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Thermal decompositions of some bioinorganic complexes of europium

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Abstract

Thermogravimetric and derivative thermogravimetric investigations for three kinds of bioinorganic complexes of europium with *N*-acetyl-DL-alanine, *N*-acetyl-DL-valine and DL-alanyl-DL-alanine have been performed. It was found that the water molecules in these solid state complexes are not directly coordinated to the europium ion and that there may be three or four steps in the thermal decomposition process of these complexes after dehydration. The possible thermal decomposition reactions of these bioinorganic complexes have been suggested and discussed.

INTRODUCTION

Research on the structures and properties of rare earth bioinorganic complexes are very significant because rare earth ions can be used as a probe in biochemical research. Thermal stability is one of most important properties for any biological complex. However, few thermogravimetric investigations on the bioinorganic complexes of rare earths with amino acids have been published.

For the study of the thermal decomposition process of the bioinorganic complexes of rare earths and an amino acid with different substituent group and of rare earths and dipeptide, we have synthesised three kinds of bioinorganic complexes of europium with *N*-acetyl-DL-alanine, *N*-acetyl-DL-valine and DL-alanyl-DL-alanine and have performed thermogravimetric investigations for these solid state complexes. From the thermogravimetric curves and derivative thermogravimetric curves, it can be found that all the water molecules in these complexes are not directly linked to the europium ion and that the thermal decomposition process of these complexes is not a simple one; the complexes undergo three or four thermal decomposition steps after dehydration.

EXPERIMENTAL

All the complexes were prepared by a conventional method described previously [1,2]. All the chemicals used in the syntheses were analytical reagent grade.

Freshly prepared europium carbonate or europium chloride was dissolved at 40 ° C by slow drop-wise addition of an aqueous solution of the corresponding biological ligand (10^{-2} M or 10^{-3} M), the biological ligand being kept slightly in excess of the stoichiometric amount. The resultant solution was then filtered and the clear filtrate was concentrated in a thermostated bath at 40 ° C. On cooling, the corresponding solid state complex was formed and was collected by filtration. The solid state complex was washed repeatedly with acetone, recrystallised from the distilled water solution, and finally dried in a vacuum desiccator over phosphorus(V) oxide.

The results of the elemental analyses for these solid state complexes indicate that the compositions of the europium bioinorganic complexes are $Eu(C_5H_8NO_3)_3 \cdot 1.5H_2O$, $Eu(C_7H_{12}NO_3)_3 \cdot 2H_2O$ and $Eu(C_6H_{12}N_2O_3)_3 \cdot 4H_2O$, respectively.

Thermal studies were carried out on a Shimadzu DT-30 thermal analyzer. The thermogravimetric curves and derivative thermogravimetric curves were registered in dynamic conditions using an air flow rate of 60 ml min^{-1} and a heating rate of 5 ° C min^{-1}, and with sample masses between 2 and 4 mg. The thermogravimetric curves and derivative thermogravimetric curves of these europium bioinorganic complexes are shown in Fig. 1.

RESULTS AND DISCUSSION

As Fig. 1 shows, all the TG and DTG curves show that the first weight loss begins when the temperature is below 50 ° C: 4.5%, 5% and 8% of the initial weight of the complex is eliminated, respectively. The experimental percentage weight loss is in agreement with the theoretically calculated water content in the complexes: 4.7% for $Eu(C_5H_8NO_3)_3 \cdot 1.5H_2O$, 5.4% for $Eu(C_7H_{12}NO_3)_3 \cdot 2H_2O$ and 8.9% for $Eu(C_6H_{12}N_2O_3)_3 \cdot 4H_2O$. Therefore, the weight loss process can be attributable to the dehydration of the complex. The fact that the dehydration temperature is so low may imply that the water molecules in these solid state complexes are not in the inner coordination sphere of the europium ion and the biological ligands and that the water molecule is not directly coordinated to the central europium ion. Sharma and Chandra [3] have found that the lysinato–neodymium dihydrate is stable up to 45 ° C and that all the water molecules can be completely lost at 90 ° C. Thus, they consider that the two water molecules in lysinato–neodymium dihydrate must be outside the coordination sphere of the neodymium ion and the ligands.

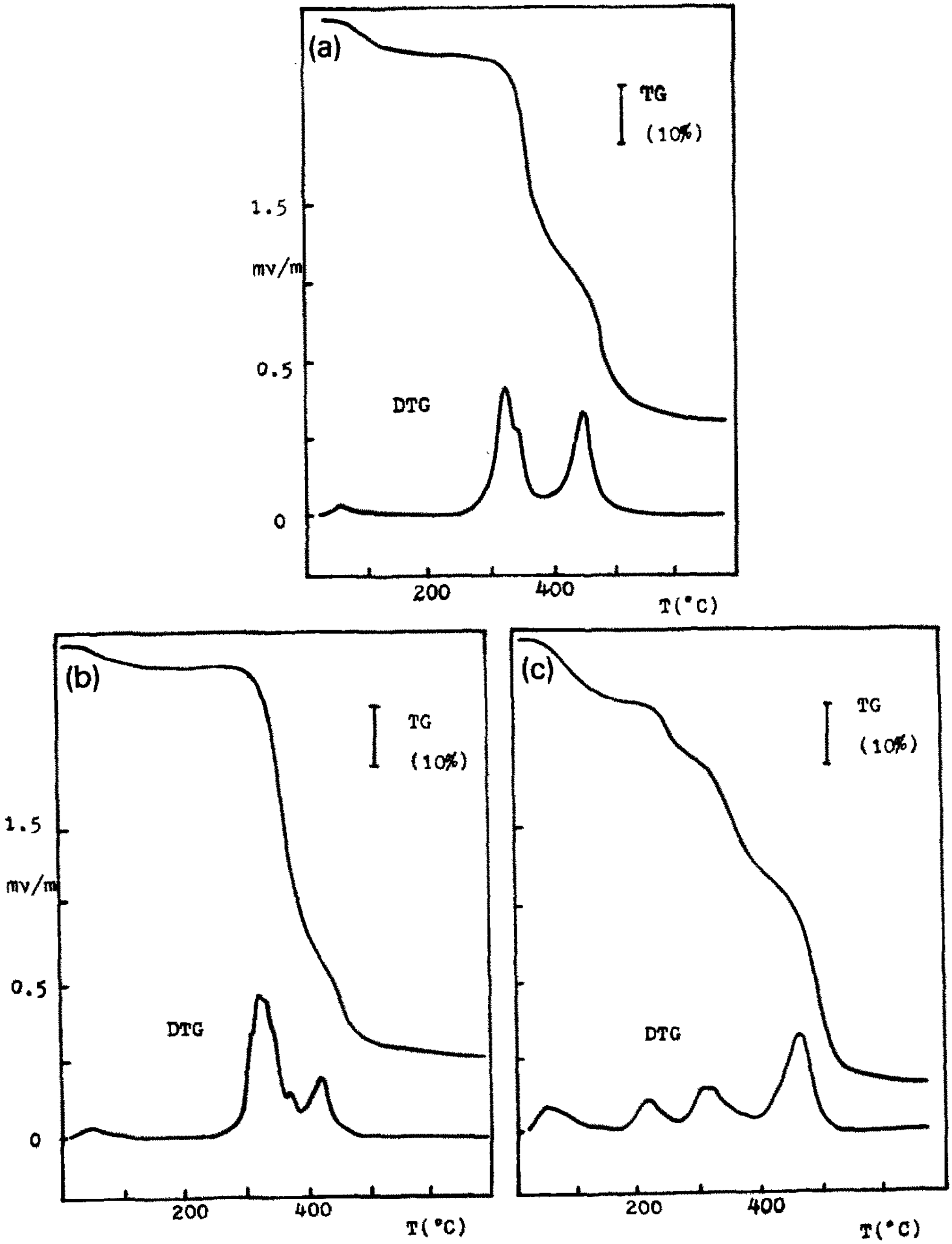

Fig. 1. The TG and DTG curves of some bioinorganic complexes of europium: (a), *N*-acetyl-DL-alanine europium complex, sample weight = 2.10 mg; (b), *N*-acetyl-DL-valine europium complex, sample weight = 3.25 mg; (c), DL-alanyl-DL-alanine europium complex, sample weight = 1.90 mg.

The TG curves for the complexes of europium with *N*-acetyl-DL-alanine and *N*-acetyl-DL-valine show that an abrupt weight loss in the sample starts at about 280 ° C. This indicates the thermal decomposition of the anhydrous complex after dehydration. However, the TG curves show that the weight loss process of the samples becomes slower when the temperature is above 380 ° C. Finally, the weight loss becomes less and less with increasing temperature when the temperature is above 600 ° C. Obviously, such a weight loss process must imply that there may be at least two or more steps in the thermal decomposition process of the sample. In the DTG curve of both the *N*-acetyl-DL-alanine and the *N*-acetyl-DL-valine complexes, a peak can be observed at about 420 ° C. This peak may corresponding to the maximum decomposition rate in the thermal decomposition process from europium propionate to europium carbonate or basic europium carbonate. This is very similar to the thermal decomposition process from europium acetate to europium carbonate or basic europium carbonate [4]. From the DTG curve of the *N*-acetyl-DL-valine europium complex, a small peak can be seen at about 370 ° C and there are two overlapping peaks at about 310 ° C and 330 ° C. The DTG curve of the *N*-acetyl-DL-alanine europium complex is similar to that of the *N*-acetyl-DL-valine complex, but there is no peak at about 370 ° C. However, in the DTG curve of the *N*-acetyl-DL-alanine europium complex, there are two closely overlapping peaks at about 310 ° C and 330 ° C.

Thus, the DTG curve of the *N*-acetyl-DL-alanine europium complex has four peaks and that of the *N*-acetyl-DL-valine europium complex has five. As mentioned above, the first peak in the two DTG curves can be assigned to the dehydration process of the complex. The second peak in the two curves may be assumed to corresponding to the elimination reaction of the carbonyl group from the aminde in the biological ligand of the complex. This reaction is very similar to the well-known Hofmann elimination reaction or degradation reaction of aminde. The thermal decomposition reaction corresponding to the third peak in the curves may relate to the elimination reaction of the amino group in the biological ligand.

The theoretically calculated weight loss of the anhydrous complex for the pyrolytic elimination reaction of the carbonyl group from the aminde in the biological ligand and of the amino group in the biological ligand is 34.8% for the *N*-acetyl-DL-alanine europium complex. The experimental percentage weight loss of the sample cannot be measured accurately from the TG curve because the pyrolytic elimination reaction of the carbonyl group and of the amino group in the ligand may take place consecutively in the decomposition process of the sample. However, we can approximate the weight loss of the sample in the two thermal decomposition processes from the TG curve of the *N*-acetyl-DL-alanine europium complex to be about 35% at about 350 ° C (Fig. 1a). This is in good agreement with the theoretical weight loss (34.8%).

The fourth peak at about 370 °C in the DTG curve (Fig. 1b) is characteristic of the *N*-acetyl-DL-valine europium complex. We consider that this may be due to the breaking of the C–C bond and the pyrolytic elimination of the methyls in the side chain of the isovaleric acid radical in the europium isovalerate formed following dehydration of the *N*-acetyl-DL-valine europium complex and the pyrolytic elimination of the carbonyl and amino groups from the ligand. In this case, the possible product of the pyrolytic decomposition is europium butyrate or europium propionate. The theoretically calculated weight loss of the sample in this step is 43.9%. The experimental weight loss measured approximately from the TG curve of the *N*-acetyl-DL-valine europium complex is about 45% at about 390 °C (Fig. 1b), if the final product is europium propionate.

We feel that this assignment for the fourth peak in the DTG curve of the *N*-acetyl-DL-valine europium complex is reasonable because the energy of the C–C bond (H_3C-CH_3) is 79 kcal mol^{-1} and the energy of the C–N bond (H_3C-NH_2) is 66.5 kcal mol^{-1} [5]. Possibly the energy of the C–C bond is larger than that of the C–N bond in the ligand of the above-mentioned complex, and the C–N bond is broken more easily than the C–C bond; thus the temperature for elimination of the methyl group from the ligand will be higher than that for elimination of the amino group from the ligand.

On the basis of the above discussion, the *N*-acetyl-DL-alanine europium complex undergoes three steps in its thermal decomposition after dehydration, while the *N*-acetyl-DL-valine europium complex undergoes four steps in its thermal decomposition after dehydration. In the last step, the complexes become europium carbonate or basic europium carbonate from europium propionate or europium butyrate, respectively.

As the Fig. 1c shows, the TG and DTG curves of the DL-alanyl-DL-alanine europium complex is somewhat different from the curves of the complexes considered above. A characteristic peak at about 215 °C in the DTG curve of the DL-alanyl-DL-alanine europium complex can be observed. This peak may be attributable to the thermal dissociation of the hydrogen chloride molecule from the complex. This possibly indicates that not only the water molecules but also the chloride anions in the complex are outside the coordination sphere of the europium ion and the biological ligands. The temperature required to eliminate the hydrogen chloride molecule from the complex must be higher than that to eliminate water because the pyrolytic elimination of the hydrogen chloride molecule from the complex may result from the breaking of the H–N bond in the amino group of the biological ligand. In this complex, the biological ligand is the dipeptide, not the amino acid; therefore, this peak may be characteristic of the DL-alanyl-DL-alanine europium complex. From the TG curve, the experimental weight loss of the DL-alanyl-DL-alanine europium complex in the thermal dissociation process of the hydrogen chloride molecules is about 11%. This is in

TABLE 1

Thermal decompositional data for some bioinorganic complexes of europium

Reaction [a]	TG temperature range (° C)	T_{max} in DTG (° C)
(1) $Eu(C_5H_8NO_3)_3 \cdot 1.5H_2O \rightarrow Eu(C_5H_8NO_3)_3 + 1.5H_2O$	40– 90	45
$Eu(C_5H_8NO_3)_3 \rightarrow Eu(C_4H_8NO_2)_3$ + d.p.	280–340	310
$Eu(C_4H_8NO_2)_3 \rightarrow Eu(C_3H_5O_2)_3$ + d.p.	300–350	330
$Eu(C_3H_5O_2)_3 \rightarrow Eu(CO_3)_3$ or $Eu_2O_3 \cdot nCO_2$ + d.p.	380–480	420
(2) $Eu(C_7H_{12}NO_3)_3 \cdot 2H_2O \rightarrow Eu(C_7H_{12}NO_3)_3 + 2H_2O$	40– 90	50
$Eu(C_7H_{12}NO_3)_3 \rightarrow Eu(C_6H_{12}NO_2)_3$ + d.p.	280–350	310
$Eu(C_6H_{12}NO_2)_3 \rightarrow Eu(C_5H_9O_2)_3$ + d.p.	300–370	330
$Eu(C_5H_9O_2)_3 \rightarrow Eu(C_4H_7O_2)_3$ or $Eu(C_3H_5O_2)_3$ + d.p.	340–390	370
$Eu(C_4H_7O_2)_3$ or $Eu(C_3H_5O_2)_3 \rightarrow Eu_2(CO_3)_3$ or $Eu_2O_3 \cdot nCO_2$ + d.p.	380–490	420
(3) $Eu(C_6H_{12}N_2O_3)_3Cl_3 \cdot 4H_2O \rightarrow Eu(C_6H_{12}N_2O_3)_3Cl_3 + 4H_2O$	40– 90	50
$Eu(C_6H_{12}N_2O_3)_3Cl_3 \rightarrow Eu(C_6H_{11}N_2O_3)_3 + 3HCl$	190–250	215
$Eu(C_6H_{11}N_2O_3)_3 \rightarrow Eu(C_5H_{11}N_2O_2)_3$ or $Eu(C_5H_{10}NO_2)_3$ + d.p.	280–350	300
$Eu(C_5H_{10}NO_2)_3 \rightarrow Eu(C_3H_5O_2)_3$ + d.p.	300–370	330
$Eu(C_3H_5O_2)_3 \rightarrow Eu_2(CO_3)_3$ or $Eu_2O_3 \cdot nCO_2$ + d.p.	380–500	450

[a] d.p., thermal decomposition product.

agreement with the theoretically calculated weight loss of the sample (13.5%).

After the dissociation of the hydrogen chloride molecules, the complex undergoes three pyrolysis steps in the thermal decomposition process which are very similar to those in the thermal decomposition process of the anhydrous complex of europium with *N*-acetyl-DL-alanine. Two closely overlapping peaks at about 300 and 330 ° C, respectively, can be found in the DTG curve of the complex. The peak at about 300 ° C may be related to the pyrolytic elimination of the carbonyl group from the aminde in the biological ligand, as for the *N*-acetyl-DL-alanine europium and the *N*-acetyl-DL-valine europium complexes. From the molecular structure of DL-alanyl-DL-alanine, it seems very likely that the pyrolytic elimination of the imido group in the side chain from the ligand may occur in this thermal decomposition step. As in the thermal decomposition of the *N*-acetyl-DL-alanine europium the *N*-acetyl-DL-valine europium complexes, the peak at about 330 ° C can be attributed to the pyrolytic elimination of the amino group from the ligand. However, the pyrolytic elimination of the imido group in the side chain of the biological ligand may complicate the assignation of the peaks in the range 300–330 ° C in the DTG curve of this complex. The peak at about 450 ° C corresponds to the thermal decomposition of europium propionate.

As mentioned above, we consider that the thermal decomposition of the bioinorganic complexes of europium with *N*-acetyl-DL-alanine, *N*-acetyl-DL-valine and DL-alanyl-DL-alanine is mainly a pyrolytic degradation process of the biological ligand in these solid state complexes. Of course, in the final pyrolysis step, the europium propionate or europium butyrate produced due to the thermal decomposition of the anhydrous complex becomes europium carbonate or basic europium carbonate.

All the possible thermal decomposition reactions in the thermal decomposition process of these bioinorganic complexes of europium and the corresponding thermal decomposition data are listed in Table 1.

Rodriguez-Mendez et al. have investigated the thermal decomposition of some amino acids [6]. They found that the temperature at maximum rate of degradation is 279 ° C for DL-alanine and 278 ° C for DL-valine. This is different from the results observed here in the DTG curves of the *N*-acetyl-DL-alanine europium and *N*-acetyl-DL-valine europium complexes. However, it is to be expected that amino acids with different substituent groups, especially the amino acid radicals in the solid state complex, will show a different thermal behaviour from the simple or free amino acids.

CONCLUSION

The thermogravimetric and derivative thermogravimetric investigations show that the dehydration reaction of all the solid state complexes studied takes place at low temperatures. This indicates that all the water molecules in these complexes are not directly coordinated to the europium ion and are outside the coordination sphere.

From the TG and DTG curves of these complexes, it is found that these bioinorganic complexes of europium undergo three or four pyrolysis steps in their thermal decomposition process. The common decomposition reactions are the pyrolytic elimination of the carbonyl group, similar to the Hofmann degradation reaction of aminde, and the pyrolytic elimination of the amino group from the biological ligand. The characteristic decomposition reaction for one of these complexes may occur in the thermal decomposition process due to the existence of different substituent groups in the side chain of the ligands. The final thermal decomposition reaction is from europium propionate or butyrate to europium carbonate or basic europium carbonate. Therefore, the thermal decomposition process of the complexes studied is mainly the result of the decomposition of the biological ligands of the complexes.

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