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Synthesis and Spectroscopic Characterization of *l*-Glutamic Acid and *l*-Phenylalanine Complexes with the Lanthanide metals La⁺³ and Yb⁺³

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ABSTRACT

The complexes between amino acids (l-glutamic acid and l-phenylalanine) and lanthanide Metals (La^{+3} and Yb^{+3}) have been prepared and characterized using a variety of techniques including, infrared spectroscopy, ¹H NMR, ¹³C NMR, elemental analysis and metal contents. The ¹H NMR and ¹³C NMR spectrum of the lanthanides complexes of l-glutamic acid and l-phenylalanine undergo a shift to lower and higher field when it was compared with free amino acids. The large upfield shift observed in the case of Ytterbium complexes, because Ytterbium metal is more contracted than Lanthanum metal. The ¹³C downfield shift indicates a lower electron density at the carbon with consequent downfield shift observed on the α -H attached to it increasing its acidity.

Keywords: *l*-glutamic acid; *l*-phenylalanine; Lanthanum; Ytterbium; Lanthanides (III) complexes; IR; NMR.

INTRODUCTION

The study of the chemical bonding between trivalent lanthanide ions (Ln^{3+}) and amino acids or peptides has its origin in the interest in using these ions as structural probes in biological systems, particularly in those systems which contain Ca^{2+} in their structure [1,2]. In biological systems Ca^{+2} often occurs bonded to proteins via aspartate or glutamate residues. The Ca^{2+} ion is optically transparent and is, therefore, not suitable for providing information through optical spectroscopic measurements about the chemical environment in which it is embedded. On the other hand, almost all Ln^{3+} ions are know to exhibit rich optical spectra, either in absorption or emission, and it occurs that, due to the similarity between ionic radii, they may substitute Ca^{2+} ions in the chemical structures. There is strong evidence that the bonding between Ln^{3+} ions and amino acids is made with the oxygens of the carboxylate group, and that the bonding via the nitrogen of the amino group is unlikely to occur at least in a range of pH values up to 5.6 [3,4].

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At high pH values, however, multiple binding of lanthanides ions by an amino acid (α -amino carboxylate, to be more exact) may be achieved with both the amino and the carboxylate groups participating in simultaneous coordination⁽⁵⁾. Such chelating effects may stabilize the metal complex by counteracting the undesirable hydrolysis and consequently high-nuclearity lanthanides clusters would form. Lanthanides clusters are expected to exhibit more promising magnetic properties as a consequence of the unique spectroscopic and electronic properties mainly associated with their 4f electronic configuration [5].

Most studies on Ln/amino acid model complexes are based on the chemical and photophysical properties of the Ln compounds, mainly efficient emission in the UV to IR regions, NMR and EPR [6]. Definite structural interpretation, however, can only be given by X-ray diffraction, a technique generally limited to crystalline complexes. Although nearly 70 structures of Ln/ amino acid complexes have been reported [7–9], only few of them are glutamates: [$\{Pr_2(Glu)_2(ClO_4)(H2O)_7\}$.3(ClO₄) 4H₂O]n [10], [$\{Sm_2(Glu)_2(H_2O)_8\}$. 4(ClO₄) .H₂O]n [11], [$\{Dy_2(Glu)_2(H_2O)_8\}$. 4(ClO₄) .H₂O]n and [Ho₂(Glu)_2(H2O)_8\}.4(ClO₄) .H₂O]n [12], [$\{Gd_2(L-Glu)_2(H_2O)_8\}$.4(ClO₄) . 2.5H₂O]n [13] and [$\{Eu_2(L-Glu)_2(H_2O)_8\}$.4(ClO₄) . 2.5H₂O]n [13], [$Er_2(Glu)_2(NO_3)_2(H_2O)_4$] (NO₃)₂·5H₂O [14], [$Er_2(Glu)_2(H_2O)_8$](ClO₄)₂·H₂O [15]. These structures are built by infinite 2D planes with pairs of metal centers of nine-coordinate geometries linked by fourfold carboxylate bridges, two in the $\eta^1:\eta^1:\mu_2$ and two in the $\eta^2:\eta^1:\mu_2$ modes. The structural motifs of phenylalanine have been described in the compound [Nd₂(Phe)₄(H₂O)₈](ClO₄)₆·H₂O which has isolated dimer structure [16].

Much progress has been recently achieved in the coordination chemistry of lanthanides. This resurgence of interest is sustained in the use of lanthanide-based reagents for different purposes, and in the preparation and study of new materials. Recently lanthanide ions and lanthanide complexes have been proposed and used in several biological and medical applications [17-20]⁻.

Due to the low stability of lanthanide complexes with amino acid and peptides, hydrolysis reactions are obvious competing processes. The smaller are the lanthanides, the more importance should be given to hydrolysis reactions [21]. The formation of $[Ln(OH)]^{2+}$, $[Ln_2(OH)_2]^{4+}$ and $[Ln_3(OH)_5]^{4+}$ have been reported for all lanthanide ions and a consistent increase in acidity is observed as the charge/radius ratio increases due to the lanthanide contraction. The lanthanide trihydroxides are only weakly amphoteric but those of the heavier metals dissolve in excess base. The interaction behaves in a purely electrostatic manner. This fact is reflected in the scarce participation of amino groups in coordination, and the dependence of K values with charge of ligand and lanthanide radius. In the solid state structure, carboxylate groups also play a very important role. Different spatial arrangements are found, but the presence of COO⁻ bridges is a common structural framework. In addition to the X-ray analysis which was discussed in the structures, also the complexes were characterized using a variety of techniques, including IR, ESI-MS, metal contents and microanalysis. The infrared spectra of these compounds have shown changes in the position and profiles of some bands, as compared to that of the free amino acids, suggesting the participation of the groups that produce these bands in the coordination bond with lanthanides. Major changes in all IR patterns, are related to the carboxylate bands [21]. In the case of *l*-phenylalanine for example, the bands at 1410 cm⁻¹ and 1565 cm⁻¹, corresponding to the carboxylate symmetrical and asymmetrical stretchings, are shifted to higher wave numbers after complexation with Eu³⁺, Tb³⁺, thus indicating coordination through that group. A strong and broad absorption appears at v = 3500-3600 cm⁻¹, which is typical of molecules of high water content. A sharp peak around 3580 cm⁻¹, usually assigned to the stretching of μ_3 -OH, was not observed in any of the these compounds. The peak is probably obscured by the broad water absorption. The presence of coordinated water molecules in all complexes is indicated by their characteristic rocking and wagging frequencies between 700 and 800 cm⁻¹ and between 500 and 650 cm⁻¹, respectively. For complexes where ionic ClO₄⁻¹ serves as the counter anion, characteristic strong Cl-O stretching frequencies between 1090 and 1145 cm⁻¹ are observed. In addition, a relatively strong peak at 903 cm⁻¹ indicates the presence of a unidentate ClO₄⁻¹ in solid state complexes. Corresponding frequencies are absent from the IR spectrum of complexes, where the counter anions are chlorides [22].

All complexes are extremely soluble in water, and an aqueous solution of the complex turns turbid after standing overnight at room temperature, presumably because of further hydrolysis of the complex. The complexes are readily soluble in common organic solvents, such as tetrahydrofuran, dichloromethane, acetone and acetonitrile, rendering product purification difficult.

The aim of this work is the synthesis of amino acids lanthanides complexes which have not been synthesized to see the effect of lanthanides metals on the spectroscopic of amino acids, which was confirmed by infrared spectra shift and nuclear magnetic resonance shift.

MATERIALS AND METHODS

Physical Measurements

IR spectra were recorded on perkin Elmer spectrum 100 instrument which an attenuated total reflection attachment, NMR data were recorded on a Bruker ANANCE III 400 MHz and 600 MHz, C, H, N, were determined by CHN elemental analysis instrument, the metal contents were determined by compleximetric titration with EDTA, using xylenol orange as indicator.

Synthesis of complexes

1. $[La_2(l-Glu)_2(H_2O)_8](ClO_4)_4$

An aqueous solution of lanthanum perchlorate was prepared by digesting (0.65gm) La₂O₃ in concentrated perchloric acid (2ml, 70 %), a suitable concentration of La (ClO₄)₃ (1.7 g, 4 mmol) was achieved by diluting the concentrated solution with 10 ml distilled water, *l*-Glutamic acid (0.294 g, 2 mmol) was added as solid to the above aqueous solution of La(ClO₄)₃, one drop of an aqueous solution of HCl (1.0M) was then added. The mixture was stirred at about 80 °C on a heating plate while an aqueous solution of NaOH (0.5M) was added dropwise to cause an incipient but permanent precipitate, pH=6. The mixture was then filtered, and the filtrate was then reduced to about 5 ml. The hot solution was tightly covered and allowed to evaporate gradually at room temperature. White precipitate appeared in about two weeks. The solid was collected by filteration, washed with cold diethyl ether, and dried under vacuum in a desiccator charged with silica gel. Yield =0.22 g (9.8%). The presence of lanthanum metal was detected by xylenol orange indicator, ¹³C (D₂O, 400 MHz, 25 °C): δ=54.33, 32.96, 26.30 ppm. Anal. Calc. for C₁₀H₃₂Cl₄La₂N₂O₃₂:C, 10.80; H, 2.90; N, 2.52; La, 24.98. Found : C, 10.14; H, 2.75; N, 1.85; La, 25.59. Main FT IR bands (KBr, cm⁻¹), *v_{max}* 3485, 3232, 2926, 2598, 2200, 1619, 1537, 1449, 1426, 1353, 1320, 1281, 1262, 1223, 1052, 982, 925, 873, 844, 762, 690, 620, 545, 508, 446, 403.

2. [La₂(*l*-Glu)₂(H₂O)₈]Cl₆

l-Glutamic acid (0.147 g, 1 mmol) was added as solid to the aqueous solution of LaCl₃.7 H₂O₁ prepared by dissolving 0.743 g in 13 ml distilled water (2 mmol), The mixture was stirred at about 80 °C on a heating plate while an aqueous solution of NaOH (0.5M) was added dropwise to cause an incipient but permanent precipitate, pH=6. The mixture was then filtered, and the hot clear filtrate solution was tightly covered and allowed to evaporate gradually at room temperature. White precipitate appeared in about one week. The solid was collected by filteration, washed with cold diethyl ether/THF;1:1, and dried under vacuum in a desiccator charged with silica gel. Yield =0.40 (43.24%) g, m.p.=129-132 °C. The presence of lanthanum metal was detected by xylenol orange indicator, ¹³C (D₂O, 400 MHz, 25 °C): δ =182.84, 174.67, 54.31, 32.92, 26.30 ppm. *Anal*. Calc. for C₁₀H₃₄Cl₆La₂N₂O₁₆: C, 12.93; H, 3.69; N, 3.02; La, 29.91. Found: C, 10.99; H, 3.76; N, 2.25; La, 30.03. Main FT IR bands (KBr, cm⁻¹), *v_{max}* 3330, 2598, 2202, 1619, 1566, 1488, 1442, 1423, 1361, 1343, 1315, 1288, 1257, 1200, 1137, 1122, 1086, 1037, 997, 962, 853, 805, 779, 718, 672, 555, 488, 459.

3. [La(*l*-phen)(H₂O)₇]Cl₃

l-phenylalanine (0.326 g, 2 mmol) was added as solid to the aqueous solution of LaCl₃ 7H₂O, prepared by dissolving 1.486 g in 15 ml distilled water (4 mmol), The mixture was stirred at about 80 °C on a heating plate while an aqueous solution of NaOH (0.5M) was added dropwise to cause an incipient but permanent precipitate, pH=6. The mixture was then filtered, and the hot clear filtrate solution was tightly covered and allowed to evaporate gradually at room temperature. White precipitate appeared in about one month. The solid was collected by filteration, washed with cold diethyl ether/THF;1:1, and dried under vacuum in a desiccator charged with silica gel. Yield =0.10 g (9.32%), m.p. = 134 °C. The presence of lanthanum metal was detected by xylenol orange indicator, ¹³C (D₂O, 400 MHz, 25 °C): δ =173.98, 135.03, 129.31, 129.07, 127.06, 55.97, 36.28 ppm, *Anal*. Calc. for C₉H₂₅Cl₃LaNO₉: C, 20.15; H, 4.7; N, 2.61; La, 25.89. Found: C, 20.64; H, 5.17; N, 2.61; La, 25.44. Main FT IR bands (KBr, cm⁻¹), *v_{max}* 3338, 3029, 2974, 2634, 2200, 1610, 1509, 1495, 1448, 1428, 1346, 1333, 1200, 1146, 1122, 1092, 1071, 1043, 981, 964, 926, 870, 842, 816, 767, 742, 698, 663, 595,531, 485, 467, 415.

4. [Yb₂(*l*-Glu)₂(H₂O)₈]Cl₆

l-Glutamic acid (0.294 g, 2 mmol) was added as solid to the aqueous solution of YbCl₃ 6 H₂O₁ prepared by dissolving 1.55 g in 13 ml distilled water (4 mmol), The mixture was stirred at about 80 °C on a heating plate while an aqueous solution of NaOH (0.5M) was added dropwise to cause an incipient but permanent precipitate, pH=6. The mixture was then filtered, and the hot clear filtrate solution was tightly covered and allowed to evaporate gradually at room temperature. White precipitate appeared in about twenty days. The solid was collected by filteration, washed with cold diethyl ether/THF; 1:1, and dried under vacuum in a desiccator charged with silica gel. Yield =0.24 g (12.01%), m. p.=131-132 °C. The presence of Yb metal was detected by xylenol orange indicator, ¹³C (D₂O, 400 MHz, 25 °C): δ =48.79, 21.50, 19.89 ppm, *Anal.* Calc. for C₁₀H₃₆Cl₆Yb₂N₂O₁₆: C, 12.04; H, 3.34; N, 2.81; Yb, 34.71. Found: C, 8.96; H, 3.33; N, 1.64; La, 35.61. Main FT IR bands (KBr, cm⁻¹), *v_{max}*2998, 2739, 1638, 1501, 1417, 1350, 1309, 1255, 1230, 1212, 1149, 1125, 1074, 1053, 945, 911, 865, 805, 758, 711, 701, 671, 536, 506, 398.

5. [Yb₂(*l*-phen)₄(H₂O)₈].3H₂OCl₆

l-phenylalanine (0.66 g, 4 mmol) was added as solid to the aqueous solution of YbCl₃ 6 H₂O prepared by dissolving 3.1 g in 15 ml distilled water (8 mmol), The mixture was stirred at about 80 °C on a heating plate while an aqueous solution of NaOH (0.5M) was added dropwise to cause an incipient but permanent precipitate, pH=6. The mixture was then filtered, and the hot clear filtrate solution was tightly covered and allowed to evaporate gradually at room temperature. White precipitate appeared in about one month. The solid was collected by filteration, washed with cold diethyl ether/THF;1:1, and dried under vacuum in a desiccator charged with silica gel. Yield = 0.43 g. (7.5%) The presence of Yb metal was detected by xylenol orange indicator, ¹³C (D₂O, 400 MHz, 25 °C): δ =134.79, 129.35, 129.29, 127.88, 35.36 ppm. *Anal.* Calc. for C₃₆H₆₆Cl₆Yb₂N₄O₁₉: C, 30.59; H, 4.42; N, 3.96; Yb, 24.48. Found: C, 28.87; H, 4.94; N, 3.66; Yb, 25.89. Main FT IR bands (KBr, cm⁻¹), *v_{max}* 3211, 1966, 1694, 1626, 1578, 1495, 1441, 1406, 1356, 1341, 1240, 1211, 1128, 1031, 964, 919, 860, 756, 696, 547, 530, 486, 395.

RESULTS AND DISCUSSION

All of the complexes are extremely soluble in water and readily soluble in common organic solvents, such as tetrahydrofuran, dichloromethane, acetone, and acetonitrile. The compounds were characterized using a variety of techniques, including IR, ¹³C NMR, ¹H NMR, microanalysis (CHN) and metal content. The metal content was determined by complexometric titration with EDTA. The results of the elemental analysis confirm the formula of the most complexes, from compound (1) to compound (5), and also confirm a 1:1 metal to ligand stoichiometry for the complexes 1, 2, 3 and 4, 1:2 metal to ligand ratio for compound 5.

Structures of complexes

The stoichiometry of complexes of glutamic acid $[La_2(l-glu)_2(H_2O)_8]Cl_6$ and $[Yb_2(l-glu)_2(H_2O)_8]Cl_6$ similar to the complex $[Sm_2(glu)_2(H_2O)_8]Cl_6.3H_2O$ [23]. 1:1 metal to ligand ratio of the complex $[La_2 (l-glu)_2(H_2O)_8](ClO_4)_4$ similar to the compounds $[Dy_2(glu)_2(H_2O)_8](ClO_4)_4.H_2O[12]$, $Ho_2(glu)_2(H_2O)_8](ClO_4)_4.H_2O[12]$, $[Er_2(glu)_2(H_2O)_8](ClO_4)_4.H_2O[15]$, $[Pr_2(glu)_2(H_2O)_8](ClO_4)_4$.4H_2O[10] and $[Sm_2(glu)_2(H_2O)_8](ClO_4)_4.3H_2O[11]$, each monoanionic glutamic residue bridges a couple of Ln atoms through its α -carboxylate, and another Ln pair through its γ -carboxylate, this results in an extended 2D arrangement.

In the case of the complexes of phenylalanine with lanthanides metal no much prepared be found in the literature, except compounds can the complex $[Nd_2(l$ $phe_4(H_2O_8)(ClO_4)_6, H_2O[16],$ our complex $[Yb_2(l-phe)_4(H_2O)_8]Cl_6, 3H_2O,$ similar to this complex, 1:2 metal to ligand ratio in the innersphere, and in the outershere, the $(ClO_4)_6$ replaced by Cl₆. The complex $[La(l-phen)(H_2O)_7]Cl_3$ with 1:1 metal to ligand ratio similar to the complexes of glutamic chlorides [23].

Characterization of the complexes by infrared spectra

In the infrared spectra, a strong and broad absorption appears at v=3300-3590 cm⁻¹, which is typical of molecules of high water content. A peak around 3505 cm⁻¹, previously reported and assigned to the stretching of a μ_3 -OH,[24)] was not observed in any of all the compounds; the peak is probably obscured by the broad water absorption. The presence of coordinated water

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molecules in all complexes is indicated by their characteristic rocking frequency at about 825 cm⁻¹. Metal coordination results in appreciable shifts of the asymmetric stretching frequency of the carboxylate moiety of the amino acids ligand, from 1610 to about 1590 cm⁻¹. The symmetric carboxylate stretching frequency shifts from 1416 to 1422 cm⁻¹. Strong and characteristic Cl-O stretching frequencies between 1050-1170 cm⁻¹ and 620-630 cm⁻¹ are observed for the ClO⁻⁴ counterions in all complexes, see supplementary materials, spectrum (1) – (7).

Characterization of complexes by nmr spectra

The ¹H NMR and ¹³C NMR spectrum of the lanthanides complexes of *l*-glutamic acid and *l*-phenylalanine undergo a shift to lower and higher field when it was compared with free amino acids.

Complexes of *l*-glutamic acid

In the complexes of *l*-Glutamic acid with the lanthanides, La^{3+} and Yb^{3+} , $[La_2(l-glu)_2(H_2O)_8]Cl_6$ and $[La_2(l-glu)_2(H_2O)_8](ClO_4)_4$, there is small upfield shift in proton nmr, but in the case of the complex $[Yb_2(l-glu)_2(H_2O)_8]Cl_6$ there is a large upfield shift in proton nmr below zero ppm, see supplementary materials, spectrum (8) – (11), the small upfield shift is due to slight increase in shielding resulting from increased donation from the carboxylic groups to the metal. Relative to the free amino acid the electron density of the chiral carbon is slightly higher. The same is true, but to a greater extent, in case of Yb resulted in the large upfield shift.

In the ¹³C-NMR spectrum of glutamic acid complexes (Table 1) the C1 signal at 177.60 ppm in the free ligand is shifted to 182.28 ppm (downfield) in compounds 2, and disappeared in the case of compound 1 and 4. The C5 signal at 174.34 ppm in the free ligand, shifted to 174.67 ppm (downfield) in compounds 2, and disappeared in the compound 1 and 4. This indicates the participation of the carboxyl oxygen into the coordination of the complexes [25]. Also there is small shift in C2, C3 and C4 in compounds 2 and 1, which is large in C2, C3 and C4 in compound 4 (upfield), because Ytterbium metal is more contracted than Lanthanum metal.

$HO - C_{5} - H_{2}C_{4} - H_{2}C_{3} - C_{1} - C_{1} - O^{-}$ $H - H_{1} - H$					
<i>l</i> -glu.	Compound 2	Compound 1	Compound 4	Assignment	
	LaCl ₃	$La(ClO_4)_3$	YbCl ₃		
177.60	182.28			C1	
174.34	174.67			C5	
54.35	54.31	54.33	48.79	C2	
30.35	32.92	32.96	21.50	C3	
26.02	26.30	26.30	19.89	C4	

Table 1. ¹³C-NMR Data of *l*-Glutamic Acid and *l*-Glutamic Acid Ln³⁺Complexes δ(ppm)

Complexes of *l*-phenylalanine

In complexes of *l*-phenylalanine with La^{3+} and Yb^{3+} , there is small upfield shift in proton nmr and ¹³C nmr in the case of $[La(l-phen)(H_2O)_7]Cl_3$, see supplementary materials, spectrum (16) –

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(21), but in the complex $[Yb_2(l-phen)_4(H_2O)_8]3H_2O.Cl_6$ the proton nmr spectrum is broad and some splitting is removed when compared with free ligand, and C1 and C2 disappeared in ¹³C nmr (table (2)).

7	5 4	$H_{2}C \xrightarrow{H} C \xrightarrow{2} H_{2}$	о со [.] `н
<i>l</i> -glu.	Compound 3	Compound 5	Assignment
	LaCl ₃	YbCl ₃	
173.89	173.98		C1
135.03	135.03	134.79	C7
129.30	129.31	129.35	C6
129.06	129.07	129.29	C5
127.64	127.06	127.88	C4
55.98	55.97		C2
36.29	36.28	35.36	C3

Table 2¹³C-NMR Data of *l*-Phenylalanine and *l*-Phenylalanine Ln³⁺Complexes δ (ppm)

The lanthanides metals generally act as a lewis acid and have the amino acids carbonyl oxygen which is coordinated to the metal acts as a lewis base. This is ideal situation for the lanthanides shift effect. It has been observed with ytterbium more than with lanthanum because of its lacks the required f-orbitals. The effect is transmitted to the α -carbon and its proton. This is the reason why the lanthanides complexes of the amino acids have been used as electronic environment probes.

CONCLUSION

The complexes of glutomic acid have 1:1 metal to ligand ratio, which contain infinite layers. The complexes of phenylalanine have 1:2 metal to ligand ratio.

Metal coordination results in appreciable shifts of the asymmetric stretching frequency of the carboxylate moiety of the glutomic acid ligand, from 1610 to about 1590 cm⁻¹. The symmetric carboxylate stretching frequency shifts from 1416 to 1422 cm^{-1} .

The shift in ¹H NMR resonance in the case of lanthanum metal is upfield and small because lanthanum is diamagnetic, but in the case of Ytterbium the upfield resonance shift is much higher. The characteristic shifts of ¹H NMR and ¹³C NMR clearly show that *l*-glutamic acid is coordinated to the lanthanides ions via the carboxylic acid oxygen.

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