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MODEL STUDIES OF THE INTERACTION OF BASE-METAL CONTAINING MINERALS WITH SOME BIOLOGICAL ALTERATION COMPOUNDS IN ORE-BODIED ENVIRONMENT

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ABSTRACT

Studies dealing with the complex behaviors of some N-benzoyl and N-formyl amino acids, and dipeptides with base-metal containing compounds were carried out. The results indicate that coordination sites of N-protected amino acids and dipeptides are different from those of the free amino acids and peptides. Complexes of Zn (II) with N-benzoyl derivatives of L-leucine, L-leucylglycine and N-formyl derivatives of DL-valine, L-phenylalanine, DL-valylglycine and L-phenylalanylglycine were prepared in the course of the studies. The possible stereochemistry of these compounds have been deduced with the help of analytical data, infrared spectra (IR), thermogravimetric analysis (TGA) and differential thermal analysis (DTA).

Keywords: dipeptide, benzoyl, stereochemistry, ligand, precipitate, spectra.

INTRODUCTION

The modeling of the interaction of base-metal containing minerals, with some biological alteration in ore-bearing zones in relatively elevated temperature, has become significant in tropical countries such as Nigeria. Microorganism found growing in soils and on rocks surfaces are all known to excrete a host of oxygen-donor ligands [1-2]. The ligands range from simple carboxylic acids to oxyacids and aromatic species. Major ones among these are oxalic, citric and tartaric acids, their analogues, and congeners, and benzoic, hydroxybenzoic and dihydroxybenzoic acids. All of these ligands form strong complexes with hard acids such as Al (III). Fe (III), Zn (II) and Ca (II) ions. thus causing their mobilization in aqueous solution. The interaction of Cu (II) ions with N-protected amino acids has previously been reported [3-5].

Many of the compounds which occur in nature or and are able to be synthesized in the laboratory are not confined to species comprising of compounds generated from atoms via loss or gain of electrons. The real elaboration of the number and kinds of compounds that can form arises from the fact that complex ions are able to form via the combination of certain elements at some specified temperatures. The conditions under which the organic compounds containing base-metal minerals would be thermo-chemically stable will need to be investigated. The relative metal-organic mobility and solubility in oxidizing sulfide ores when large quantities of organics are available in solution need to be reassessed. Unfortunately, most of the agricultural and mineral resources richly endowed in Nigeria, are in their natural states which are not the usable forms in terms of quality and specification.

The aim of this study was to investigate the interaction at the coordination sites in base-metal containing minerals especially those in the oxidation zones with elevated temperature of Nigerian ore deposits. Models for their coordination in weathered environments have been developed in the process. Therefore, this work on the base-metal containing organic compounds using IR, TGA and DTA set to reconnaissance, prospect and appraise minerals in Western zone of Nigeria.

MATERIALS AND METHODS

Ammonium hydrogen (100cm^3) was added to a solution (100cm^3) of Zn (II) chloride in 10% hydrochloric acid. The resulting gelatinous precipitate produced Zn (II) hydroxide. Complexes of Zn (II) were prepared by the addition of a mixture of N-benzoyl (20cm^3), N-formyl (40cm^3), and amino acid (200cm^3) to a suspension of freshly prepared Zn $(OH)_2$ in methanol. The resulting solution was agitated with magnetic stirrer, for 10 hrs. The complexes (Tables 1-3) were prepared in the same way by substituting the amino acid with dipeptides at weights in ratio (1:2:10). Excess Zn $(OH)_2$ was evaporated under vacuum. The residues left were washed with acetone and recrystallized using methanol. Amounts of zinc were determined by complex metric titration with EDTA. Total zinc, carbon. hydrogen and nitrogen were analyzed.

Table-1. The yield found and expected percentages for Zn, C, H and N.

S. No.	Complex	% Yield	% Observed				% Expected			
			Zn	C	H	N	Zn	C	H	N
1	Zn (Bz-LeuO)$_2$	60	12.1	58.22	5.89	5.10	12.19	58.53	6	6.25
2	Zn (Bz-Leu GlyO)$_2$	60	10.4	55.4	58.88	8.60	10.04	55.64	6.87	8.05
3	Zn (For-ValO)$_2$.2H$_2$O	63	16.45	36.95	6.36	7.16	16.17	37.01	6.16	7.17
4	Zn (For-Val GlyO)$_2$.2H$_2$O	67	12.8	38.1	6.09	11.10	12.92	38.17	5.96	11.12
5	Zn (For-PheO)$_2$.2H$_2$O	70	13.2	49.64	5.08	5.70	13.4	49.48	4.94	5.77
6	Zn (For-PheGlyO)$_2$.2H$_2$O	65	10.7	47.96	4.98	9.20	10.85	48.08	5.01	9.31

Table-2. Frequency of infrared spectra for the ligands.

S. No.	Complex/Legends	Infrared spectra (cm^{-1})					
		Nco	V$_{NH}$	Ncooasym	Vcoosym	Vcoo	NcooH
1	Bz-Leu	1645	3320	1540	1320	220	1720
2	Zn (Bz-LeuO)$_2$	1645	3320	1530	1380	150	
3	Bz-Leu Gly	1645	3180	1560	1380	200	1730
4	Zn (Bz-Leu GlyO)$_2$	1645	3180	1545	1400	145	
5	For-Val	1625	3160	1570	1370	200	1730
6	Zn (For-ValO)$_2$.2H$_2$O	1630	3160	1555	1410	145	
7	For-Val Gly	1640	3300	1570	1370	200	1730
8	Zn (For-Val GlyO)$_2$.2H$_2$O	1640	3300	1545	1395	150	
9	For-Phe	1615	3330	1550	1340	210	1730
10	Zn (For-PheO)$_2$.2H$_2$O	1620	3330	1535	1390	145	
11	For-PheGly	1645	3330	1550	1330	220	1745
12	Zn (For-PheGlyO)$_2$.H$_2$O	1650	3330	1540	1395	145	

The infrared spectra, IR, using KBr were recorded with FT-IR spectrometer (Nicollet-TM 380). Similarly, the peak temperatures were obtained, Differential Thermal Analysis, (DTA) using a Precision electronic balance (Thermo Fisher) apparatus. Thermo Gravimetric Analysis (TGA) studies were carried on a manual instrument (Scrooge and West). The amounts of Zn were determined by complexometric titration with EDTA. Carbon, hydrogen, nitrogen were analyzed using micro analytical methods [6].

Table-3. Physical properties of metal/legend complexes.

S. No.	Complex	Melting point / decomposition temperature (t^{0}C)	DTA peak temperature (t^{0}C)	% Loss observed in TGA at temp (t^{0}C)	% Loss calculated (due to)
1	Zn (Bz-LeuO)$_2$	222-224	-	-	-
2	Zn (Bz-Leu GlyO)$_2$	215-218	-	-	-
3	Zn (For-ValO)$_2$.2H$_2$O	188-190	150,180,470 460 (endo)	(4.70)180	(4.6)H$_2$O
4	Zn (For-Val GlyO)$_2$.2H$_2$O	185-188	180,240,530 450 (exo)	(7.25)180	(7.15)2H$_2$O
5	Zn (For-PheO)$_2$.2H$_2$O	192-194	160,180,290 630 (endo)	-	-
6	Zn (For-PheGlyO)$_2$.2H$_2$O	194-196	150, 190, 280, 570, (endo) 440	(3.10)150	(3.10)1H$_2$O

RESULTS AND DISCUSSIONS

The complexes, their yields and analytical data are reported for Zn, C, H and N in Table-1. These are presented in histogram forms in Figures 1 to 4. The bar charts plotted from the data in the Tables are equal to the amounts of the complex.

Figure-1. The yield observed and expected percent for Zn.

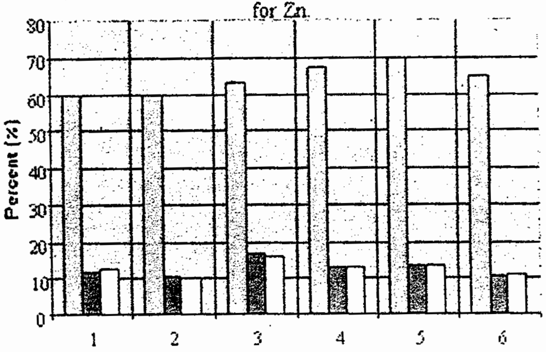
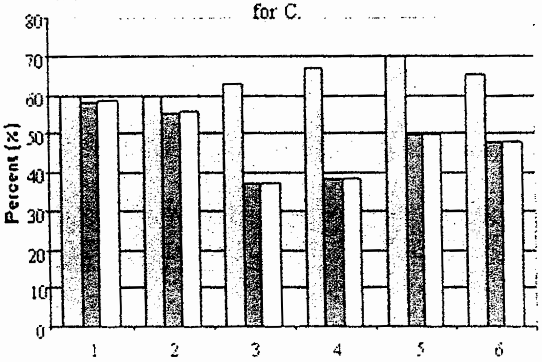


Figure-2. The yield observed and expected percent for C.



Legend ☐ % Yield ▨ % Observed ☐ % Expected
1. - Zn (Bz-LeuO) 2; 2. - Zn (Bz-LeuGlyO) 2; 3. - Zn (For-ValO) 2.2H2O
4. - Zn (For-Val GlO) 2.2H2O 5. - Zn (For-PheO) 2.2H2O 6. - Zn (For-Val GlO) 2.2H2O

Figure-3. The yield, observed and expected percent for H

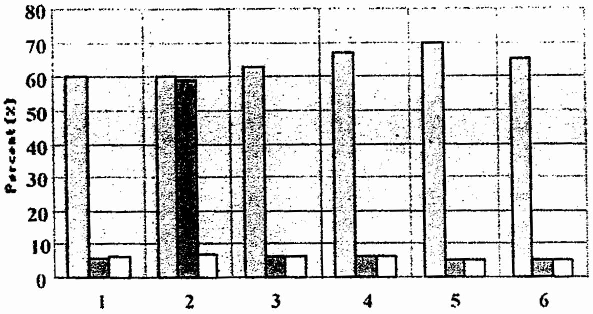
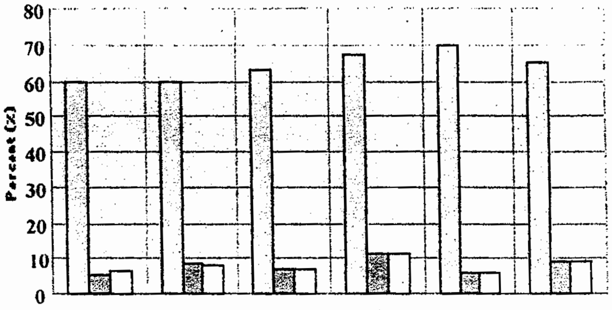


Figure-4. The Yield, observed and expected percent for N



LEGEND: ☐ **% Yield** ▨ **% Observed** ☐ **% Expected**
1. - Zn(Bz-LeuO)2; **2. - Zn(Bz-LeuGlyO)2;** **3. - Zn(For-ValO)2.2H2O**
4. - Zn(For-Val GlO)2.2H2O **5. - Zn(For-PheO)2.2H2O** **6. - Zn(For-Val GlO)2.2H2O**

Since limited amounts of the synthesized complex are available hence the plots of the bar chart to show the frequency of values in successive small ranges of concentration. Many types of organic containing base metal compounds have been recognized in some natural compounds [2, 7]. Even trace amounts of organic materials can have effects on the chemistry of the trace elements as demonstrated in this work. These effects include complexion of trace ions by dissolved organic matter, resulting in increase immobilization of element; adsorption or formation of organic compounds and reduction of lower valence states with resulting changes in chemical properties. Major types of natural organic compounds include the following, carbohydrates, hydrocarbons, alcohols, organic acids, fats, waxes, amino acids, proteins, humic substances, porphyries, vitamins, pigments and other complex compounds. Most of these compounds are found in or associated with living organisms.

However, the elemental content of metals in particular of natural water may be enhanced under arid climate condition by evaporation and resulting concentration of all the dissolved solids. It may also vary in response to variations in the content of soluble organic matter.

The corresponding infrared spectra are in Table-2. The melting point, (mp), DTA and TGA are reported in Table-3.

The infrared spectra absorption bands of N-protected amino acids and peptides 1720-1745 cm^{-1}, 1320-1370 cm-1 (ν_{COOH} and $\nu_{COO\ sym}$. [8] and 1615-1645 cm^{-1} (ν_{CO}) indicate the co-ordination behaviors of amino acids and peptides. The absorption bands at 1530-1555 cm^{-1} and 1380-1410 cm^{-1} have been assigned to ν_{COO}

respectively. The positions of the bands and the difference between the asymmetric and symmetric stretching frequencies i.e. 145-150cm.$^{-1}$ indicate the bidentate co-ordinate of carboxylate group [9-10]. In all these complexes positions of NH and carbonyl stretching frequencies remain unchanged as compared with those of the free ligands (Table-2), indicating the lack of co-ordination at the benzoyl-amino group, formyl-amino acids two absorption bands at 790 and 2280cm^{-1} are observed with the characteristic bands of coordinated water. These are illustrated in Figure-5.

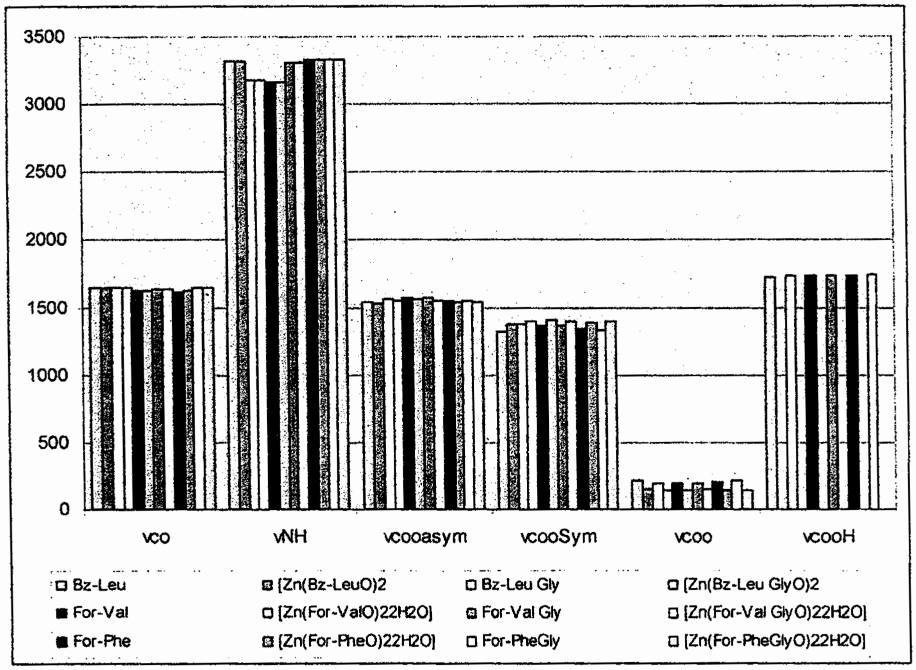


Figure-5. Frequency of infrared spectra for the Legends.

In the Zn (II) complexes with N-formyl-DL-valine and N-formyl-L-phenylalanine, the weight loss in thermo gravimetric analysis between 120^{0}C to 180^{0}C corresponds to two water molecules. In the Zn (II) complex with N-formyl-DL-valine, two endothermic peaks at 150^{0}C and 180^{0}C are recorded, whereas in the complex of N-formyl-L-phenylalanine two water molecules present in those complexes are coordinated to the metal ion.

In the differential thermal analyses of Zn (II) complex with N-formyl-L-phenylalanine, a strong endothermic peak is recorded at 180^{0}C and corresponding loss in weight observed in TGA, two to two water molecules, whereas for Zn (II) complex of N-formyl-L-phenylalanyglycerine, two endothermic peaks at 150^{0}C to 190^{0}C is recorded on DTA. These peaks are assigned to the loss of coordinated water molecules. Further heating of these complexes results in their decomposition and ultimately the formation of metal oxides with the loss of the ligands. Some endothermic and exothermic peaks are observed during this process of decomposition on DTA curves but since the loss in weight in TGA above 190^0 is different to make assignment to any of these peaks.

The result indicated that the co-ordination sites of N-protected amino acids and peptides are different from those of free amino acids and peptides. The coordination governed by the nature of the protecting group. In amino acids, coordination occurs through the amino group and the carboxylate oxygen. In free peptide coordination also exits the peptide group oxygen [6].

The infrared spectroscopic studies on N-substituted dipeptides complexes clearly indicate that peptide group oxygen is also not involved in coordination. The most probable explanation for these behaviors is that peptide form a stable five-member ring by involving both the nitrogen of the alpha-amino and the oxygen of the amide groups in coordination with the metal ion as shown in the structure in Figure-6(a).

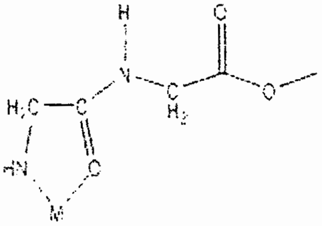


Figure-6a. Structure of interaction of base metals with biological alteration compound, M (B_Z-LeuO)$_2$.

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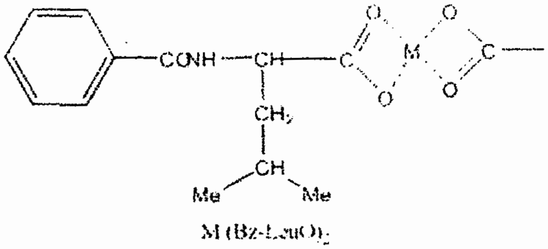

Figure-6b. Structure of interaction of base metals with biological alteration compound, M (B_Z-LeuO)$_2$.

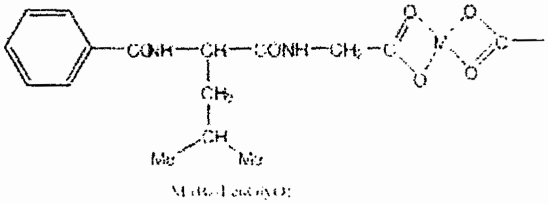

Figure-6c. Structure of interaction of base metals with biological alteration compound, M (B_Z-LeuGlyO)$_2$.

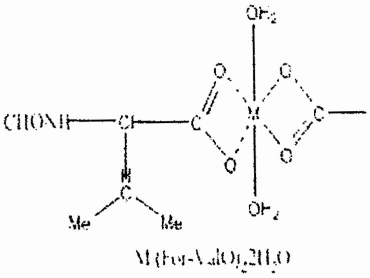

Figure-6d. Structure of interaction of base metals with biological alteration compound, M (For-ValO)$_2$H$_2$O.

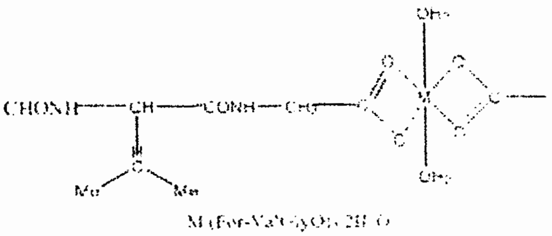

Figure-6e. Structure of interaction of base metals with biological alteration compound, M (For-ValGlyO)$_2$H$_2$O

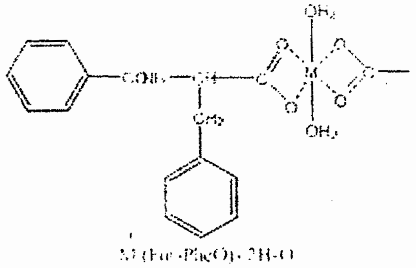

Figure-6f. Structure of interaction of base metals with biological alteration compound, M (For-PheO)$_2$H$_2$O.

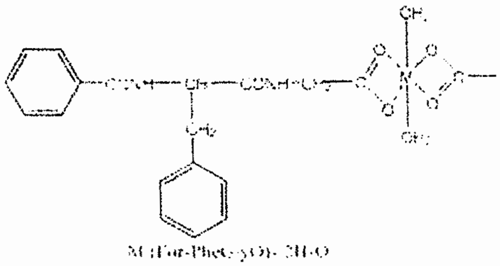

Figure-6g. Structure of interaction of base metals with biological alteration compound, M (For-PheGlyO)$_2$H$_2$O.

Unlike free amino acids and their peptides, there are no marked differences in the coordination sites of N-protected amino acids and their peptides. This is because the amido side chain is not involved in coordination to the metal ion.

These complexes possess 1:2 stoichiometry irrespective of the metal/ligands ratio used. The N-formyl N-benzoyl dipeptides and N-benzoyl amino acids, coordination occurs through the carboxylate group in bidentate manner. In the case of N-formyl dipeptides and N- formyl amino acids, in addition to carboxylate oxygen two water molecules are also involved in the coordination. This same kind of consideration as applied to the formation of Zn (II) compound may be extended to those of Pb (II) and Cu (II) containing mineral formation as few organic compounds or coordination complexes have been described as separate minerals [11]. Furthermore, further degradation in soils leads to the release of monomers including benzoic and hydroxyl benzoic acids, which may readily be extracted and characterized. Not surprisingly, there are elaborately substituted, especially by alkane and alkoxyl groups on fulmic acid using nuclear magnetic resonance, (NMR), techniques [12].

On the basis of the above studies and discussion distorted tetrahedral structures are suggested for base-metal containing complexes with N-benzoyl-DL-valine and N-benzoyl-DL-valylglycine. These are shown in Figure-6(b) and Figure-6(c). Similar coordination of Zinc (II) ion has been reported with enzymes and other bimolecular complexes, [4, 7].

An octahedral coordination of Zn (II) ion is suggested for formyl amino acid and formyl dipeptide complexes Figure-6(d), Figure-6(e), Figure-6(f) and Figure-6(g).

CONCLUSIONS

On the basis of the above studies distorted tetrahedral structures are proposed for M (II) complexes with N-benzoyl-DL-valine and N-benzoyl-DL-valyglycine. An octahedral coordination of M (II) ion is suggested for formyl amino acid and formyl dipeptide complexes. It is also sufficient to state from the on going discussion that alteration of minerals is due in part to microbiological activity and the leaching process, leading to the formation of the complexes in the oxide zone. It is therefore the case that similar mechanisms are involved in the formation and breakdown of gauge minerals containing these complexes in the supergene zone. These complex formations in this environment may be facilitated due to nutrient requirement by the plants in the oxidized environment by the uptake of the base metal ions.

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REFERENCES

[1] Krumbien W. E. 1983. Microbial geochemistry. Blackwell, Oxford.

[2] Said E. L., Kamal H.E., Salah A. E. Razika B. J. 2007. Carbohydrate Chem. 26: 1-16.

[3] Zhenjiang L., Weisi L., Yingjie S, He H, Pingkai O. J. 2008. Heterocycl. Chem. 45: 286-300.

[4] Lidija P., Uros G. Anton M., Branko S. and Jurij S. J. 2008. Heterocycl. Chem. 45: 154-160.

[5] Deng X. and Mani N. S. 2006. Org. Lett. 8: 3504-3509.

[6] Sandhu S. S., Hundal M. S., Sood G. and Dhillon J. 1989. J. Chem. Soc. Dalton Trans. p. 1341.

[7] Freeman H. C. 1976. Adv. Protein Chem. 22: 257.

[8] Bellamy W. J. 1975. The Infrared Spectra of Complex Molecules. Wiley, New York.

[9] Belleau B. and Malek G., J. Amer. 1968. Chem Soc. 90: 1651.

[10] Udupa M.R. and Krebs I. 1978. Inorg. Chem. Acta. 31: 1730.

[11] Christman R.F. and Gjessing C. 1983. Aquatic and Terrestrial Humic Material. Ann Arbor Science.

[12] Wilson M.A. Barron P. F. and Gillam A. A. 1981. Geochim Cosmochim. Acta. 45: 1743.