Research on the thermal decomposition of the bioinorganic complex of europium and L-glutamine by Mössbauer spectroscopy

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Abstract

Mössbauer spectroscopy has been used to investigate the thermal decomposition of the bioinorganic complex of europium and L-glutamine. The Mössbauer parameters can demonstrate that the water molecules in the complex and the chlorine anion in the hydrogen chloride molecule, dissociated from the complex below 200°C, are not linked directly to the europium atom. The thermal decomposition process of the complex is discussed and a possible coordination model for the europium L-glutamine complex is also proposed on the basis of the thermogravimetric and derivative thermogravimetric curves, and from some evidence obtained from the Mössbauer effects of some decomposition products of the complex.

INTRODUCTION

In investigations of the thermal decomposition processes of inorganic and organic compounds using thermogravimetry, some modern analytical methods, for example, powder X-ray diffractometry and gas chromatography, are often used to characterize and determine the composition and structure of the thermal decomposition products. The results obtained by means of these techniques can provide important information for interpreting and understanding the most probable thermal decomposition process of the compound.

Mössbauer spectroscopy can reveal some comparatively weak interactions between the Mössbauer atom and the surrounding atoms; therefore, it has been widely applied in many fields of chemical research, for example in investigating phase transition processes and the properties of chemical bonds in some compounds [1].

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TABLE 1

Analytical data for the complex of europium and L-glutamine

Formula		Eu (%)	C (%)	H (%)	N (%)	Cl (%)
$Eu(C_5H_{10}N_2O_3)_3Cl_3 \cdot 2H_2O$	Found	20.75	24.87	4.71	11.11	14.03
	Calc.	20.74	24.58	4.69	11.47	14.51

Research on the thermal decomposition of rare earth bioinorganic complexes is very interesting, because the rare earth ion can be used as a probe in some biochemical investigations.

Therefore, we have applied Mössbauer spectroscopy to research on the thermal decomposition of the bioinorganic complex of europium and L-glutamine and have obtained some interesting results.

EXPERIMENTAL

The solid state complex of europium and L-glutamine was synthesized using a conventional method described previously [2]. All the chemicals used were analytical reagent grade.

Europium chloride was dissolved in 25 ml of L-glutamine aqueous solution, with a metal:ligand mole ratio of 1:3, with stirring in a thermostated bath at 70°C for 6 h. The resultant solution was concentrated at room temperature by natural evaporation of the solvent and the solid state complex was precipitated from the solution. The solid state complex was filtered off, washed repeatedly with absolute ethanol and ether, and then dried in a vacuum desiccator over phosphorus(V) oxide to constant weight. The results of elemental analyses are listed in Table 1; they indicate that the composition of the solid state complex is $Eu(C_5H_{10}N_2O_3)_3Cl_3 \cdot 2H_2O$.

The thermal decomposition studies were carried out on a Shimadzu DT-30 thermal analyzer. The thermogravimetric and derivative thermogravimetric curves were recorded in dynamic conditions using an air flow rate of 30 ml min^{-1}, a heating rate of 5°C min^{-1} and a sample mass between 2 and 3 mg. The thermogravimetric and derivative thermogravimetric curves of the complex of europium and L-glutamine are shown in Fig. 1.

The Mössbauer spectrum was recorded using an Oxford MS-500 model constant acceleration Mössbauer spectrometer with a 1024 multichannel analyzer. The radiation source was SmF_3 (^{151}Sm, about 100 mCi ^{151}Eu); a xenon (methane) proportional counter was used as a detector. The sample was prepared in a thin absorber containing about 20 mg cm^{-2} europium. After the Mössbauer spectrum of the sample had been measured, the sample was placed in a baking oven and kept at about 100°C for 10 h. Then, the Mössbauer spectrum of this treated sample was measured.
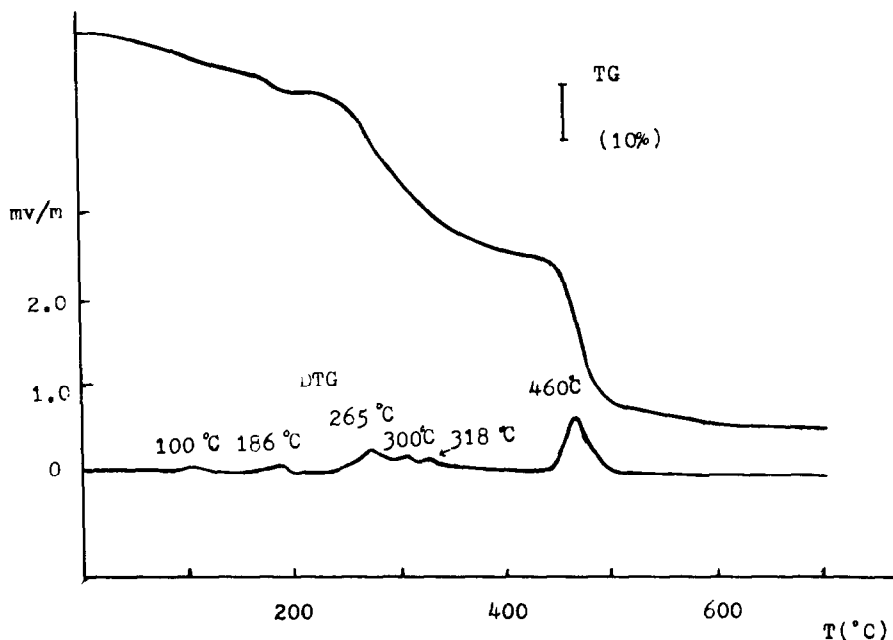
Fig. 1. The TG and DTG curves of the complex of europium and L-glutamine (sample weight, 2.65 mg).

Finally, the sample was placed in the baking oven again, and kept at about 180°C for 10 h. The Mössbauer spectrum of this sample was also measured. The experimental penetration Mössbauer spectra of the samples above are shown in Fig. 2. Glentworth et al. have taken into account the quadrupole splitting of the [151]Eu nucleus in Mössbauer effect studies of complexes of europium with some organic ligands [3]. Therefore, we have used a modified method in fitting the experimental Mössbauer spectra of the complex of europium and L-glutamine [4]. We found that each experimental Mössbauer spectrum is mainly composed of the six main subspectra. All the Mössbauer parameters, such as the isomer shift, the electric quadrupole splitting and the asymmetric parameter of the electric field gradient at the [151]Eu nucleus, derived directly from the fitting to the experimental spectra, are listed in Table 2.

RESULTS AND DISCUSSION

From the derivative thermogravimetric curve, it can be determined that the solid state complex of europium and L-glutamine has six steps in the thermal decomposition process between 20 and 700°C.

The first step can be considered to be dehydration of the hydrous complex of europium and L-glutamine. The thermogravimetric curve indicates that the first weight loss starts below 50°C. The experimental percent-
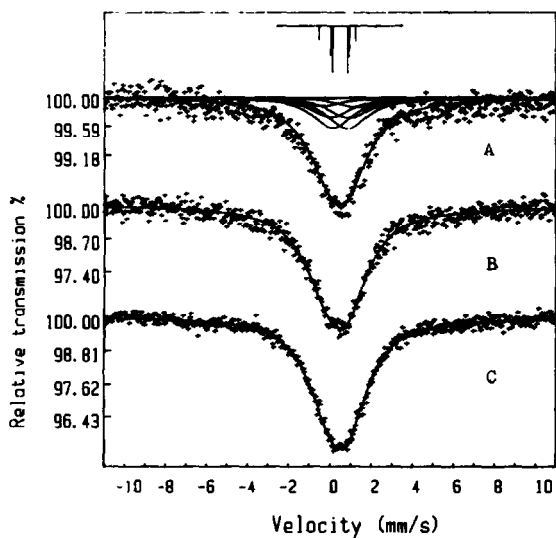
Fig. 2. Mössbauer spectrum of the solid state complex of europium and L-glutamine (at room temperature): **A** hydrous complex of europium and L-glutamine; **B** anhydrous complex of europium and L-glutamine; **C** anhydrous complex of europium and L-glutamine after a hydrogen chloride molecule has been dissociated from the complex. The six main subspectra for the Mössbauer spectrum of the hydrous complex of europium and L-glutamine are shown at the top of the figure.

age weight loss at 100°C (about 4.8%) is in good agreement with the theoretically calculated water content (4.9%) of the hydrous complex of europium and L-glutamine. The second weight loss is attributable to the thermal dissociation of the hydrogen chloride molecule from the anhydrous complex of europium and L-glutamine. The experimental weight loss determined from the thermogravimetric curve is about 5.3% at 200°C. This corresponds to the theoretically calculated weight loss (5.2%) due to dissociation of one hydrogen chloride molecule from the complex of

TABLE 2

The Mössbauer parameters of the solid state complex of europium and L-glutamine at room temperature
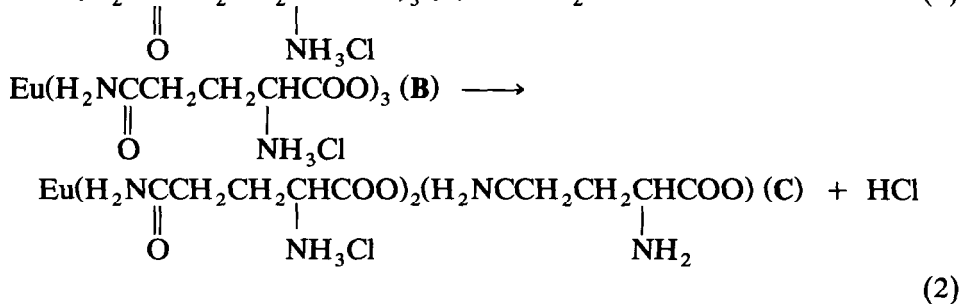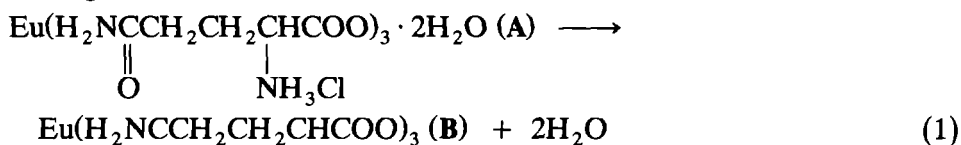
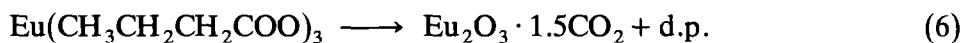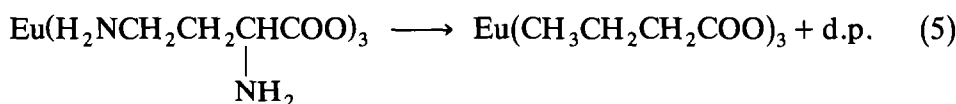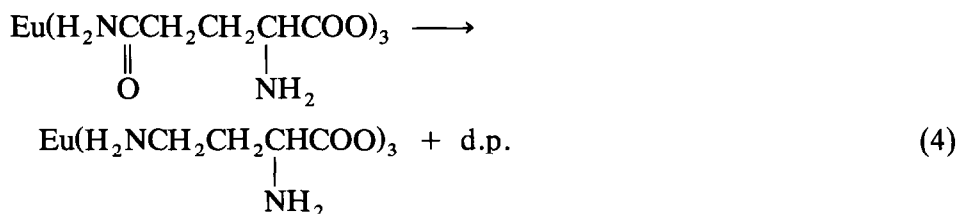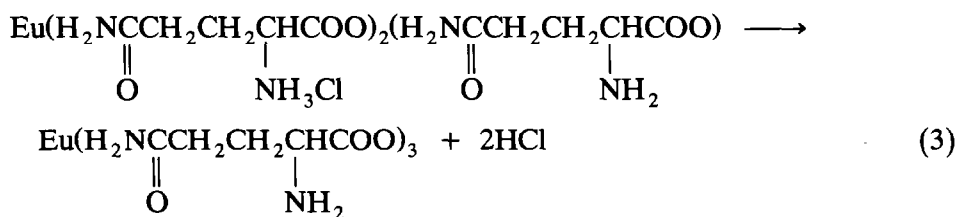| Complex	Isomer shift IS(EuF$_3$) (mm s^{-1}) (± 0.03)	Electric quadrupole splitting eQV_{zz} (mm s^{-1}) (± 0.3) [a]	Asymmetric parameter η (± 0.15)
A: Eu(C$_5$H$_{10}$N$_2$O$_3$)$_3$Cl$_3\cdot$2H$_2$O	+0.54	5.1	0.82
B: Eu(C$_5$H$_{10}$N$_2$O$_3$)$_3$Cl$_3$	+0.51	5.6	0.62
C: Eu(C$_5$H$_9$N$_2$O$_3$)(C$_5$H$_{10}$N$_2$O$_3$)$_2\cdot$Cl$_2$	+0.55	5.4	0.72

[a] Q is the quadrupole moment of the ground state of the ^{151}Eu nucleus, $Q = 1.16 \times 10^{-24}$ cm^2.

europium and L-glutamine. Therefore, the peak at about 186°C in the DTG curve may be assigned to the thermal dissociation of one hydrogen chloride molecule from the complex. The third peak in the DTG curve at 265°C can be considered to be related to the thermal dissociation of the other two hydrogen chloride molecules from the complex. In this step, the total weight loss of the sample should be 20.2% if two hydrogen chloride molecules are dissociated from the complex. From the thermogravimetric curve, it can be found that the experimental weight loss at 265°C is about 20%. There are two even peaks in the derivative thermogravimetric curve in the range 280–330°C. The peak at about 300°C can be assumed to relate to the elimination reaction of the carbonyl group from the amide in the organic ligand of the solid state complex. This reaction is very similar to the well known Hofmann elimination reaction or degradation reaction of the amide [5]. The fifth DTG peak (at about 318°C) can be assigned to the pyrolytic elimination of the amino group of the organic ligand.

Both the thermogravimetric and the derivative thermogravimetric curves suggest that the solid state sample becomes europium butyrate at about 400°C. The theoretically calculated total weight loss is 44.1% at 400°C, when the hydrous complex of europium and L-glutamine becomes europium butyrate by the thermal decomposition reaction. We can estimate an approximate total weight loss from the thermogravimetric curve. The experimental weight loss of the sample is about 41% at 400°C which is very close to the calculated total weight loss of sample. At high temperature, the europium butyrate becomes $Eu_2O_3 \cdot nCO_2$, as in the thermal decomposition of all carboxylates of rare earths [6]. We have also noted that the total weight loss of the sample is about 71.5% at 700°C. In this case, the theoretically calculated weight loss of the sample is in good agreement with the experimental weight loss, if we assume that the decomposition product at 700°C is $Eu_2O_3 \cdot 1.5CO_2$.

On the basis of the results described above, we can conclude that the entire thermal decomposition process of the hydrous complex of europium and L-glutamine is described as follows:

$$Eu(H_2NCCH_2CH_2CHCOO)_3 \cdot 2H_2O \text{ (A)} \longrightarrow$$
$$\qquad\quad \overset{\|}{O} \qquad\quad \overset{|}{NH_3Cl}$$

$$Eu(H_2NCCH_2CH_2CHCOO)_3 \text{ (B)} + 2H_2O \qquad\qquad (1)$$
$$\qquad\quad \overset{\|}{O} \qquad\quad \overset{|}{NH_3Cl}$$

$$Eu(H_2NCCH_2CH_2CHCOO)_3 \text{ (B)} \longrightarrow$$
$$\qquad\quad \overset{\|}{O} \qquad\quad \overset{|}{NH_3Cl}$$

$$Eu(H_2NCCH_2CH_2CHCOO)_2(H_2NCCH_2CH_2CHCOO) \text{ (C)} + HCl$$
$$\qquad\quad \overset{\|}{O} \qquad\quad \overset{|}{NH_3Cl} \qquad\qquad\qquad \overset{|}{NH_2}$$

$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad (2)$$

$$Eu(H_2NCCH_2CH_2CHCOO)_2(H_2NCCH_2CH_2CHCOO) \longrightarrow$$
$$\underset{\underset{O}{\|}}{} \underset{NH_3Cl}{|} \underset{\underset{O}{\|}}{} \underset{NH_2}{|}$$

$$Eu(H_2NCCH_2CH_2CHCOO)_3 + 2HCl \qquad (3)$$
$$\underset{\underset{O}{\|}}{} \underset{NH_2}{|}$$

$$Eu(H_2NCCH_2CH_2CHCOO)_3 \longrightarrow$$
$$\underset{\underset{O}{\|}}{} \underset{NH_2}{|}$$

$$Eu(H_2NCH_2CH_2CHCOO)_3 + d.p. \qquad (4)$$
$$\underset{NH_2}{|}$$

$$Eu(H_2NCH_2CH_2CHCOO)_3 \longrightarrow Eu(CH_3CH_2CH_2COO)_3 + d.p. \qquad (5)$$
$$\underset{NH_2}{|}$$

$$Eu(CH_3CH_2CH_2COO)_3 \longrightarrow Eu_2O_3 \cdot 1.5CO_2 + d.p. \qquad (6)$$

where d.p. indicates the decomposition product.

It is assumed that the two water molecules in the hydrous complex of europium and L-glutamine are not linked directly to the central europium atom because of the low dehydration temperature of the complex. However, further experimental evidence is required if we want to understand whether the chlorine anion in the first hydrogen chloride molecule dissociated from the complex is linked directly to the europium atom in the hydrous complex, or why this hydrogen chloride molecule is so easily dissocated from the complex.

It is well known that the isomer shift (IS) of the Mössbauer nucleus is very sensitive to the coordination environment about the Mössbauer atom and to the chemical bond of the Mössbauer atom with the coordination atom [1]. The dehydration and the dissociation of the hydrogen chloride molecule must cause a detectable change in the isomer shift of the complex, if the oxygen atom in the water molecule and the chlorine anion in the complex are linked directly to the europium atom. We have found that the differences between the isomer shifts of all the samples are either very small or are within the errors. As mentioned in the experimental section, sample A is the hydrous complex of europium and L-glutamine, sample B is the anhydrous complex of europium and L-glutamine, and sample C is the anhydrous complex of europium and L-glutamine from which a hydrogen chloride molecule has been dissociated, that is, the anhydrous complex with two chlorine atoms. The fact that the isomer shifts of these samples are so close to each other indicates that neither the presence nor the absence of the water molecule or the chlorine anion in

the first dissociated hydrogen chloride molecule in the solid state complex of europium and L-glutamine, have any effect on the charge density at the Mössbauer atom or on the chemical bonds of the europium atom with the surrounding atoms. Therefore, we can conclude that neither the oxygen atom of the water molecules nor the chlorine anion of the first dissociated hydrogen chloride molecule are linked directly to the europium atom. In addition we have noted that the values of the isomer shifts of all the samples fall within the same range as the isomer shifts of europium complexes with some carboxylic acids with different substituent groups [3]. As Glentworth et al. have suggested, the chemical bonds between the europium atom and the surrounding atoms may possess a strong ionic character or a little covalent character [3]. Although the change in the isomer shifts before and after dehydration of the sample is very small, the change in both the electric quadrupole splitting and the asymmetric parameter of the electric field gradient at the ^{151}Eu nucleus is outside the errors and cannot be ignored. Why the change in the isomer shift after dehydration of the sample is not large yet the change in the electric quadrupole splitting and the asymmetric parameter after dehydration of the sample is appreciable, is not clear. We feel that the electric quadrupole splitting of the Mössbauer nucleus depends not only on the charge distribution about the nucleus and the atom, but also on the coordination structure about the Mössbauer atom. Although the two water molecules are not coordinated directly to the europium atom, dehydration may change the coordination structure about the europium atom. We can assume that the presence or absence of the water molecules will not lead to any change in the structure of the inner coordination sphere, if the two water molecules are outside the inner coordination sphere composed of the three L-glutamines. Therefore, the water molecules may occupy the interstices in the inner coordination sphere, i.e. they are interstitial water. In this case, the loss of these water molecules will lead to a small movement of the atoms in the main or side chains of the large organic ligands and can cause a small change in the inner coordination sphere; hence, the electric field gradient at the europium nucleus created by all the atoms around the europium atom will be changed. Perhaps this is why the electric quadrupole splitting and the asymmetric parameter of the sample after dehydration are different from those before dehydration. Because the two water molecules are situated at the interstices of the inner coordination sphere composed of the large, flexible organic ligands, the reason why the dehydration temperature of the hydrous complex has a rather broad range (about 40–100°C) can be explained.

From Table 2, it can be seen that the electric quadrupole splitting and the asymmetric parameter of the sample after dissociation of the first hydrogen chloride molecule from the anhydrous complex are not considerably different from those before dissociation of the first hydrogen chloride

molecule. The difference between the isomer shifts or the asymmetric parameters before and after dissociation of the first hydrogen chloride molecule are just inside the errors. This may imply that neither the presence nor the absence of the chlorine anion in the first dissociated hydrogen chloride molecule in the complex of europium and L-glutamine has any detectable effect on the charge distribution and the coordination structure about the europium atom. Therefore, we can be sure that the chlorine anion of the first dissociated hydrogen chloride molecule must be outside the inner coordination sphere and far from the central europium, both in the hydrous complex and in the anhydrous complex of europium and L-glutamine. The dissociation temperature of the first hydrogen chloride molecule from the complex is higher because this dissociation must be accompanied by breaking of the H–N bond in the amino groups of the ligand.

Unfortunately, we cannot check whether the other two chlorine anions in the complex are coordinated directly to the europium atom, because we cannot obtain a pure sample without any hydrogen chloride molecule at about 260°C, because of the consecutive thermal decomposition process of the complex in this temperature range. However, we can assume that the two chlorine anions in the complex of europium and L-glutamine may both be associated with the hydrogen atom in the amino group of the organic ligand and coordinated to the central europium atom; hence, the dissociation of the two hydrogen chloride molecules from the complex will occur at a higher temperature.

On the basis of the results above, we can suggest a possible coordination model for the complex of europium and L-glutamine (Fig. 3). In the hydrous complex of europium and L-glutamine, the six oxygen atoms from the three carboxylic acid radicals of the L-glutamines may form a coordina-
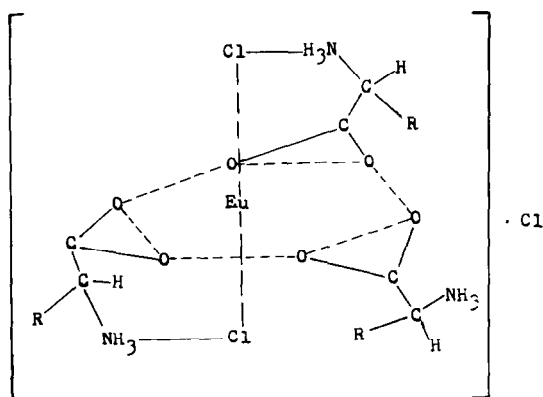

Fig. 3. A possible coordination model for the complex of europium and L-glutamine. The two interstitial water molecules in the inner coordination sphere are not shown. R is $-CH_2CH_2CONH_3$.

tion plane, with the europium atom situated at the center of the coordination plane. The two chlorine anions associated with the hydrogen atoms in the amino group of the L-glutamine are above and below the coordination plane and are coordinated directly to the europium atom. The bending carbon chains of the three organic ligands fill most of the free space in the inner coordination sphere. The two water molecules may be in small interstices between the three organic ligands, and may form weak hydrogen bonds with the hydrogen atoms in the amino groups of the terminals of the L-glutamines. The third chlorine anion, may be outside the inner coordination sphere composed of the europium atom and three L-glutamines, and may be associated with a hydrogen atom in the amino group of an L-glutamine. According to this coordination model, the coordination number of the europium atom will be eight. It is well known that rare earth ions with eight coordination are often found in the coordination chemistry of the rare earths.

CONCLUSIONS

The thermogravimetric and derivative thermogravimetric curves of the complex of europium and L-glutamine indicate that the solid state complex has six steps in its thermal decomposition process. These steps are: dehydration, dissociation of the first hydrogen chloride molecule, dissociation of the second and third hydrogen chloride molecules, elimination of the carbonyl group from the amide, pyrolytical elimination of the amino group in the side chain or the terminal of the ligands and, finally, the solid state complex transforms from europium butyrate to $Eu_2O_3 \cdot 1.5CO_2$.

The results from different Mössbauer spectra of the same sample after different heat treatments demonstrate that the two water molecules in the complex are interstitial waters, inside the inner coordination sphere but not linked to the europium atom, and that the chlorine anion in the first dissociated hydrogen chloride molecule is not coordinated directly to the europium atom and is outside the coordination sphere composed of the europium and L-glutamines.

On the basis of the results of the thermal decomposition and the evidence from Mössbauer effect studies, a possible coordination model is proposed for the complex of europium and L-glutamine. In this complex, the europium may be coordinated by six oxygen atoms from the three carboxylic acid radicals of the L-glutamines and by two chlorine anions associated with the hydrogen atoms in the amino groups of the L-glutamines; the coordination number of the europium atom is eight.

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