Complexation of Lanthanide(III) Ions with Polyhydroxy Carboxylic Acids in Aqueous Solutions

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Keywords: Lanthanides / Cations / Acidity / Complexation / NMR spectroscopy

The complexation of lanthanum(III), europium(III), dysprosium(III), erbium(III), and lutetium(III) with D-gluconic acid (LH) was studied by pH potentiometry and NMR. The set of complexes formed in aqueous solutions and their stability constants β were determined, and the results were compared to those previously found for praseodymium(III) (S. Giroux et al., Polyhedron **2000**, *19*, 1567). A regular evolution of the β values was observed along the lanthanide series, particularly for the neutral complex MLH_{-2} (where two hydroxy functions were deprotonated) with a selectivity similar to that of EDTA. For the ML_2^+ complex, where the ligand was coordinated via the carboxylate groups, the analysis of the ^{13}C NMR pseudocontact shift showed that the carboxylate group was not bidentate and that there was a participation of the α-hydroxy group in the coordination. The study of the complexation of Pr^{III} with other hydroxy carboxylic acids: glyceric, threonic, 2-hydroxybutanoic, and 3-hydroxybutanoic acids confirms that in the complex MLH_{-2} the deprotonated hydroxy groups, that intervene in the coordination with the metal ion, are those in α and γ positions relative to the carboxylate group. (© Wiley-VCH Verlag GmbH, 69451 Weinheim, Germany, 2002)

Introduction

Polyhydroxycarboxylic acids, particularly D-gluconic acid (**I**), have good complexing properties, and find more and more practical applications in the industrial domain.[1] The complexing ability of gluconic acid towards metallic ions is well known[2−11] even if the structure of the complexes formed in solution is not always well reported. The determination of the role and the nature of the alcohol groups concerned by the coordination to the metal ion is a difficult problem to solve. The combination of several techniques (potentiometry, NMR, circular dichroism) has proved to be efficient in obtaining such information.[7,11]

Lanthanide(III) ions are hard acids and their interaction with carboxylate groups or deprotonated hydroxy functions is strong.[2,10−12] The complexation of the praseodymium(III) ion with D-gluconic acid in aqueous solutions has been thoroughly studied[11] by potentiometry, UV/Vis spectrophotometry, NMR, and circular dichroism (CD) experiments. It was shown that six different complexes are formed in solution. Among them there are species where deprotonated OH groups participate in the coordination. It must also be noted that at neutral pH values, the formation of a neutral complex takes place that could, using a more hydrophobic ligand, allow for the extraction of this species into an organic phase.[13]

This work is devoted to a study of the complexation of the La^{III}, Eu^{III}, Dy^{III}, Er^{III}, and Lu^{III} ions with D-gluconic acid in order to know if there is an evolution of the complexing ability of this ligand along the lanthanide series, and whether this induces a possible selectivity. The complexes and their stability constants were determined by pH potentiometry. An NMR study allowed us to draw conclusions on the structure of the complexes.

In order to enhance our knowledge on the binding sites of gluconic acid in complexes where alcohol functions are deprotonated, we also studied the complexation of the praseodymium(III) ion with glyceric acid (**II**), threonic acid (**III**), 2-hydroxybutanoic acid (**IV**), and 3-hydroxybutanoic acid (**V**). Gluconic acid and threonic acid are polyhydroxylated carboxylic acids with three or four carbon atoms, and two or three OH functions, respectively. The presence of a primary alcohol function in the β or γ position relative to the carboxylic function, instead of a secondary alcohol one in gluconic acid, may generate variations in the complexing abilities. The two studied butanoic acids have only one OH function in α or β position relative to the carboxylic function. It was interesting to see if the presence of only one OH group in the ligand considerably lowered the complexation power of these molecules.

Results

Complexes of La^{III}, Pr^{III}, Eu^{III}, Dy^{III}, Er^{III}, and Lu^{III} with D-Gluconic Acid

Potentiometric measurements were made on mixtures of lanthanide(III) cations and D-gluconic acid as a function of

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pH and for several ligand to metal ratios. For ligand/metal ratios smaller than 5:1 a precipitate was observed at $pH < 11$ (Table 1). For higher ratios no precipitation occurred. In the case of the Dy^{III} and Er^{III} cations, for small ligand/metal ratios, high concentrations, and for $pH > 9$, the viscosity of the solutions increased with time, and the formation of a gel was observed after a few minutes or a few tens of minutes.

Table 1. pH of precipitation for solutions of gluconic acid (L) and lanthanide(III) ions (M) for different [L]/[M] ratios; the metal ion concentration was varied from ca. 1×10^{-3} to ca. 5×10^{-3} $mol{\cdot}L^{-1}$ for a nearly constant gluconic acid concentration of ca. $6-8 \times 10^{-3}$ $mol{\cdot}L^{-1}$

[L]/[M]	La^{III}	Pr^{III}	Eu^{III}	Dy^{III}	Er^{III}	Lu^{III}
1:1	9.0	8.5	7.4	8.2	7.4	7.4
1.5:1	9.9	8.5	8.2	8.3	7.5	[a]
3:1	10.1	8.9	9.5	[b]	[b]	7.8
5:1	[b]	[b]	[b]	[b]	[b]	[b]

[a] Not measured. [b] No precipitation observed up to pH = 11.3.

These experiments allowed us to determine that the same set of six complexes was formed for the La^{III}, Eu^{III}, Dy^{III}, Er^{III}, and Lu^{III} cations as for the Pr^{III} cation:[11] ML^{2+}, MLH_{-1}^{+}, MLH_{-2}, ML_2^{+}, ML_2H_{-1}, and $ML_2H_{-3}^{2-}$, and in addition, the complex $M_2L_2H_{-5}^{-}$. There were two exceptions: $ML_2H_{-3}^{2-}$ could not be found for Eu^{III} and MLH_{-1}^{+} for Lu^{III}. The formation constants of all these species are summarized in Table 2.

Distribution diagrams of these complexes as a function of pH are represented by Figure 1. At pH = 4, and for a gluconic acid concentration of 0.5 $mol{\cdot}L^{-1}$, and for large ligand/metal ratios, the complex ML_2 was formed in 100% yield.

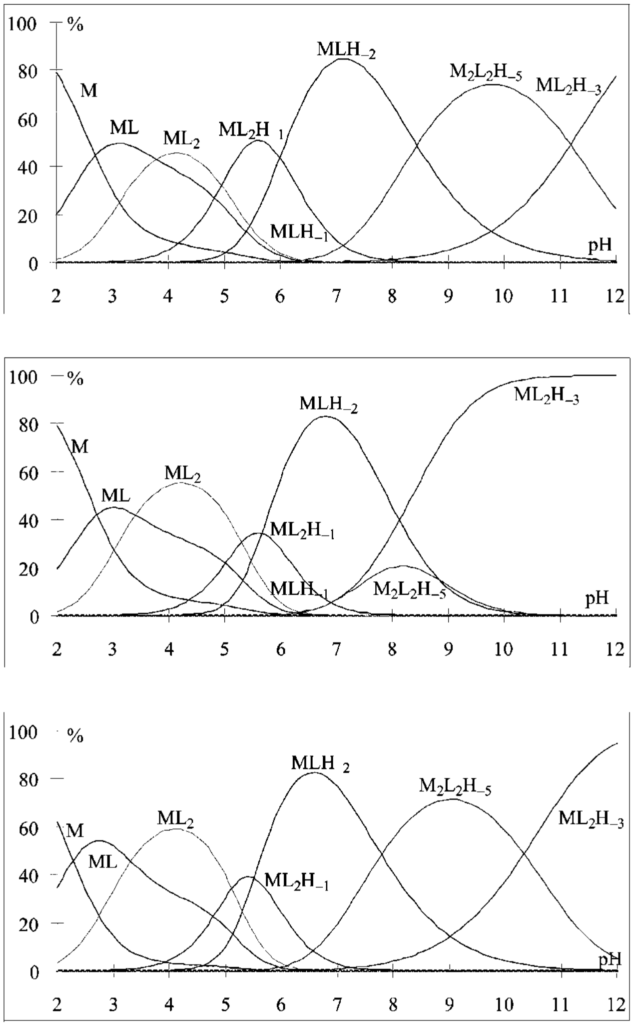


Figure 1. Distribution diagrams of the complexes formed at 25 °C between gluconic acid (5.10^{-3} $mol{\cdot}L^{-1}$) and Dy^{III} (top), Er^{III} (center), and Lu^{III} (bottom) as a function of pH, for a ligand/metal ratio of 5:1

A ^{13}C NMR study of this complex was performed. For the diamagnetic cations, La^{3+} and Lu^{3+}, no shifts relative to the free ligand were observed, but for the paramagnetic ions the peaks were considerably shifted and broadened. To observe the signals, large ligand/metal ratios (10:1 to 250:1) were used. Only one mean signal for each carbon atom was detected because of a rapid exchange between free and bound gluconic acid. With an excess of free ligand the signals are reasonably shifted and broadened.

The chemical shift δ of the signals is related to the chemical shift of free (δ_f) and bound (δ_b) gluconic acid, as well as the molar fraction of free (p_f) and bound (p_b) ligand: $\delta = p_b\,\delta_b + p_f\,\delta_f$. As $p_f = 1 - p_b$, δ can be written as $\delta = \delta_f + p_b \cdot \Delta\delta$, where $\Delta\delta = \delta_b - \delta_f$.

Table 2. Formation constants ($\log \beta_{pqr}$) for the different complexes formed in the system Ln^{III}/gluconic acid [$T = 25$ °C, $I = 0.1$ $mol{\cdot}L^{-1}$ ($NaClO_4$) determined from pH potentiometry measurements]

	La^{III}	Pr^{III} [a]	Eu^{III}	Dy^{III}	Er^{III}	Lu^{III}
ML	2.91 ± 0.02	2.78 ± 0.03	2.82 ± 0.05	3.21 ± 0.03	3.20 ± 0.02	3.58 ± 0.03
MLH_{-1}	−4.25 ± 0.03	−3.34 ± 0.02	−2.53 ± 0.03	−2.46 ± 0.10	−2.42 ± 0.04	X
MLH_{-2}	−11.65 ± 0.01	−10.09 ± 0.01	−8.65 ± 0.01	−7.58 ± 0.01	−7.45 ± 0.01	−6.69 ± 0.02
ML_2	4.85 ± 0.08	5.57 ± 0.03	5.74 ± 0.04	5.82 ± 0.04	5.97 ± 0.02	6.41 ± 0.03
ML_2H_{-1}	−2.29 ± 0.15	−0.67 ± 0.05	0.33 ± 0.05	0.87 ± 0.05	0.67 ± 0.04	1.28 ± 0.04
ML_2H_{-3}	−19.84 ± 0.05	−19.13 ± 0.08	X	−14.94 ± 0.09	−13.13 ± 0.07	−13.30 ± 0.06
$M_2L_2H_{-5}$	−31.44 ± 0.11	X	−26.21 ± 0.25	−20.59 ± 0.04	−20.21 ± 0.03	−18.16 ± 0.07
MH_{-1}	−9.33	−8.82	−8.58	−8.37	−8.26	−8.17

[a] From ref.[11]

The plot of δ as a function of p_b for each carbon atom for the Pr^{III}, Eu^{III}, and Dy^{III} complexes gives straight lines, the slope of which allows the determination of Δδ. An example of plot is given in Figure 2. The Δδ values are summarized in Table 3.

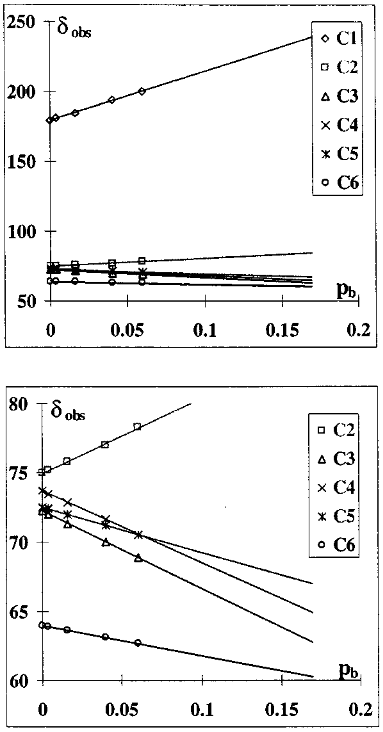


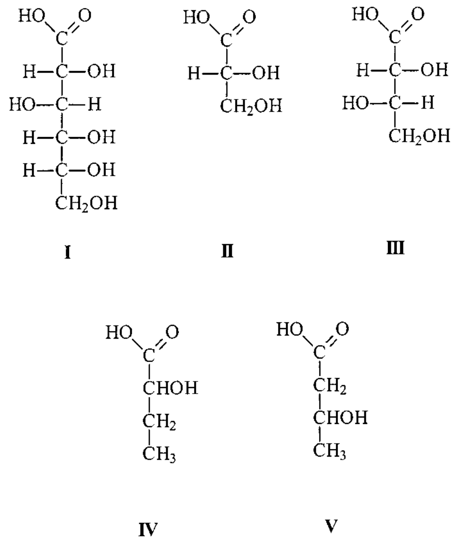
Figure 2. NMR chemical shifts of the different gluconic acid ^{13}C nuclei as a function of p_b, the molar fraction of gluconic acid bound to Dy^{III}

Table 3. ^{13}C NMR chemical shift difference Δδ (in ppm) between free gluconic acid and this ligand bound to various Ln^{III} ions in the ML_2 complexes

	Pr^{III}	Eu^{III}	Dy^{III}
C^1	32.7	−21.2	349.9
C^2	20.2	−7.8	54.0
C^3	2.5	−6.7	−55.4
C^4	−4.8	4.4	−51.8
C^5	−2.4	1.2	−32.4
C^6	−1.9	1.0	−22.0

Complexation of Pr^{III} with Glyceric, Threonic, 2-Hydroxybutanoic and 3-Hydroxybutanoic Acids

In order to determine the influence of the number and the position of hydroxy groups on the complexation behaviour of the polyhydroxy carboxylic acids, a potentiometric study of the complexation of Pr^{III} by D-glyceric acid (**II**), L-threonic acid (**III**), 2-hydroxybutanoic acid (**IV**), and (*R*)-3-hydroxybutanoic acid (**V**) was performed (Scheme 1).



Scheme 1

The pK_a values of these acids are 3.52, 3.48, 3.64, and 4.34, respectively (gluconic acid: $pK_a = 3.47$). These values are in agreement with those reported in the literature. For glyceric acid, values of 3.32 ($I = 0.1$ mol·L^{-1}, KNO_3)[14] and 3.54 ($I = 2$ mol·L^{-1}, $NaClO_4$) are reported.[15] The pK_a value of 2-hydroxybutanoic acid from the literature data was found to be 3.70 or 3.80[16] at 25 °C and $I = 0.1$ mol·L^{-1}, that of 3-hydroxy-butanoic acid is reported to be 4.31 for an ionic strength of $I = 0.5$ mol L^{-1} in $NaClO_4$ at 25 °C[17] and 4.40 at 31 °C for $I = 0.1$ mol·L^{-1}.[18]

In the presence of Pr^{III}, the formation of a precipitate was observed at pH ≈ 8 for glyceric and threonic acids, and at pH ≈ 7 for the two butanoic acids. For **III**, **IV**, and **V** the complex ML was formed (the ligands, where the carboxylic function is not deprotonated, are noted LH) with $\log \beta_{110} = 2.76 \pm 0.04$, 2.56 ± 0.01, and 2.08 ± 0.02, respectively (2.78 ± 0.03 for gluconic acid[11]). It was the only complex that could be detected with **IV** and **V**. For **III**, the complexes MLH_{-1} and MLH_{-2} were also present ($\log \beta_{11-1} = -3.97 \pm 0.03$ and $\log \beta_{11-2} = -11.78 \pm 0.02$, compared to the corresponding values found for gluconic acid, −3.34 and −10.0[11]). Additionally the ML_2 species ($\log \beta_{120} = 5.19 \pm 0.04$) was also formed in the case of glyceric acid ($\log \beta_{120} = 5.11 \pm 0.02$; for gluconic acid, $\log \beta_{120} = 5.57$). For **II**, in addition to ML_2, the complex ML_2H_{-2} and the binuclear species M_2L_2 and $M_2L_2H_{-2}$ were also detected ($\log \beta_{12-2} = -10.82 \pm 0.06$, $\log \beta_{220} = 7.79 \pm 0.04$, and $\log \beta_{22-2} = -6.61 \pm 0.04$, respectively). It should be noted that in this case, M_2L_2 and $M_2L_2H_{-2}$ could be replaced by ML and MLH_{-1}, but the fit is not as good, and the formation constant for ML is too low and not consistent with that of ML_2.

The ^1H and ^{13}C NMR study of these systems was made under conditions where the signals were not too broad nor significantly shifted, i.e. for large L/M ratios. For such L/M ratios, from the potentiometric results at pH < 7, the mean species was ML_2 for glyceric acid, a mixture of ML and ML_2 (ML_2 predominant) for threonic acid, and ML for the butanoic acids (Figure 3). This study confirms the complexation by the carboxylate group. The most shifted ^{13}C NMR signals are those corresponding to the COO^- group and those corresponding to hydrogen atoms (^1H NMR) on the carbon atom adjacent to the carboxylate group.

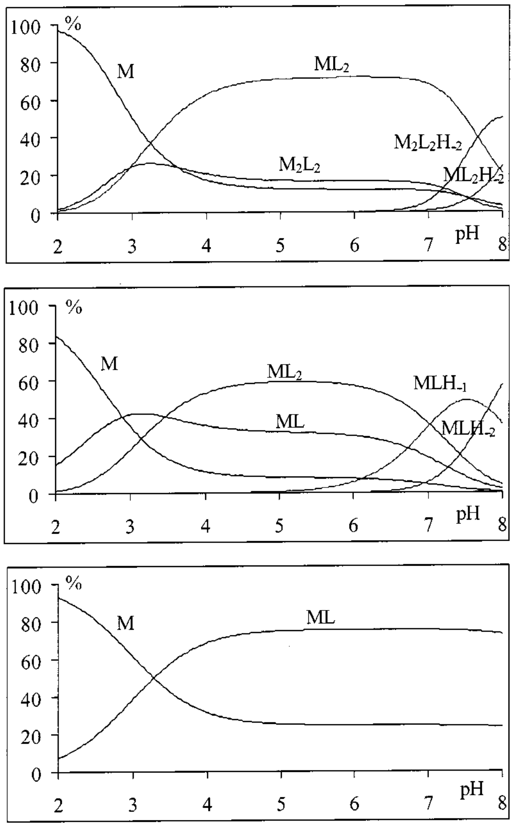


Figure 3. Distribution diagrams for the complexes formed at 25 °C between Pr^{III} and glyceric acid (top), threonic acid (center), and 2-hydroxybutanoic acid (bottom) as a function of pH; the concentration of the ligand was 0.01 mol·L^{-1} and the ligand/metal ratio was 5:1

Discussion

The systems of complexes formed between the six studied trivalent lanthanides and gluconic acid are very similar from one cation to another; only one species among seven is missing for Pr^{3+} ($M_2L_2H_{-5}$), Eu^{3+} (ML_2H_{-3}), and Lu^{3+} (MLH_{-1}). For an individual species, the formation constants are of the same order of magnitude, but show a regular increase along the lanthanide series with very few exceptions (Table 2). This can be put in relation with the increase in electrostatic interaction between the hard lanthanide ions, the radii of which decrease along the series, and the negatively charged oxygen atoms of the ligand that act as hard bases.

This continuous increase in the formation constants is shown for the complex MLH_{-2} in Figure 4. The amplitude in the variation from La^{3+} to Lu^{3+} is practically equal to five logarithmic units in this case, a value that can be compared to that obtained with the ethylenediamine tetraacetate ion (EDTA), 4.38.[19-20] The selectivity of gluconic acid towards lanthanide(III) ions through the formation of MLH_{-2} complexes is better than that of EDTA. This is important if one notes that MLH_{-2} is a non-charged species that can be extracted into an organic solvent. Gluconic acid, or a more hydrophobic form of this ligand, would be a good candidate for the liquid-liquid extraction of the trivalent lanthanide ions.[13]

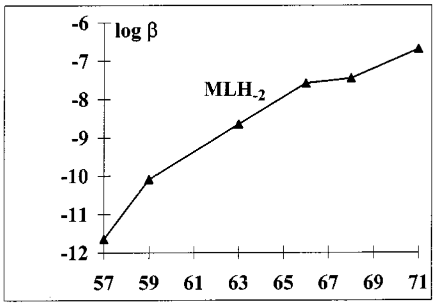


Figure 4. Variation of the log β_{11-2} value (MLH_{-2} complex) as a function of the lanthanide atomic number

The structure of the different Pr^{III} complexes has been largely discussed in a previous publication,[11] from potentiometric, NMR, UV/Vis, and CD experiments. For the ML_2 complex it is clear that the coordination takes place via the carboxylate group as demonstrated earlier,[11] but there is a presumption that the hydroxy group in α-position relative to the carboxylate group participates in the coordinating to the metal ion. Moreover, this OH function is that one that loses a proton, giving rise to the MLH_{-1} complex. The NMR study of systems with various paramagnetic cations may allow us to obtain more information on the structure of the ML_2 complex that can be formed at 100% without the presence of any other species at pH = 4.0. As was shown above, we could obtain the $\Delta\delta$ value for the different carbon atoms of gluconic acid ($\Delta\delta = \delta_b - \delta_f$). From these values it is possible to determine the part of the contact shift and that of the pseudo-contact shift in $\Delta\delta$:[21-23] $\Delta\delta_i^j = f_i \langle S_z \rangle_j + D_j \cdot g_i$.

The first term of the sum represents the contact shift, $\langle S_z \rangle_j$ is the projection of the total electron spin magnetization of the lanthanide j on the direction of the external magnetic field, and f_i is the product of the hyperfine coupling constant of carbon C_i and a coefficient. The second term is related to the dipolar (pseudo-contact) contribution. D_j is a constant for the lanthanide j, and g_i for a complex with an axial symmetry is defined as $g_i = k\,[3\cos^2(\theta - 1)]/r^3$, where k is a crystal field coefficient that is supposed to be constant along the lanthanide series; θ the angle between the principal axis of symmetry and the vector $C_i{-}Ln^{3+}$ and r, the distance $C_i{-}Ln^{3+}$. The f and g coefficients can be determined from the plot $\Delta\delta_i^j/\langle S_z \rangle_j$ as a function of $D_j/\langle S_z \rangle_j$. In this case this plot must be a straight line, the slope of which is g_i. The structure of the complexes was not supposed to vary along the lanthanide series. The plot for the

C^1 (carboxylate) and C^2 carbon atoms are shown in Figure 5. The f and g values deduced from these plots and the corresponding contact and pseudo-contact contributions to the total shift are reported in Table 4. With the exception of the C^3 carbon atom, the pseudo-contact term is always larger than the contact term for the Pr^{3+} and Dy^{3+}ions. In the case of Eu^{3+}, the pseudo-contact part overcomes the contact term only for the C^1, C^4, and C^6 carbon atoms.

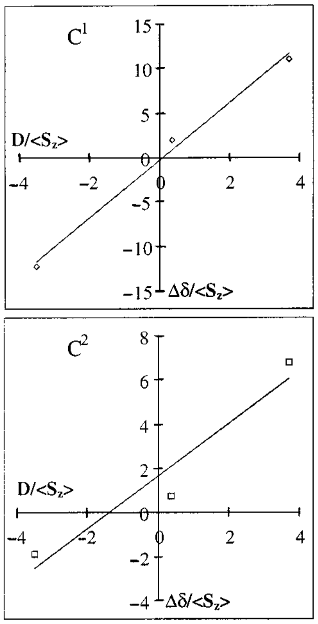


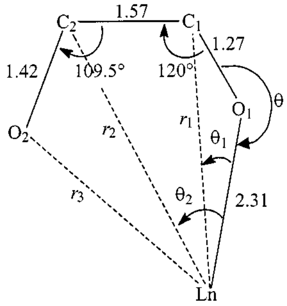
Figure 5. Plots $\Delta\delta/\langle S_z\rangle$ as a function of $D/\langle S_z\rangle$ for the C^1 (carboxylate) and C^2 carbon atoms of gluconic acid (L) in the complex PrL_2^+

Table 4. The f and g parameters for the ML_2 complex; contact and pseudo-contact contributions to the ^{13}C NMR chemical shift (M = Pr, Eu, and Dy)

	f	g	Pr^{III}		Eu^{III}		Dy^{III}	
			contact	pseudo	contact	pseudo	contact	pseudo
C^1	−0.3803	3.2406	−1.13	35.61	4.06	−13.12	10.86	324.1
C^2	1.6539	1.1935	4.91	13.11	−17.67	−4.83	47.21	119.4
C^3	1.1666	−0.1579	3.47	−1.73	−12.46	0.64	−33.30	−15.79
C^4	0.0245	−0.4783	0.07	−5.26	−0.26	1.94	−0.70	−47.83
C^5	0.1243	−0.2712	0.37	−2.98	−1.33	1.10	−3.55	−27.12
C^6	0.0542	−0.1952	0.16	−2.14	−0.58	0.79	−1.55	−19.52

From the g value, structural information can be obtained for the ML_2 complex. The question arises whether the gluconic acid carboxylate group acts as a bidentate ligand, as observed in the case of the acetate ion,[24] or if it can be envisaged that there is a participation of the hydroxy group borne by the C^2 carbon atom, leading to a monodentate coordination of the carboxylate head. The second type of coordination was observed in the solid state for manganese(II) D-gluconate dihydrate[25] and lead D-gluconate,[26] where there is a strong interaction of the hydroxy group with the metal ions leading to the formation of a five-membered chelate ring; in this case the metal−oxygen distances are of the same order of magnitude either for one of the oxygen atoms of the carboxylate group or the oxygen atom of the α-hydroxy group.

In the solid $Pr(acetate)_3{\cdot}H_2O$, two acetate ions are bidentate (one of the oxygen atoms is bonded to a second Pr^{3+} ion) and the Pr−O−C−O planes are planar to within 0.06 Å.[24] If the situation is the same for the Pr gluconate system, the ratio of the g values for the C^1 and C^2 carbon atoms can be easily calculated; the angles θ for these two carbon atoms are the same regardless of the position of the principal axis of the complex (since the C^2 carbon atom is also in the Pr−O−C−O plane because of the planar structure of the carboxylate group). The distances r may be evaluated from the data of ref.[24] The calculated ratio is ca. 3.6, to be compared to the experimental value of 2.7 (Table 4). Obviously, the calculated value is too high, indicating that the C^2 carbon atom is probably closer to the lanthanide(III) ion in the gluconate complex than in the acetate complex. This leads us to propose a structure in which the carboxylate ion is monodentate and the α-hydroxy group interacts with the Ln^{III} ions. Nevertheless, this interaction in probably weaker than that observed in the solid state for the manganese(II) and lead(II) species, probably due to a competition with the hydrogen bonding of the water molecules. Indeed, no CD effect was observed for this complex in the case of Pr^{III} ion, indicating that the α-hydroxy group is not tightly bound to the cation. The position of the C^2 carbon atom (and that of the O^2 oxygen atom of the α-hydroxy group; see Scheme 2) may be evaluated from the g_1 and g_2 values ($g_1/g_2 \approx 2.7$). We made the assumption of an axial symmetry around the $Ln{-}O^1$ (acetate) bond, justified by fluxionality (rapid rotation) about this bond and by the fact that the coordination interaction with the carboxylate group is strong, compared to the other possible interactions.



Scheme 2

The calculation of θ_1, θ_2, r_1, and r_2 was made by varying the angle θ, according to Scheme 2. The indicated angles and distances were estimated from the crystallographic structure discussed in ref.[26] for lead gluconate after correcting for the differences in the ionic radii of the Pb^{2+} and Pr^{3+} ions. There are two solutions for θ (130° and 210°), but only the second one gives rise to an interaction with the O^2 oxygen atom. The following values are consequently found: $\theta_1 = 10°$, $\theta_2 = 30°$; $r_1 = 3.46$ Å, $r_2 = 4.06$ Å, $r_3 = 3.39$ Å. It can be noted that the $Ln{-}O^2$ distance (ca. 3.4

Å) is much larger than the Ln−O^1 distance (2.3 Å), but that this weak interaction with the α-hydroxy group probably hinders the bidentate coordination of the carboxylate group and predisposes the OH group to be deprotonated in order to form the ML_2H_{-1} species.

The complexation of the lanthanide cations by hydroxy groups is important for the stability of the complex and it is probably a crucial stage before the deprotonation of these functions leading to an interaction with an alkoxide ion. We have just seen that in the complex ML_2 the complexation occurs via the carboxylate group, but that the cation also interacts with the α-hydroxy group. Previously, we concluded on the basis of CD results[11] that in the complex MLH_{-2} for the system Pr^{3+}/gluconic acid, the complexation occurred via a second deprotonated hydroxy function in addition to the deprotonated α-hydroxy group. Furthermore, this function was probably that in γ-position relative to the carboxylate group. If it is effectively the case, there is probably an interaction between the γ-hydroxy group and the cation, which occurs before the deprotonation of this function. If there is no tertiary alcohol function in γ-position, the complexation would undoubtedly occur via a β-hydroxy group, but it is probably energetically less favourable. In order to prove these assumptions, we studied some hydroxylated carboxylic acid ligands. The formation constants of the complexes ML and ML_2 for gluconic acid, threonic acid, and glyceric acid, which have nearly identical pK_a values, are very similar (practically identical for ML and slightly higher for ML_2 in the case of gluconic acid compared to the two other ligands with a difference of about 0.4 pK units).

It must be noted that all these ligands have a hydroxy function in α-position relative to the carboxylate group. For the two hydroxybutanoic acids the log β values are smaller than for the other ligands, contrary to what is generally observed: in the case of a hard base−hard acid interaction, log β(M + L → ML) usually increases when pK_a increases for ligands having comparable structures. The lower value observed for 2-hydroxybutanoic acid compared to **I**, **II** and **III**, seems to indicate that the OH groups other than those in the α-position also have a (weak) participation in complexation. The 3-hydroxybutanoic acid exhibits a significantly lower log β value because of the lack of an OH group in α-position relative to the carboxylate group. It must also be noted that the two hydroxybutanoic acids do not form MLH_{-1} and MLH_{-2} complexes.

The log β_{11-1} values ($M^{3+} + L^- \leftrightarrow MLH_{-1}{}^+ + H^+$) for threonic acid is ca. 0.6 logarithm units lower than that for gluconic acid, indicating a small difference in the complexation strength of the two molecules. For gluconic acid, the γ-OH group plays a role in the complexation of Pr^{3+} in MLH_{-1} (this group deprotonates to form MLH_{-2}). For threonic acid the γ-OH group is not a secondary alcohol function, but a primary alcohol function with a higher acidity constant.

We can consider two possibilities: either the β-OH group intervenes in the complexation of the Pr^{3+} ion, inducing geometrical constraints due to the complexation of two consecutive OH functions (less favourable than those observed with the α- and γ-OH coordinations), or the γ-OH group interacts with the metal ion with a lower strength than in the case of gluconic acid. This second possibility would probably be due to the fact that there is a loss in hydrogen bonding with the solvent water molecules (there are no other OH groups in δ- and ε-positions unlike gluconic acid).

The difference in the complexation behaviour is amplified if we consider the formation of the MLH_{-2} complex: the β_{11-2} value for threonic acid is much lower than that for gluconic acid with a difference in the log β values of 1.8 logarithmic unit. All these remarks seem to prove that the hydroxy group in the γ-position is effectively the second deprotonated hydroxy function in gluconic acid.

Conclusion

This study confirms the view that gluconic acid is a good complexing agent towards the trivalent lanthanide ions. It also shows that the presence of five hydroxy functions in the chain is important for the stability of the complexes, either by their direct intervention in the complexation or by their interaction with solvent molecules in aqueous solutions. Polyhydroxy carboxylic acids with a smaller number of carbon atoms (and consequently of hydroxy functions) are less efficient.

The observation of a relative selectivity of complexation along the lanthanide series allows us to envisage using gluconic acid derivatives as extracting selective agents for lanthanides. For this purpose, hydrophobic derivatives must be synthesized − keeping the complexing ability of this molecule, but with a high solubility in organic solvents − for a use in liquid-liquid extraction. We already reported the preparation of hydrophobic derivatives of tartaric acid, HOOC−CHOH−CHOH−CONHR, where R is a long alkyl chain.[13] The preparation of hydrophobic ligands with a longer hydrophilic chain (with more OH functions) is in progress.

Experimental Section

Materials: Lanthanum, praseodymium, europium, dysprosium, and erbium nitrates (Strem Chem, 99.9%), lutetium perchlorate (Alfa Products, 99.9%), and sodium perchlorate (Fluka, 99%) were used without further purification. The concentration of the lanthanide(III) solutions was determined by a standard procedure using EDTA (Merck). pH-metric titrations were performed with NaOH (Merck or SDS) standard solutions. Potassium D-gluconate (99%), D-glyceric acid hemicalcium salt (≥ 98%), L-threonic acid hemicalcium salt (> 97%), and sodium 2-hydroxybutanoate (> 97%) were Fluka products. Sodium (*R*)-3-hydroxybutanoate (99%) was purchased from Aldrich.

pH-Metric Measurements: The acidity and complex formation constants were determined by pH-metric titrations at 298.0 ± 0.1 K and at an ionic strength $I = 0.1$ mol·L^{-1} ($NaClO_4$) under argon, using an automatic titration set, including a Metrohm Dosimat 665 autoburette and a Mettler Toledo Inlab 422 type combined glass electrode. The different equilibria were characterized by Equation (1), where M denotes the lanthanide(III) ion and L the ligand in the carboxylate form. Generally, charges were omitted, but they can be easily calculated.

$$pM + qL + rH \rightleftharpoons M_pL_qH_r$$

$$\beta_{pqr} = \frac{[M_p\ L_q\ H_r]}{[M]^p\ [L]^q\ [H]^r} \qquad (1)$$

The description of the procedure for data evaluation using the PSEQUAD[27] computer program was described earlier.[28,29] The acidity and complex formation constants were determined, respectively, from four and six to eight independent titrations (about 100 data points per titration). The concentration of the ligands was about $5-8 \times 10^{-3}$ mol·L^{-1} and the ligand/metal (L/M) ratio was varied form 1:1 to 5:1. The pH-metric data between pH = 2 and 11.3 (or between pH = 2 and the pH of precipitation when precipitation occurred in the presence of a metal ion) were used for the evaluation of the acidity and complexation constants. The errors indicated for the complexation constants are those given by the PSEQUAD computer program. It was verified that the use of hemicalcium salts for glyceric and threonic acids had no consequence on the determination of the complexation constants. The acidity constants for compounds in the presence or absence of the calcium(II) ion are nearly identical. 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 constant (log β_{10-1}): −9.33, −8.82, −8.58, −8.37, −8.26, and −8.17 for La^{III}, Pr^{III}, Eu^{III}, Dy^{III}, Er^{III}, and Lu^{III}, respectively.[30]

NMR Spectroscopy: ^{1}H and ^{13}C NMR spectra were recorded with a Bruker DRX400 apparatus at 400 and 100.6 MHz, respectively. The gluconic acid concentration, for the shift analysis, was 0.5 mol·L^{-1} and the L/M ratios varied from 10:1 to 250:1. The solvent was a mixture of H_2O/D_2O (80:20, v/v) and the pH was adjusted to 4.0 with NaOH or $HClO_4$. For the determination of the pseudocontact and contact contributions to the chemical shift, the parameters D and $\langle S_z \rangle$ are D = 2.972, −10.682, and −28.545, and $\langle S_z \rangle$ = 10.99, −4.05, and 100 for Pr ^{III}, Eu^{III}, and Dy^{III}, respectively.[22−23,31,32]

Acknowledgments

NMR spectra were recorded with the apparatus of the "Service Commun de RMN" of the University Henri Poincaré-Nancy 1. The authors are grateful to Stephane Parant for his technical assistance.

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Received October 1, 2001
[I01383]