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Amino acid–lanthanide interactions—2. The X-ray crystal structures of lanthanide and calcium complexes of 1-amino cyclohexane-1-carboxylic acid (Acc6), [Nd2(Acc6)6(H2O)6](ClO4)6 · (H2O)6 (1), [Er2(Acc6)4(H2O)8](ClO4)6 · (H2O)11 (2) and [Ca5(Acc6)12(H2O)6](ClO4)10 · (H2O)4 (3)

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Abstract—The structures of $[Nd_2(Acc^6)_6(H_2O)_6](ClO_4)_6 \cdot (H_2O)_6$ (**1**) $[Er_2(Acc^6)_4(H_2O)_8](ClO_4)_6 \cdot (H_2O)_{11}$ (**2**) and $[Ca_5(Acc^6)_{12}(H_2O)_6](ClO_4)_{10} \cdot (H_2O)_4$ (**3**) (Acc6 = 1-aminocyclohexane-1-carboxylic acid) have been determined by X-ray crystallography. The lanthanide complexes **1** and **2** are dimeric in which two lanthanide cations are bridged by four carboxylato groups of Acc6 molecules. In addition, the neodymium complex (**1**) features the unidentate coordination of the carboxyl group of an Acc6 molecule in place of a water molecule in the erbium complex (**2**). The coordination number in both **1** and **2** is eight. The calcium Acc6 complex (**3**) is polymeric ; three different calcium environments are observed in the asymmetric unit. Two calcium ions are hexa-coordinated and one is hepta-coordinated. Considerable differences are observed between the solid state structures of Ln^{III} and Ca^{II} complexes of Acc6. Copyright © 1996 Elsevier Science Ltd

Lanthanide ions are often used as probes of Ca^{II} binding sites in biological systems. The ability of lanthanides to mimic Ca^{II} in diverse situations arises from the similarity in the sizes of the ions and their strong affinity to form complexes with oxygen donor ligands [1,2]. In continuation of our studies on amino acid [3] and peptide [4] complexes of lanthanides, we report here the structures of the lanthanide and calcium complexes of 1-aminocyclohexane-1-carboxylic acid (Acc6).

The use of non-protein amino acid residues in the synthesis of peptides with restricted conformational flexibility has acquired increasing importance in the design of specifically folded analogues of biologically active peptides [5]. α,α-Dialkylated residues [—NH—CR¹R²—CO—) have proved valuable in the construction of conformationally constrained peptide backbones [6–8]. The studies on Acc6 residues of the N-blocked amino acids and peptides showed that the amino function is almost always found in the axial position [9–11]. The zwitterionic amino acid (Acc6) is the only case where the amino function is equatorial [9]. In this context, it would be interesting to study the metal complexes of zwitterionic Acc6 to assess the conformational preference of the amino group.

EXPERIMENTAL

Lanthanide perchlorates were prepared from the respective lanthanide oxides. 1-Aminocyclohexane 1-

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carboxylic acid (Acc[6]) was prepared according to the literature procedure [12, 13].

Synthesis of $[Nd_2(Acc^6)_6(H_2O)_6](ClO_4)_6 \cdot (H_2O)_6$ (1) and $[Er_2(Acc^6)_4(H_2O)_8](ClO_4)_6 \cdot (H_2O)_{11}$ (2)

Lanthanide perchlorate hexahydrate $(3.64 \times 10^{-4}$ mol) and Acc[6] (0.05 g, 3.64×10^{-4} mol) were dissolved in 5 cm^3 of distilled water. On slow evaporation of the solution at room temperature, crystals of lanthanide-Acc[6] complexes were obtained. Yield: $\approx 75\%$.

Synthesis of $[Ca_5(Acc^6)_{12}(H_2O)_6](ClO_4)_{10} \cdot (H_2O)_4$ (3)

Calcium perchlorate (0.09 g, 2.80×10^{-4} mol) and Acc[6] (0.04 g, 2.80×10^{-4} mol) were dissolved in 5 cm^3 of distilled water. On slow evaporation of the solution at room temperature crystals of calcium perchlorate-Acc[6] complex were isolated. Yield: 70%.

Satisfactory C, H, N analysis could not be obtained for the complexes because of their hygroscopic nature. Lanthanide metal contents were determined by titration with EDTA using xylenol orange as the indicator and correspond to the empirical formulae noted above.

X-ray crystal structure analysis of 1–3

A suitable crystal of each compound was mounted in a Lindemann capillary and sealed to protect it from moisture. The data were collected on an Enraf-Nonius CAD-4 diffractometer using graphite mono-chromated Mo-K_α radiation. The structures were solved by Patterson and Fourier techniques and refined by full matrix least squares procedures [14, 15]. All the non-hydrogen atoms were refined aniso-tropically. The methylene hydrogen atoms of the cyclohexane ring were fixed at geometrically cal-culated positions (C—H = 0.9 Å) and included in the structure factor calculations. The water and NH$_3^+$ hydrogen atoms were not located. This may be the reason for the high R-factor observed for complex 3, which contains the relatively lighter calcium atoms compared to the other heavy atom structures 1 and 2. The details pertaining to the data collection and refinement are given in Table 1.

RESULTS AND DISCUSSION

Spectroscopic data for the complexes

The Acc[6] complexes of neodymium (1), erbium (2) and calcium (3) perchlorates are prepared by dis-solving stoichiometric amounts of Acc[6] and the respective metal salt in water. Slow evaporation of the resultant solution gave crystalline complexes in high yield. These complexes possess the characteristic color of the lanthanide ion.

The infrared spectra of the complexes show a broad and strong absorption in the 3300–2300 cm^{-1} region which can be assigned to the O—H and NH$_3^+$ stret-ching vibrations superimposed on each other. The strong band in the region 1600–1500 cm^{-1} arises from the asymmetric stretching vibration of the carboxylato group. The strong absorptions in the region of 1170–1050 and 620–630 cm^{-1} are assigned to ν_3 and ν_4 vibrations of the perchlorate ion.

The structure of the lanthanide-Acc[6] complexes in solution has been investigated by ^{13}C NMR spec-troscopy. For this purpose, the ^{13}C resonances of Acc[6] are monitored upon successive addition of praseo-dymium perchlorate solution. The praseodymium complexes are expected to have a similar structure to that of the neodymium complex [16]. The advantage of using Pr^{3+} for NMR measurements is that it induces large chemical shifts, without causing appreci-able line broadening compared to the Nd^{3+} ion [16]. Upon successive addition of praseodymium per-chlorate solution, the resonances of carboxyl carbon (δ value in free Acc[6]: 177.6 ppm, $\Delta\delta$: 1 ppm) and the carbon which is directly bonded to the carboxyl group (δ value in free Acc[6]: 61.6 ppm, $\Delta\delta$: 6 ppm) show maximum chemical shift variations compared to the other resonances. Irrespective of the concentration of the praseodymium salt, only a single resonance is observed for the carboxyl carbon. This observation suggests that there is a dynamic equilibrium between differently coordinated carboxyl groups of the Acc[6] in solution. The X-ray crystal structure of the neo-dymium-Acc[6] complex shows two different types of coordination of the carboxyl group of Acc[6] (see below).

X-ray crystal structures

X-ray crystal structure analysis of neodymium-Acc^6 (1) and erbium-Acc^6 (2) complexes. The structures of neodymium and erbium complexes were determined by X-ray crystallography. Perspective views of the molecules are shown in Figs 1 and 2. The selected bond distances and angles are listed in Table 2.

In both neodymium and erbium complexes, the two lanthanide ions are bridged by the carboxylato groups of four Acc[6] molecules. In the neodymium complex, in addition, each neodymium ion is also coordinated to a unidentate carboxyl group of an Acc[6] molecule. Such a unidentate coordination of the carboxyl group of an amino acid to lanthanides is observed for the first time. However, this type of unidentate car-boxylato group is present in the solid state structures of the trifluoroacetato and *meta*-hydroxybenzoato complexes, $[Pr(O_2CCF_3)_3 \cdot 3H_2O]$ [17] and $[Ln_2(O_2C C_6H_4OH-3)_6(H_2O)_6] \cdot 2H_2O$ (Ln = Sm or Er) [18].

The metal to ligand ratio is 1:3 in the neodymium-Acc[6] complex but in the erbium-Acc[6] complex, it is decreased to 1:2 and the unidentate Acc[6] molecule is replaced by a water molecule. This difference is a

Table 1. Crystal data, details of intensity data collection, structure solution and refinement for **1**, **2** and **3**

	1	**2**	**3**
Molecular formula	$C_{42}H_{98}Cl_6Nd_2N_6O_{48}$	$C_{28}H_{90}Cl_6Er_2N_4O_{51}$	$C_{84}H_{176}Ca_{5\cdot}Cl_{10}N_{12}O_{74}$
Molecular weight	1956.5	1846.3	3093.3
Crystal system	Triclinic	Orthorhombic	Triclinic
a (Å)	11.429(1)	11.356(4)	14.952(5)
b (Å)	12.900(2)	22.707(7)	15.408(3)
c (Å)	14.653(2)	27.008(4)	16.109(4)
α (°)	71.87(1)	—	65.43(2)
β (°)	85.47(1)	—	83.73(2)
γ (°)	68.68(1)	—	82.23(2)
V (Å^3)	1911(13)	6964(3)	3338(10)
Space group	$P\bar{1}$	$Pcnn$	$P\bar{1}$
Z	1	4	1
D_c (g cm^{-3})	1.70	1.76	1.54
$F(000)$	992	3808	1622
Temperature (°C)	20	20	20
Radiation (graphite monochromator)	Mo-K_α(0.7107 Å)	Mo-K_α(0.7107 Å)	Mo-K_α(0.7107 Å)
Scan technique	$\omega/2\theta$	ω	$\omega/2\theta$
Octants (collected)	$+h, \pm k, \pm l$	$+h, +k, +l$	$+h, \pm k, \pm l$
2θ range (°)	2–50	2–50	2–50
Decay	<1%	<1%	<1%
Color	Rose	Pale pink	Colorless
Size (mm)	0.20 × 0.50 × 0.40	0.18 × 0.88 × 0.25	0.40 × 0.40 × 0.40
Linear abs. coeff. (μ cm^{-1})	16.11	27.70	4.82
Total number of reflections	7246	6999	12019
Unique reflections	6244	6128	10115
Observed reflections	6235 $\{F_o > 5\sigma(F_o)\}$	3833 $\{F_o > 5\sigma(F_o)\}$	8017 $\{F_o > 5\sigma(F_o)\}$
No. of parameters	469	456	870
R^a	0.033	0.051	0.086
$R_w{}^{b,c}$	0.038	0.052	0.092
Residual peak in final diff. map (e/Å^3)	1.0	1.9	1.0
Shifts/e.s.d.(max)	0.1	0.1	0.1

[a] $R = \Sigma(\|F_o|-|F_c\|)/\Sigma|F_o|$.

[b] $R_w(\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2)^{1/2}$.

[c] w for **1** = $2.3568/(\sigma^2(F)+0.000441F^2)$; **2** = $2.7828/(\sigma^2(F)+0.000000F^2)$; **3** = $4.7977/(\sigma^2(F)+0.001727F^2)$.

consequence of the decreased ionic radius of the Er^{3+} ion compared to the Nd^{3+} ion as a result of "lanthanide contraction". In both **1** and **2**, the coordination number of the lanthanide ion is eight and the geometry around the metal is that of a square antiprism. The amino acids exist in the zwitterionic form and the perchlorate ions are outside the coordination sphere. In the neodymium complex **1**, the distance between the unidentate carboxylato oxygen [O(5)] and the neodymium ion is (2.485(3) Å) which is longer than the average distance of the bridging carboxylato oxygens to the neodymium ion (Table 2). The latter distances fall into two ranges [the mean of Nd(1)—O(2) and Nd(1)—O(3) is 2.447(3) Å; the mean of Nd(1)—O(1)′ and Nd(1)—O(4)′ is 2.375(4) Å]. The non-bonding distance between O(6) and Nd(1) ion is 3.912(4) Å. In both neodymium and erbium complexes, the average distance between the carboxylato oxygens and metal ion is shorter than the distance of the coordinated water oxygen to the metal.

X-ray crystal structure analysis of calcium-Acc[6] (**3**) *complex.* The structure of the calcium-Acc[6] complex (**3**) is shown in Fig. 3. The Acc[6] molecules are in their zwitterionic form and the perchlorate groups are outside the coordination sphere. The unit cell consists of five calcium atoms with one of them (Ca(3)) lying at the centre of inversion so that the asymmetric unit corresponds to the formula $[Ca_{2.5}(Acc^6)_6(H_2O)_3](ClO_4)_5 \cdot (H_2O)_2$. Unlike the lanthanide complexes of Acc[6], the calcium complex is polymeric with carboxylato bridges. Three different calcium environments are observed in the asymmetric unit, two calcium ions are hexa-coordinated with an octahedral geometry and one calcium ion is hepta-coordinated with pentagonal bipyramidal geometry. The Ca(1) and Ca(2) are bridged by three carboxylato groups of Acc[6] and Ca(2) and Ca(3) are bridged by two carboxylato groups. Each of the two centrosymmetrically related calcium ions Ca(1) and Ca(1)′ bears a chelated carboxylato group which also bridges

Fig. 1. The molecular structure of $[Nd_2(Acc^6)_6(H_2O)_6](ClO_4)_6 \cdot (H_2O)_6$ (**1**) omitting the perchlorate groups and lattice water molecules.
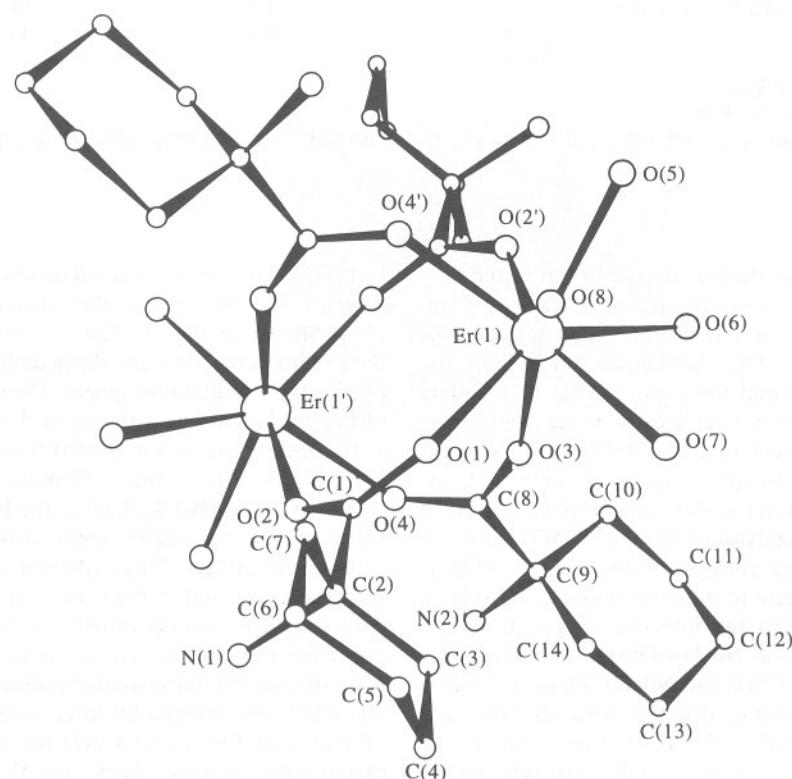
Fig. 2. The molecular structure of $[Er_2(Acc^6)_4(H_2O)_8](ClO_4)_6 \cdot (H_2O)_{11}$ (**2**) omitting the perchlorate groups and lattice water molecules.

Table 2. Selected bond distances (Å) and angles (°) in [Nd$_2$(Acc^6)$_6$(H$_2$O)$_6$](ClO$_4$)$_6$ · (H$_2$O)$_6$ (1) and [Er$_2$(Acc^6)$_4$(H$_2$O)$_8$](ClO$_4$)$_6$ · (H$_2$O)$_{11}$ (2)

Complex (1)

Nd(1)—O(1) = 2.377(3)	O(1)—Nd(1)—O(4) = 73.7(1)
Nd(1)′—O(2) = 2.447(2)	O(4)—Nd(1)—O(8) = 84.8(1)
Nd(1)′—O(3) = 2.447(3)	Nd(1)—O(1)—C(1) = 173.1(3)
Nd(1)—O(4) = 2.372(4)	Nd(1)—O(4)—C(8) = 145.1(3)
Nd(1)—O(5) = 2.485(3)	Nd(1)—O(5)—C(15) = 138.8(4)
Nd(1)—O(7) = 2.544(3)	O(3)—C(8)—O(4) = 127.3(4)
Nd(1)—O(8) = 2.442(3)	O(5)—C(15)—O(6) = 125.5(4)
Nd(1)—O(9) = 2.508(3)	
Nd(1)···O(6) = 3.912(4)	
O(3)—C(8) = 1.245(6)	
O(4)—C(8) = 1.254(7)	
O(5)—C(15) = 1.256(5)	
O(6)—C(15) = 1.248(5)	

Complex (2)

Er(1)—O(1) = 2.256(8)	O(1)—Er(1)—O(2)′ = 76.9(3)
Er(1)′—O(2) = 2.315(8)	O(3)—Er(1)—O(4)′ = 77.5(3)
Er(1)′—O(3) = 2.268(7)	Er(1)′—O(2)—C(1) = 136.9(6)
Er(1)′—O(4) = 2.300(7)	Er(1)′—O(4)—C(8) = 135.2(6)
Er(1)—O(5) = 2.393(7)	O(1)—C(1)—O(2) = 128.5(9)
Er(1)—O(6) = 2.431(8)	O(3)—C(8)—O(4) = 126.0(9)
Er(1)—O(7) = 2.359(8)	
Er(1)—O(8) = 2.408(6)	
O(1)—C(1) = 1.266(13)	
O(2)—C(1) = 1.243(13)	
O(3)—C(8) = 1.244(12)	
O(4)—C(8) = 1.262(12)	

the other calcium ion. Thus the carboxylato groups between Ca(1) and Ca(1)′ act as tridentate ligands.

The selected bond distances and angles are listed in Table 3. The distance between Ca(1)···Ca(1)′ (4.046(3) Å) is shorter than the distance between Ca(1)···Ca(2) (4.382(3) Å) or Ca(2)···Ca(3) (4.487 (2) Å). The Ca(1)—O(2) distance (2.365(6) Å) is shorter than the Ca(1)′—O(2) distance (2.737(4) Å).

Cyclohexyl ring conformation

The endocyclic cyclohexane ring angles in 1, 2 and 3 are close to an almost perfect chair conformation for the cyclohexane ring. The mean value is ±54(1)° as found for several Acc^6 containing compounds [9–12].

The amino functional group in the complexes 1–3 occupies an axial position with respect to the Acc^6 moiety. This feature is also observed in other Acc^6 containing compounds [10–12] except in the free zwitterionic Acc^6 where the amino functional group is in an equatorial position [9].

Comparison of the structures of lanthanide–amino acid complexes

Prior to this study, the structures of the lanthanide complexes of glycine [19], L-alanine [20] and α-amino

isobutyric acid (Aib) [3] have been reported. In all these complexes, the amino acids exist in their zwitterionic form and the perchlorate or chloride ions reside outside the coordination sphere of the metal.

The glycine complex [Nd$_2$(Gly)$_6$(ClO$_4$)$_6$ · 9H$_2$O] [19] is polymeric with carboxylato bridges between two neodymium ions. The asymmetric unit consists of dimers in which neodymium ions are bridged by four glycine molecules; two of them act as bidentate ligands while the other two act as tridentate ligands chelating to one metal and bridging to the other metal. Each of the neodymium ion dimers, is linked to another such dimer by two carboxylato bridges. The L-Ala [20] and Aib [3] complexes of lanthanides are dimeric with four bridging carboxylato groups. The same feature is also observed in the lanthanide complexes of Acc^6 reported here. In addition, in the Nd-Acc^6 complex, a unidentate Acc^6 is present.

Comparison of the structures of calcium–amino acid complexes

The calcium-Acc^6 complex (3) shows considerable differences from the Ca-glycine complex. In the Ca-Acc^6 complex, bidentate and tridentate mode of bonding of the carboxylato groups are observed whereas in the calcium-glycine complex bidentate and unidentate bonding of the aminoacid are observed. In the calcium
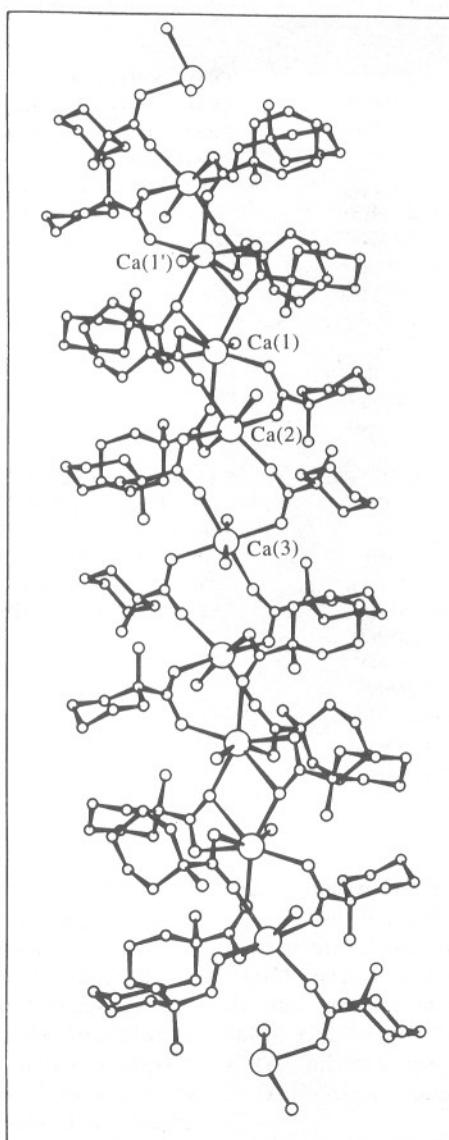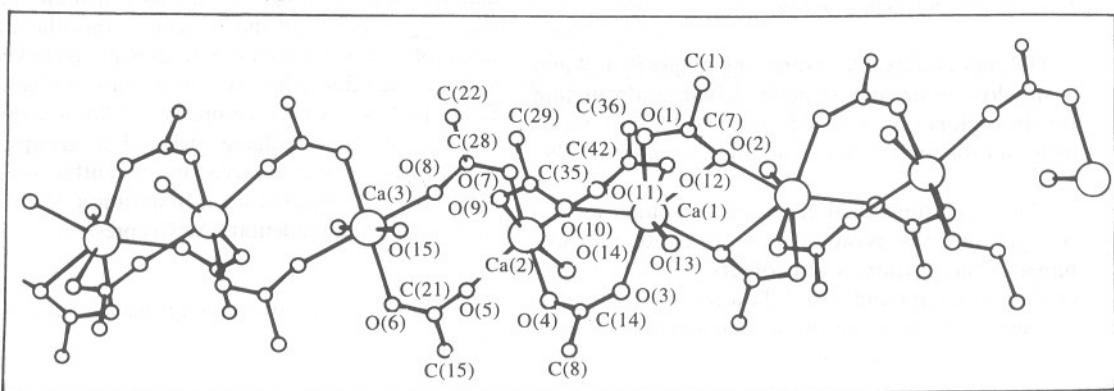
Fig. 3. (a) The molecular structure of $[Ca_5(Acc^6)_{12}(H_2O)_6](ClO_4)_{10} \cdot (H_2O)_4$ **(3)** omitting the perchlorate groups and lattice water molecules. (b) The molecular structure of $[Ca_5(Acc^6)_{12}(H_2O)_6](ClO_4)_{10} \cdot (H_2O)_4$ **(3)** omitting the perchlorate groups, lattice water molecules and ring carbon atoms.

Table 3. Selected bond distances (Å) and angles (°) in [Ca$_5$(Ac-c^6)$_{12}$(H$_2$O)$_6$](ClO$_4$)$_{10}$ · (H$_2$O)$_4$ (**3**)

Ca(1)—O(1) = 2.426(5)	Ca(1)—O(1)—C7 = 100.4(4)
Ca(1)—O(2) = 2.365(6)	Ca(1)—O(2)—C7 = 169.0(4)
Ca(1)—O(3) = 2.363(6)	Ca(1)—O(3)—C14 = 131.9(5)
Ca(1)—O(10) = 2.359(6)	Ca(1)—O(10)—C35 = 143.0(4)
Ca(1)—O(12) = 2.395(4)	Ca(1)—O(12)—C42 = 108.6(4)
Ca(1)—O(13) = 2.374(5)	O(1)—C(7)—O(2) = 123.1(6)
Ca(2)—O(4) = 2.321(4)	O(5)—C(21)—O(6) = 122.9(6)
Ca(2)—O(5) = 2.304(5)	O(7)—C(28)—O(8) = 122.6(6)
Ca(2)—O(7) = 2.370(4)	O(9)—C(35)—O(10) = 125.9(7)
Ca(2)—O(9) = 2.326(7)	O(11)—C(42)—O(12) = 122.3(6)
Ca(2)—O(11) = 2.365(4)	
Ca(2)—O(14) = 2.356(9)	
Ca(3)—O(6) = 2.301(5)	
Ca(3)—O(8) = 2.312(4)	
Ca(3)—O(15) = 2.380(5)	
Ca(1)′—O(2) = 2.737(4)	

glycine complex [21], the coordination number for calcium is seven but in the calcium-Acc^6 complex, both six and seven coordinated calcium ions are observed.

Comparison of the structures of lanthanide and calcium amino acid complexes

Lanthanide complexes of Acc^6 show considerable structural differences from the calcium complex of Acc^6. The neodymium and erbium complexes of Acc^6 are dimeric whereas the Ca–Acc^6 complex is polymeric. In the Ca–Acc^6 complex both bi- and tridentate carboxylato bridges are present; in contrast, only bidentate carboxylato groups are present in the erbium-Acc^6 complex and bidentate and unidentate carboxylato groups are present in the neodymium–Acc^6 complex. Pronounced differences are also observed between the modes of binding of glycine to lanthanides and calcium as revealed by the structures of [Nd$_2$(Gly)$_6$(ClO$_4$)$_6$ · 9H$_2$O] [19] and [CaI$_2$(Gly)$_3$H$_2$O] [21]. In the calcium–glycine complex, only one glycine carboxylato group bridges two calcium ions while the other two glycine molecules are coordinated to a calcium ion in a unidentate fashion. On the other hand, the neodymium–glycine complex contains both bidentate and tridentate carboxyl groups (see above).

CONCLUSION

The results reported here reinforce our earlier conclusion [3,4] that there can be considerable variation in the modes of binding of amino acids to lanthanides as compared to calcium ions. The difference in the precise binding geometries suggests that structural alterations may accompany the interaction of lanthanides with calcium ion binding sites in biological systems.

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