) Table (1) .

Table 1: Some physical properties of the prepared complexes

Empirical formula	Colour	m.p (C ^o)	Wt of product (g)	Yield (%)
[Mn (GLY H ₂ O) ₂]	Brown	296	0.7618	53
[Cu (GLY H ₂ O) ₂]	Brown	290	0.94	58
[Co (GLY H ₂ O) ₂]	Pink	245	0.205	56
[Ni (GLY H ₂ O) ₂]	Green	280	0.45	58
[Zn (GLY H ₂ O) ₂]	White	< 330	0.38	55
[Cd (GLY H ₂ O) ₂]	White	280	0.72	54
[Pb (GLY H ₂ O) ₂]	white	< 330	2.07	53

RESULTS AND DISCUSSION

The various EI device allows the quantitative determination of the carbon, nitrogen and hydrogen in various operating modes. For the synthesized copper, cobalt, Nickel, manganese, zinc, cadmium and lead Complexes the elemental analysis results confirm the 1:2 copper ion to ligand composition Data of the elemental analysis for metal ion amino acids complexes are illustrated in Table (2).

Table 2: Elemental analysis for Copper, Cobalt, Nickel, Manganese, Zinc, Cadmium and Lead complexes

Complex Proposed formula	Molecular weight	%C		%H		%N	
		Calc.	Meas.	Calc.	Meas.	Calc	Meas.
Glycine	75	32	30.12	6.66	7.1	18.6	17.60
Cu.(Gly) ₂ .2H ₂ O	247.5	19.39	18.92	4.84	4.62	11.3	11.8
Co.(Gly) ₂ .2H ₂ O	243.3	19.72	19.12	4.93	4.52	11.5	11.32
Ni.(Gly) ₂	206.7	23.20	24.21	3.87	3.51	13.5	13.91
Mn.(Gly) ₂ .2H ₂ O	239	20.10	20.51	5.02	4.91	11.70	12.10
Zn.(Gly) ₂	213.3	22.51	23.01	3.75	3.61	13.12	13.91
Cd.(Gly) ₂ .2H ₂ O	296.4	16.19	17.21	4.04	3.95	9.44	10.01
Pb.(Gly) ₂ .2H ₂ O	391.12	12.27	13.01	3.07	3.41	7.15	7.51

The metal ions complexes theoretical concentrations have similar values with those of the synthesized complexes. Which demonstrates the complete reaction took place Table (3).

The I.R spectra for glycine and its complexes are shown in figs (1-7), and the assignment of the characteristic bands are summarized in Table (4). As it was postulated, for amino acid, the difference between the vibrational frequencies $\nu_{\text{as}}(\text{Coo}^-)$ and $\nu_{\text{s}}(\text{Coo}^-)$, generally increase when the M-o bond strength increases depending on the

carboxylate coordination which can be monodentate or bidentate (8). The monodentate coordination gives rise to values closer to those found for ionic carboxylate compounds, as for instance for amino acid.

Table 3: Metal ions complexes concentration obtained by means of atomic spectroscopy

Proposed formula	Metal ions complexes %	
	Synthesized	Theoretical
Cu.(Gly) ₂ .2H ₂ O	26.61	25.6
Co.(Gly) ₂ .2H ₂ O	25.31	24.24
Ni.(Gly) ₂	27.91	28.39
Mn.(Gly) ₂ .2H ₂ O	24.50	23.01
Zn.(Gly) ₂	31.14	30.64
Cd.(Gly) ₂ .2H ₂ O	38.01	37.92
Pb.(Gly) ₂ .2H ₂ O	53.21	52.95

The vibrational frequencies related to $V_{as}(\text{Coo}^-)$ and $V_s(\text{Coo}^-)$ in glycine occur at (1611 and 1414) cm^{-1} , while for Mn (II) complex observed at (1634 and 1364) cm^{-1} , for Cu (II) complex at (1623 and 1384) cm^{-1} , for Co (II) complex observed at (1657 and 1422) cm^{-1} for Ni (II) complex observed at (1627 and 1399) cm^{-1} and for Zn (II) complex observed at (1680 and 1391) cm^{-1} .

So for glycine $\nu = 197$ and for metal complexes occur in the range $\nu = 17-289$. These values are an indication that both oxygen atoms of the carboxyl group are involved in coordination to the metal ions, as it occurs for polymeric metal complexes with methionine [8], for such complexes two metal ions as bidentate – bridging group forming a polymeric structure [8].

Two very well resolved bands at 1500 cm^{-1} and broad at 3100 cm^{-1} are an indication of the amino group to the metal ion (7). In the infrared spectrum of glycine the broad band at 3170-2529 cm^{-1} and a medium band 1507 cm^{-1} correspond to ν NH_2 stretching and bending vibration respectively for free ligand is shifted in the spectra of the complexes and appears at (3420 and 1438) cm^{-1} for Mn (II) complex, (3344 and 1450) cm^{-1} for Cu (II) complex, (3289 and 1850) cm^{-1} for Co (II) complex, (3436 and 3640_(b)) cm^{-1} for Ni (II) complex and (3413_(b) and 1507_(s)) cm^{-1} for Zn (II) complex.

These shifted compared to those of the free ligand, which means that ($-\text{NH}_2$) group is involved in metal-ligand formation. The absence of $\delta(\text{NH}_3^+)$ band at 2128 cm^{-1} in the spectra of the complexes in comparison to the free as ligand, also constitute another valuable to the free ligand, also constitute another valuable proof of the involvement of NH_2 group coordination.

Infrared spectra of the complexes were also measured in the region 400-700 cm^{-1} in order to identify frequencies related to M-O and M-N bands. The M-O frequencies for Mn (II), Cu (II), Co (II), Ni (II) and Zn (II) complexes were observed respectively at 527 cm^{-1} , 527 cm^{-1} , 531 cm^{-1} , 531 cm^{-1} , 570 cm^{-1} and 620 cm^{-1} respectively. While M – N frequencies were identified at range (300 – 500) cm^{-1} . These results are in agreement with literature value, being similar to other metal complexes with amino acid [9].

The ν (O-H) stretching vibration do not appear in the ligand, Ni (II) complex and Zn (II) complex spectra, but they do in spectra of other complexes at range (3450 – 3750) cm^{-1} suggesting the presence of the crystal and coordinated water in these compounds.

Table 4: Some important IR bands of glycine and its metal complexes

Compounds	$V_{as}(\text{COO}^-)$	$V_s(\text{COO}^-)$	$V(\text{C=O})$	$V_6(\text{NH}_2)$	$V_{st}(\text{NH}_2)$
glycine	1414	1611	1715	1507	3170-2520 (br)
Mn.gly	1364	1634	1715	1438	3420 (br)
Cu.gly	1384	1623	—	1450	3344, 3443
Co.gly	1422	1657	—	1580	3197, 3123, 3289
Ni.gly	1399	1627	1708	—	3436-3640 (br)
Zn.gly	1391	1680	—	1507	3413 (br)
Cd.gly	1438, 1399	—	1793	1565	3478
Pb.gly	1391	—	1685	1507	3413

as = asymmetric br = broad b = binding s = symmetric st = stretching

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