Amphiphilic Amide Derivatives of D-Glucaric Acid. Synthesis and Complexing Properties Toward Lanthanide(III) Ions

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Hydrophobic derivatives of D-glucaric acid, HOOC–$(CHOH)_4$–CONHR,where R is an alkyl chain having 3, 8, 10, or 12 carbon atoms, have been synthesized from D-glucaro-1,4-lactone and the corresponding amines. The complexing abilities of these compounds toward trivalent lanthanide cations have been studied, using the water-soluble propyl compound, and compared to that of gulonic acid, which corresponds to the complexing part of these molecules. The formation constants of the complexes have been determined and their structures discussed. The surfactant properties of the C_8, C_{10} and C_{12} glucaramides and their extracting ability toward Ln^{III} ions have also been evaluated.

Introduction

Polyhydroxylated carboxylic acids are good complexing agents toward metallic ions.[1] For instance, gluconic acid is largely used in the industrial and food domains. Moreover, sugars and sugar derivatives are increasingly being used as hydrophilic heads for synthesizing amphiphilic molecules that display good biodegradability [2] and low environmental impact.[3] The preparation of glucidoamphiphilic molecules [4,5] has been the subject of numerous research aimed toward obtaining molecules having complementary properties, in which the sugar head brings about specific properties, such as molecular recognition in biology[6–8] or the complexation of cations[1,9].

In this field, we propose the use of new amphiphilic agents, hydrophobic derivatives of aldaric acids having a sugar-type hydrophilic part, for liquid–liquid extraction of metallic ions.

In a previous paper, we showed that aldonic acids are efficient complexing molecules for the lanthanide(III) cations and that there is a significant evolution of the stability constants for complexation along the series.[10]

Indeed, the search for molecules that present selective complexing and extracting properties toward these ions is important for the separation of these elements, which have very similar chemical properties. This search is also of interest for nuclear waste management: the separation of lanthanide(III) and actinide(III) ions is a difficult problem to solve because of their close chemical behaviour.

Our challenge was to prepare hydrophobic derivatives without losing the complexing properties of aldonic acids, i.e., by keeping the carboxylate and hydroxy groups free. In a previous study, we prepared tartaric acid derivatives that were rendered hydrophobic by the reaction of a fatty amine with one of the two carboxylic functions, which led to the formation of an amide function.[9] In these compounds, one carboxylate and two potentially ionizable hydroxy groups, in α and β positions relative to the carboxylate unit, are available for complexation, but we have demonstrated that the complexation of gluconic acid occurred at the carboxylate group, followed by deprotonation of the α- and γ-OH groups. Thus, to retain the full complexing ability of gluconic acid, evidently the hydrophobic derivatives must have at least three OH groups in addition to the carboxylate group; in contrast, the tartaric acid derivatives have only two OH functions. We also demonstrated that the greater the number of hydroxy groups the molecule has, the higher is the complexing power of this kind of molecule. Compounds prepared from aldaric acids, which are C_6 diacids having four OH groups, fulfil this condition. Therefore, we decided to prepare monoamide derivatives of D-glucaric acid. The preparation of monoesters was also envisaged, but eventually rejected, because of the larger sensitivity to hydrolysis of these compounds relative to that of amides.

In this paper, we present the synthesis of fatty monoamides that are derivatives of aldaric acids, HOOC–$(CHOH)_4$–CO–NHR, where R contains a C_3, C_8, C_{10} or C_{12} alkyl chain.

The C_3 derivative is soluble enough in water to allow us to study its complexing properties with lanthanide(III) ions in aqueous solutions. The other three molecules are only slightly soluble in water; because they present the potential for amphiphilic character, their surfactive properties in water were evaluated from surface tension measurements.

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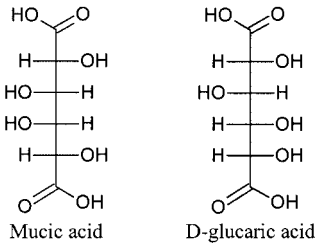
The aims of the complexation study were to verify that if a neutral complex is formed, as for gluconic acid, it will allow the extraction of metal cations into an organic medium and also to test whether the strength of the interaction is close to that of the generic compound. We studied the complexation of four different lanthanide(III) cations: Pr^{3+}, Eu^{3+}, Dy^{3+} and Lu^{3+}. A comparison of the complexation strength of the C_3-compound toward these different ions was conducted to see if selective complexation behaviour may be detected along the lanthanide series. Finally, in a prospective work, we evaluated the potential of the long-chain compounds as extracting agents for lanthanide(III) ions.

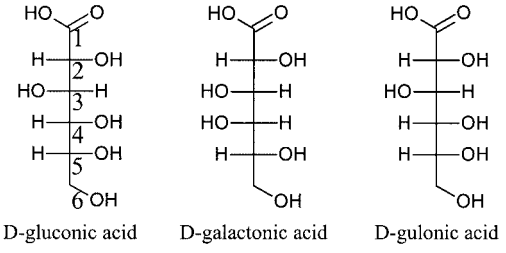
Results and Discussion

Synthesis of Amide Derivatives of D-Glucaric Acid

As starting materials, we considered only two commercially available aldaric acids, mucic acid and D-glucaric acid (Scheme 1). Our aim was to synthesize a unique monoamide form, the complexing part of which (i.e., the carboxylic and four OH functions) corresponds to that of the aldonic acids (gluconic, gulonic or galactonic acids; Scheme 2). The hydrophobic part would be provided by a fatty amine.



Scheme 1. Fischer representations of two aldaric acids

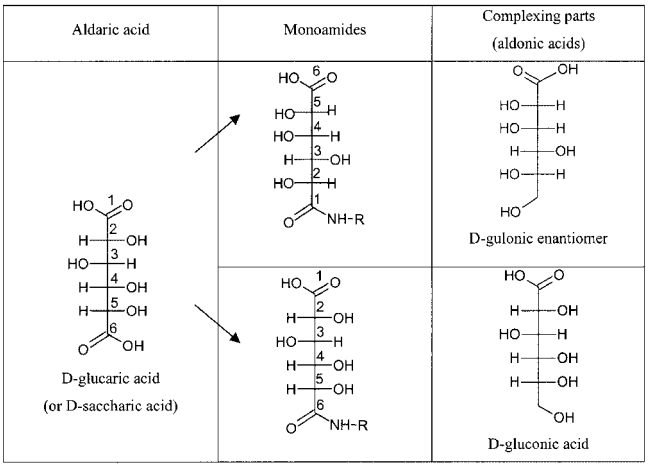


Scheme 2. Fischer representations of three aldonic acids

The simple method described by us previously[9] for the preparation of monoamide derivatives of tartaric acid was not applicable for mucic and glucaric acids. This method consists of the direct reaction of tartaric acid with the corresponding amines in the absence of a coupling agent. The first step involves simply mixing the amine and tartaric acid to form an ammonium salt. The second step is the pyrolysis of this salt under azeotropic reflux in either toluene or heptane.

In fact, the insolubility of mucic acid in most solvents does not allow the monoamide synthesis to be conducted in such a simple and applicable way.

The difficulty in synthesising a unique monoamide from glucaric acid resides in the unsymmetrical structure of the molecule. In fact, the synthesis would lead to two different monoamides that have different complexing parts (gluconic acid and gulonic acid); their separation would not be easy (Scheme 3).



Scheme 3. Monoamide derivatives of D-glucaric acid and their corresponding complexing units.

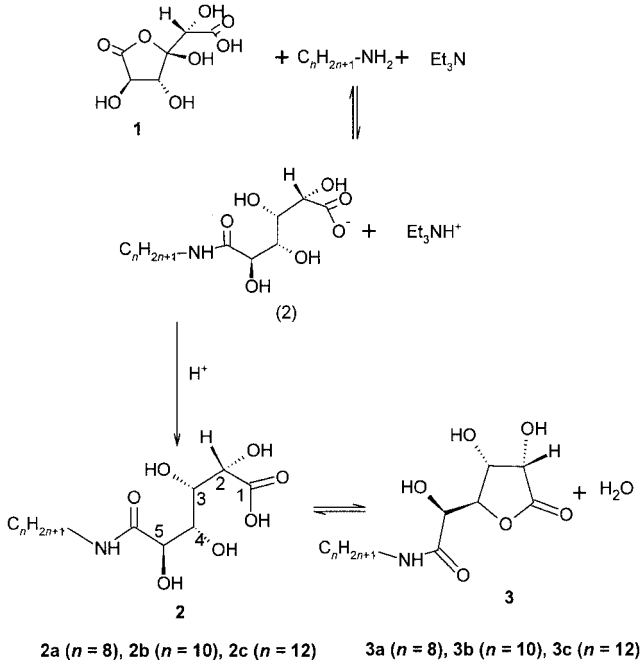
Thus, our strategy for synthesizing a unique monoamide consisted of the use of the lactone form of glucaric acid. Since the synthesis depends on the chain length, first we describe the synthesis of monoamides having a long chain and then the preparation of the propylamide.

Synthesis of the Long-Chain Monoamides

Glucaro-1,4-lactone acid (**1**) was dissolved in a minimum amount of methanol and then we slowly added one equiv. of the amine together with two equiv. of triethylamine dissolved in methanol (Scheme 4). The mixture was heated under reflux for 8 h. Triethylamine was added to avoid requiring an excess of fatty amine, which might allow the formation of the diamide. After evaporation, the residual product was dispersed in water and the pH was adjusted to 2 by adding HCl. In its acidic form, compound **2** could be extracted by ethyl acetate. The by-product (triethylammonium chloride) and the excess of compound **1** remained in the aqueous phase. To avoid formation of lactone **3**, which occurs relatively fast in acidic solutions, this extraction had to be performed quickly. The overall yields from compound **1** were 40−66%.

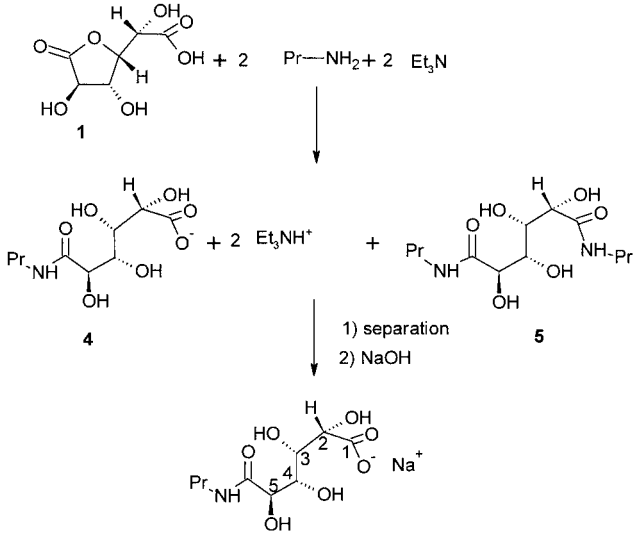
Synthesis of Propylamide

The previous strategy was not applicable here because the reaction is not quantitative and the separation of the starting reagent **1** from the monoamide is not straightforward, on account of their very small differences in solubility. The



Scheme 4. Synthesis of the octyl-, decyl-, dodecylmonoamides.

separation of the diamide **5** from the monoamide **4** was relatively easier. For this reason, we applied the same protocol, but with two equiv. of amine and a longer reaction time. In this way, glucaro-1,4-lactone acid reacted completely with the amine to form monoamide **4** as the major product and diamide **5** as the minor one (Scheme 5).



Scheme 5. Propylamide synthesis

The residual product was washed with cold acetonitrile. The diamide **5** was insoluble under these conditions. The monoamide **4** was obtained after evaporation of the acetonitrile in presence of an excess of amine.

The residual product was dissolved in a minimum amount of water and the pH was adjusted to 12.7 by adding NaOH. The excess amine was extracted with diethyl ether. (The use of ethyl acetate must be avoided because of its hydrolysis when it contacts the basic aqueous phase).

The monoamide **6**, which remained in the aqueous phase, was obtained in very good yield (ca. 80%) after freeze-drying.

Solubility and Surfactant Properties

The propyl derivative is soluble in water. The solubility of the other products in water is low, particularly when they are in their acidic forms; their solubility does not exceed 1 mM in basic solutions.

All of the amides are soluble in methanol and those having a long chain are also soluble in long-chain alcohols, such as heptanol. The amides are insoluble in most other common organic solvents.

We studied the surfactant properties of the C_8, C_{10} and C_{12} derivatives to verify their amphiphilic character and to see whether they can form micelles in water. Indeed, the formation of complexing micelles is interesting for the separation of ions by ultrafiltration.

The surface tension of solutions of the octyl, decyl and dodecyl compounds was measured, at 25 °C and pH 8 to prevent lactone formation, as a function of concentration. For the C_8 and C_{10} compounds, the solutions were limpid at concentrations $< 5 \times 10^{-3}$ mol·L^{-1}. The surface tension decreases when the concentration increases, which reveals the surfactant character of these molecules. At the solubility limit, the surface tensions of the C_8, C_{10} and C_{12} compounds are ca. 38, 33 and 39 mN·m^{-1}, respectively. No threshold of the surface tension was observed and, consequently, the eventual formation of micelles was not detected.

From the slope of the straight line obtained from a plot of the variation of the surface tension as a function of the logarithm of the concentration (i.e., the Gibbs formula),[11] we determined that the areas per polar head are 63 and 80 Å^2 for the decyl and the octyl amides, respectively. These values are on the same order of magnitude as those obtained for carboxylate surfactants, such as sodium dodecanoylsarcosinate (81 Å^2).[12] The values are greater than that found for octyltartramide (48 Å^2),[9] probably because of the bulkier hydrophilic part.

Complexation Properties in Aqueous Solutions

It was important to verify that the synthesized amides retain the complexing ability of the aldonic acids. The amide having a C_3 chain is soluble enough in water, without the formation of organized molecular systems, to allow a study of its complexation behaviour to be performed in this solvent. It was also important to verify whether a neutral complex is formed. Since these molecules were designed to be used for liquid−liquid extraction of metal ions, the formation of a neutral complex that is potentially soluble in organic solvents is an essential condition.

The aldonic acid that corresponds to the complexing part of the amides synthesized in this study is L-gulonic acid.

Table 1. Logarithm of the formation constants ($\log\beta_{pqr}$) of the complexes in the Ln^{III}/propylamide system at 25 °C in 0.1 M aqueous $NaClO_4$, obtained from potentiometric measurements

	Pr^{3+}	Eu^{3+}	Dy^{3+}	Lu^{3+}
ML_2^+	5.63 ± 0.06	5.84 ± 0.05	5.76 ± 0.04	5.06 ± 0.08
MLH_{-1}^+	−3.52 ± 0.09	−2.37 ± 0.07	−2.28 ± 0.05	−1.82 ± 0.04
MLH_{-2}	−9.44 ± 0.06	−7.88 ± 0.06	−7.60 ± 0.02	−7.35 ± 0.04
MLH_{-3}^-	−20.11 ± 0.09	−18.04 ± 0.08	−14.89 ± 0.04	−17.49 ± 0.05
The acidity constant of the ligand is 3.57 ± 0.01				

Table 2. Logarithm of the formation constants ($\log\beta_{pqr}$) of the complexes in the Ln^{III}/gulonic acid system at 25 °C in 0.1 M aqueous $NaClO_4$, obtained from potentiometric measurements

	Pr^{3+}	Eu^{3+}	Dy^{3+}	Lu^{3+}
ML_2^+	5.31 ± 0.09	5.72 ± 0.07	5.35 ± 0.09	5.98 ± 0.09
MLH_{-1}^+	−3.49 ± 0.07	−2.63 ± 0.07	−2.43 ± 0.07	−1.10 ± 0.07
MLH_{-2}	−9.40 ± 0.05	−8.35 ± 0.04	−7.83 ± 0.05	−6.97 ± 0.07
MLH_{-3}^-	−17.16 ± 0.09	−19.41 ± 0.09	−17.99 ± 0.09	−15.89 ± 0.09
The acidity constant of the ligand is 3.60 ± 0.01				

The complexation of Pr^{III}, Eu^{III}, Dy^{III} and Lu^{III} ions was studied individually with both the propylamide and gulonic acid. We have reported previously[13] a study of the Pr^{3+}/gluconic acid system in which the complexes formed in aqueous solutions were examined extensively and carefully as a function of pH.[10] This previous study helped us to investigate the Ln^{3+}/gulonic acid and propylglucaramide systems.

The set of complexes and their formation constants determined from pH-potentiometry experiments are presented in Table 1 for the propylamide and in Table 2 for gulonic acid. The distribution diagrams obtained in the case of the Pr^{3+} cation are displayed in Figure 1 and 2.

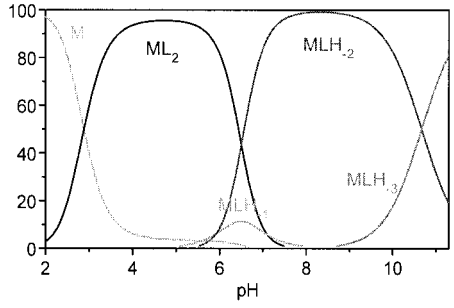


Figure 1. Distribution diagrams for Pr^{III}/propylamide (0.01 M) drawn from the results listed in Table 1 for a metal-to-ligand ratio of 1:10

We note that the gulonic acid and propylglucaramide ligands form the same system of complexes and that their formation constants are close. We conclude that the complexing properties of aldonic acids are conserved and that the presence of the amide group on the opposite side of the carboxylate group does not significantly modify their ability to complex cations.

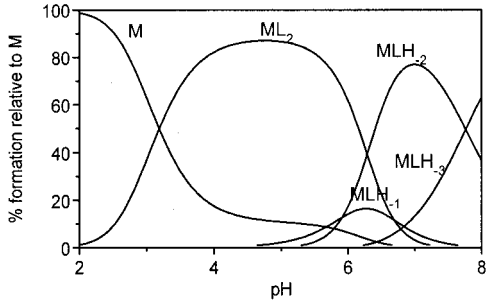


Figure 2. Distribution diagrams for Pr^{III}/gulonic acid (0.01 M) drawn from the results listed in Table 2 for a metal-to-ligand ratio of 1:5

In the acidic range of pH values, the predominant complex is ML_2. In a previous study,[13] the formation of the complex ML of gulonic acid, in addition to ML_2, was also detected, but this complex would be present in noticeable quantities only at low ligand-to-metal ratios. Under the conditions of our present experiments, it was not possible to detect the formation of this complex, probably because, if it exists, its proportion is low in the presence of the ML_2 species.

The existence of the ML_2 complex (L = gulonic acid) was confirmed by spectroscopic studies. First the stoichiometry of this species was determined by the Job method using UV/Vis spectrophotometry (see Exp. Sect.).[14] Aqueous Pr^{3+} solutions give rise to four absorption bands that can be used in applying the Job method. The pH was fixed at 4. The absorbance was measured for solutions having a total concentration of gulonic acid and Pr^{III} of 0.05 M and for different Pr^{3+}-to-ligand ratios. The results obtained at 443.9 nm are shown in Figure 3. The ligand-to-metal molar ratios measured at 443.9, 468.9 and 481.4 nm were found to be 2.27, 1.93 and 2.03, respectively, which allows us to

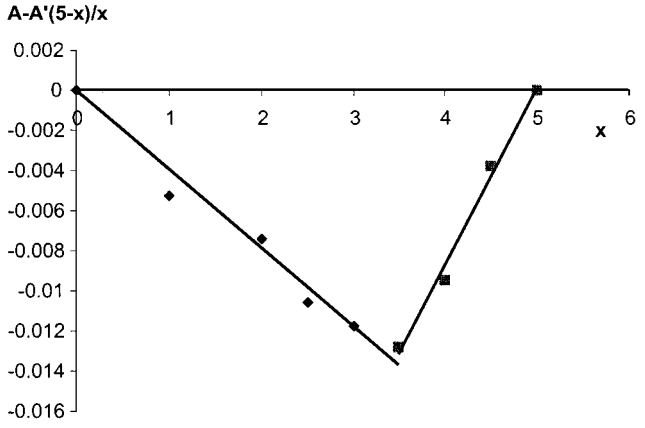


Figure 3. A plot of $[A - A'(5 - x)/x]$ as a function of x measured at $\lambda = 443.9$ nm. A: the absorbance of the solution; A′: the absorbance of the praseodynium(III) solution in the absence of ligand; x: the volume (mL) of the gulonic acid solution mixed with the Pr^{III} solution. The total volume of the solutions was 5 mL.

deduce a stoichiometry of two ligands per cation and to confirm the existence of the ML_2 species.

The interaction of gulonic acid or propylamide with the lanthanide(III) ions in the ML_2 species probably occurs through the carboxylate group. This supposition was confirmed by ^1H and ^{13}C NMR spectroscopy (Table 3−5). The ^{13}C NMR spectra indicate that the carboxylate signal is the one that is shifted the most by the presence of the paramagnetic Pr^{3+} cation, but the signal of the C-2 carbon atom is also shifted significantly, which indicates that the OH group in the α position with respect to the carboxylate function is implicated in the complexation process. The same conclusions are drawn from an analysis of the ^1H NMR spectra: the chemical shifts of the H-2 protons are affected significantly by the interaction with the Pr^{3+} cation.

Table 3. Chemical shifts (ppm) of the ^1H NMR spectroscopic signals of gulonic acid at different metal-to-ligand (M:L) ratios at pH 4

M:L	H2	H3	H4	H5	H6	H6′
0	4.17	3.88	3.82	3.83	3.72	3.62
1/25	−	3.95	3.89	3.92	3.73	3.62
1/10	6.09	4.16	3.96	4.01	3.76	3.63
$\delta = \delta_{1/10} - \delta_0$	1.92	0.28	0.14	0.18	0.04	0.01

Table 4. Chemical shifts (ppm) of the ^{13}C NMR spectroscopic signals of gulonic acid at different metal-to-ligand (M:L) ratios at pH 4.

M:L	C1	C2	C3	C4	C5	C6
0	180.92	75.79	75.11	73.14	75.32	65.31
1/25	183.13	77.28	75.39	73.16	75.27	65.36
1/10	186.26	79.49	75.76	73.17	75.19	65.38
$\delta = \delta_{1/10} - \delta_0$	5.34	3.7	0.65	0.03	−0.13	0.07

Table 5. Chemical shifts (ppm) of the ^{13}C NMR spectroscopic signals of propylamide at different metal-to-ligand (M:L) ratios at pH 4

M:L	C1	C2	C3	C4	C5	C6
0	178.41	73.69	74.29	71.90	73.60	174.89
1/100	178.59	73.81	74.32	71.92	73.61	174.91
1/15	181.03	74.60	75.40	72.05	73.61	175.01
$\delta = \delta_{1/15} - \delta_0$	2.62	0.91	1.11	0.15	0.01	0.12

Our hypothesis that the α-hydroxy group participates in coordination to the metal ion in the ML_2 complex is also supported by the fact that this OH function can lose a proton, giving rise to the MLH_{-1} complex.[10] This hypothesis may be confirmed by ^{13}C NMR spectroscopy. The ML_2 species is the only complex formed at pH 4.

In the case of complexes with paramagnetic cations, the ^{13}C NMR spectroscopic signals are shifted considerably and broadened. Only one signal for each carbon atom is observed because of the rapid exchange between the free and bound ligand molecules. With an excess of ligand these peaks are reasonably shifted and broadened. The chemical shift of the signals is related to the chemical shift of free (δ_f) and bound (δ_b) ligand and to the molar fraction of free (p_f) and bound (p_b) ligand:

$$\delta = p_b\delta_b + p_f\delta_f$$

Because $p_f = 1 - p_b$, the equation can be written as $\delta = \delta_f + p_b\,\Delta\delta$, where $\Delta\delta = \delta_b - \delta_f$.

The variation of δ for each carbon atom was studied for the Pr^{III}, Eu^{III} and Dy^{III} complexes of propylglucaramide. In all the cases, the plot of δ as a function of p_b gives straight lines, the slopes of which allow Δδ to be determined (Figure 4).

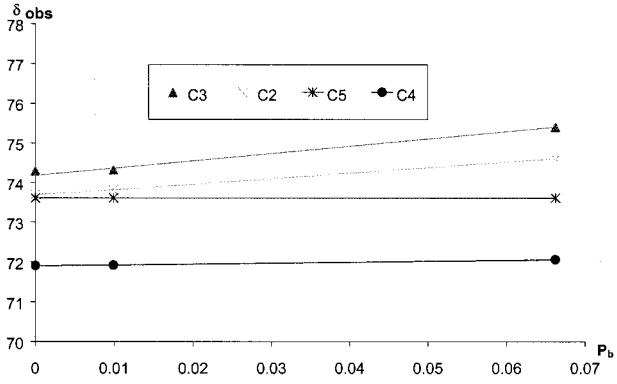


Figure 4. NMR spectroscopic chemical shifts of the different propylglucaramide ^{13}C nuclei as a function of p_b, the molar fraction of propylglucaramide bound to Pr^{III}

The values of Δδ for each carbon atom are summarized in Table 6. From these values, the part of the contact shift and that of the pseudo-contact shift can be determined.[15−18]

Table 6. Chemical shift difference (Δδ) between free ligand molecules and those engaged in the ML_2^+ complex for the different propylglucaramide ^{13}C nuclei at pH 4

		Praseodyme(III)	Europium(III)	Dysprosium(III)
Δδ	C1	40.84	−7.14	161.78
	C2	13.81	−7.64	47.89
	C3	17.57	−3.25	−49.86
	C4	2.34	−1.79	−22.02
	C5	0.07	−0.37	−3.99
	C6	1.76	−1.39	1.63

Indeed, Δδ can be written according to the following expression:

$$\Delta\delta_i^j = f_i\langle S_z\rangle_j + D_j g_i$$

The first term represents the contact shift, $\langle S_z\rangle_j$, being the projection of the total electron spin magnetization of lanthanide *j* in the direction of the external magnetic field (this value is a constant for a given lanthanide: $\langle S_z\rangle$ = 2.972, −16.685 and −28.545 for Pr, Eu and Dy, respectively); f_i is the product of the hyperfine coupling constant of carbon C_i and a coefficient.

The second term concerns the pseudo-contact (dipolar) contribution. D_j is a constant for lanthanide *j* (D_j = 10.99, −4.05 and 100 for Pr, Eu and Dy, respectively) and $g_i = k[(3\cos^2\theta - 1)/r^3]$ for an axially symmetric complex. The term *k* is a crystal field coefficient, which is supposed to be constant along the lanthanide series, θ is the angle between the principal axis of symmetry and the vector C_i-Ln^{3+}, and *r* is the distance $C_i\cdots$cation. The plot of $\Delta\delta_i^j/\langle S_z\rangle$ as a function of $D_i/\langle S_z\rangle_j$ allows the *g* coefficient to be determined from the slope of the expected straight line. The value of *f* can be determined from the intercept point. The structures of the complexes were assumed not to vary on proceeding from Pr^{III} to Dy^{III}. For the C1 (carboxylate) and C2 carbon atoms, we obtained effectively straight lines (Figure 5). The corresponding values of *f* and *g*, as well as the contact and pseudo-contact contributions, are given in Table 7.

As discussed previously[10] for the Pr^{3+}/gluconate complex, bidentate coordination of the carboxylate group would lead to a ratio of the geometrical g parameters (see Exp. Sect.) for the C1 and C2 carbon atoms that is equal to 3.6. The experimental value for the propylamide complex with Pr^{III} is ca. 3.0, which indicates that the C2 carbon atom is actually closer to the lanthanide(III) ion in the considered complex than it is in a complex having bidentate coordination of the COO^- group. This finding can be explained by monodentate coordination of the carboxylate group and an interaction of the α-OH group with the cation, but this interaction is probably weaker than that observed for manganese(II) and lead(II) species, in which five-membered chelate rings are formed.[19,20] Indeed, we detected no circular dichroism effect for the Pr^{3+}/gulonate complex at pH 4.2.[13] This observation indicates that the interaction of the α-OH group with the cation is not very strong.

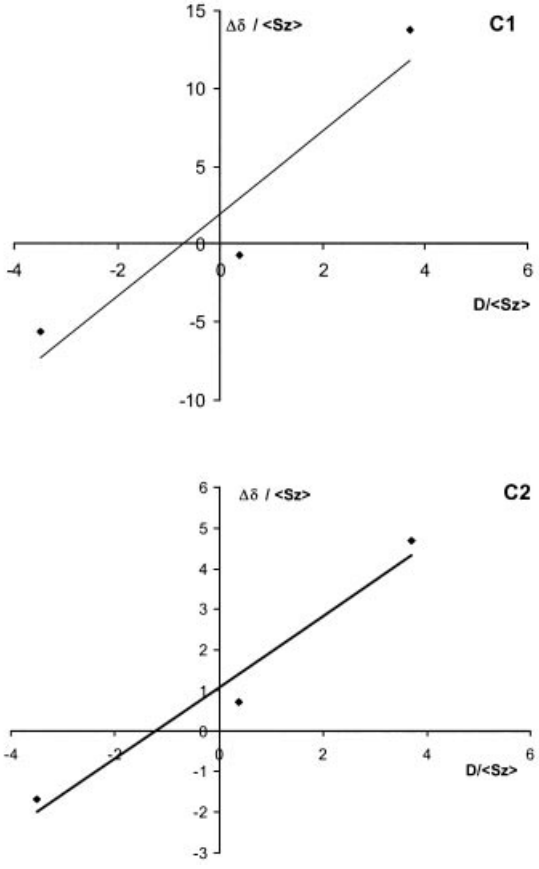


Figure 5. Δδ as a function of $D/\langle S_z\rangle$ for the C1 (top) and C2 carbon atoms of the propylamide−Ln^{III} complexes ML_2^+. For definitions of *D* and $\langle S_z\rangle$, see the text.

Table 7. Parameters f and g for the ML_2^+ propylamide complex; contact and pseudo-contact contributions to the ^{13}C NMR spectroscopic chemical shift (M = Pr, Eu and Dy). For definitions of *f* and *g*, see the text

	f	g	Pr^{III}		Eu^{III}		Dy^{III}	
			contact	pseudo	contact	pseudo	contact	pseudo
C1	1.961	2.656	5.83	29.19	−20.94	−10.76	−55.97	265.57
C2	1.072	0.876	3.19	9.62	−11.45	−3.55	−30.59	87.56
C5	0.069	−0.016	0.21	−0.18	−0.74	0.07	−1.98	−1.64
C6	0.205	0.089	0.61	0.98	−2.19	−0.36	−5.86	8.92

The hypothesis of axial symmetry around the the Ln−O (carboxylate) bond, which is justified by fluxionality about this bond and by the strong interaction of the carboxylate group when compared with the other interactions, allows us to evaluate the position of both the C2 carbon atom and the O2 oxygen atom of the α-OH group (Figure 6).

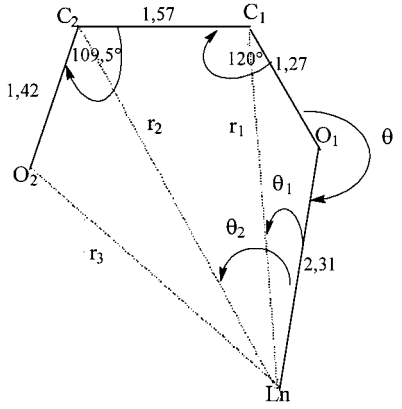


Figure 6. Representation of the complexing part of gulonic acid in its interaction with Ln^{III} cations

The values of θ_1, θ_2, r_1, and r_2 can be calculated from the value of θ. The other distances and angles indicated in Figure 6 could be evaluated from crystallographic data[20] according to a procedure described previously.[10]

We varied the value of θ to obtain the experimental g_1/g_2 ratio. The following results were obtained: θ = 219°, r_1 = 3.39 Å, r_2 = 3.85 Å, r_3 = 3.09 Å, θ_1 = 14°, and θ_2 = 38°. These values are close to those obtained for gluconic acid.[10] Although the Ln−O2 distance is much larger than the Ln−O1 distance, there is an interaction between the α-hydroxy group and the lanthanide(III) ion that probably prevents bidentate coordination of the carboxylate group and favors its deprotonation, which leads to the formation of the MLH_{-1} species. We note that coordination of the deprotonated α-OH group of one ligand to the Ln^{III} cation leads to expulsion of the other ligand molecule.

The MLH_{-1} complex is always formed concomitantly with other species, ML_2 and MLH_{-2}, in the pH range 5−8 and could not be studied in solution, either by UV/Vis or NMR spectroscopy.

At pH 8, the MLH_{-2} species is formed quantitatively. In its ^1H NMR spectra, the signals corresponding to this complex are not shifted and appear at the same value of chemical shift as those of the free ligand. By measuring the peak integrals with respect to that of an internal reference (dioxan), we determined that only the signal corresponding to the free ligand was observed. This finding means that the signals due to the bound molecules are very broad and/or shifted significantly and are not observed, with the rate of exchange between bound and free molecules being relatively slow on the NMR spectroscopic time scale.

It has been demonstrated for gluconic acid[10] that, in the MLH_{-1} complex, the coordination occurs through the carboxylate unit and the deprotonated α-OH function. Additionally, in the MLH_{-2} species, the deprotonated γ-OH function intervenes in the coordination sphere.

A study of the complexation of four different lanthanide(III) ions, from the beginning (Pr^{3+}) to the end (Lu^{3+}) of the series, with the propylamide allowed us to evaluate the evolution of the complexation strength along the series. Considering the MLH_{-2} species, we note that the formation constant β_{11-2} increases from Pr^{3+} (−9.44) to Lu^{3+} (−7.35). This complex is electronically neutral and potentially can be extracted into an organic phase. The evolution of the formation constants along the series reveals that a relative selectivity can be expected for lanthanide(III) extraction. The difference between log β_{11-2} (Lu^{3+}) and log β_{11-2} (Pr^{3+}) is ca. 2.1 for propylamide, which is a value similar to that observed for gulonic acid (2.4), but lower than that observed for EDTA (3.4).

Extraction Properties

We have shown that the amides synthesized in this work are good molecules for complexing lanthanide(III) ions. Indeed, at a ligand-to-metal ratio of 10:1, 99.9% of the metal ions are complexed. Moreover, a neutral complex (MLH_{-2}) is formed in aqueous solutions. Consequently, we envisaged that these ligands could act as extracting agents of these ions.

The first step was to find a good solvent for these molecules. The glucaramides are insoluble in dichloromethane, nitromethane, hexane, chloroform, toluene, diethyl ether, alkanes, methyl isobutyl ketone, and ethyl acetate, but they are soluble in a heptanol/nitrobenzene (50:50, v/v) mixture. The decyl derivative was more soluble than the dodecyl compound and so we used the former molecule in the extraction experiments.

First, we studied the extraction of praseodymium nitrate; the pH of the aqueous solution was varied. The results of the extractions are summarized in Table 8.

Table 8. Percentage of extracted praseodynium(III) cation as a function of pH of the aqueous solution before extraction

Value of pH before extraction	% Pr^{III} ion extracted
2.21	17
3.68	50
5.82	87

The extraction yield depends on the initial pH of the aqueous solution and decreases with pH. After extraction, the pH of the aqueous solution is lower than it was before extraction. This observation can be explained by a cation-exchange mechanism. The change in pH is compatible with the exchange of two H^+ ions per Pr^{3+} cation. The extraction reaction can be written:

$$Pr^{3+} + \overline{LH} + NO_3^- = \overline{PrLH_{-1}^+, NO_3^-} + 2H^+$$

or

$$Pr^{3+} + 2\overline{LH} + NO_3^- = \overline{PrL_2^+, NO_3^-} + 2H^+$$

The observation of a slight precipitate in the organic phase after extraction is explained by the formation of species that are too hydrophobic to be soluble in water but are still not soluble enough in the organic phase.

Extractions conducted in the presence of a co-extractant, such as tributyl phosphate or terpyridine (in a molar ratio

Table 9. Percentage of extracted Eu^{III} cations as a function of pH of the aqueous solution before extraction. The concentrations of Eu^{III} in the solutions before and after extraction were determined by atomic absorption spectrometry

Value of pH before extraction	Value of pH after extraction	% Eu^{III} ion extracted	$nH^+_{released}/nEu^{3+}_{extracted}$
5.64	2.74	91.9	2.5
5.29	2.76	83.5	2.6
3.52	2.71	78.0	2.6
3.07	2.70	74.4	1.9
2.61	2.49	40	2.5

of 2:1 with respect to the metal ion), are better because there is no more Pr^{3+} remaining in the aqueous solution after extraction (at the limit of the sensitivity of the technique used for the measurement of the praseodymium ion concentration). In this case, the extraction corresponds to the exchange of one H^+ ion. A synergistic effect occurs between decylamide and terpyridine or tributyl phosphate: the latter compounds have no efficiency when they are used alone.

In a second step, we investigated the extraction of europium(III) at a ratio of the number of moles of extractant to metal of 10. Table 9 summarizes the results of the extraction yield as a function of the initial value of pH of the aqueous phase.

The extraction yield increases with the value of pH to reach ca. 92% at an initial pH value of 5.6. For an extractant-to-metal ratio of 30 and a value of pH of 5.3, the yield is 99.9%. The value of the pH of the aqueous solution decreases after extraction and the number of H^+ ions produced by the extraction reaction was evaluated to be ca. 2.5. Consequently, we believe that, in addition to the MLH_{-1} or ML_2 species, the complex MLH_{-2} or ML_3 (although the formation of this species was not detected in the previous complexation study) is probably extracted in the organic phase. Europium(III) ions are extracted more efficiently than praseodymium(III) ions, as is expected from the formation constants of their corresponding complexes.

If terpyridine or tributyl phosphate are added to the decylamide solution, the extraction yield increases. At an initial value of pH of 5.3, these yields increase from 83% to 92% for terpyridine and 90% for tributyl phosphate; is also a synergistic effect in this case. Tributyl phosphate is commonly used in the extraction of uranium and terpyridine is among a class of molecules that have promising properties for a selective separation of lanthanides(III) and actinides(III).[21,22] The molecules we have prepared could be used as co-extractants. The presence of carboxylic groups having values of pK_a that are relatively low ($pK_a = 3.5$), could provide neutrality to the complexes and, thereby, facilitate the extraction with neutral ligands such as those mentioned above.

Conclusion

If the formation constants are considered, polyhydroxylated carboxylic acids, such as gluconic or gulonic acids and their hydrophobic derivatives, are good complexing agents for lanthanide(III) ions. Indeed, at pH 6.5, near-total complexation occurs at a ligand-to-metal ratio of only 5:1.

The branching of an alkyl chain to one end of the glucaric acid molecule, which renders it hydrophobic, does not modify the complexing properties of these compounds as demonstrated by pH potentiometry and UV/Vis and NMR spectroscopy studies.

The results obtained in liquid−liquid extraction experiments clearly show that these molecules can be considered as agents for the extraction of lanthanide(III) ions, either alone or with other compounds acting as synergetic agents. Owing to their carboxylic functions having a relative low value of pK_a (ca. 3.5), they can form mixed neutral complexes with ligands, such as pyridine and triazine derivatives, that display selective behavior toward lanthanide(III) and actinide(III) ions. Additional work is in progress to find better solvents for the glucaramides presented in this paper so that we can improve the extraction procedure.

We have also to study the potential of the hydrophobic glucaramides to act as surfactant molecules that are able to form molecularly organized systems. The separation and extraction of cations by ultrafiltration of complexing micelles is envisaged.

Experimental Section

General Remarks: All reagents and solvents were reagent grade and were used without purification. NMR spectra (^1H and ^{13}C) were recorded with a Bruker AM 400 spectrometer. The chemical shifts are reported in ppm downfield from tetramethylsilane (TMS). The IR spectra were recorded with a Perkin−Elmer 1600 FTIR spectrometer. Melting points were determined with an Electrothermal electronic apparatus and are not corrected. Elemental analyses were performed by the Centre National de la Recherche Scientifique (CNRS) at Vernaison (France). Specific rotatory power was measured on a Perkin−Elmer 141 polarimeter.

Procedure for the Preparation of Propyl-Glucaramide: Glucaro-1,4-lactone acid (**1**) (2 g, 9.5 mmol) was added to methanol (20 mL) in a round-bottom flask, and then triethylamine (1.93 g, 19 mmol) and propylamine (1.12 g, 19 mmol) in methanol were added dropwise to the mixture using a spherical dropping funnel. The reaction mixture was heated under reflux for 15 h.

The solvents were evaporated under reduced pressure; the residual product was washed with acetonitrile and then the solvent is evaporated again. The product was treated with 0.1 M aqueous NaOH

(20 mL) to obtain pH 12.7. The aqueous solution was washed with diethyl ether (10 × 10 mL) and then freeze-dried. The solid obtained was dried under vacuum.

Procedure for the Preparation of Octyl-, Decyl-, and Dodecylglucaramides: Glucaro-1,4-lactone acid (**1**) (2 g, 9.5 mmol) was added to methanol (20 mL) in a round-bottom flask and then triethylamine (1.93 g, 19 mmol) and fatty amine (9.5 mmol) in methanol were added dropwise to the mixture using a spherical dropping funnel. The reaction mixture was heated under reflux for 8 h with stirring.

The solvents were evaporated under reduced pressure. The residual product was dispersed in water and treated with 1 M HCl to obtain pH 2. The aqueous phase was extracted with ethyl acetate (4 × 30 mL) and the solvent was evaporated under reduced pressure.

Characterization of the Products

Common Characteristics: IR: $\tilde{\nu}$ = 3200−3500 (br, NH/OH), 1720 (COOH), 1620 (COO^-),1650 (CONH), 1780 (CO lactone) cm^{-1}.
Octylglucaramide (Lactone) 3a: Yield starting from **1**: 66%. M.p. 154 °C (dec.). $[\alpha]_D^{20}$ = 45.9 (*c* = 0.15, CH_3OH). ^1H NMR (CD_3OD, 25 °C): δ = 0.94 (t, $^3J_{H,H}$ = 6.9 Hz, 3 H, $CONHCH_2CH_2(CH_2)_5CH_3$), 1.37 (br. m, 10 H, $CONHCH_2CH_2(CH_2)_5CH_3$), 1.58 (br. m, 2 H, $CONHCH_2CH_2(CH_2)_5CH_3$), 3.28 (t, $^3J_{H,H}$ = 6.9 Hz, 2 H, $CONHCH_2CH_2(CH_2)_5CH_3$), 4.51 (dd, $^3J_{H,H}$ = 4.9, $^4J_{H,H}$ = 3.1 Hz, 1 H, HOOC−CHOH−CHOH−CHOH−CHOH−CONH), 4.55 (dd, $^3J_{H,H}$ = 5.9, $^4J_{H,H}$ = 3.1 Hz, 1 H, HOOC−CHOH−CHOH−CHOH−CHOH−CONH), 4.56 (d, $^3J_{H,H}$ = 4.9 Hz, 1 H, HOOC−CHOH−CHOH−CHOH−CHOH−CONH), 4.48 (d, $^3J_{H,H}$ = 5.9 Hz, 1 H, HOOC−CHOH−CHOH−CHOH−CHOH−CONH) ppm. ^{13}C NMR (CD_3OD, 25 °C): δ = 15.24 [$CONHCH_2CH_2(CH_2)_5CH_3$], 24.51−31.24 [$CONHCH_2CH_2(CH_2)_5CH_3$], 33.79 [$CONHCH_2CH_2(CH_2)_5CH_3$], 40.98 [$CONHCH_2CH_2(CH_2)_5CH_3$], 72.42, 72.73, 72.90, 82.76 (CHOH), 178.42 (CONH), 173.71 (COOH) ppm. $C_{14}H_{27}NO_7$ (303.35): calcd. C 53.32, H 8.47, N 4.36; found C 53.00, H 8.68, N 4.55.

Decylglucaramide 2b: Yield starting from **1**: 50%. M.p. 138 °C (dec.). $[\alpha]_D^{20}$ = 36.5 (*c* = 0.15, CH_3OH). ^1H NMR (CD_3OD, 25 °C): δ = 0.94 [t, $^3J_{H,H}$ = 7.1 Hz, 3 H, $CONHCH_2CH_2(CH_2)_7CH_3$], 1.37 [br. m, 14 H, $CONHCH_2CH_2(CH_2)_7CH_3$], 1.57 [br. m, 2 H, $CONHCH_2CH_2(CH_2)_7CH_3$], 3.27 [2 ddd, 2 H, $CONHCH_2CH_2(CH_2)_7CH_3$], 3.98 (dd, $^3J_{H,H}$ = 6.4, $^4J_{H,H}$ = 3.4 Hz, 1 H, HOOC−CHOH−CHOH−CHOH−CHOH−CONH), 4.14 (t, $^3J_{H,H}$ = 3.4 Hz, 1 H, HOOC−CHOH−CHOH−CHOH−CHOH−CONH), 4.24 (d, $^3J_{H,H}$ = 6.4 Hz, 1 H, HOOC−CHOH−CHOH−CHOH−CHOH−CONH), 4.25 (d, $^3J_{H,H}$ = 3.4 Hz, 1 H, HOOC−CHOH−CHOH−CHOH−CHOH−CONH) ppm. ^{13}C NMR (CD_3OD): δ = 15.24 [$CONHCH_2CH_2(CH_2)_5CH_3$], 24.55−31.52 [$CONHCH_2CH_2(CH_2)_7CH_3$], 33.88 [$CONHCH_2CH_2(CH_2)_7CH_3$], 40.96 [$CONHCH_2CH_2(CH_2)_7CH_3$], 72.98, 73.86, 75.26, 75.62 (CHOH), 175.71 (CONH), 177.11 (COOH) ppm. $C_{16}H_{31}NO_7$ (349.42): calcd. C 54.99, H 8.94, N 4.01; found C 55.73, H 8.93, N 3.96.

Dodecylglucaramide 2c : Yield starting from **1**: 40%. M.p. 126 °C (dec.). $[\alpha]_D^{20}$ = 28.5 (*c* = 0.15, CH_3OH). ^1H NMR (CD_3OD, 25 °C): δ = 0.94 [t, $^3J_{H,H}$ = 7.1 Hz, 3 H, $CONHCH_2CH_2(CH_2)_9CH_3$], 1.37 [br. m, 18 H, $CONHCH_2CH_2(CH_2)_9CH_3$], 1.57 [br. m, 2 H, $CONHCH_2CH_2(CH_2)_9CH_3$], 3.27 [2 ddd, 2 H, $CONHCH_2CH_2(CH_2)_9CH_3$], 3.98 (dd, $^3J_{H,H}$ = 6.4, $^4J_{H,H}$ = 3.4 Hz, 1 H, HOOC-CHOH−CHOH−CHOH−CHOH−CONH), 4.14 (t, $^3J_{H,H}$ = 3.4 Hz, 1 H, HOOC−CHOH−CHOH−CHOH−CHOH−CONH), 4.24 (d, $^3J_{H,H}$ = 6.4 Hz, 1 H, HOOC−CHOH−CHOH−CHOH−CHOH−CONH), 4.25 (d, $^3J_{H,H}$ = 3.4 Hz, 1 H, HOOC−CHOH−CHOH−CHOH−CHOH−CONH) ppm. ^{13}C NMR (CD_3OD, 25 °C): δ = 15.24 [$CONHCH_2CH_2(CH_2)_9CH_3$], 24.54−31.59 [$CONHCH_2CH_2(CH_2)_9CH_3$], 33.88 [$CONHCH_2CH_2(CH_2)_7CH_3$], 40.96 [$CONHCH_2CH_2(CH_2)_9CH_3$], 72.98, 73.86, 75.27, 75.623 (CHOH), 175.70 (CONH), 177.12 (COOH) ppm. $C_{18}H_{35}NO_7$ (377.47): calcd. C 57.27, H 9.44, N 3.71; found C 58.26, H 9.65, N 3.72.

Propylamide Glucarate Sodium Salt 6: Yield starting from **1**: 80%. M.p. 138 °C (dec.). $[\alpha]_D^{20}$ = 15.5 (*c* = 2, H_2O). ^1H NMR (CD_3OD,25 °C): δ = 0.98 (t, $^3J_{H,H}$ = 7.5 Hz, 3 H, $CONHCH_2CH_2CH_3$), 1.59 (s, 2 H, $CONHCH_2CH_2CH_3$), 3.24 [2 ddd, 2 H, $CONHCH_2CH_2CH_3$], 3.86 (dd, $^3J_{H,H}$ = 6.4, $^4J_{H,H}$ = 2.6 Hz, 1 H, HOOC−CHOH−CHOH−CHOH−CHOH−CONH), 4.17 (t, $^3J_{H,H}$ = 2.6 Hz, 1 H, HOOC−CHOH−CHOH−CHOH−CHOH−CONH), 3.99 (d, $^3J_{H,H}$ = 6.4 Hz, 1 H, HOOC−CHOH−CHOH−CHOH−CHOH−CONH), 4.25 (d, $^3J_{H,H}$ = 2.6 Hz, 1 H, HOOC−CHOH−CHOH−CHOH−CHOH−CONH) ppm. ^{13}C NMR (D_2O, 25 °C): δ = 11.37 ($CONHCH_2CH_2CH_3$), 22.74 ($CONHCH_2CH_2CH_3$), 41.71 ($CONHCH_2CH_2CH_3$), 71.91 (HOOC−CHOH−CHOH−CHOH−CHOH−CONH), 73.65 (HOOC−CHOH−CHOH−CHOH−CHOH−CONH), 73.77 (HOOC−CHOH−CHOH−CHOH−CHOH−CONH), 74.29 (HOOC−CHOH−CHOH−CHOH−CHOH−CONH), 174.59 (CONH), 178.71 (COOH) ppm. $C_{10}H_{27}NNa_2O_9$ (345.25): calcd. C 34.79, H 6.13, N 4.06, Na 13.31; found C 35.33, H 5.89, N 4.00, Na 13.79.

Potentiometric pH Measurements: The protonation and coordination equilibria were investigated by potentiometric titrations in aqueous solutions at a constant ionic strength (0.1 M $NaClO_4$; *T* = 298.0 ± 0.1 K) under argon atmospheres using an automatic titration apparatus including a 721 NET Titrino (Metrohm) autoburette and Orion 9103SC type combined glass electrode. The species formed in the systems were characterized by the following general equilibrium process:

$$p\,M + q\,L + r\,H \Leftrightarrow M_pL_qH_r \quad (\beta_{pqr})$$

$$\beta_{pqr} = \frac{[M_pL_qH_r]}{[M]^p[L]^q[H]^r}$$

[where M denotes the lanthanide(III) cation and L is the non-protonated ligand molecule]. Charges are sometimes omitted for simplicity, but they can be calculated readily by taking into account that the fully protonated ligands are denoted LH. A detailed description of the experimental procedure and the data evaluation (using the PSEQUAD computer program[23]) has been reported earlier.[24]

The protonation and the complex formation constants were determined from five and ten independent titrations (ca. 100 data points per titration), respectively. The metal-to-ligand ratios were varied between 1:1 and 1:10, using lanthanide(III) concentrations ranging from 5 × 10^{-4} to 5 × 10^{-3} M. Potentiometric data obtained between pH 2 and 11.3 were used for the evaluation.

For the analysis of the titration curves, the formation of the hydroxo complex $MOH^{2+}(MH_{-1})$ was taken into consideration, with the following values for the formation constants (log β_{10-1}): −8.82, −8.58, −8.37, and −8.17 for Pr^{3+}, Eu^{3+}, Dy^{3+}, and Lu^{3+}, respectively.[25]

The solutions were kept at pH 7 to avoid lactonization. Perchloric acid was added just before titration to begin measurements at pH 2.

In the case of the propylamide ligand, and for low ligand-to-metal ratios or high metal concentrations, the complex MLH_{-1} precipitates in the solution and redissolution occurs when the MLH_{-2} complex is formed, even though this species is a neutral one. The presence of the propyl group could explain the more hydrophobic character of the corresponding complex relative to that of gulonic acid.

UV/Vis Spectrophotometry (Job method[14]): Visible absorption spectra were recorded with a Varian Cary 3E UV/Vis spectrophotometer. Solutions were obtained by mixing different volumes of Pr^{III} (0.05 M) and D-gulonic acid (0.05 M). The value of pH was adjusted to 4 by the addition of NaOH. The total volume was 5 mL. The term A represents the absorbance of the solution; x is the volume of the gulonic acid solution; A' corresponds to the absorbance of the praseodynium(III) solution in the absence of ligand. The plot of $A - A'[(5 - x)/x]$ as a function of x gives two straight lines, the intersection point of which corresponds to the x_e value. The x_e value allows us to determine n from the following formula: $n = x_e/(5 - x_e)$.

NMR Spectroscopy: ^{13}C and ^{1}H NMR spectra for the complexation studies were recorded with a Bruker DRX 400 apparatus at 100.6 and 400 MHz, respectively. ^{1}H NMR spectroscopic chemical shifts in aqueous solutions were measured relative to DSS (sodium 3-trimethylsilyl-1-propanesulfonate).

Surface Tension Measurements: The surface tension was measured at 25 °C using the Wilhelmy plate method (Krüss digital tensiometer K10T).

Extraction Experiments: A 2×10^{-3} M $Pr(NO_3)_3$ solution (2 mL) was placed in contact with an 8×10^{-3} M decylamide solution (5 mL) in a heptanol/nitrobenzene mixture at 20 °C. Under these conditions, the extractant-to-cation ratio was 10:1. The Pr^{III} concentration in the aqueous phase was monitored by UV/Vis spectrometry. Europium nitrate solution ($[Eu^{III}] = 8 \times 10^{-4}$ M; 5 mL) was shaken at 20 °C with a 3.2×10^{-3} M decylamide solution (12.5 mL) in a 50:50 heptanol/nitrobenzene mixture. The Eu^{III} concentration was measured by atomic absorption spectrometry.

Atomic Absorption: Measurements were performed on a Varian AA-1275 atomic absorption spectrophotometer, calibrated using 5×10^{-5}, 10^{-4}, and 2×10^{-4} M europium(III) solutions.

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