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Review

Structure and thermodynamic stability of lanthanide complexes with amino acids and peptides

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Contents

Abstract

The interaction of lanthanide ions with biologically active ligands is of the utmost relevance to understand and develop new complexes based on these ions. In this paper the thermodynamic and structural properties of Ln(III) complexes with amino acids and peptides is critically reviewed. Mixed-ligand and heteropolynuclear complexes containing amino acids or peptides in the coordination sphere are also included. Equilibrium data in aqueous solution have been collected, showing the formation of species with low thermodynamic stability. The solid state structures are dominated by the formation of carboxylate bridges which connect lanthanide cations. Different nuclearities are found, from discrete dimers to infinite 2D structures.

Keywords: Lanthanides; Amino acids; Peptides; Complexation thermodynamics; Structure

1. Introduction

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. Over the past 10 years lanthanide ions and lanthanide complexes have been proposed and used in several biological and medical applications, namely:

a. The high-spin paramagnetism and the ability of lanthanide complexes to enhance the longitudinal relaxation rate of water protons, especially in the case of Gd(III), have been

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fully used to develop new contrast agents in conjunction with magnetic resonance imaging [1–4].

b. Radiolanthanides are excellent candidates for radiotherapy because of their desirable physical characteristics and ready availability. Sm, ^{165}Dy, ^{166}Ho, and ^{177}Lu complexes have been used for palliative treatment of pain from metastatic bone cancer, radiation synovectomy and radioimmunotherapy [5,6].
c. Lanthanide tris(β-diketonates) and porphyrinates are effective receptors which offer chiral recognition and chirality sensing of biological substrates, including amino acids [7–10].
d. Lanthanide ions can induce perforation of the cell membranes as does the Ca(II) ion, but at a very low concentration [7].
e. Lanthanides are scavengers of reactive oxygen species, with the characteristic that they interact with free radicals and peroxides but they cannot become radicals [11].
f. Due to the special photophysical properties of lanthanide complexes, they are being used as luminescent labels in various fluoroimmunoassays [11].
g. Lanthanide complexes are, up to now, the best non-enzymatic agents which selectively hydrolyse DNA and RNA with high specificity [12–19].

In all these applications two main points should be taken into account to optimize the success of a lanthanide complex for achieving a specific objective. First, thermodynamic stability is crucial to assure that the complex can reach the target point (an organ, a cell, etc.) unchanged. Second, the structure of the complex is very important to determine the in vivo behavior of the agent. For example, the coordination number, the presence of coordinated water and the formation of polynuclear species can dramatically change the usefulness of the compound.

With this in mind, in this review we focus our attention on the thermodynamic and structural properties of lanthanide(III) complexes with the biologically relevant ligands, amino acids and peptides. This review enlarges and updates previous reports in this field [20,21]. A good understanding of the direct interaction between these ligands and the lanthanide ions is of utmost importance to rationalize the transport and biological activity of the species.

The revised literature does not contain a uniform nomenclature for the ligands. In this review, H_nL (for example, HAla or H_2Glu) will represent the zwitterionic form of the amino acid. *n* indicates the number of acidic protons for the species H_3N^+–CHR–COO^-. This is very useful to describe the equilibria in solution. On the other hand, a generic name L (for example, Ala or Glu) is used to formulate the structures. This is the most widely used nomenclature in the crystallographic papers. Ln will be used to refer in general to the lanthanide elements, including the elements from La to Lu, and amino acids will generally be referred to as aa.

An apology is offered to those authors whose work has been inadvertently omitted.

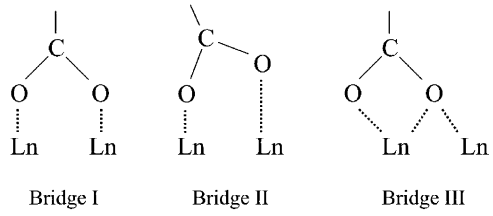
2. Structure of simple Ln(III) species containing amino acids in the coordination sphere

The strong hydrolysis undergone by Ln(III) ions in aqueous media has been an important restriction to the preparation of Ln(III)–aa complexes. In this section, we will review the structures reported for those compounds prepared under acidic conditions. Table 1 lists the complexes together with the main structural characteristics. Sixty structures can be found in the literature, covering all Ln with the exceptions of Ce, Pm, Tm and Lu.

The synthesis of the complexes is carried out in aqueous solution at pH always below 5. Different ligand to metal ratios have been used, but this does not seem to be determining in the stoichiometry and structure of the complexes. Coordination number 8 is the most common (41 of the 60) among the structures. This fact is more remarkable at the end of the series (but not exclusive), reflecting the smaller size of the cations.

Some general comments can be made regarding the structures. In spite of the presence of an amino group in the ligand, it does not participate in the coordination. The amino acids may be regarded as zwitterions coordinated through the carboxylate group. Nevertheless, the $–NH_3^+$ group of the amino acid usually has an active participation in the formation of H bonds, which gives further stability to the crystal structure. Another general point is the almost ubiquitous presence of carboxylate-bridged polynuclear units. The only exception is the complex $[Nd(Gly)_3(H_2O)_2]Cl_3$ [35]. It contains three glycine ligands acting as bidentate to the same central atom. In all the other structures, the carboxylate bridges Ln ions resulting in dinuclear units, infinite chains or infinite 2D structures.

A detailed analysis of the structures listed in Table 1 allows one to recognize three kinds of carboxylate bridges. They are shown in Scheme 1. In the type I bridge, both oxygen atoms of the carboxylate lie quite symmetrically with respect to the Ln atoms. In the type II bridge, there is a considerable difference between the two Ln–O distances, being an asymmetric μ_2-coordination mode. We have fixed an arbitrary limit of 3% difference between Ln–O distances to distinguish between type I and type II bridges. Finally, in some structures,



Scheme 1. Carboxylate bridges found in Ln–aa structures.

Table 1
Structural data of Ln–aa complexes

Compound	Ln CN	Molecular structure	Bridges connecting Ln ions	Ref.
$[La(Gly)_3(H_2O)_2]Cl_3{\cdot}H_2O$	9	Infinite chain	Three bridges (I, II, III)	[22]
$[La(Gly)_3(H_2O)_2](ClO_4)_3$	10	Infinite chain	Two bridges (III, III) alternating with four bridges (I, I, III, III)	[23]
$[La_2(Ala)_4(H_2O)_8](ClO_4)_6$	8	Isolated dimer	Four bridges (I, I, I, I)	[24]
$[Pr_2(Gly)_6(H_2O)_4](ClO_4)_6{\cdot}5H_2O$	9	Infinite chain	Two bridges (I, I) alternating with four bridges (I, I, II, III)	[25]
$[Pr(Gly)_3(H_2O)_2]Cl_3{\cdot}H_2O$	9	Infinite chain	Two bridges (I, II)	[26]
$[Pr_2(Gly)_6(H_2O)_4](ClO_4)_6{\cdot}5H_2O$	8	Infinite chain	Two bridges (I, I) alternating with four bridges (I, I, II, III)	[27]
$[Pr_2(Thr)_2(H_2O)_{12}]Cl_6$	9	Infinite zigzag chain	Two different simple bridges (I)	[28]
$[Pr_2(Pro)_6(H_2O)_4](ClO_4)_6$	8	Infinite chain	Two bridges (I, II) alternating with four bridges (I, II, II, II)	[29,30]
$[Pr_2(Glu)_2(ClO_4)\ (H_2O)_7](ClO_4)_3{\cdot}4H_2O$	9	Infinite 2D planes	Two bridges (I) through Cα, and two bridges (III) through Cγ	[31,32]
$[Nd_2(Gly)_6(H_2O)_4](ClO_4)_6{\cdot}5H_2O$	9	Infinite chain	Two bridges (I, I) alternating with four bridges (I, I, II, III)	[33]
$[Nd(Gly)(H_2O)_7]Cl_3$	9	Infinite chain	Simple bridge (I)	[34]
$[Nd(Gly)_3(H_2O)_2]Cl_3{\cdot}H_2O$	8	Isolated monomer	No bridge	[35]
$[Nd_2(Gly)_4Cl_2(H_2O)_2]Cl_3$	9	Isolated dimer	Four bridges (I, I, III, III)	[36]
$[Nd_2(Ala)_4(H_2O)_8](ClO_4)_6$	8	Isolated dimer	Four bridges (I, I, I, I)	[37]
$[Nd_2(Phe)_4(H_2O)_8](ClO_4)_6{\cdot}H_2O$	8	Isolated dimer	Four bridges (II, II, II, II)	[38]
$[Nd_2(Ile)_4(H_2O)_8](ClO_4)_6$	8	Isolated dimer	Four bridges (I, I, II, II)	[39]
$[Nd(Pro)_3(H_2O)_2](ClO_4)_6$	8	Infinite chain	Two bridges (I, II) alternating with four bridges (I, II, II, II)	[40]
$[Nd_4(Pro)_4Cl_2(H_2O)_{22}]Cl_{10}$	8	Two non-equivalent isolated dimers	Two bridges (II, II) for both dimers	[41]
$[Sm_2(Gly)_6(H_2O)_4](ClO_4)_6{\cdot}5H_2O$	9	Infinite chain	Two bridges (I, I) alternating with four bridges (I, I, II, III)	[42]
$[Sm_2(Ala)_4(H_2O)_8](ClO_4)_4Cl_2$	8	Isolated dimer	Four bridges (I, I, I, II)	[43]
$[Sm_2(Val)_4(H_2O)_8](ClO_4)_6$	8	Isolated dimer	Four bridges (I, I, I, II)	[44]
$[Sm_2(Pro)_6(H_2O)_6](ClO_4)_6$	8	Infinite chain	Two bridges (II, II) and one Pro monodentate	[45]
$[Sm_2(Glu)_2(H_2O)_8](ClO_4)_4{\cdot}3H_2O$	9	Infinite 2D planes	Two bridges (II, II) through Cα, and two bridges (III, III) through Cγ	[46]
$[Sm(Asp)(H_2O)_4]Cl_2$	8	Infinite 2D planes	One bridge (I) through Cα, and one bridge (I) through Cβ	[45]
$[Eu_2(Ala)_4(H_2O)_8](ClO_4)_6$	8	Isolated dimer	Four bridges (I, I, I, I)	[47]
$[Eu_2(Ile)_4(H_2O)_8](ClO_4)_6$	8	Isolated dimer	Four bridges (I, I, II, II)	[39]
$[Eu_2(Pro)_4(H_2O)_8](ClO_4)_6{\cdot}4H_2O$	8	Isolated dimer	Four bridges (I, I, I, I)	[48]
$[Eu_2(Pro)_4(H_2O)_8](ClO_4)_6{\cdot}4H_2O$	8	Infinite chain	Two bridges (I, I) and one Pro monodentate	[48]
$[Eu(Thr)(H_2O)_5]Cl_3$	8	Zig-zag chain	simple bridge (I)	[49]
$[Gd_2(Ala)_4(H_2O)_8](ClO_4)_6$	8	Isolated dimer	Four bridges (I, I, I, I)	[50]
$[Gd(Gly)_3(H_2O)_2]Cl_3{\cdot}H_2O$	8	Infinite chain	Three bridges (I, II, II)	[51]
$[Gd_2(Pro)_6(H_2O)_6](ClO_4)_6$	8	Infinite chain	Two bridges (II, II) and one Pro monodentate	[52]
$[Dy_2(Gly)_6(H_2O)_4](ClO_4)_6{\cdot}2H_2O$	9	Infinite chain	Two bridges (I, II) alternating with four bridges (I, I, II, II)	[53]
$[Dy_2(Ala)_2(H_2O)_{12}]Cl_6$	8	Infinite chain	Simple bridge (II)	[54]
$[Dy(Pro)_2(H_2O)_5]Cl_3$	8	Infinite zig-zag chain	Simple bridge (I) and pro monodentate	[55]
$[Dy_2(Glu)_2(H_2O)_8](ClO_4)_4{\cdot}H_2O$	9	Infinite 2D planes	Two bridges (I, I) through Cα, and two bridges (III, III) through Cγ	[56]
$[Ho_2(Gly)_6(H_2O)_4](ClO_4)_6{\cdot}2H_2O$	9	Infinite chain	Two bridges (I, II) alternating with four bridges (I, I, II, II)	[53]
$[Ho_2(Ala)_4(H_2O)_8]Cl_6$	8	Isolated dimer	Four bridges (I, I, I, II)	[57]
$[Ho(Thr)(H_2O)_5]Cl_3$	8	Infinite zigzag chain	Simple bridge (I)	[58]
$[Ho(Ser)(H_2O)_5]Cl_3$	8	Infinite zigzag chain	Simple bridge (I)	[59]
$[Ho(Pro)_2(H_2O)_5]Cl_3$	8	Infinite zigzag chain	Simple bridge (I) and Pro monodentate	[55]
$[Ho_2(Glu)_2(H_2O)_8](ClO_4)_4{\cdot}H_2O$	9	Infinite 2D planes	Two bridges (I, I) through Cα, and two bridges (III, III) through Cγ	[56]
$[Ho(Asp)(H_2O)_5]Cl_2{\cdot}H_2O$	8	Infinite 2D planes	One bridge (I) through Cβ, and one α-COO monodentate	[60]
$[Er_2(Gly)_4(H_2O)_8](ClO_4)_6{\cdot}C_4H_8O_2$	8	Isolated dimer	Four bridges (I, I, I, I)	[61]
$[Er_2(Gly)_6(H_2O)_8](ClO_4)_6{\cdot}5H_2O$	10	Infinite chain	Two bridges (I, II) alternating with four bridges (I, I, II, II)	[62]

Table 1 (*Continued*)

Compound	Ln CN	Molecular structure	Bridges connecting Ln ions	Ref.
$[Er_2(Gly)_2(H_2O)_{12}](ClO_4)_6{\cdot}4H_2O$	8	Isolated dimer	Two bridges (I, I)	[63]
$[Er_2Y_2(Gly)_{12}(H_2O)_8](ClO_4)_{12}{\cdot}10H_2O$	8	Infinite chain	Four bridges (I, I, II, II) Er-Y alternating with Y-Y double bridge (I, II) and Er-Er double bridge (I, II)	[64]
$[Er_2(Ala)_4(H_2O)_8](ClO_4)_6$	8	Isolated dimer	Four bridges (I, I, I, I)	[47,65]
$[ErY(Ala)_4(H_2O)_4](ClO_4)_6$	8	Isolated dimers containing Er or Y	Four bridges (I, I, I, I)	[66]
$[Er_4(Met)_6(Gly)_2(H_2O)_{16}](ClO_4)_{12}$	8	Two independent isolated dimers	One quadruple Met bridge (I, I, II, II) and one with two Gly bridges (I, I) and two Met bridges (II, II)	[67]
$[Er_2(Ser)_3(H_2O)_8](ClO_4)_6$	7	Isolated dimer	Three bridges (I, I, II)	[68]
$[Er(Pro)_2(H_2O)_5]Cl_3$	8	Infinite zigzag chain	Simple bridge (I) and Pro monodentate	[69]
$[Er_2(Pro)_6(H_2O)_6](ClO_4)_6$	8	Infinite chain	Two bridges (II, II) and Pro monodentate	[70]
$[ErY(Pro)_6(H_2O)_6](ClO_4)_6$	8	Infinite chain	Two bridges (alternating I, I, and II, II) and Pro monodentate	[71]
$[ErY(Pro)_4(H_2O)_8](ClO_4)_6$	8	Infinite chain	Two bridges (II, II)	[72]
$[Er_2(Glu)_2(NO_3)_2(H_2O)_4](NO_3)_2{\cdot}5H_2O$	9	Infinite 2D planes	Two bridges (I, II) through Cα, and two bridges (III, III) through Cγ	[73]
$[Er_2(Glu)_2(H_2O)_8](ClO_4)_2{\cdot}H_2O$	9	Infinite 2D planes	two bridges (I, II) through Cα, and two bridges (III, III) through Cγ	[74]
$[Yb(Gly)_3(H_2O)_2]Cl_3{\cdot}H_2O$	8	Infinite chain	Three bridges (I, II, II)	[75]
$[Yb(Thr)(H_2O)_5]Cl_3$	8	Infinite zig-zag chain	Simple bridge (I)	[49]
$[Yb(Pro)_2(H_2O)_5]Cl_3$	8	Infinite zig-zag chain	Simple bridge (I) and Pro monodentate	[76]

Compounds are formulated according to the crystallographic basic unit. The nomenclature of bridges follows Scheme 1. CN represents the coordination number.

the disposition of the O atoms is very different. One of them is almost in the middle of the metal centres at bond distance of both metals. It can be considered to be a μ_3-carboxylate group occupying three coordination positions belonging to two different ions. The type III bridge is much more frequent for lighter Ln. They have larger ionic radii, favouring the possibility that an oxygen atom forms two bonds with two metal centres. Regardless of the type of bridge, the distance Ln–Ln is great enough to rule out a direct metal–metal bond.

We can begin with the different structures containing the simplest amino acid, glycine. Besides the above mentioned tris chelate compound $[Nd(Gly)_3(H_2O)_2]Cl_3$, all the other structures are polymeric, mostly infinite chains. $[La(Gly)_3(H_2O)_2](ClO_4)_3$ [23], $[Pr_2(Gly)_6(H_2O)_4](ClO_4)_6{\cdot}5H_2O$ [25,27], $[Nd_2(Gly)_6(H_2O)_4](ClO_4)_6{\cdot}5H_2O$ [33], $[Sm_2(Gly)_6(H_2O)_4](ClO_4)_6{\cdot}5H_2O$ [42], $[Dy_2(Gly)_6(H_2O)_4](ClO_4)_6{\cdot}2H_2O$, $[Ho_2(Gly)_6(H_2O)_4](ClO_4)_6{\cdot}2H_2O$ [53], and $[Er_2(Gly)_6(H_2O)_8](ClO_4)_6{\cdot}5H_2O$ [62] exhibit the same structural motif, resulting in a Ln:aa molar ratio of 1:3. The Ln ions in the chain are linked by four or two carboxylate groups, in an alternate way. This is shown in Fig. 1. The double bridge is usually symmetric (type I), but the quadruple bridge tends to be more asymmetric. For the first lanthanides, with a larger ionic radius, a type III bridge can be found (La, Pr, Nd, and Sm).

A similar structure is displayed in $[Er_2Y_2(Gly)_{12}(H_2O)_8](ClO_4)_{12}{\cdot}10H_2O$ [64]. A quadruple bridge joins Er and Y, alternating with Er–Er and Y–Y double bridges.

Some variations of this chain can be observed in other structures. In $[La(Gly)_3(H_2O)_2]Cl_3{\cdot}H_2O$ [22], $[Yb(Gly)_3(H_2O)_2]Cl_3{\cdot}H_2O$ [75], and $[Gd(Gly)_3(H_2O)_2]Cl_3{\cdot}H_2O$ [51], there are only triple bridges connecting La atoms, while in $[Pr(Gly)_3(H_2O)_2]Cl_3{\cdot}H_2O$ [26] the chain is sustained by two bridges. On the other hand, Nd atoms in $[Nd(Gly)(H_2O)_7]Cl_3$ [34] are connected by a simple type I bridge.

In the case of Er, besides the chain structure, two isolated dimers have been reported. $[Er_2(Gly)_4(H_2O)_8](ClO_4)_6{\cdot}C_4H_8O_2$ [61] possesses a double bridge while in $[Er_2(Gly)_2(H_2O)_{12}](ClO_4)_6{\cdot}4H_2O$ [63] four bridges connect two Er atoms. Neodymium also presents a structure based

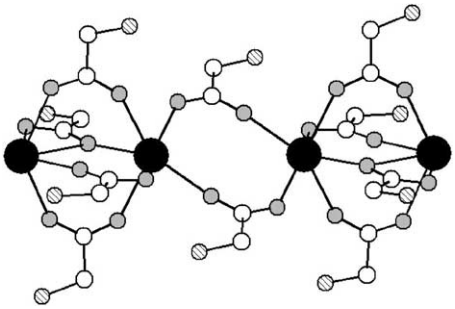


Fig. 1. Schematic disposition of atoms in $[Pr_2(Gly)_6(H_2O)_4](ClO_4)_6{\cdot}5H_2O$. Water molecules, H atoms, and counterions are omitted for clarity. Pr: black; O: grey; C: white; N: dashed. In this case, the double bridge is symmetric (I, I). The quadruple bridge includes two type I bridges, one type II, and another type III bridge.

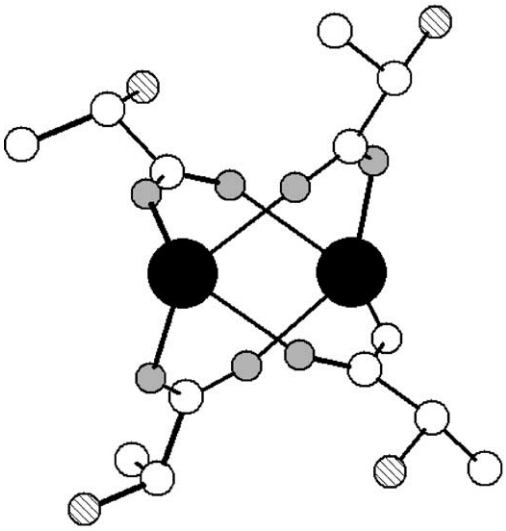


Fig. 2. Schematic disposition of atoms in $[Sm_2(Ala)_4(H_2O)_8](ClO_4)_4Cl_2$. Only the carboxylate bridges are shown; water molecules, H atoms, and counterions are omitted for clarity. Sm: black; O: grey; C: white; N: dashed.

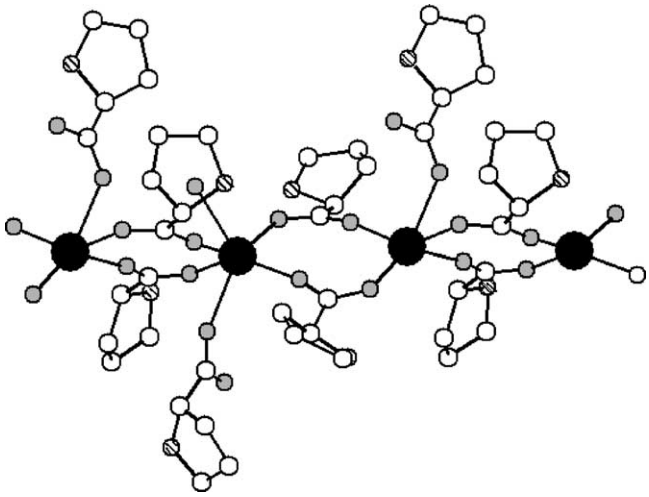


Fig. 3. Schematic disposition of atoms in $[Sm_2(Pro)_6(H_2O)_6](ClO_4)_6$. Only the carboxylate bridges are shown; water molecules, H atoms, and counterions are omitted for clarity. Sm: black; O: grey; C: white; N: dashed.

on isolated dimers, $[Nd_2(Gly)_4Cl_2(H_2O)_2]Cl_3$ [36], with a quadruple bridge.

Structures containing dimers are very commonly found in alanine complexes. $[La_2(Ala)_4(H_2O)_8](ClO_4)_6$ [24], $[Nd_2(Ala)_4(H_2O)_8](ClO_4)_6$ [37], $[Sm_2(Ala)_4(H_2O)_8](ClO_4)_4Cl_2$ [43], $[Eu_2(Ala)_4(H_2O)_8](ClO_4)_6$ [47], $[Gd_2(Ala)_4(H_2O)_8](ClO_4)_6$ [50], $[Ho_2(Ala)_4(H_2O)_8]Cl_6$ [57], and $[Er_2(Ala)_4(H_2O)_8](ClO_4)_6$ [47,65] are built on the basis of dimers in which two Ln are joined by four carboxylate groups belonging to four amino acids. The final stoichiometry (Ln:aa) in these compounds is 1:2. The four bridges are very symmetric, generally type I bridges. This is shown in Fig. 2. The same structure is found in the compound $[ErY(Ala)_4(H_2O)_4](ClO_4)_6$ [64], in which half of the units are Er dimers and the other half Y dimers.

Only one infinite chain has been reported for alanine complexes. In $[Dy_2(Ala)_2(H_2O)_{12}]Cl_6$ [54], a simple bridge connects the dysprosium atoms.

Other simple amino acids also show the formation of isolated dimers at solid state. $[Nd_2(Phe)_4(H_2O)_8](ClO_4)_6{\cdot}H_2O$ [38], $[Nd_2(Ile)_4(H_2O)_8](ClO_4)_6$ [39], $[Sm_2(Val)_4(H_2O)_8](ClO_4)_6$ [43], and $[Eu_2(Ile)_4(H_2O)_8](ClO_4)_6$ [39] display the same structural motif containing four carboxylate bridges connecting two Ln ions. Once more, these dimers exhibit a 1:2 (Ln:aa) molar ratio. It has been reported an interesting compound which has two different aa in the coordination sphere. $[Er_4(Met)_6(Gly)_2(H_2O)_{16}](ClO_4)_{12}$ [67] is a mixture of two dimers. One dimer has two Er atoms connected by four Met molecules, and the other one has two Er atoms connected by two Met and two Gly molecules.

Proline should be considered to be a special case because many different structures are observed in their complexes with lanthanides, resulting in stoichiometries varying from 1:1 to 1:3. The lighter ions exhibit structures quite similar to those found for Gly and Ala complexes. $[Pr_2(Pro)_6(H_2O)_4](ClO_4)_6$ [29,30], and $[Nd(Pro)_3(H_2O)_2](ClO_4)_6$ [40] are infinite chains with alternating quadruple and double bridges, $[Nd_4(Pro)_4Cl_2(H_2O)_{22}]Cl_{10}$ [41] is a dimer with a double bridge, and $[Eu_2(Pro)_4(H_2O)_8](ClO_4)_6{\cdot}4H_2O$ is also a dimer but with a quadruple bridge. In the structure of $[ErY(Pro)_4(H_2O)_8](ClO_4)_6$ [72], containing two lanthanides, a double bridge forms an infinite chain which alternates one Er and one Y.

The structures reported for the other Ln–Pro complexes include a monodentate proline ligand. This is a unique case in the Ln–aa complexes. The most common disposition is an infinite chain in which a double bridge connects the metal ions and another Pro is bonded to each Ln only through one O of the carboxylate (Fig. 3). This structure is observed in $[Sm_2(Pro)_6(H_2O)_6](ClO_4)_6$, [45], $[Eu_2(Pro)_4(H_2O)_8](ClO_4)_6{\cdot}4H_2O$ [48], $[Gd_2(Pro)_6(H_2O)_6](ClO_4)_6$ [52], $[Er_2(Pro)_6(H_2O)_6](ClO_4)_6$ [70], and $[ErY(Pro)_6(H_2O)_6](ClO_4)_6$ [71]. Another group of complexes have a similar chain disposition with a monodentate proline, but with a simple bridge between the Ln atoms: $[Dy(Pro)_2(H_2O)_5]Cl_3$, $[Ho(Pro)_2(H_2O)_5]Cl_3$ [55], $[Er(Pro)_2(H_2O)_5]Cl_3$ [69], and $[Yb(Pro)_2(H_2O)_5]Cl_3$ [76].

When the amino acid possesses another potential coordinating group, the structures can have higher nuclearity, up to the formation of infinite planes. If Thr or Ser is the amino acid, the additional –OH group also coordinates to the Ln. Hence, one molecule of Thr coordinates by two points (one O of the carboxylate and OH of the alcohol residue) to the same Ln. The other O of the carboxylate coordinates to other Ln, resulting in an infinite zigzag chain. This is shown in Fig. 4. The resulting molar ratio Ln:aa is 1:1. This structure is observed in all complexes containing Thr: $[Pr_2(Thr)_2(H_2O)_{12}]Cl_6$

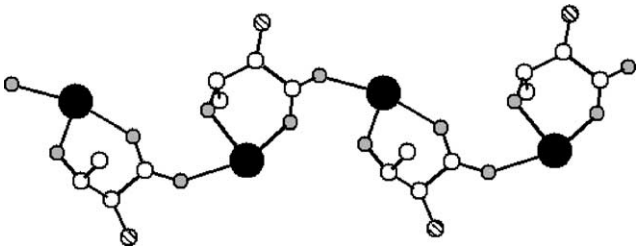


Fig. 4. Schematic disposition of atoms in $[Yb(Thr)(H_2O)_5]Cl_3$. Only the carboxylate bridges are shown; water molecules, H atoms, and counterions are omitted for clarity. Yb: black; O: grey; C: white; N: dashed.

[28], $[Eu(Thr)(H_2O)_5]Cl_3$ [49], $[Ho(Thr)(H_2O)_5]Cl_3$ [58], $[Yb(Thr)(H_2O)_5]Cl_3$ [49], and $[Ho(Ser)(H_2O)_5]Cl_3$ [59]. The complex $[Er_2(Ser)_3(H_2O)_8](ClO_4)_6$ [68] constitutes a particular case in which Er(III) atoms (with CN = 7) are coupled by three Ser bridges without intervention of −OH groups. The final molar ratio Ln:aa is 1:1.5.

The incorporation of a second carboxylate group in glutamic acid produces the formation of well-defined layers in the structure. This is the disposition found in the structures of the complexes $[Pr_2(Glu)_2(ClO_4)(H_2O)_7](ClO_4)_3{\cdot}4H_2O$ [31,32], $[Sm_2(Glu)_2(H_2O)_8](ClO_4)_4{\cdot}3H_2O$ [46], $[Dy_2(Glu)_2(H_2O)_8](ClO_4)_4{\cdot}H_2O$, $[Ho_2(Glu)_2(H_2O)_8](ClO_4)_4{\cdot}H_2O$ [56], $[Er_2(Glu)_2(NO_3)_2(H_2O)_4](NO_3)_2{\cdot}5H_2O$ [73], and $[Er_2(Glu)_2(H_2O)_8](ClO_4)_2{\cdot}H_2O$ [74]. Each monoanionic Glu residue bridges a couple of Ln atoms through its α-carboxylate, and another Ln pair through its γ-carboxylate. Hence, each metal centre is linked to another one by four carboxylate bridges, two α-carboxylate and two γ-carboxylate. This results in an extended 2D arrangement as shown in Fig. 5.

The structures of aspartic acid complexes $[Sm(Asp)(H_2O)_4]Cl_2$ [45], and $[Ho(Asp)(H_2O)_5]Cl_2{\cdot}H_2O$ [60] also contain infinite layers. In the case of the Sm complex, both α and β-carboxylates bridge metal ions. The structure is quite different from those found in Glu complexes because there is only one bridge between adjacent Sm atoms. On the other hand, in the Ho compound the β-carboxylate is the only group that bridges Ho centres. α-Carboxylate (belonging to a second aa residue) acts as monodentate, and allows the formation of infinite layers. Both sets of complexes, containing Glu or Asp lead to a 1:1 stoichiometry.

It is important to discuss a few points in relation to these structures. In Fig. 6, a plot of the O–C–O carboxylate angles reported for all the structures in Table 1 is shown. The distances are grouped according to the type of bridge they belong to, regardless of the aa and the Ln. As can be seen, type I bridges are the most frequent, type III being much more scarce. Thus, the symmetric μ_2-COO^- coordination mode of the aa should be taken as the most common one. Now we can compare the mean value of the O–C–O angles in the three different bridges (126.1°, 125.2°, and 122.8° for type I, type II, and type III, respectively) with the same angle for those structures which contain a monodentate aa (126.3°). It

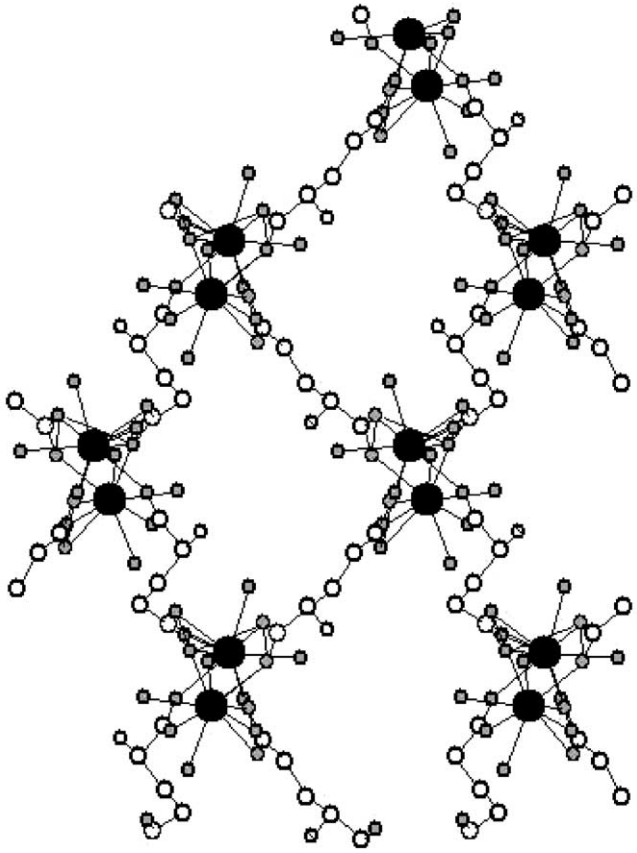


Fig. 5. Schematic disposition of atoms in $[Pr_2(Glu)_2(ClO_4)(H_2O)_7](ClO_4)_3{\cdot}4H_2O$. Only the carboxylate bridges are shown; water molecules, H atoms, and counterions are omitted for clarity. Pr: black; O: grey; C: white; N: dashed.

is possible to conclude that the formation of a bridge does not represent a large distortion of the carboxylate group in the aa. Indeed, the mean values indicate that the COO^- group in bridge I is almost undisturbed. On the other hand, in bridge III where the COO^- occupies three coordination positions, is the most distorted situation. The O–C–O angle should be smaller in order to reach the three positions. It is important to note that these results are independent of the Ln and the aa.

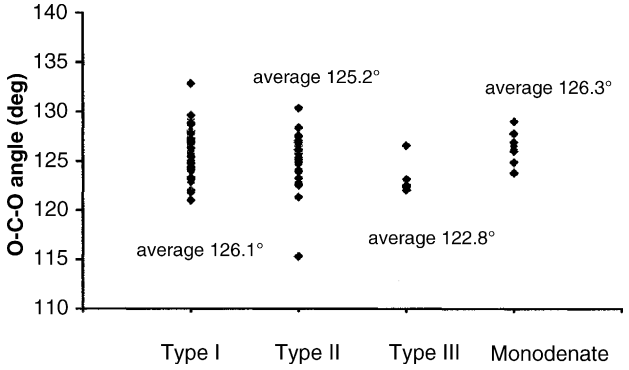


Fig. 6. O—C—O angle in the coordinating carboxylate group for the different types of bridges. The angle for monodentate amino acids (in Ln complexes) is also shown.

Table 2
Relation between Shannon's ion radii (coordination number 8) [77], and the average distance Ln—O

	La	Pr	Nd	Sm	Eu	Gd	Dy	Ho	Er	Yb
Shannon's ion radii	1.160	1.126	1.109	1.079	1.066	1.053	1.027	1.015	1.004	0.985
Ln—O distance in type I bridge	2.500	2.439	2.410	2.382	2.362	2.356	2.320	2.319	2.283	2.336
Ln—O distance in type II bridge	2.501	2.445	2.415	2.390	2.402	2.376		2.315	2.310	2.314

For every type of bridge, distances from structures in Table 1 were averaged.

In conclusion, aa behave as a two-points negative charge toward Ln(III) ions. The ligand tries to fit two coordination positions of adjacent lanthanides without much distortion. Only in the type III bridges, a distortion in the carboxylate group is forced in order to fit three coordination positions. The predominantly ionic interaction is also reflected in the variation of Ln–O distances. This is shown in Table 2. There is a close relation between the ionic radius of the central atom, and Ln–O distances. Regardless of the aa, a monotonous decrease in Ln–O distance is observed with a diminishing ionic radius.

The different structural motifs we can find have been described above. For example, the aa glycine, alanine, phenylalanine, valine, isoleucine, and proline only have the carboxylate to coordinate the Ln ion. They differ in the alkyl group (–R) attached to the C in the α position. The question is why even small changes in R lead to quite different structures. The different steric hindrance of the R groups seems not to be definitive in the final result. The addition of a $-CH_3$ (from Gly to Ala) should not justify a change from chains to dimers, taking into account the rather large ionic radius of the lanthanides. As we will see in Section 8 there is no great difference among the ligand capabilities of the different aa towards Ln(III). Thus, the diverse stoichiometries and structures cannot be considered to be a direct function of the basicity of the aa. Perhaps the final structure is the result of a delicate balance of interactions, some of which may not be immediately obvious. The comparison of the structures reveals another important factor that can influence the solid state structure of the complexes, the nature of the counterion. The preparation of all these cationic compounds is quite similar, but chloride or perchlorate have been used as counterions. A similar preparation of a Ln with amino acid in the same molar ratio, but starting from $LnCl_3$ instead of $Ln(ClO_4)_3$ yields different structures. Perchlorate is always involved in well-defined H bonds, either with crystallization water or with protonated $-NH_3^+$ groups. These interactions confer further stabilization to the lattice and can favour one structure over the other.

A further comment should be deserved to the influence of the chirality of the aa on the structure of the complexes. This fact has been studied on the dimeric structure of $[Nd_2(Ala)_4(H_2O)_8]^{6+}$ [37], and $[Eu_2(Ile)_4(H_2O)_8]^{6+}$ [39]. Using of L-aa instead of DL-aa results in subtle differences in the structure. The dimeric structural motif is retained. However, a non-centrosymmetric dimer is obtained with the L-ligand, while a centrosymmetric one is found in the case of the racemic ligand. This change affects the spectroscopic properties of the system. This phenomenon was undoubtly demonstrated by high resolution spectroscopy at 4 K [37,39].

3. Structure of other Ln(III) species containing amino acids in the coordination sphere

Mixed-ligand species in which an auxiliary ligand gives sufficient stability to the Ln ion while some coordination positions are still free in order to bind an amino acid have been developed. Some of such complexes have been obtained in order to design new radiotherapeutic agents [78] or lanthanide probe complexes for biomolecules [79].

Research in that area produced three novel structures. Two of them contain Yb as the central atom, [YbL(Gly)] $(CF_3SO_3)_2{\cdot}H_2O{\cdot}CH_3OH$, and [YbL(Ser)]$(CF_3SO_3)_2{\cdot}H_2O{\cdot}CH_3OH$ [79]. L is a heptadentate derivative of cyclen, 1,4,7-tris[(R)-(1-phenyl)ethylcarbamoylmethyl]-1,4,7,10-tetraazacyclodecane. The ligand occupies seven coordination positions of the Yb (using the four N of the cyclen ring and three amide oxygens, belonging to each substitute). Bound water molecules can be displaced by an amino acid yielding a mixed-ligand complex. The aa is fully deprotonated in the complex, as a result of preparing the complex in a neutral water:methanol solution. In addition, the aa coordinates both through the O and through the nitrogen atom. This is a rare N, O-bidentate coordination of an aa to a lanthanide ion.

The third structure is the Eu compound $[Eu(Val)(phen)_2(H_2O)_3]{\cdot}(ClO_4)_3{\cdot}3phen{\cdot}2H_2O$ (phen = 1,10-phenanthroline) [80]. The species can be seen as a $[Eu(phen)_2]^{3+}$ block with the addition of valine. The aa acts as bidentate using only the carboxylate in a μ_2-coordination mode.

$[Eu_2(Met)_3(glycylato)(H_2O)_8](ClO_4)_6$ [81] also belongs to this group. It shows the presence of isolated dimers with four COO^- bridges, three belonging to Met and the other to one molecule of glycylate.

4. Polynuclear complexes containing Ln(III), amino acids and a 3d metal ion

New materials based on Ln polynuclear coordination compounds have been developed for many purposes. They contain, besides Ln(III), a 3d-metal ion. These structures can

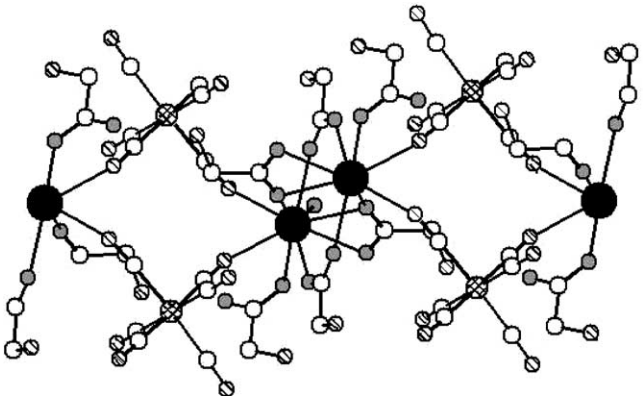


Fig. 7. Schematic disposition of atoms in $[La\{Fe(CN)_6\}(Gly)_3(H_2O)]_2{\cdot}2H_2O$. Water molecules, and H atoms are omitted for clarity. La: black; Fe: squared; O: grey; C: white; N: dashed.

be seen to be derived from the basic ones described in Section 2.

In the complexes $[Ni_3La_2(dto)_6(Gly)_2(H_2O)_8]{\cdot}Gly{\cdot}7H_2O$, and $[Ni_3Yb_2(dto)_6(Gly)_2(H_2O)_4]{\cdot}8H_2O$ (dto = dithiooxalate) [82] we can recognize infinite chains of La or Yb, connected by carboxylate bridges. In the La compound, a simple carboxylate bridge (type I) forms the chain ···O–La–O–C–O–Ln···. dto, which is coordinated to the Ni atoms, is also bonded to La in a bis-bidentate way, connecting the La chains. The Yb complex is quite similar, but in this case a double bridge Yb–Yb through two carboxylates of Gly builds the chain.

In the polynuclear complexes we can also find structures with simple dimers connected by a quadruple bridge. $[La\{Fe(CN)_6\}(Gly)_3(H_2O)]_2{\cdot}2H_2O$ [83] and $[Ce\{Fe(CN)_6\}(Gly)_3(H_2O)]_2{\cdot}H_2O$ [84] possess Ln–Ln dimers connected by four type I bridges. In addition, one molecule of monodentate Gly also coordinates to the central atom. Cyanide provides an additional Ln–Fe bridge. This is shown in Fig. 7.

Several samarium–nickel and europium–nickel polynuclear complexes with formula $[Ln\{Ni(Pro)_2\}_6]X_3$ (Ln = Sm, Eu; X = ClO_4^-, BF_4^-, PF_6^-, NO_3^-, I^-) [85–87] have been reported. The heteronuclear complexes contain $[Ni(Pro)_2]$ moieties, six per Ln atom. One carboxylate of every Pro bridges the Ni unit with the Ln atom, resulting in an icosahedral metal centre. Related with this structure are those observed in $[La_6Cu_{26}(Gly)_{18}(\mu_3\text{-}OH)_{30}(H_2O)_{24}(ClO_4)](ClO_4)_{21}{\cdot}26H_2O$ [88], $Na_4[PrNi_6(Gly)_9(\mu_3\text{-}OH)_3(H_2O)_6](ClO_4)_7$, $Na_2[PrNi_6(Gly)_8(\mu_3\text{-}OH)_3(\mu_2\text{-}OH_2)_2(H_2O)_6](ClO_4)_6{\cdot}2H_2O$, $Na[DyNi_6(Gly)_7(\mu_3\text{-}OH)_3(\mu_2\text{-}OH_2)_2(H_2O)_6](ClO_4)_6{\cdot}H_2O$, $[SmNi_6(Gly)_6(\mu_3\text{-}OH)_3Cl_3(H_2O)_6]Cl_3{\cdot}9H_2O$, and $[ErNi_6(Gly)_6(\mu_3\text{-}OH)_3Cl_3(H_2O)_6]Cl_3{\cdot}9H_2O$ [89]. In these heteronuclear complexes, some glycine molecules act as bridges between M(II) and Ln(III).

5. Complexes featuring a cubane-like $[Ln_4(\mu_3\text{-}OH)_4]^{8+}$ core

Very recently, the design of lanthanide complexes whose core structure resembles that of the active site of phosphodiesterases, led to the synthesis and characterization of a new series of compounds based on the $[Ln_4(\mu_3\text{-}OH)_4]^{8+}$ core, and containing amino acids. An excellent review [90] accounts for the development of such complexes. In this section we will only describe the main structural features in order to compare them with other Ln–aa species.

The synthesis of these complexes is the result of a subtle balance between the hydrolysis of Ln(III) and its coordination with the amino acid. They are prepared at pH values near 6–7, where $Ln(OH)_3$ and other hydrolysed species coexist with the complexes. The simplest examples of the species are $[Sm_4(\mu_3\text{-}OH)_4(Gly)_5(H_2O)_{11}(ClO_4)](ClO_4)_7{\cdot}NaClO_4$, $[Nd_4(\mu_3\text{-}OH)_4(Ala)_6(H_2O)_{10}](ClO_4)_8{\cdot}4NaClO_4{\cdot}23H_2O$, $[Er_4(\mu_3\text{-}OH)_4(Val)_5(H_2O)_{10}]Cl_8{\cdot}15H_2O$ [19], $[Er_4(\mu_3\text{-}OH)_4(Ala)_6(H_2O)_8](ClO_4)_8{\cdot}3H_2O$ [91], $[Gd_4(\mu_3\text{-}OH)_4(Val)_6(H_2O)_8](ClO_4)_5{\cdot}8H_2O$ [92], $[Er_4(\mu_3\text{-}OH)_4(Pro)_6(H_2O)_7](ClO_4)_6{\cdot}6H_2O$ [93], and $[Gd_4(\mu_3\text{-}OH)_4(Pro)_6(H_2O)_7](ClO_4)_6{\cdot}6H_2O$ [94]. Structurally, the complexes may be viewed as derived from the tetranuclear cubane-like $[Ln_4(\mu_3\text{-}OH)_4]^{8+}$ core, in which four Ln(III) ions occupy the alternate vertices of a distorted cube. Four OH bridging groups occupy the other four vertices. Amino acids are linked to this cube by bridging two lanthanides (via carboxylate group) of the same cube. This is exemplified in Fig. 8. The bridges are usually asymmetric (type II), corresponding to a μ_2-coordination mode. The synthesis at higher pH values allows the presence of both the zwitterionic form of the ligands, and the fully deprotonated one.

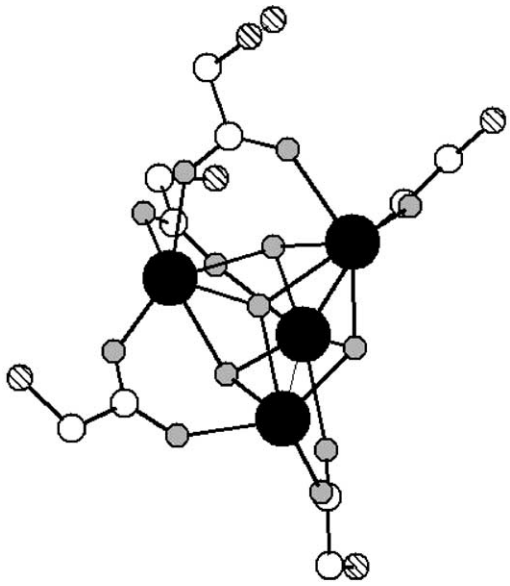


Fig. 8. Schematic disposition of atoms in $[Sm_4(\mu_3\text{-}OH)_4(Gly)_5(H_2O)_{11}(ClO_4)](ClO_4)_7{\cdot}NaClO_4$. Water molecules, counterions, and H atoms are omitted for clarity. Sm: black; O: grey; N: dashed; C: white.

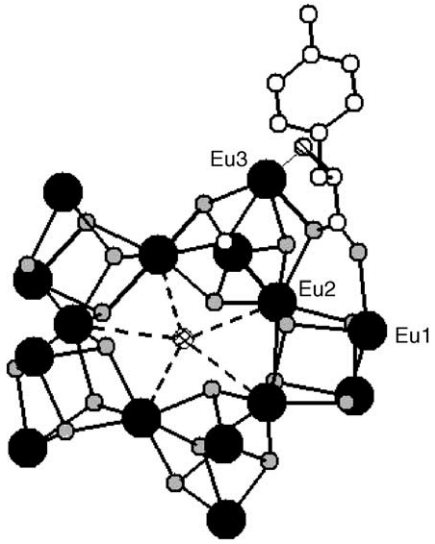


Fig. 9. Schematic disposition of atoms in $[Eu_{15}(\mu_3\text{-}OH)_{20}(\mu_5\text{-}Cl)(Tyr)_{10}(OH)_2(\mu_2\text{-}H_2O)_5(H_2O)_{18}](ClO_4)_{12}\cdot 9H_2O$. Water molecules, and H atoms are omitted for clarity. Only one Tyr molecule is shown. Eu: black; Cl: squared; O: grey; N: dashed; C: white.

As in the case of the simple Ln–aa complexes, the inclusion of glutamic or aspartic acid leads to the formation of molecular structures with higher dimensionality. The aa uses both COO^- groups to bridge Ln in the same cube, and also to interlink $[Ln_4(\mu_3\text{-}OH)_4]^{8+}$ cores. Two such structures are $[Er_4(\mu_3\text{-}OH)_4(Glu)_3(H_2O)_8](ClO_4)_5\cdot 6H_2O$ [19] and $[Dy_4(\mu_3\text{-}OH)_4(Asp)_3(H_2O)_8](ClO_4)_5\cdot 10H_2O$ [94].

If tyrosine is used as amino acid, and is assisted by a templating halide, different structures are obtained. They are mostly pentadecanuclear lanthanide-hydroxo complexes consisting of five vertex-sharing $[Ln_4(\mu_3\text{-}OH)_4]^{8+}$ cubane units centred on a $\mu_5\text{-}X^-$ ion (X = Cl, Br) [90]. Fig. 9 shows the example of $[Eu_{15}(\mu_3\text{-}OH)_{20}(\mu_5\text{-}Cl)(Tyr)_{10}(OH)_2(\mu_2\text{-}H_2O)_5(H_2O)_{18}]^{12+}$ [95]. Tyr is attached to the cubes acting as tetradentate ligand. One of the O coordinates to one Eu (Eu1), while the other coordinates to another Eu (Eu2, the common vertex of the cubes), and another Eu ion (Eu3) of the adjacent cube. N atom (now deprotonated) also coordinates to Eu3. This coordination mode is different from those described above. Six reports are found with this structural motif: $[Eu_{15}(\mu_3\text{-}OH)_{20}(\mu_5\text{-}Cl)(Tyr)_{10}(OH)_2(\mu_2\text{-}H_2O)_5\ (H_2O)_{18}](ClO_4)_{12}\cdot 9H_2O$, $[Nd_{15}(\mu_3\text{-}OH)_{20}(\mu_5\text{-}Cl)(Tyr)_{10}(OH)_3(\mu_2\text{-}H_2O)(H_2O)_{23}]Cl_3(ClO_4)_8\cdot 2H_2O$, $[Gd_{15}\ (\mu_3\text{-}OH)_{20}(\mu_5\text{-}Cl)(Tyr)_{10}(OH)(\mu_2\text{-}H_2O)_5(H_2O)_{19}]\ (ClO_4)_{13}\cdot 12H_2O$, $[Pr_{15}(\mu_3\text{-}OH)_{20}(\mu_5\text{-}Br)(Tyr)_{12}(\mu_2\text{-}H_2O)_3(H_2O)_{20}](ClO_4)_{14}\cdot 8H_2O$, $[Eu_{15}(\mu_3\text{-}OH)_{20}(\mu_5\text{-}Br)(Tyr)_{10}(\mu_2\text{-}H_2O)_5(H_2O)_{20}](ClO_4)_{14}\cdot 2H_2O$, and $[Eu_{15}(\mu_3\text{-}OH)_{20}(\mu_5\text{-}Cl)(Tyr)_{10}(OH)_{12}(\mu_2\text{-}H_2O)_5(H_2O)_8](ClO_4)_2\cdot 56H_2O$ [96]. When I^- is utilized, dodecanuclear complexes with the encapsulation of two iodide guests in the centre of a four-cubane wheel are obtained: $[Dy_{12}(\mu_3\text{-}OH)_{16}(I)_2(Tyr)_8(H_2O)_{20}](ClO_4)_{10}\cdot 8H_2O$, and $[Er_{12}(\mu_3\text{-}OH)_{16}(I)_2(Tyr)_8(H_2O)_{20}](ClO_4)_{10}\cdot 12H_2O$ [95].

6. Ln(III) species containing peptides in the coordination sphere

Only five structures are known of complexes containing Ln and peptides. One of the reasons for this small number is the difficulty to isolate the compounds due to their extreme aqueous solubility. The preparation is analogous to those mentioned for complexes with amino acids, i.e., the direct combination of the metal and the ligand in aqueous solution at pH below 5. The structures resemble those described in Section 2, but the inclusion of an additional carbonyl group (originated in the amide linkage of the peptide bond) can provide a new linkage point.

From the structural point of view, $[Sm_2(Gly\text{–}Val)_4(H_2O)_8](ClO_4)_6\cdot 2H_2O$ [97] is the simplest complex. It consists of isolated dimers completely analogous to those found in Ln–aa complexes. In the dimer, Sm atoms are bridged by four COO^- groups belonging to four independent peptides. Two of the bridges are type I, while the others are type II. The carbonyl group does not participate in the coordination. The carboxylate group in Gly–Val belongs to the Val residue. Thus, the structure is analogous to that found in $[Sm_2(Val)_4(H_2O)_8](ClO_4)_6$ [44], also formed by isolated dimers. In this case, the rest of the peptide is not significant to determine the solid state structure.

The other four structures display the formation of infinite chains, in which the carbonyl group plays a determinant structural role. In $[Ho(Gly\text{–}Tyr)(H_2O)_5]Cl_3\cdot H_2O$ [98], Ho atoms are linked by a single carboxylate bridge (type I). In addition, the carbonyl group also coordinates to one of the Ho of the chain. This is shown in Fig. 10. $[Nd_2(Gly\text{–}Gly)_4(H_2O)_4](ClO_4)_6\cdot 2H_2O$ [99] consists of dimers connected by four carboxylate bridges, two of them bidentate (type I) and the other two tridentate (type III). This structure is quite similar to those found with amino acids (Table 1). However, the presence of the carbonyl produces the

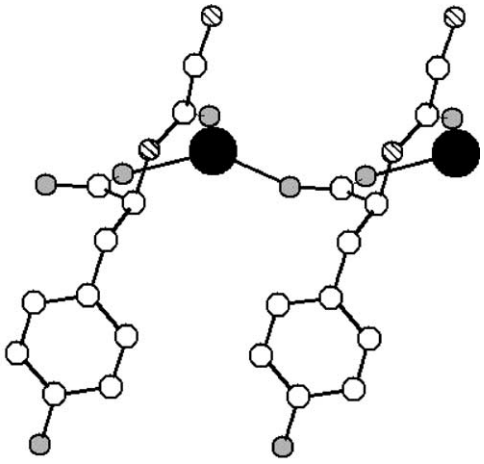


Fig. 10. Schematic disposition of atoms in $[Ho(Gly\text{–}Tyr)(H_2O)_5]Cl_3\cdot H_2O$. Water molecules, counterions, and H atoms are omitted for clarity. Ho: black; O: grey; N: dashed; C: white.

Table 3
Equilibrium constants for Ln(III) complexation reactions with amino acids

aa	Ln	Method	T (°C)	Medium	Equilibrium constant	log K	Ref.
Gly	La	gl	30	0.10 M KCl	K_1	3.23	[104]
Gly	La	gl	30	0.10 M KCl	β_2	6.15	[104]
Gly	La	gl	35	0.10 M KNO_3	K(Ln + HL)	3.23	[105]
Gly	La	gl	20	0.1 M NaCl	K_1	3.54	[106]
Gly	La	gl	25	0.20 M $NaClO_4$	K_1	5.32	[107]
Gly	La	gl	30	0.20 M $NaClO_4$	K_1	3.85	[108]
Ala	La	gl	25	0.20 M $NaClO_4$	K_1	5.82	[107]
Ala	La	gl	20	0.10 M $NaClO_4$	K_1	3.20	[109]
Ala	La	gl	20	0.10 M $NaClO_4$	β(LnHL)	6.49	[109]
Ala	La	gl	25	0.1 M KNO_3	K_1	4.5	[110]
His	La	gl	35	0.10 M KNO_3	K(Ln + HL)	3.41	[105]
His	La	gl	25	3.00 M $NaClO_4$	K_1	4.10	[111]
His	La	gl	25	3.00 M $NaClO_4$	β_2	5.40	[111]
His	La	gl	25	3.00 M $NaClO_4$	β(LnHL)	11.75	[111]
His	La	gl	37	3.00 M $NaClO_4$	K_1	3.40	[112]
His	La	gl	37	3.00 M $NaClO_4$	β_2	6.85	[112]
His	La	gl	37	3.00 M $NaClO_4$	β(LnHL)	11.07	[112]
Pro	La	gl	25	0.10 M $NaClO_4$	β_2	3.9	[113]
Leu	La	gl	25	0.20 M $NaClO_4$	K_1	5.61	[107]
Lys	La	gl	20	0.10 M $NaClO_4$	K_1	5.8	[114]
Phe	La	gl	25	0.10 M KCl	K_1	3.8	[115]
Pro	La	gl	25	0.10 M $NaClO_4$	K_1	4.32	[116
Ser	La	gl	20	0.10 M $NaClO_4$	β(LnHL)	3.18	[109]
Trp	La	gl	25	0.10 M KCl	K_1	4.45	[115]
Trp	La	gl	25	0.10 M KCl	β_2	8.55	[115]
Tyr	La	gl	25	0.10 M KCl	K(Ln + HL)	4.2	[113]
Tyr	La	gl	25	0.10 M KNO_3	K(Ln + HL)	3.82	[117]
Val	La	gl	25	0.20 M $NaClO_4$	K_1	5.94	[107]
Val	La	gl	25	0.10 M KCl	K_1	3.73	[118]
Gly	Ce	gl	30	0.10 M KCl	K_1	3.40	[104]
Gly	Ce	gl	30	0.10 M KCl	β_2	6.40	[104]
Gly	Ce	gl	25	0.20 M $NaClO_4$	K_1	5.38	[107]
Gly	Ce	gl	30	0.20 M $NaClO_4$	K_1	4.46	[108]
Gly	Ce	dis	25	2.0 M $NaClO_4$	K(Ln + HL)	0.53	[119]
Ala	Ce	gl	30	0.10 M KCl	β_2	6.4	[104]
Ala	Ce	gl	25	0.20 M $NaClO_4$	K_1	6.03	[107]
Ala	Ce	gl	37	0.15 M NaCl	K_1	3.01	[120]
Arg	Ce	gl	20	0.10 M KCl	K_1	2.7	[121]
Leu	Ce	gl	25	0.20 M $NaClO_4$	K_1	5.84	[107]
Lys	Ce	gl	20	0.10 M $NaClO_4$	K_1	6.42	[114]
Lys	Ce	gl	20	0.10 M KCl	K_1	2.6	[121]
Met	Ce	gl	20	0.10 M KCl	K_1	4.4	[121]
Phe	Ce	gl	20	0.10 M KCl	K_1	3.52	[122]
Pro	Ce	gl	25	0.10 M $NaClO_4$	K_1	4.87	[116]
Pro	Ce	ix	20	0.10 M KCl	K_1	5.65	[123]
Pro	Ce	ix	20	0.10 M KCl	β_2	8.8	[123]
Tre	Ce	gl	20	0.10 M KCl	K_1	3.7	[121]
Trp	Ce	gl	20	0.10 M KCl	K_1	4.55	[122]
Tyr	Ce	gl	25	0.10 M KNO_3	K(Ln + HL)	4.17	[117]
Val	Ce	gl	25	0.20 M $NaClO_4$	K_1	6.05	[107]
Val	Ce	gl	25	0.10 M KCl	K_1	3.96	[118]
Gly	Pr	gl	30	0.1 M KCl	K_1	3.64	[104]
Gly	Pr	gl	30	0.1M KCl	β_2	6.96	[104]
Gly	Pr	gl	35	0.10 M KNO_3	K(Ln + HL)	3.53	[105]
Gly	Pr	gl	25	0.20 M $NaClO_4$	K_1	5.55	[107]
Gly	Pr	gl	30	0.20 M $NaClO_4$	K_1	4.50	[108]
Ala	Pr	gl	25	0.20 M $NaClO_4$	K_1	6.36	[107]
Ala	Pr	gl	25	0.10 M KNO_3	K_1	4.7	[110]
Ala	Pr	gl	37	0.15 M NaCl	K_1	3.49	[120]
Ala	Pr	gl	37	0.15 M NaCl	β_2	6.68	[120]
His	Pr	gl	35	0.10 M KNO_3	K(Ln + HL)	3.56	[105]

Table 3 (*Continued*)

aa	Ln	Method	T (°C)	Medium	Equilibrium constant	log K	Ref.
His	Pr	gl	25	3.00 M $NaClO_4$	K_1	4.36	[111]
His	Pr	gl	25	3.00 M $NaClO_4$	β_2	6.2	[111]
His	Pr	gl	25	3.00 M $NaClO_4$	β(LnHL)	11.77	[111]
His	Pr	gl	37	3.00 M $NaClO_4$	K_1	3.69	[112]
His	Pr	gl	37	3.00 M $NaClO_4$	β_2	7.78	[112]
His	Pr	gl	37	3.00 M $NaClO_4$	β(LnHL)	11.04	[112]
Leu	Pr	gl	25	0.20 M $NaClO_4$	K_1	5.99	[107]
Lys	Pr	gl	20	0.10 M $NaClO_4$	K_1	7.37	[114]
Lys	Pr	gl	20	0.10 M $NaClO_4$	β_2	13.93	[114]
Pro	Pr	gl	25	0.10 M $NaClO_4$	β_2	5.1	[113]
Pro	Pr	gl	25	0.10 M $NaClO_4$	K_1	5.22	[116]
Tyr	Pr	gl	25	0.10 M KCl	K(Ln + HL)	4.35	[124]
Tyr	Pr	gl	25	0.10 M KCl	K(LnHL + HL)	3.88	[124]
Val	Pr	gl	25	0.20 M $NaClO_4$	K_1	6.28	[107]
Val	Pr	gl	25	0.10 M KCl	K_1	3.92	[118]
Gly	Nd	gl	30	0.10 M KCl	K_1	3.71	[104]
Gly	Nd	gl	30	0.10 M KCl	β_2	7.01	[104]
Gly	Nd	gl	35	0.10 M KNO_3	K(Ln + HL)	3.71	[105]
Gly	Nd	gl	25	0.20 M $NaClO_4$	K_1	5.68	[107]
Gly	Nd	gl	30	0.20 M $NaClO_4$	K_1	4.62	[108]
Gly	Nd	gl	25	0.15 M $NaClO_4$	K_1	3.26	[125]
Gly	Nd	gl	25	0.15 M $NaClO_4$	β(LnHL)	10.43	[125]
Gly	Nd	gl	25	0.15 M $NaClO_4$	$\beta(LnH_{-1}L)$	−4.96	[125]
Ala	Nd	gl	25	0.20 M $NaClO_4$	K_1	6.52	[107]
Ala	Nd	gl	37	0.15 M NaCl	K_1	3.90	[120]
Ala	Nd	gl	37	0.15 M NaCl	β_2	7.80	[120]
Ala	Nd	gl	25	0.10 M KNO_3	K_1	4.8	[110]
His	Nd	gl	35	0.10 M KNO_3	K(Ln + HL)	3.79	[105]
His	Nd	gl	25	3.00 M $NaClO_4$	K_1	4.40	[111]
His	Nd	gl	25	3.00 M $NaClO_4$	β_2	6.59	[111]
His	Nd	gl	25	3.00 M $NaClO_4$	β(LnHL)	11.77	[111]
His	Nd	gl	37	3.00 M $NaClO_4$	K_1	3.95	[112]
His	Nd	gl	37	3.00 M $NaClO_4$	β_2	8.12	[112]
His	Nd	gl	37	3.00 M $NaClO_4$	β(LnHL)	11.2	[112]
Leu	Nd	gl	25	0.20 M $NaClO_4$	K_1	6.03	[107]
Lys	Nd	gl	20	0.10 M $NaClO_4$	K_1	7.12	[114]
Lys	Nd	gl	20	0.10 M $NaClO_4$	β_2	12.99	[114]
Phe	Nd	gl	25	0.10 M KCl	K_1	4.2	[115]
Pro	Nd	gl	25	0.10 M $NaClO_4$	β_2	5.18	[113]
Pro	Nd	gl	25	0.10 M $NaClO_4$	K_1	5.32	[116]
Trp	Nd	gl	25	0.10 M KCl	K_1	4.45	[115]
Trp	Nd	gl	25	0.10 M KCl	β_2	8.85	[115]
Tyr	Nd	gl	25	0.10 M KCl	K(Ln + HL)	4.1	[115]
Tyr	Nd	gl	25	0.10 M KCl	K(LnHL + HL)	3.5	[115]
Tyr	Nd	gl	25	0.10 M KCl	K(Ln + HL)	4.54	[124]
Tyr	Nd	gl	25	0.10 M KCl	K(LnHL + HL)	4.01	[124]
Val	Nd	gl	25	0.20 M $NaClO_4$	K_1	6.52	[107]
Val	Nd	gl	25	0.10 M KCl	K_1	3.88	[118]
Gly	Pm	dis	25	2.0 M $NaClO_4$	K(Ln + HL)	0.67	[119]
Gly	Sm	gl	37	0.15 M $NaClO_4$	$\beta(Ln_2(HL)_6)$	13.3	[43]
Gly	Sm	gl	37	0.15 M $NaClO_4$	K(Ln + HL)	1.6	[43]
Gly	Sm	gl	37	0.15 M $NaClO_4$	$\beta(LnH_{-1}(HL)_3)$	1.36	[43]
Gly	Sm	gl	35	0.10 M KNO_3	K(Ln + HL)	3.82	[105]
Gly	Sm	gl	25	0.20 M $NaClO_4$	K_1	5.84	[107]
Ala	Sm	gl	37	0.15 M $NaClO_4$	$\beta(Ln(HL)_2)$	1.67	[43]
Ala	Sm	gl	37	0.15 M $NaClO_4$	$\beta(Ln_2(HL)_4)$	5.02	[43]
Ala	Sm	gl	25	0.20 M $NaClO_4$	K_1	6.68	[107]
Ala	Sm	gl	25	1.00 M $R_4N.X$	β_2	11.70	[126]
Ala	Sm	gl	25	1.00 M $R_4N.X$	K_1	7.04	[126]
Ala	Sm	gl	25	0.10 M KNO_3	K_1	4.7	[110]
Arg	Sm	gl	37	0.15 M $NaClO_4$	K_1	5.91	[45]
Arg	Sm	gl	37	0.15 M $NaClO_4$	β(LnHL)	9.84	[45]

Table 3 (*Continued*)

aa	Ln	Method	T (°C)	Medium	Equilibrium constant	log K	Ref.
Cys	Sm	gl	37	0.15 M $NaClO_4$	K(Ln + HL)	1.443	[43]
Cys	Sm	gl	37	0.15 M $NaClO_4$	$\beta(LnH_{-1}(HL)_3)$	−1.71	[43]
His	Sm	gl	37	0.15 M $NaClO_4$	β(LnHL)	11.63	[45]
His	Sm	gl	37	0.15 M $NaClO_4$	$\beta(LnH_2L)$	17.43	[45]
His	Sm	gl	37	0.15 M $NaClO_4$	$\beta(LnH_3L_3)$	33.42	[45]
His	Sm	gl	37	0.15 M $NaClO_4$	$\beta(Ln_2H_6L_4)$	59.25	[45]
His	Sm	gl	35	0.10 M KNO_3	K(Ln + HL)	3.85	[105]
His	Sm	gl	25	3.00 M $NaClO_4$	K_1	4.46	[111]
His	Sm	gl	25	3.00 M $NaClO_4$	β_2	8.71	[111]
His	Sm	gl	25	3.00 M $NaClO_4$	β(LnHL)	11.78	[111]
His	Sm	gl	37	3.00 M $NaClO_4$	K_1	4.37	[112]
His	Sm	gl	37	3.00 M $NaClO_4$	β_2	8.78	[112]
His	Sm	gl	37	3.00 M $NaClO_4$	β(LnHL)	11.18	[112]
Leu	Sm	gl	25	0.20 M $NaClO_4$	K_1	6.18	[107]
Lys	Sm	gl	20	0.10 M $NaClO_4$	K_1	7.71	[114]
Lys	Sm	gl	20	0.10 M $NaClO_4$	β_2	14.66	[114]
Phe	Sm	gl	37	0.15 M $NaClO_4$	β(LnHL)	11.49	[45]
Phe	Sm	gl	37	0.15 M $NaClO_4$	β_2	7.95	[45]
Pro	Sm	gl	37	0.15 M $NaClO_4$	K(Ln + HL)	2.95	[43]
Pro	Sm	gl	37	0.15 M $NaClO_4$	$\beta(Ln(HL)_2)$	3.71	[43]
Pro	Sm	gl	25	0.10 M $NaClO_4$	β_2	5.53	[113]
Ser	Sm	gl	37	0.15 M $NaClO_4$	β(LnHL)	11.05	[45]
Ser	Sm	gl	37	0.15 M $NaClO_4$	$\beta(LnH_2L_3)$	25.65	[45]
Ser	Sm	gl	37	0.15 M $NaClO_4$	$\beta(LnH_3L_3)$	31.72	[45]
Ser	Sm	gl	37	0.15 M $NaClO_4$	$\beta(LnH_{-1}L)$	−3.7	[45]
Trp	Sm	gl	37	0.15 M $NaClO_4$	K(Ln + HL)	1.72	[43]
Trp	Sm	gl	37	0.15 M $NaClO_4$	$\beta(LnH_{-1}(HL)_3)$	0.67	[43]
Tyr	Sm	gl	25	0.10 M KCl	K(Ln + HL)	4.71	[124]
Tyr	Sm	gl	25	0.10 M KCl	K(LnHL + HL)	4.13	[124]
Val	Sm	gl	37	0.15 M $NaClO_4$	K(Ln + HL)	1.64	[43]
Val	Sm	gl	37	0.15 M $NaClO_4$	$\beta(LnH_{-1}(HL)_3)$	0.67	[43]
Val	Sm	gl	25	0.20 M $NaClO_4$	K_1	6.68	[107]
Val	Sm	gl	25	0.10 M KCl	K_1	3.9	[118]
Gly	Eu	dis	25	2.0 M $NaClO_4$	K(Ln + HL)	0.7	[119]
Ala	Eu	sp	25	1.00 M R_4NX	K_1	6.07	[126]
Ala	Eu	sp	25	1.00 M R_4NX	β_2	11.73	[126]
Ala	Eu	dis	25	2.0 M $NaClO_4$	K_1	0.74	[127]
Ala	Eu	gl	25	0.10 M KNO_3	K_1	4.7	[110]
Ala	Eu	sp	25	1.0 M $NaClO_4$	K(Ln + HL)	0.33	[128]
Pro	Eu	gl	25	0.10 M $NaClO_4$	β_2	5.57	[113]
Pro	Eu	vlt	25	0.20 M $NaClO_4$	K_1	0.3	[129]
Pro	Eu	vlt	25	0.20 M $NaClO_4$	β_2	1.78	[129]
Trp	Eu	vlt	25	0.20 M $NaClO_4$	K_1	6.80	[129]
Trp	Eu	gl	25	0.10 M $NaClO_4$	K_1	6.78	[130]
Val	Eu	gl	25	0.10 M KCl	K_1	3.85	[118]
Gly	Gd	gl	35	0.10 M KNO_3	K(Ln + HL)	3.72	[105]
Gly	Gd	gl	25	0.10 M $NaClO_4$	K(Ln + HL)	0.73	[131]
Ala	Gd	gl	15	0.10 M KNO_3	K_1	4.6	[110]
His	Gd	gl	35	0.10 M KNO_3	K(Ln + HL)	3.76	[105]
His	Gd	gl	25	3.00 M $NaClO_4$	K_1	4.39	[111]
His	Gd	gl	25	3.00 M $NaClO_4$	β_2	8.61	[111]
His	Gd	gl	27	3.00 M $NaClO_4$	β(LnHL)	11.47	[111]
His	Gd	gl	37	3.00 M $NaClO_4$	K_1	4.94	[112]
His	Gd	gl	37	3.00 M $NaClO_4$	β_2	9.16	[112]
His	Gd	gl	37	3.00 M $NaClO_4$	β(LnHL)	11.3	[112]
Lys	Gd	gl	20	0.10 M $NaClO_4$	K_1	7.42	[114]
Lys	Gd	gl	20	0.10 M $NaClO_4$	β_2	14.03	[114]
Phe	Gd	gl	25	0.10 M KCl	K_1	4.25	[115]
Pro	Gd	gl	25	0.10 M $NaClO_4$	β_2	5.6	[113]
Pro	Gd	gl	25	0.10 M $NaClO_4$	K_1	5.58	[116]
Trp	Gd	gl	25	0.10 M KCl	K_1	5.0	[115]
Trp	Gd	gl	25	0.10 M KCl	β_2	9.6	[115]

Table 3 (*Continued*)

aa	Ln	Method	T (°C)	Medium	Equilibrium constant	log K	Ref.
Tyr	Gd	gl	25	0.10 M KCl	K(Ln + HL)	4.35	[115]
Tyr	Gd	gl	25	0.10 M KCl	K(LnHL + HL)	4.2	[115]
Tyr	Gd	gl	25	0.10 M KCl	K(Ln + H_2L)	4.63	[132]
Tyr	Gd	gl	25	0.10 M KCl	K(LnH_2L + H_2L)	4.17	[132]
Tyr	Gd	gl	25	0.10 M KNO_3	K(Ln + HL)	4.92	[133]
Tyr	Gd	gl	25	0.10 M KNO_3	K(LnHL + HL)	4.43	[133]
Val	Gd	gl	25	0.10 M KCl	K_1	3.96	[118]
Ala	Tb	gl	25	0.10 M KNO_3	K_1	4.7	[110]
Phe	Tb	gl	25	0.10 M KCl	K_1	4.3	[115]
Phe	Tb	gl	25	0.10 M KCl	β_2	7.80	[115]
Pro	Tb	gl	25	0.10 M $NaClO_4$	β_2	5.62	[113]
Trp	Tb	gl	25	0.10 M KCl	K_1	5.0	[115]
Trp	Tb	gl	25	0.10 M KCl	β_2	9.7	[115]
Tyr	Tb	gl	25	0.10 M KCl	K(Ln + HL)	4.35	[115]
Tyr	Tb	gl	25	0.10 M KCl	K(LnHL + HL)	4.3	[115]
Val	Tb	gl	25	0.10 M KCl	K_1	4.00	[118]
Gly	Dy	gl	35	0.10 M KNO_3	K(Ln + HL)	3.86	[105]
Ala	Dy	gl	25	0.10 M KNO_3	K_1	4.7	[110]
His	Dy	gl	35	0.10 M KNO_3	K(Ln + HL)	3.99	[105]
His	Dy	gl	25	3.00 M $NaClO_4$	K_1	4.40	[111]
His	Dy	gl	25	3.00 M $NaClO_4$	β_2	9.14	[111]
His	Dy	gl	27	3.00 M $NaClO_4$	β(LnHL)	11.16	[111]
His	Dy	gl	37	3.00 M $NaClO_4$	K_1	5.09	[112]
His	Dy	gl	37	3.00 M $NaClO_4$	β_2	9.85	[112]
His	Dy	gl	37	3.00 M $NaClO_4$	β(LnHL)	11.56	[112]
Pro	Dy	gl	25	0.10 M $NaClO_4$	K_1	5.77	[116]
Pro	Dy	gl	25	0.10 M $NaClO_4$	β_2	5.67	[113]
Tyr	Dy	gl	25	0.10 M KCl	K(Ln + H_2L)	4.74	[132]
Tyr	Dy	gl	25	0.10 M KCl	K(LnH_2L + H_2L)	4.30	[132]
Tyr	Dy	gl	25	0.10 M KNO_3	K(Ln + HL)	5.04	[133]
Tyr	Dy	gl	25	0.10 M KNO_3	K(LnHL + HL)	4.57	[133]
Val	Dy	gl	25	0.10 M KCl	K_1	4.03	[118]
Pro	Ho	gl	25	0.10 M $NaClO_4$	β_2	5.75	[113]
Val	Ho	gl	25	0.10 M KCl	K_1	4.10	[118]
Ala	Er	gl	25	0.10 M KNO_3	K_1	4.7	[110]
Gly	Er	gl	35	0.10 M KNO_3	K(Ln + HL)	3.93	[105]
His	Er	gl	35	0.10 M KNO_3	K(Ln + HL)	4.06	[105]
His	Er	gl	25	3.00 M $NaClO_4$	K_1	4.49	[111]
His	Er	gl	25	3.00 M $NaClO_4$	β_2	8.99	[109]
His	Er	gl	27	3.00 M $NaClO_4$	β(LnHL)	11.18	[109]
His	Er	gl	37	3.00 M $NaClO_4$	K_1	4.99	[112]
His	Er	gl	37	3.00 M $NaClO_4$	β_2	9.91	[112]
His	Er	gl	37	3.00 M $NaClO_4$	β(LnHL)	11.40	[112]
Phe	Er	gl	25	0.10 M KCl	K_1	4.35	[115]
Phe	Er	gl	25	0.10 M KCl	β_2	8.25	[115]
Pro	Er	gl	25	0.10 M $NaClO_4$	β_2	5.90	[113]
Trp	Er	gl	25	0.10 M KCl	K_1	5.1	[115]
Trp	Er	gl	25	0.10 M KCl	β_2	9.6	[115]
Tyr	Er	gl	25	0.10 M KCl	K(Ln + HL)	4.4	[115]
Tyr	Er	gl	25	0.10 M KCl	K(LnHL + HL)	4.1	[115]
Tyr	Er	gl	25	0.10 M KCl	K(Ln + H_2L)	4.83	[132]
Tyr	Er	gl	25	0.10 M KCl	K(LnH_2L + H_2L)	4.51	[132]
Tyr	Er	gl	25	0.10 M KNO_3	K(Ln + HL)	5.15	[133]
Tyr	Er	gl	25	0.10 M KNO_3	K(LnHL + HL)	4.86	[133]
Val	Er	gl	25	0.10 M KCl	K_1	4.19	[118]
Ala	Tm	gl	25	0.10 M KNO_3	K_1	4.7	[110]
Pro	Tm	gl	25	0.10 M $NaClO_4$	β_2	6.08	[113]
Ala	Yb	gl	25	0.10 M KNO_3	K_1	4.9	[110]
His	Yb	gl	25	3.00 M $NaClO_4$	K_1	4.23	[111]
His	Yb	gl	25	3.00 M $NaClO_4$	β_2	9.83	[111]
His	Yb	gl	25	3.00 M $NaClO_4$	β(LnHL)	11.40	[111]
His	Yb	gl	37	3.00 M $NaClO_4$	K_1	4.76	[112]

Table 3 (*Continued*)

aa	Ln	Method	T (°C)	Medium	Equilibrium constant	log K	Ref.
His	Yb	gl	37	3.00 M $NaClO_4$	β_2	10.31	[112]
His	Yb	gl	37	3.00 M $NaClO_4$	β(LnHL)	11.60	[112]
Tyr	Yb	gl	25	0.10 M KNO_3	K_1	5.00	[132]
Tyr	Yb	gl	25	0.10 M KNO_3	β_2	9.70	[132]
Tyr	Yb	gl	25	0.10 M KNO_3	K(Ln + HL)	5.35	[133]
Tyr	Yb	gl	25	0.10 M KNO_3	K(LnHL + HL)	5.00	[133]
Val	Yb	gl	25	0.10 M KCl	K_1	4.3	[118]
Phe	Lu	gl	25	0.10 M KCl	K_1	4.45	[115]
Phe	Lu	gl	25	0.10 M KCl	β_2	7.95	[115]
Pro	Lu	gl	25	0.10 M $NaClO_4$	β_2	6.15	[113]
Trp	Lu	gl	25	0.10 M KCl	K_1	5.2	[115]
Trp	Lu	gl	25	0.10 M KCl	β_2	9.90	[115]
Tyr	Lu	gl	25	0.10 M KCl	K(Ln + HL)	4.55	[115]
Tyr	Lu	gl	25	0.10 M KCl	K(LnHL + HL)	4.5	[115]
Val	Lu	gl	25	0.10 M KCl	K_1	4.30	[118]

Method abbreviations are: gl, glass electrode; dis, distribution experiments; ix, ion exchange; vlt, voltammetry; sp, spectrophotometry.

formation of infinite chains. The carbonyl C=O group of the peptide molecule which joins Nd atoms by a type III bridge, is also linked to the same Nd atom (in this case the peptide occupies four coordination positions in two Nd atoms). But carbonyl groups of peptides acting as a type I bridge interlink cationic dimers, resulting in an infinite chain. This structure is also found in $[Eu(Gly–Gly)_2(H_2O)_2](ClO_4)_3{\cdot}2H_2O$ [100].

$[Eu(Gly–Gly–Gly)(H_2O)_4](ClO_4)_3{\cdot}H_2O$ [101] is the only structure which contains a tripeptide. Eu atoms are connected by a double COO^- bridge (type II). The overall structure is built by the union of both carbonyl groups of a peptide with another Eu atom belonging to a different dimer. Thus, the tripeptide is tetradentate. It uses the carboxyl group to bridge two metallic centres and the two carbonyl groups to chelate another Eu ion.

Equilibrium	Equilibrium constant
$Ln^{3+} + L^{n-} \rightarrow [LnL]^{(3-n)+}$	K_1
$Ln^{3+} + 2L^{n-} \rightarrow [LnL_2]^{(3-2n)+}$	β_2
$[LnL_2]^{(3-2n)+} + L^{n-} \rightarrow [LnL_3]^{(3-3n)+}$	K_3
$mLn^{3+} + pL^{n-} \rightarrow [Ln_mL_p]^{(3m-np)+}$	$\beta(Ln_mL_p)$
$Ln^{3+} + H_nL \rightarrow [Ln(H_nL)]^{3+}$	$K(Ln+H_nL)$
$[Ln(H_nL)]^{3+} + H_nL \rightarrow [Ln(H_nL)_2]^{3+}$	$K(LnH_nL+H_nL)$
$mLn^{3+} + rH_nL \rightarrow [Ln_m(H_nL)_r]^{3m+}$	$\beta(Ln_m(H_nL)_r)$
$mLn^{3+} + pL^{n-} + rH^+ \rightarrow [Ln_mH_rL_p]^{(3m-np+r)+}$	$\beta(Ln_mH_rL_p)$
$Ln^{3+} + mL^{n-} \rightarrow [Ln(OH)L]^{(3-n-1)+} + H^+$	$\beta(LnH_{-1}L)$
$[Ln(OH)]^{2+} + L^{n-} \rightarrow [Ln(OH)L]^{(2-n)+}$	$K(LnOH+L)$
$[Ln(OH)]^{2+} + mH_nL \rightarrow [Ln(OH)(H_nL)_m]^+$	$K(LnOH+mH_nL)$
$Ln^{3+} + mH_nL \rightarrow [Ln(H_{mn-q}L_m)]^{3-q+} + qH^+$	$\beta(LnH_{-q}(H_nL)_m)$

Scheme 2. Definition of equilibrium constants used in this review. H_nL is the neutral form of the ligands.

7. General information about equilibrium data

In the present and following sections, we will discuss the stability of coordination compounds of lanthanide ions in oxidation state +3 with different ligands. A problem generally found upon collecting thermodynamic equilibrium data is the difficulty to compare them. They come from different sources and have been obtained under different experimental conditions. Regarding the formation constants of coordination compounds, we will express them as they were reported, except when needed for comparison. Scheme 2 shows the corresponding nomenclature.

Another point should be taken into account. Due to the low stability of lanthanide complexes with aa and peptides, hydrolysis reactions are obvious competing processes. Of course, the extension of hydrolysis depends on the particular ion since the acidity of these f-transition metal ions increases with decreasing ionic radii. Thus, the smaller are the lanthanides, the more importance should be given to hydrolysis reactions. 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. There is evidence for the formation of $[Ln(OH)_4]^-$ [102].

Hydrolysis is mostly governed by two reactions:

$$Ln^{3+} + H_2O \rightleftarrows [Ln(OH)]^{2+} + H^+ \; {}^*K_1,$$

$$Ln(OH)_3 + 3H^+ \rightleftarrows Ln^{3+} + 3H_2O \; {}^*K_{s0}$$

$p({}^*K_1)$ is near 8.5, while $p({}^*K_{s0})$ is quoted as having a value near −17. Even when numerous data on hydrolysis constants are available in the literature [103], most of the experimental work on Ln–aa systems does not take them into account.

With this in mind, in the following sections we will discuss the available themodynamic data on the complexation of Ln in oxidation state 3+ with aa and peptides. In addition, we have included equilibrium data obtained from ternary systems, i.e., mixed-ligand systems containing auxiliary ligands bound to the metal ions and the aa ligand. For such experiments we will focus on the effective formation constant of the complexes:

$$[Sm(A)] + aa \rightleftarrows [Sm(A)(aa)]$$

where A represents the auxiliary ligand (charges and protons are omitted for clarity). A is generally a polycarboxylate, and the amino acid can participate as H_nL or L^- in these complexes.

8. Thermodynamic stability of lanthanide complexes with amino acids

Tables 3 and 4 show the data on complexation of lanthanides with aa, together with the experimental method used, and the experimental conditions. Asp and Glu are presented in a separate table, considering their additional carboxylate group.

As can be seen in Table 3, the behavior of lanthanide ions in the presence of these ligands is almost the same, reflecting their well-known chemical similarity. So, even when small differences among them will be pointed out later, we shall begin with the general trends. Formation of the monomeric species $[Ln(H_nL)]^{3+}$ or $[Ln(H_{n-1}L)]^{2+}$ with 1:1 stoichiometry has been reported for all amino acids, these species being the most prominent Ln–aa species under acidic conditions. Concerning the charge of the coordinated aa, the data are not fully consistent. The most reliable data suggest that aa are coordinated as neutral zwitterions. Only a few reports have detected the existence of soluble species with higher ligand to metal molar ratios [43,45,104,111–115,123,124,126,129] for simple amino acids.

Little attention has been paid to hydroxylated and polymeric species in these systems. Nevertheless they appear in some reports [43,45,126]. Even though hydroxylated species are generally not predominant, they are important when the pH is raised.

Aspartic and glutamic acid (Table 4) also show the formation of complexes with ligand to metal molar ratios 1 and 2. Much greater consistency exists in these systems regarding complex formation with deprotonated forms of the ligands, due to their additional acid groups. Indeed, some authors have simultaneously detected both kinds of coordinated ligands, H_2L, and HL^- [45,120,135,140].

On the other hand, hydroxyl groups, present in serine and tyrosine (as well as the thiol group of cysteine and methionine) do not deprotonate by metal interaction. These groups, therefore, do not participate in coordination. Conversely, for tyrosine, coordination compounds with partially protonated ligands were detected [132]. Basic amino acids

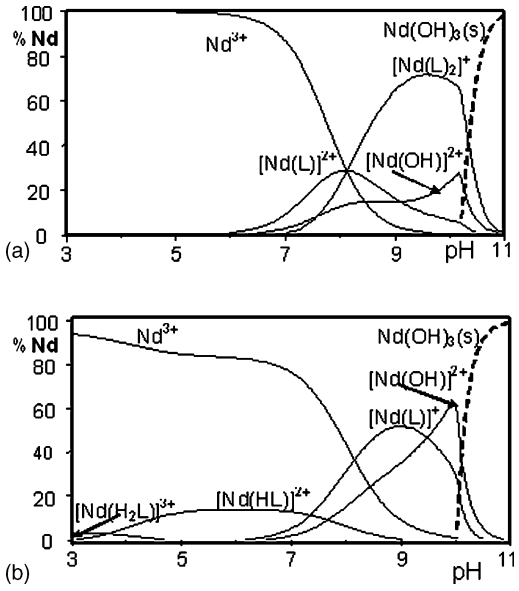


Fig. 11. Species distribution diagrams of Nd with alanine, HL (a) and glutamic acid, H_2L (b). Stability data were taken from Ref. [120] and hydrolysis data of the metal from Refs. [141,142]. T = 37.0 °C, I = 0.15 M NaCl, [Nd] = 1 mM, [Ala] or [Glu] = 3 mM.

(lysine, arginine, histidine) do not generally form species with protonated ligands with the exception of $[Sm(His)]^{4+}$ [45].

Tables 3 and 4 reflect the strong analogy among all Ln–aa complexes. We can take two examples to show the dependence of speciation at different pH values. Fig. 11 displays the species distribution diagram of the systems Nd–Ala and Nd–Glu. For both systems, and even under excess of ligand, a high percentage of the metal is still free, especially in acid media. This is a direct consequence of the low thermodynamic stability of the complexes. As pH is raised, hydrolysis competes with the formation of complexes. $[Nd(OH)]^{2+}$ becomes detectable, and finally $Nd(OH)_3$ precipitates. In Nd–Ala (Fig. 11a) two complex species are formed. Obviously, for lower ligand to metal molar ratios, the 1:1 species appears as predominant. But, when a large excess of the ligand is present, species containing more than one ligand per metal ion are favoured. $[Nd(Ala)_2]^+$ coexists with $[Nd(Ala)]^{2+}$ and $[Nd(OH)]^{2+}$. When acidic ligands are present, as in the case of glutamic acid, complexed metal is present over a wider interval of pH. Besides, even when a species containing two ligands was not detected, deprotonation of the ligand causes the retention of an important percentage of the metal in solution (Fig. 11b).

In general, amino acids show a weak binding to lanthanide metals. Formation constant values are always low and variations for different amino acids are quite small. Despite this, it is possible to observe that the interaction of lanthanides with these ligands is mostly determined by electrostatic interaction. Some observed trends support this idea:

Table 4
Equilibrium constants for Ln(III) complexation reactions with Asp and Glu

aa	Ln	T (°C)	Medium	Equilibrium constant	log K	Ref.
Asp	La	30	0.10 M KCl	K_1	4.84	[104]
Asp	La	30	0.10 M KCl	β_2	8.26	[104]
Asp	La	25	0.20 M $NaClO_4$	K_1	5.61	[107]
Asp	La	25	0.10 M KCl	K_1	5.0	[134]
Asp	La	25	0.10 M KCl	β_2	9.20	[134]
Asp	La	20	0.10 M $NaClO_4$	K_1	4.53	[135]
Asp	La	22	0.10 M $NaClO_4$	β(LnHL)	12.49	[135]
Asp	La	30	0.10 M $NaClO_4$	K_1	4.47	[136]
Asp	Ce	30	0.10 M KCl	K_1	5.13	[104]
Asp	Ce	30	0.10 M KCl	β_2	8.78	[104]
Asp	Ce	30	0.10 M KCl	K_3	2.75	[104]
Asp	Ce	25	0.20 M $NaClO_4$	K_1	5.77	[107]
Asp	Ce	25	0.10 M KCl	K_1	5.2	[134]
Asp	Ce	25	0.10 M KCl	β_2	9.80	[134]
Asp	Ce	30	0.10 M $NaClO_4$	β_2	8.91	[136]
Asp	Ce	30	0.10 M $NaClO_4$	K_1	4.77	[136]
Glu	Ce	37	0.15 M NaCl	K_1	3.81	[120]
Asp	Pr	30	0.10 M KCl	K_1	5.23	[104]
Asp	Pr	30	0.10 M KCl	β_2	9.07	[104]
Asp	Pr	30	0.10 M KCl	K_3	2.72	[104]
Asp	Pr	25	0.20 M $NaClO_4$	K_1	5.90	[107]
Asp	Pr	25	0.10 M KCl	K_1	5.4	[134]
Asp	Pr	25	0.10 M KCl	β_2	10.20	[134]
Asp	Pr	20	0.10 M $NaClO_4$	K_1	5.14	[135]
Asp	Pr	20	0.10 M $NaClO_4$	β(LnHL)	12.62	[135]
Asp	Pr	30	0.10 M $NaClO_4$	K_1	4.90	[136]
Asp	Pr	30	0.10 M $NaClO_4$	β_2	9.44	[136]
Asp	Pr	25	0.10 M KCl	K_1	5.20	[137]
Asp	Pr	25	0.10 M KCl	β_2	8.80	[137]
Glu	Pr	37	0.15 M NaCl	K_1	3.85	[120]
Glu	Pr	37	0.15 M NaCl	β(LnHL)	11.05	[120]
Asp	Nd	30	0.10 M KCl	K_1	5.40	[104]
Asp	Nd	30	0.10 M KCl	β_2	9.48	[104]
Asp	Nd	30	0.10 M KCl	K_3	3.06	[104]
Asp	Nd	25	0.20 M $NaClO_4$	K_1	6.04	[107]
Asp	Nd	25	0.10 M KCl	K_1	5.5	[134]
Asp	Nd	25	0.10 M KCl	β_2	10.40	[134]
Asp	Nd	30	0.10 M $NaClO_4$	K_1	5.02	[136]
Asp	Nd	30	0.10 M $NaClO_4$	β_2	9.24	[136]
Asp	Nd	25	0.10 M KCl	K_1	5.36	[137]
Asp	Nd	25	0.10 M KCl	β_2	9.26	[137]
Asp	Nd	30	0.10 M $NaClO_4$	K_1	5.66	[138]
Asp	Nd	30	0.10 M $NaClO_4$	β_2	10.46	[138]
Glu	Nd	37	0.15 M NaCl	K_1	3.94	[120]
Glu	Nd	37	0.15 M NaCl	β(LnHL)	11.27	[120]
Glu	Nd	37	0.15 M NaCl	$\beta(LnH_2L)$	14.88	[120]
Asp	Sm	37	0.15 M $NaClO_4$	K_1	5.56	[45]
Asp	Sm	37	0.15 M $NaClO_4$	β(LnHL)	11.84	[45]
Asp	Sm	37	0.15 M $NaClO_4$	$\beta(LnH_{-1}L)$	−1.8	[45]
Asp	Sm	37	0.15 M $NaClO_4$	$\beta(LnH_2L)$	14.89	[45]
Asp	Sm	25	0.20 M $NaClO_4$	K_1	6.16	[107]
Asp	Sm	30	0.10 M $NaClO_4$	K_1	5.13	[136]
Asp	Sm	30	0.10 M $NaClO_4$	β_2	9.64	[136]
Asp	Sm	25	0.10 M KCl	K_1	5.55	[137]
Asp	Sm	25	0.10 M KCl	β_2	9.72	[137]
Asp	Sm	40	0.10 M $NaClO_4$	K_1	9.45	[138]
Asp	Sm	40	0.10 M $NaClO_4$	β_2	15.85	[138]
Glu	Sm	37	0.15 M $NaClO_4$	$\beta(Ln_2(H_2L)_4)$	10.05	[43]
Glu	Sm	37	0.15 M $NaClO_4$	$\beta(LnH_{-1}(H_2L)_2)$	0.48	[43]
Glu	Sm	37	0.15 M $NaClO_4$	$\beta(LnH_{-2}(H_2L)_2)$	−3.4	[43]
Asp	Eu	30	0.10 M $NaClO_4$	K_1	5.20	[136]

Table 4 (*Continued*)

aa	Ln	T (°C)	Medium	Equilibrium constant	log K	Ref.
Asp	Eu	30	0.10 M $NaClO_4$	β_2	9.8	[136]
Asp	Eu	25	0.10 M KCl	K_1	5.62	[137]
Asp	Eu	25	0.10 M KCl	β_2	9.77	[137]
Asp	Gd	30	0.10 M $NaClO_4$	K_1	5.30	[136]
Asp	Gd	30	0.10 M $NaClO_4$	β_2	9.80	[136]
Asp	Gd	25	0.10 M KCl	K_1	5.74	[137]
Asp	Gd	25	0.10 M KCl	β_2	10.50	[137]
Asp	Tb	30	0.10 M $NaClO_4$	K_1	5.45	[136]
Asp	Tb	30	0.10 M $NaClO_4$	β_2	10.12	[136]
Asp	Tb	25	0.10 M KCl	K_1	5.8	[137]
Asp	Tb	25	0.10 M KCl	β_2	10.28	[137]
Asp	Dy	30	0.10 M $NaClO_4$	β_2	10.24	[136]
Asp	Dy	25	0.10 M KCl	β_2	10.78	[137]
Asp	Dy	25	0.10 M KCl	K_1	5.85	[137]
Asp	Dy	30	0.10 M $NaClO_4$	K_1	5.54	[136]
Asp	Ho	30	0.10 M $NaClO_4$	K_1	5.68	[136]
Asp	Ho	30	0.10 M $NaClO_4$	β_2	10.47	[136]
Asp	Ho	25	0.10 M KCl	K_1	5.91	[137]
Asp	Ho	25	0.10 M KCl	β_2	10.81	[137]
Asp	Ho	30	0.10 M $NaClO_4$	K_1	6.36	[139]
Glu	Ho	25	0.10 M KCl	K_1	4.57	[140]
Glu	Ho	25	0.10 M KCl	β(LnHL)	11.36	[140]
Asp	Er	30	0.10 M $NaClO_4$	K_1	5.71	[136]
Asp	Er	30	0.10 M $NaClO_4$	β_2	10.54	[136]
Asp	Er	25	0.10 M KCl	K_1	6.08	[137]
Asp	Er	25	0.10 M KCl	β_2	10.93	[137]
Asp	Tm	30	0.10 M $NaClO_4$	K_1	5.87	[136]
Asp	Tm	30	0.10 M $NaClO_4$	β_2	10.80	[136]
Asp	Tm	25	0.10 M KCl	K_1	6.10	[137]
Asp	Tm	25	0.10 M KCl	β_2	11.10	[137]
Asp	Yb	30	0.10 M $NaClO_4$	K_1	5.93	[136]
Asp	Yb	30	0.10 M $NaClO_4$	β_2	10.93	[136]
Asp	Yb	25	0.10 M KCl	K_1	6.18	[137]
Asp	Yb	25	0.10 M KCl	β_2	11.45	[137]
Asp	Yb	30	0.10 M $NaClO_4$	K_1	7.00	[139]
Asp	Lu	20	0.10 M $NaClO_4$	β(LnHL)	12.71	[135]
Asp	Lu	30	0.10 M $NaClO_4$	K_1	6.07	[136]
Asp	Lu	30	0.10 M $NaClO_4$	β_2	10.90	[136]
Asp	Lu	25	0.10 M KCl	K_1	6.25	[137]
Asp	Lu	25	0.10 M KCl	β_2	11.58	[137]

In all cases, potentiometric titrations (glass electrode) were used to obtain K values.

a. An increase in formation constant values is observed as the basicity of the ligand increases (Fig. 12).
b. Stability is also enhanced when more negatively charged ligands are bound to the metal (Fig. 13). Asp and Glu provide a good example of this point. We can find reported values of K_1 for the species $[Ln(H_2L)]^{4+}$, $[Ln(HL)]^{3+}$, and $[Ln(L)]^{2+}$. K values for $[Ln(L)]^{2+}$ (containing L^-), are at least two orders of magnitude greater than those for $[Ln(HL)]^{3+}$.
c. A steady increase in formation constants is observed as ionic radii of the lanthanide ions decreases [136].

The linearity of the three relations supports that Ln–aa bonds are largely electrostatic. They can be understood in terms of simple electrostatic considerations [145].

We have seen in Section 2 that solid state structures are governed by Ln–OCO binding, mostly as μ_2-carboxylate

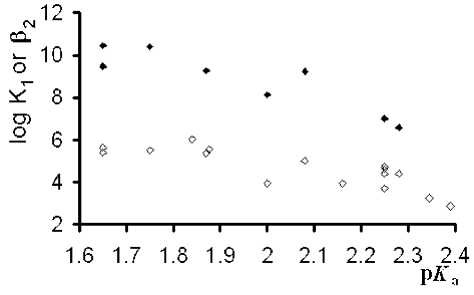


Fig. 12. Variation of complexes stability with the basicity of the ligands. log K_1 (empty squares) or β_2 (filled squares) for Gly, Glu, Asp and His are plotted vs. K_a of the ligands. Data were taken from Refs. [43,45,104,105,107,108,111,112,120,125,134,136–138,143,144]. K_a data were taken from the same reference when possible. Alternatively, data in similar conditions were used [103].

Table 5
Stability constants of Ln(III) mixed-ligand complexes

aa	Ln	Auxiliary ligand (A)	Method	T (°C)	Medium	Equilibrium constant	log K	Ref.
Gly	La	edta	gl	25	0.20 M $NaClO_4$	K(Ln(A) + L)	4.09	[107]
Gly	La	cyt	gl	35	0.10 M KNO_3	K(Ln + A + HL)	8.27	[105]
Ala	La	edta	gl	25	0.20 M $NaClO_4$	K(Ln(A) + L)	4.28	[107]
Asp	La	edta	gl	25	0.20 M $NaClO_4$	K(Ln(A) + L)	4.55	[107]
His	La	cyt	gl	35	0.10 M KNO_3	K(Ln + A + HL)	8.47	[105]
Leu	La	edta	gl	35	0.10 M KNO_3	K(Ln + A + HL)	4.31	[105]
Val	La	edta	gl	25	0.20 M $NaClO_4$	K(Ln(A) + L)	5.10	[107]
Gly	Ce	edta	gl	25	0.20 M $NaClO_4$	K(Ln(A) + L)	4.32	[107]
Ala	Ce	edta	gl	25	0.20 M $NaClO_4$	K(Ln(A) + L)	4.40	[107]
Asp	Ce	edta	gl	25	0.20 M $NaClO_4$	K(Ln(A) + L)	4.71	[107]
Leu	Ce	edta	gl	25	0.20 M $NaClO_4$	K(Ln(A) + L)	4.59	[107]
Val	Ce	edta	gl	25	0.20 M $NaClO_4$	K(Ln(A) + L)	5.33	[107]
Gly	Pr	edta	gl	25	0.20 M $NaClO_4$	K(Ln(A) + L)	4.63	[107]
Gly	Pr	cyt	gl	35	0.10 M KNO_3	K(Ln + A + HL)	8.34	[105]
Ala	Pr	edta	gl	25	0.20 M $NaClO_4$	K(Ln(A) + L)	4.99	[105]
Ala	Pr	cyt	gl	35	0.10 M KNO_3	K(Ln + A + HL)	8.34	[105]
Asp	Pr	edta	gl	25	0.20 M $NaClO_4$	K(Ln(A) + L)	4.91	[107]
Cys	Pr	but-diol	gl	25	Unknown	β(Ln(A)L)	17.41	[159]
Cys	Pr	but-diol	gl	25	Unknown	β(Ln$(A)_2$L)	22.99	[159]
Cys	Pr	but-diol	gl	25	Unknown	β(Ln(A)L_2)	24.32	[159]
Cys	Pr	eth-diol	gl	25	Unknown	β(Ln(A)L)	17.80	[159]
Cys	Pr	eth-diol	gl	25	Unknown	β(Ln$(A)_2$L)	22.82	[159]
Cys	Pr	eth-diol	gl	25	Unknown	β(Ln(A)L_2)	25.04	[159]
Cys	Pr	hex-diol	gl	25	Unknown	β(Ln(A)L)	17.57	[159]
Cys	Pr	hex-diol	gl	25	Unknown	β(Ln$(A)_2$L)	22.05	[159]
Cys	Pr	hex-diol	gl	25	Unknown	β(Ln(A)L_2)	23.92	[159]
Cys	Pr	pent-diol	gl	25	Unknown	β(Ln(A)L)	16.60	[159]
Cys	Pr	pent-diol	gl	25	Unknown	β(Ln$(A)_2$L)	21.72	[159]
Cys	Pr	pent-diol	gl	25	Unknown	β(Ln(A)L_2)	24.29	[159]
Cys	Pr	prop-diol	gl	25	Unknown	β(Ln(A)L)	16.68	[159]
Cys	Pr	prop-diol	gl	25	Unknown	β(Ln$(A)_2$L)	23.37	[159]
Cys	Pr	prop-diol	gl	25	Unknown	β(Ln(A)L_2)	25.02	[159]
Cys	Pr	2-but-diol	gl	25	Unknown	β(Ln(A)L)	17.88	[159]
Cys	Pr	2-but-diol	gl	25	Unknown	β(Ln$(A)_2$L)	25.60	[159]
Cys	Pr	2-but-diol	gl	25	Unknown	β(Ln(A)L_2)	27.77	[159]
His	Pr	cyt	gl	35	0.10 M KNO_3	K(Ln + A + HL)	8.50	[105]
Leu	Pr	edta	gl	25	0.20 M $NaClO_4$	K(Ln(A) + L)	4.72	[107]
Val	Pr	edta	gl	25	0.20 M $NaClO_4$	K(Ln(A) + L)	5.45	[107]
Gly	Nd	edta	gl	25	0.20 M $NaClO_4$	K(Ln(A) + L)	4.89	[107]
Gly	Nd	cyt	gl	35	0.10 M KNO_3	K(Ln + A + HL)	8.41	[105]
Ala	Nd	edta	gl	25	0.20 M $NaClO_4$	K(Ln(A) + L)	5.17	[107]
Asp	Nd	edta	gl	25	0.20 M $NaClO_4$	K(Ln(A) + L)	4.98	[107]
His	Nd	cyt	gl	35	0.10 M KNO_3	K(Ln + A + HL)	8.54	[105]
Leu	Nd	edta	gl	25	0.20 M $NaClO_4$	K(Ln(A) + L)	4.92	[107]
Val	Nd	edta	gl	25	0.20 M $NaClO_4$	K(Ln(A) + L)	5.86	[107]
Gly	Sm	ida	gl	37	0.15 M $NaClO_4$	β(Ln(A)$H_{-2}$$(HL)_2$)	−10.3	[78]
Gly	Sm	edta	gl	37	0.15 M $NaClO_4$	K(Ln(A) + 2L + HL)	5.96	[78]
Gly	Sm	edta	gl	37	0.15 M $NaClO_4$	K(Ln(A) + 3L)	5.85	[78]
Gly	Sm	edta	gl	37	0.15 M $NaClO_4$	K(Ln(A) + HL)	1.58	[78]
Gly	Sm	edta	gl	37	0.15 M $NaClO_4$	K(Ln(A) + L + 2HL)	5.36	[78]
Gly	Sm	edta	gl	25	0.20 M $NaClO_4$	K(Ln(A) + L)	4.97	[107]
Gly	Sm	ida	gl	37	0.15 M $NaClO_4$	K(Ln(A) + 2HL)	4.68	[78]
Gly	Sm	ida	gl	37	0.15 M $NaClO_4$	K(Ln(A) + HL)	2.85	[78]
Gly	Sm	ida	gl	37	0.15 M $NaClO_4$	K(Ln(A)$(OH)_2$ + 2HL)	5.0	[78]
Gly	Sm	nta	gl	37	0.15 M $NaClO_4$	K(Ln(A) + 2HL + H_2L)	5.55	[78]
Gly	Sm	nta	gl	37	0.15 M $NaClO_4$	K(Ln(A) + HL)	1.83	[78]
Gly	Sm	nta	gl	37	0.15 M $NaClO_4$	K(Ln$(A)_2$ + HL)	2.25	[78]
Gly	Sm	cyt	gl	35	0.10 M KNO_3	K(Ln + A + HL)	8.51	[105]
Ala	Sm	edta	gl	37	0.15 M $NaClO_4$	K(Ln(A) + HL)	0.86	[78]
Ala	Sm	edta	gl	37	0.15 M $NaClO_4$	K(Ln(A) + L)	1.08	[78]
Ala	Sm	edta	gl	25	0.20 M $NaClO_4$	K(Ln(A) + L)	5.37	[107]
Ala	Sm	nta	gl	37	0.15 M $NaClO_4$	K(Ln(A) + HL)	1.68	[78]

Table 5 (*Continued*)

aa	Ln	Auxiliary ligand (A)	Method	T (°C)	Medium	Equilibrium constant	log K	Ref.
Ala	Sm	nta	gl	37	0.15 M $NaClO_4$	$K(Ln(A)_2 + 2HL)$	1.84	[78]
Ala	Sm	nta	gl	37	0.15 M $NaClO_4$	$K(Ln(A)(OH) + HL)$	2.08	[78]
Arg	Sm	edta	gl	37	0.15 M $NaClO_4$	$K(Ln(A) + HL)$	1.88	[78]
Arg	Sm	edta	gl	37	0.15 M $NaClO_4$	$K(Ln(A) + L)$	1.9	[78]
Arg	Sm	nta	gl	37	0.15 M $NaClO_4$	$K(Ln(A) + HL)$	3.40	[78]
Arg	Sm	nta	gl	37	0.15 M $NaClO_4$	$K(Ln(A)_2 + HL)$	3.76	[78]
Arg	Sm	nta	gl	37	0.15 M $NaClO_4$	$K(Ln(A)(OH) + 2HL)$	7.94	[78]
Asp	Sm	edta	gl	25	0.20 M $NaClO_4$	$K(Ln(A) + L)$	5.37	[107]
Cys	Sm	edta	gl	37	0.15 M $NaClO_4$	$K(Ln(A) + 2HL)$	4.06	[78]
Cys	Sm	edta	gl	37	0.15 M $NaClO_4$	$K(Ln(A) + 2L)$	5.19	[78]
Cys	Sm	edta	gl	37	0.15 M $NaClO_4$	$K(Ln(A) + H_2L)$	2.36	[78]
Cys	Sm	edta	gl	37	0.15 M $NaClO_4$	$K(Ln(A) + HL)$	2.26	[78]
Cys	Sm	edta	gl	37	0.15 M $NaClO_4$	$K(Ln(A) + L)$	2.72	[78]
Cys	Sm	edta	gl	37	0.15 M $NaClO_4$	$K(Ln(A) + L + HL)$	5.13	[78]
Cys	Sm	nta	gl	37	0.15 M $NaClO_4$	$K(Ln(A) + H_2L)$	4.97	[78]
Cys	Sm	nta	gl	37	0.15 M $NaClO_4$	$K(Ln(A)_2 + 2HL + H_2L)$	8.6	[78]
Cys	Sm	nta	gl	37	0.15 M $NaClO_4$	$K(Ln(A)_2 + 2H_2L)$	6.8	[78]
Cys	Sm	nta	gl	37	0.15 M $NaClO_4$	$K(Ln(A)_2 + HL)$	4.40	[78]
His	Sm	cyt	gl	35	0.10 M KNO_3	$K(Ln + A + HL)$	8.63	[105]
Leu	Sm	edta	gl	25	0.20 M $NaClO_4$	$K(Ln(A) + L)$	5.09	[107]
Pro	Sm	edta	gl	37	0.15 M $NaClO_4$	$K(Ln(A) + L)$	3.4	[78]
Pro	Sm	nta	gl	37	0.15 M $NaClO_4$	$K(Ln(A) + 2HL)$	4.56	[78]
Pro	Sm	nta	gl	37	0.15 M $NaClO_4$	$K(Ln(A) + HL)$	2.68	[78]
Pro	Sm	nta	gl	37	0.15 M $NaClO_4$	$K(Ln(A)_2 + 2HL)$	4.55	[78]
Pro	Sm	nta	gl	37	0.15 M $NaClO_4$	$K(Ln(A)_2 + HL)$	2.77	[78]
Val	Sm	edta	gl	25	0.20 M $NaClO_4$	$K(Ln(A) + L)$	6.05	[107]
Gly	Gd	cyt	gl	35	0.10 M KNO_3	$K(Ln + A + HL)$	8.49	[105]
His	Gd	cyt	gl	35	0.10 M KNO_3	$K(Ln + A + HL)$	8.47	[105]
Gly	Dy	cyt	gl	35	0.10 M KNO_3	$K(Ln + A + HL)$	8.59	[105]
Asp	Tb	dga	cpl	25	0.10 M $NaClO_4$	$K(Ln(A)_2 + L)$	1.33	[160]
Asp	Tb	ide	cpl	25	0.10 M $NaClO_4$	$K(Ln(A)_2 + L)$	1.16	[160]
Asp	Tb	py-dca	cpl	25	0.10 M $NaClO_4$	$K(Ln(A)_2 + L)$	0.75	[160]
Asp	Tb	ssa	cpl	25	0.10 M $NaClO_4$	$K(Ln(A)_2 + L)$	1.62	[160]
His	Dy	cyt	gl	35	0.10 M KNO_3	$K(Ln + A + HL)$	8.76	[105]
Gly	Er	cyt	gl	35	0.10 M KNO_3	$K(Ln + A + HL)$	8.64	[105]
His	Er	cyt	gl	35	0.10 M KNO_3	$K(Ln + A + HL)$	8.81	[105]

Method abbreviations are: gl, glass electrode; cpl, circularly polarized luminescence spectroscopy. Auxiliary ligands abbreviations are: edta (ethylenediamine tetraacetic acid), cyt (cytidine), but-diol (butane-2,3-diol), eth-diol(ethanediol), hex-diol (hex-1,6-diol), pent-diol (pent-2,4-diol), prop-diol (prop-1,2-diol), 2-but-diol (2-butene-1,4-diol), ida (iminodiacetic acid), nta (nitrilotriacetic acid), dga (diglycolic acid), ide (iminodiethanoic acid), py-dca (pyridine-2,6-dicarboxylic acid), ssa (sulfosalicylic acid). A denotes the fully deprotonated form of auxiliary ligands.

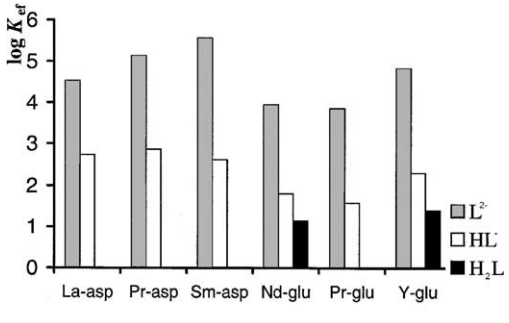


Fig. 13. Variation of complexes stability with the charge of incoming ligand for Asp and Glu with various metals. K_{ef} means the effective formation constant: $Ln^{3+} + L^{2-}$ (or HL^- or H_2L) → $[M(L, HL \text{ or } H_2L)]^{+,\,2+\text{ or }3+}$. Data were taken from Refs. [45,120,135].

bridges. The majority of reports in aqueous solution reveal the presence of 1:1 species. Several studies using UV–vis spectra [146], ^{13}C NMR [147], ^{1}H NMR [148–153], absorption and circular dichroic spectra [154,155], and luminescence spectra [156,157] demonstrate that complexing takes place through the carboxylate group. Perhaps the best evidence of Ln(III) binding to the carboxylate group has been obtained from circularly polarized luminescence and total luminescence spectroscopy. The fundamental work in this area has been previously reviewed [158].

9. Stability of other Ln(III) species containing amino acids in the coordination sphere

As already discussed, due to the low stability of these coordination compounds, hydrolysis processes are always

Table 6
Equilibrium constants for Ln(III) complexation reactions with peptides

Peptide	Ln	Method	T (°C)	Medium	Equilibrium constant	log K	Ref.
Gly–Gly	La	gl	30	0.10 M $NaClO_4$	K_1	3.35	[162]
Gly–Gly	La	gl	30	0.10 M $NaClO_4$	β_2	5.85	[162]
Gly–Gly	La	gl	30	0.10 M $NaClO_4$	K_3	2.43	[162]
Gly–Gly	Ce	gl	30	0.10 M $NaClO_4$	K_1	3.60	[162]
Gly–Gly	Ce	gl	30	0.10 M $NaClO_4$	β_2	6.17	[162]
Gly–Gly	Ce	gl	30	0.10 M $NaClO_4$	K_3	2.50	[162]
Gly–Gly	Pr	gl	30	0.10 M $NaClO_4$	K_1	3.75	[162]
Gly–Gly	Pr	gl	30	0.10 M $NaClO_4$	β_2	6.50	[162]
Gly–Gly	Pr	gl	30	0.10 M $NaClO_4$	K_3	2.64	[162]
Tyr–Val–Asp–Ala	Pr	nmr	25	0.50 M KCl	K_1	3.15	[163]
Tyr–Val–Asp–Ala	Pr	nmr	25	0.50 M KCl	K(Ln + HL)	2.50	[163]
Tyr–Val–Asp–Ala	Pr	nmr	25	0.50 M KCl	K(Ln + H_2L)	0.75	[163]
Asp–Gly–Tyr–Val–Asp–Ala	Pr	nmr	25	0.50 M KCl	K(Ln + HL)	3.13	[163]
Asp–Gly–Tyr–Val–Asp–Ala	Pr	nmr	25	0.50 M KCl	K(Ln + H_2L)	2.47	[163]
Asp–Gly–Tyr–Val–Asp–Ala	Pr	nmr	25	0.50 M KCl	K(Ln + H_3L)	0.78	[163]
Gly–Gly	Nd	gl	25	0.10 M KCl	K_1	2.35	[164]
Ala–Gly	Nd	gl	25	0.10 M KCl	K_1	2.30	[164]
Gly–Ala	Nd	gl	25	0.10 M KCl	K_1	2.30	[164]
Gly–Leu	Nd	gl	25	0.10 M KCl	K_1	2.4	[164]
Gly–Met	Nd	gl	25	0.1 M KCl	K_1	2.40	[164]
Gly–Ser	Nd	gl	25	0.10 M KCl	K_1	2.25	[164]
Gly–Tyr	Nd	gl	25	0.10 M KCl	K(Ln + HL)	2.70	[164]
Leu–Gly	Nd	gl	25	0.10 M KCl	K_1	1.85	[164]
Pro–Gly	Nd	gl	25	0.10 M KCl	K_1	2.75	[164]
Gly–Gly–Gly	Nd	gl	25	0.10 M KCl	K_1	2.15	[164]
Leu–Gly–Gly	Nd	gl	25	0.10 M KCl	K_1	1.75	[164]
Gly–Gly	Sm	gl	37	0.15 M $NaClO_4$	β(LnHL)	9.53	[97]
Gly–Gly	Sm	gl	37	0.15 M $NaClO_4$	β(LnH_2L_2)	18.7	[97]
Gly–Gly	Sm	gl	30	0.10 M $NaClO_4$	K_1	4.08	[162]
Gly–Gly	Sm	gl	30	0.10 M $NaClO_4$	β_2	6.93	[162]
Gly–Gly	Sm	gl	30	0.10 M $NaClO_4$	K_3	2.80	[162]
Ala–Gly	Sm	gl	37	0.15 M $NaClO_4$	β(LnHL)	9.35	[97]
Gly–Val	Sm	gl	37	0.15 M $NaClO_4$	β(LnHL)	9.67	[97]
Pro–Gly	Sm	gl	37	0.15 M $NaClO_4$	K_1	5.44	[97]
Pro–Gly	Sm	gl	37	0.15 M $NaClO_4$	β(LnHL)	10.95	[97]
Arg–Asp	Sm	gl	37	0.15 M $NaClO_4$	β(LnHL)	13.7	[97]
Arg–Asp	Sm	gl	37	0.15 M $NaClO_4$	β(LnH_2L)	21.07	[97]
Val–Glu	Sm	gl	37	0.15 M $NaClO_4$	β(LnHL)	10.48	[97]
Val–Glu	Sm	gl	37	0.15 M $NaClO_4$	β(LnH_2L)	14.38	[97]
Asp–Glu	Sm	gl	37	0.15 M $NaClO_4$	β(LnHL)	12.24	[97]
Asp–Glu	Sm	gl	37	0.15 M $NaClO_4$	β(LnH_2L)	15.98	[97]
Asp–Glu	Sm	gl	37	0.15 M $NaClO_4$	β(LnH_3L)	19.02	[97]
Gly–Gly–Gly	Sm	gl	37	0.15 M $NaClO_4$	β(LnHL)	9.68	[97]
Ala–Gly	Eu	gl	25	0.10 M KCl	K_1	2.55	[164]
Gly–Ala	Eu	gl	25	0.10 M KCl	K_1	2.60	[164]
Gly–Gly	Eu	gl	25	0.10 M KCl	K_1	2.65	[164]
Gly–Leu	Eu	gl	25	0.10 M KCl	K_1	2.45	[164]
Gly–Met	Eu	gl	25	0.1 M KCl	K_1	2.60	[164]
Gly–Phe	Eu	gl	25	0.10 M KCl	K_1	2.65	[164]
Gly–Ser	Eu	gl	25	0.10 M KCl	K_1	2.50	[164]
Gly–Tyr	Eu	gl	25	0.10 M KCl	K(Ln + HL)	2.85	[164]
Leu–Gly	Eu	gl	25	0.10 M KCl	K_1	2.45	[164]
Pro–Gly	Eu	gl	25	0.10 M KCl	K_1	3.10	[164]
Gly–Gly–Gly	Eu	gl	25	0.10 M KCl	K_1	2.55	[164]
Leu–Gly–Gly	Eu	gl	25	0.10 M KCl	K_1	2.40	[164]
Ala–Gly	Gd	gl	25	0.10 M KCl	K_1	2.40	[164]
Gly–Ala	Gd	gl	25	0.10 M KCl	K_1	2.40	[164]
Gly–Gly	Gd	gl	25	0.10 M KCl	K(Ln + HL)	0.58	[131]
Gly–Gly	Gd	gl	25	0.10 M KCl	K_1	2.35	[164]
Gly–Leu	Gd	gl	25	0.10 M KCl	K_1	2.30	[164]
Gly–Met	Gd	gl	25	0.1 M KCl	K_1	2.50	[164]
Gly–Phe	Gd	gl	25	0.10 M KCl	K_1	2.40	[164]

Table 6 (*Continued*)

Peptide	Ln	Method	T (°C)	Medium	Equilibrium constant	log K	Ref.
Gly–Ser	Gd	gl	25	0.10 M KCl	K_1	2.50	[164]
Gly–Tyr	Gd	gl	25	0.10 M KCl	K(Ln + HL)	2.65	[164]
Leu–Gly	Gd	gl	25	0.10 M KCl	K_1	2.25	[164]
Pro–Gly	Gd	gl	25	0.10 M KCl	K_1	3.00	[164]
Gly–Gly–Gly	Gd	gl	25	0.10 M $NaClO_4$	K(Ln + HL)	0.43	[131]
Gly–Gly–Gly	Gd	gl	25	0.10 M KCl	K_1	2.20	[164]
Leu–Gly–Gly	Gd	gl	25	0.10 M KCl	K_1	1.95	[164]
Tyr–Val–Asp–Ala	Dy	nmr	25	0.50 M KCl	K(Ln + H_2L)	0.70	[164]
Tyr–Val–Asp–Ala	Dy	nmr	25	0.50 M KCl	K(Ln + HL)	2.48	[163]
Tyr–Val–Asp–Ala	Dy	nmr	25	0.50 M KCl	K_1	3.11	[163]
Asp–Gly–Tyr–Val–Asp–Ala	Dy	nmr	25	0.50 M KCl	K (Ln + H_3L)	0.75	[163]
Asp–Gly–Tyr–Val–Asp–Ala	Dy	nmr	25	0.50 M KCl	K(Ln + H_2L)	2.42	[163]
Asp–Gly–Tyr–Val–Asp–Ala	Dy	nmr	25	0.50 M KCl	K(Ln + HL)	3.09	[163]
Ala–Gly	Ho	gl	25	0.10 M KCl	K_1	2.45	[164]
Gly–Ala	Ho	gl	25	0.10 M KCl	K_1	2.55	[164]
Gly–Gly	Ho	gl	25	0.10 M KCl	K_1	2.65	[164]
Gly–Leu	Ho	gl	25	0.10 M KCl	K_1	2.60	[164]
Gly–Met	Ho	gl	25	0.1 M KCl	K_1	2.60	[164]
Gly–Phe	Ho	gl	25	0.10 M KCl	K_1	2.45	[164]
Gly–Ser	Ho	gl	25	0.10 M KCl	K_1	2.60	[164]
Leu–Gly	Ho	gl	25	0.10 M KCl	K_1	2.40	[164]
Pro–Gly	Ho	gl	25	0.10 M KCl	K_1	3.25	[164]
Gly–Gly–Gly	Ho	gl	25	0.10 M KCl	K_1	2.35	[164]
Leu–Gly–Gly	Ho	gl	25	0.10 M KCl	K_1	2.0	[164]
Ala–Gly	Yb	gl	25	0.10 M KCl	K_1	2.80	[164]
Gly–Ala	Yb	gl	25	0.10 M KCl	K_1	2.80	[164]
Gly–Gly	Yb	gl	25	0.10 M KCl	K_1	2.75	[164]
Gly–Met	Yb	gl	25	0.1 M KCl	K_1	2.85	[164]
Gly–Leu	Yb	gl	25	0.10 M KCl	K_1	2.85	[164]
Gly–Phe	Yb	gl	25	0.10 M KCl	K_1	2.75	[164]
Gly–Ser	Yb	gl	25	0.10 M KCl	K_1	2.80	[164]
Gly–Tyr	Yb	gl	25	0.10 M KCl	K(Ln + HL)	2.85	[164]
Leu–Gly	Yb	gl	25	0.10 M KCl	K_1	2.60	[164]
Pro–Gly	Yb	gl	25	0.10 M KCl	K_1	3.50	[164]
Gly–Gly–Gly	Yb	gl	25	0.10 M KCl	K_1	2.50	[164]
Leu–Gly–Gly	Yb	gl	25	0.10 M KCl	K_1	2.30	[164]

Method abbreviations are: gl, glass electrode; nmr, nuclear magnetic resonance.

observed for Ln–aa systems. But when mixed-ligand complexes with an auxiliary ligand such as edta are prepared, precipitation of hydroxide is not observed, even in alkaline media. Polycarboxylic ligands stabilize the metals, and they are retained in solution even for relatively high pH values. Obviously, this fact depends on the auxiliary ligands employed. As the coordination numbers of the lanthanide metals are high, formation of mixed-ligand complexes from these stable cores is possible.

Table 5 shows the reported thermodynamic data on these systems. Interaction of the cores with amino acids is still weak. Even though overall formation constants may be apparently high, the effective formation constant from the primary complex is always low. It can be exemplified by the equilibria [78]:

$$Sm^{3+} + nta^{3-} \rightleftarrows [Sm(nta)] \log K = 9.85,$$

$$[Sm(nta)] + HGly \rightleftarrows [Sm(nta)(HGly)] \log K = 1.83$$

The last constant is comparable to [41]:

$$Sm^{3+} + HGly \rightleftarrows [Sm(HGly)]^{3+} \log K = 1.6$$

With this in mind, a large excess of the aa should be used to make the mixed-ligand species predominant (Fig. 14). When a large excess of amino acids is employed, mixed-ligand complexes predominate even for high pH values, due to the high affinity of the auxiliary ligand for the metals.

Binding of amino acids to these stable cores appears to be still governed by electrostatic interaction. The same dependence of stability on the size of the metal is observed, as stated in Section 8.

10. Thermodynamic stability of lanthanide complexes with peptides

Interaction of Ln with peptides is very similar to that found for amino acids. Thus, even though available data for peptides are still scarce, all results show the same behavior. Table 6 presents the compiled thermodynamic data.

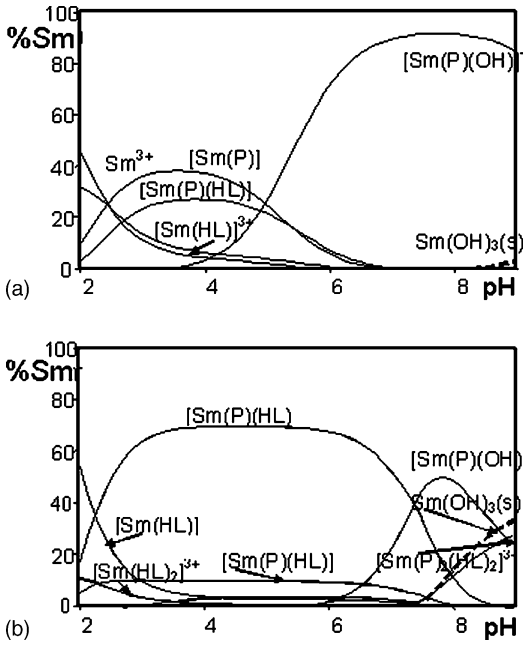


Fig. 14. Species distribution diagrams of mixed-ligand complexes of Sm with nta (H_3P), and Pro (HL). Stability data were taken from Refs. [43,78], and hydrolysis data of the metal from Ref. [161]. (a) [Sm] = 3 mM, [nta] = 3 mM, [Pro] = 3 mM. (b) [Sm] = 3 mM, [nta] = 3 mM, [Pro] = 90 mM. T = 37.0 °C, I = 0.15 M $NaClO_4$.

For peptides with no additional carboxylic group, species with 1:1 stoichiometry are the most important compounds. Only for Gly–Gly, the smallest peptide, have the species $[Sm(H_nL)_n]^{3+}$ (n = 2, 3) also been reported [97,162]. As in the studies with amino acids, hydrolysis is always observed, reflecting again the hard Lewis acid character of the metal ion and the high coordination number requirement of these large ions. Thus, these complexes are detected from the deprotonation of the ligand pH value until the precipitation of the hydroxides. For peptides containing additional carboxylic groups, deprotonated species are also detected [97].

The behavior of Ln complexes with simple peptides is determined by the identity of the C-terminal amino acid of the ligand. For example [97]:

$$Sm^{3+} + HPro–Gly \rightleftarrows [Sm(HPro–Gly)]^{3+} \log K = 2.23$$

is quite similar to

$$Sm^{3+} + HGly \rightleftarrows [Sm(HGly)]^{3+} \log K = 1.6$$

In both cases, coordination is supported by a COO^- belonging to a glycine residue.

11. Concluding remarks

Ln(III) ions are typical hard metals. Consequently, they preferentially interact with the harder residue of amino acids and peptides. Most reported data in either aqueous solution or solid state support this. In consequence, the interaction is rather independent of the amino acid, and only slightly dependent on the metal. Small changes appear when the ligand possesses an additional carboxylate group (aspartic and glutamic acid). In any case, the thermodynamic stability is low, but the formation of stable compounds containing amino acids can be reached in mixed-ligand complexes.

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 radium.

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.

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