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Multinuclear magnetic resonance study of the complexation of lanthanum (III) by D-glucitol and ribitol in aqueous solution

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Abstract

A multinuclear magnetic resonance study (^{1}H, ^{13}C, ^{139}La) of the interactions of La(III) with D-glucitol and ribitol in aqueous solution is presented and is compared with recently published calorimetric data. The thermodynamic data were determined by ^{139}La NMR, and are in excellent agreement with the calorimetric results: $\Delta H° = -10.3 \pm 1.2$ kJ mol^{-1} and $\Delta S° = -25.7 \pm 3.9$ J K^{-1} mol^{-1} (^{139}La NMR); $\Delta H° = -10.2$ kJ mol^{-1} and $\Delta S° = -25.8$ J K^{-1} mol^{-1} (calorimetry; from Rongère et al., op. cit.). A conformational analysis of D-glucitol shows that the complexation of La(III) results from a 120° rotation of the C_2–C_3 bond in the most stable conformation of D-glucitol, thus providing three hydroxyl groups in a suitable spatial arrangement for the occupancy of the first coordination sphere of La(III) and the concurrent replacement of water molecules. © 1997 Elsevier Science Ltd.

Keywords: Lanthanum cation; Multinuclear magnetic resonance; ^{139}La NMR; Complexation; Alditols; D-Glucitol; Ribitol; Conformational analysis; Thermodynamics

1. Introduction

A suitable spatial pre-organization of several metal complexing moieties in a ligand can dramatically increase the complexation efficiency of that ligand. Some macrocyclic compounds, such as crown ethers, cryptands, or calixarenes are examples of molecules built to provide a spatial organization of complexing groups, i.e. ether oxygens, particularly well suited for the complexation of metallic cations. Usually, they provide large stability constants for the formation of the complex [1]. Even if they can also provide several ligating groups in close proximity for the complexation of a metal cation, polyfunctional acyclic compounds, such as polyols, do not provide pre-organization of these groups to the same extent as do macrocyclic compounds, and therefore usually form much weaker complexes with metal cations [2]. However, in order to compete efficiently with water molecules for the occupancy of the first coordination sphere of a metallic cation, these acyclic ligands must show some pre-organization, and contain particular spatial arrangements of the ligating groups. Notable in that

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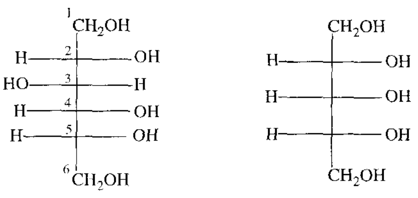

(1) (D-glucitol) (2) (ribitol)

Scheme 1.

respect is the *axial–equatorial–axial* arrangement of a sequence of three hydroxyl groups in the pyranose form of sugars [3], or, in the furanose form, the arrangement of three *cis–cis* hydroxyl groups [3]. These isomers form weak complexes with cations in aqueous solution [4].

A *threo–threo* arrangement of three consecutive hydroxyl groups, as found in alditols [5] such as xylitol or D-glucitol (**1**), is particularly suitable for the complexation of metallic cations, leading to stability constants of complex formation with divalent and trivalent cations in water in the range 2–8 [6].

A combined approach of calorimetry and multinuclear magnetic resonance spectroscopy (NMR) is particularly useful to characterize the interactions between sugars and metallic cations in aqueous solution [7]. NMR can also provide information on the structure of the complex in solution. If it contains an NMR active nuclide, and is diamagnetic, the metallic cation itself provides a very sensitive probe for the characterization of weak complexes in solution [8]. Among the lanthanide series, the quadrupolar ^{139}La nucleus ($I = 7/2$; $Q = 0.21 \times 10^{-28}$ m^2) is the best candidate to be such a probe, and this approach was used recently to study the interactions of La(III) and D-ribose in aqueous solution by ^{139}La NMR [7].

In the present work, a multinuclear NMR study (^{1}H, ^{13}C, ^{139}La) of the interactions of La(III) with D-glucitol (**1**) and ribitol (**2**) is presented (see Scheme 1) and is compared with recently published calorimetric data [6]. D-Glucitol contains the *threo–threo* sequence which is not present in ribitol. The thermodynamic data have been determined both by NMR and calorimetry in the two cases, showing an excellent agreement. A conformational analysis of D-glucitol, based on vicinal ^{1}H–^{1}H coupling constants before and after complexation, showed that the complexation of La(III) results from a 120° rotation of the C_2–C_3 bond in the most stable conformation of D-glucitol, thus providing three hydroxyl groups in a suitable spatial arrangement for the occupancy of the first coordination sphere of La(III) and the concurrent replacement of water molecules.

2. Results and discussion

The ^{13}C NMR spectra of D-glucitol (**1**) at 300 K are shown in Fig. 1 in the absence and in the presence of increasing quantities of La(III) ($\rho = [\text{La(III)}]_{tot}/[\text{D-glucitol}]_{tot}$). The asymmetric configuration of D-glucitol results in a distinct resonance for each of the six carbons [9]. The primary carbons (C_1 and C_6) resonate upfield (63–65 ppm), and the secondary carbons (C_2–C_5) downfield (71–75 ppm) [10]. The assignments of the six peaks observed were made based on data in the literature [11–13]. Carbons C_1–C_6 correspond, respectively, to chemical shifts of 63.82, 74.31, 71.03, 72.51, 72.39, and 64.61 ppm.

The presence of a trivalent cation markedly affects the chemical shifts of the carbons C_2 and C_4, whose resonances move downfield upon addition of La(III), suggesting the involvement of the corresponding oxygens in the coordination of La(III) by D-glucitol. The chemical shifts of the other carbons are also affected, albeit to a lesser degree. One should note here that the chemical shift of C_3 was essentially unaffected by the presence of La(III). This result has been previously mentioned by Kieboom et al. [15]. Since D-glucitol contains the *threo–threo* sequence of three

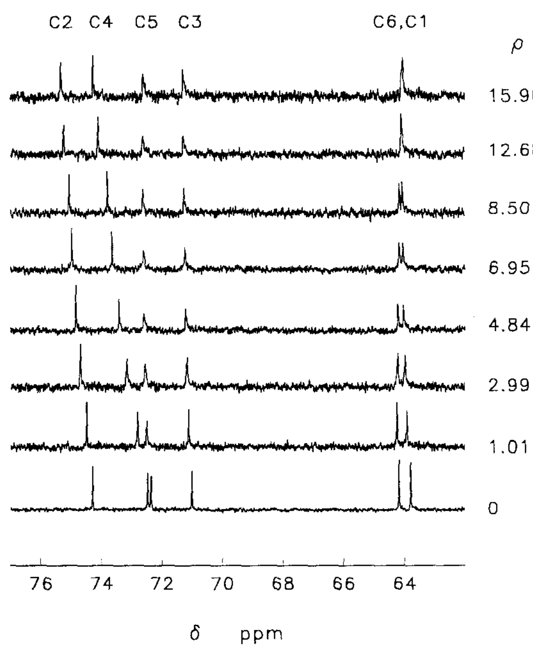

Fig. 1. ^{13}C NMR spectra of D-glucitol (2.99×10^{-2} M) for various ratios $\rho = [\text{LaCl}_3]_{tot}/[\text{D-glucitol}]_{tot}$. $T = 300$ K.

hydroxyl groups on contiguous carbons, it is expected to be particularly well suited to complex lanthanide trivalent cations [3]. In order to verify that the changes observed in the NMR spectra when various quantities of La(III) are added to the solution could be attributed to complexation, the same experiments were performed on ribitol. Lacking the *threo–threo* sequence, ribitol is a much poorer complexing agent of metallic cations than D-glucitol [6]. Indeed, in the case of ribitol, the ^{13}C NMR study did not show any significant change in the spectra after addition of similar amounts of La(III).

The stability constant of complexation, K, can be determined on the basis of a 1:1 stoichiometry model:

$$\underset{\text{G}}{\text{D-glucitol}} + \text{La(III)} \rightleftarrows \underset{\text{GLa(III)}}{[\text{D-glucitol, La(III)}]}$$

$$K = \frac{[\text{GLa(III)}]}{[\text{G}][\text{La(III)}]}. \quad (1)$$

It was assumed that the solutions were at high enough dilution to neglect the ionic factor, γ_i, thus allowing the use of concentrations instead of activities.

$$[\text{G}]_0 = [\text{G}] + [\text{GLa(III)}] \quad (2)$$

with $[\text{G}]_0 = 2.99 \times 10^{-2}$ M,

$$\rho[\text{G}]_0 = [\text{La(III)}] + [\text{GLa(III)}]. \quad (3)$$

Eq. (4) is obtained by the replacement of [G] and [La(III)] in Eq. (1) by their expressions derived from Eqs. (2) and (3):

$$[\text{GLa(III)}] = 0.5C - (0.25C^2 - \rho D)^{1/2} \quad (4)$$

where $C = [\text{G}]_0 + \rho[\text{G}]_0 + K^{-1}$ and $D = [\text{G}]_0^2$.

Under fast exchange conditions, the observed chemical shift is the population average of the chemical shifts of the glucitol in its complexed (δ_B) and uncomplexed forms (δ_A):

$$\delta_{obs} = \frac{[\text{G}]_0 - [\text{GLa(III)}]}{[\text{G}]_0} \cdot \delta_A + \frac{[\text{GLa(III)}]}{[\text{G}]_0} \cdot \delta_B. \quad (5)$$

The stability constant, K, and the chemical shift of the complex, δ_B, were determined from Eqs. (4) and (5) using a non-linear regression on the observed chemical shifts of C_2 and C_4 ($K = 4.3 \pm 0.3$ and 4.4 ± 0.4 and $\delta_B = 75.76 \pm 0.06$ and 74.97 ± 0.12 for C_2 and C_4, respectively).

The values of K determined from δ_{C_2} and δ_{C_4} are identical in the error limits. In order to verify the validity of the assumption on the ionic activity factors γ_i, the same experiments were performed using an initial concentration of D-glucitol of 8.89×10^{-3} M instead of 2.99×10^{-2} M, for various values of ρ ($\rho = 4.04$, 6.00, and 7.94). These experiments led to a stability constant of 5.5 obtained from both C_4 and C_2, a value similar to those measured previously.

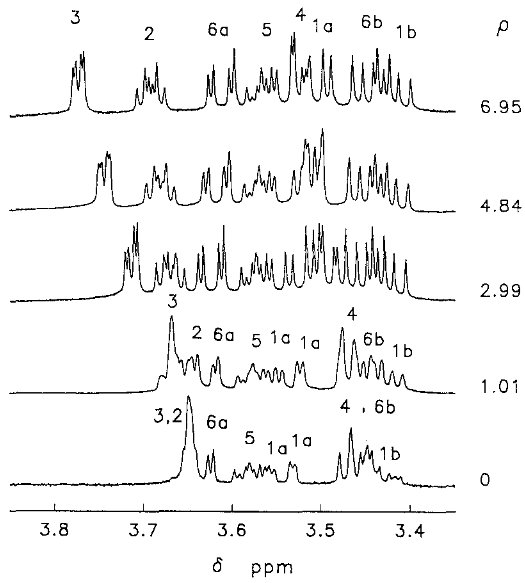

Fig. 2. ^1H NMR spectra of D-glucitol (2.99×10^{-2} M) for various ratios $\rho = [LaCl_3]_{tot}/[\text{D-glucitol}]_{tot}$. $T = 300$ K.

The ^1H NMR spectrum (500 MHz) of D-glucitol at 300 K is shown in Fig. 2, in the absence and in the presence of increasing quantities of La(III). All of the protons resonate between 3.4–3.7 ppm. Several methods have been used in the literature to assign the ^1H NMR signals of D-glucitol: shift reagents [14,15], spectral simulation [17] or a combination of 2D experiments (^1H–^{13}C correlation) and extensive spin simulation of 1D spectra [12]. The addition of La(III) to aqueous solutions of D-glucitol led to a spectrum characterized by a larger chemical shift dispersion. The signals of the protons H_2, H_3, and H_4 shift downfield, while that of H_{6a} shifts slightly upfield, as shown in Fig. 2. All of the signals could be predicted from a simulation based on data in the earlier work of Hoffman et al. [12]. Tables 1 and 2 give the ^1H NMR chemical shifts, and the geminal and vicinal coupling constants, of D-glucitol under the experimental conditions of this study.

A simulation of the spectra corresponding to $\rho = 2.99$, 4.84, and 6.95 allowed the determination of all of the chemical shifts and coupling constants, ^2J and ^3J, in each case. Under fast exchange conditions, the chemical shifts and coupling constants are population averaged for values of D-glucitol in its complexed

Table 1
^{1}H NMR chemical shifts of D-glucitol and of the D-glucitol–La(III) complex in aqueous solution [a]

	δ(ppm) D-glucitol	δ(ppm) (D-glucitol–La(III))
H_{1a}	3.541	3.431
H_{1b}	3.430	3.402
H_2	3.650	3.762
H_3	3.650	4.001
H_4	3.457	3.651
H_5	3.578	3.537
H_{6a}	3.636	3.558
H_{6b}	3.460	3.425

[a] 2.99×10^{-2} M; 300 K.

and uncomplexed forms. Moreover, knowledge of the percentage of complexed form from the stability constant obtained by calorimetry [6] allow the determination of all of the chemical shifts and coupling constants for the complex, D-glucitol–La(III). An example of a simulation is shown in Fig. 3 for $\rho = 6.95$. Results are given in Tables 1 and 2. As expected, geminal coupling constants are not affected by complexation. In Table 2, the dihedral angles determined from the crystal structure of D-glucitol [18] are also indicated, with the corresponding values of ^3J for the closest ideal dihedral angle (staggered conformation) calculated from modified Karplus equations [18,21], $J_{\theta'}$. Upon complexation, only two vicinal coupling constants change significantly, those involving H_{1a} and H_2, and H_2 and H_3. The values of the dihedral angles, θ'', of an idealized staggered conformation associated with the vicinal coupling constants, $J_{\theta''}$, for the complexed D-glucitol are also given in Table 2. The comparison between θ' and θ'' shows that the complexation process corresponds mainly to a single

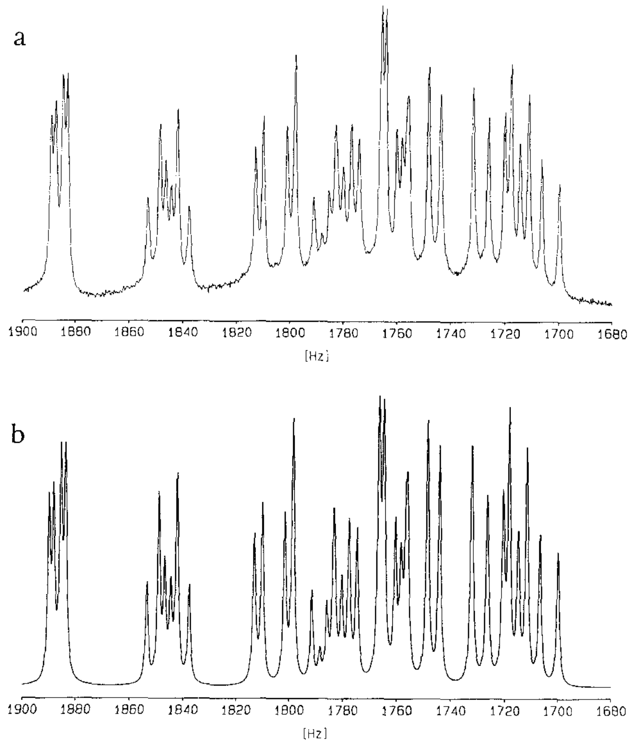

Fig. 3. (a) ^{1}H NMR spectrum of D-glucitol (2.99 10^{-2} M) in the presence of La(III) ($\rho = 6.95$). (b) Simulated spectrum.

rotation around the C_2–C_3 bond. The change in the coupling constants involving H_1 is a consequence of this rotation. The remainder of the molecule, from C_3 to C_6, retains the same conformation after complexation. This fact, coupled with the almost constant ^{13}C chemical shifts, suggests that this part of the molecule is not involved in the binding of La(III).

From the values of the dihedral angles before, θ', and after, θ'', complexation, molecular modeling of

Table 2
^{1}H–^{1}H geminal and vicinal coupling constants and dihedral angles for D-glucitol and for the D-glucitol–La(III) complex [a]

	J_{free}	$J_{complex}$	θ_{XR} [b]	θ' [c]	$J_{\theta'}$ [d]	θ'' [c]	$J_{\theta''}$ [d]
H_{1a}–H_{1b}	−12.0	−11.8					
H_{1a}–H_2	3.5	7.7	−58.1	−60	3.1	−180	10.7
H_{1b}–H_2	6.5	7.5	−178.9	−180	10.7	60	5.0
H_2–H_3	6.0	1.2	−169.6	−180	9.6	60	0.5
H_3–H_4	2.1	1.1	−56.6	−60	0.5	−60	0.5
H_4–H_5	8.3	7.5	−180.4	−180	9.6	−180	9.6
H_5–H_{6a}	3.2	2.9	66.7	60	0.9	60	0.9
H_5–H_{6b}	6.3	5.7	−173.7	−180	10.7	−180	10.7
H_{6a}–H_{6b}	−12.0	−11.8					

[a] At 300 K.
[b] Determined by X-ray crystallography [17].
[c] θ' and θ'' are dihedral angles given for idealized staggered conformations.
[d] Taken from ref. [12].

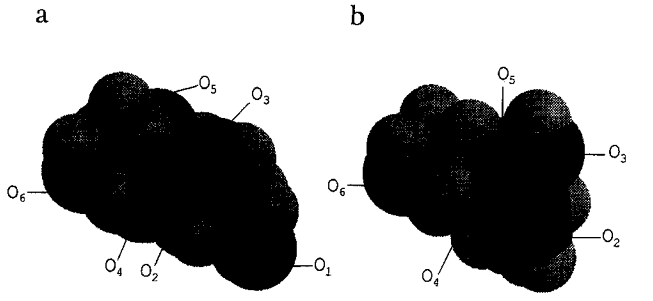

Fig. 4. Conformation of D-glucitol in aqueous solution at 300 K. (a) Uncomplexed. (b) Complexed.

D-glucitol was performed using the SPARTAN software (Fig. 4). The rotation of the C_2–C_3 bond by 120° brings the hydroxyl group of C_2 in a position such that three consecutive hydroxyl groups, O_2, O_3, and O_4, are placed in a suitable configuration for the complexation of La(III). These results are in good agreement with those observed by ^{13}C NMR and those obtained from ^{1}H NMR studies of the complexation of D-glucitol with Pr(III) [15] and Eu(III) [14]. The X-ray crystal structure of an alditol–lanthanide complex has been determined (galactitol, $2PrCl_3$), showing a structure similar to that described above [16].

Fig. 5 shows the changes in ^{1}H chemical shifts as a function of ρ. The proton H_3 attached to the central atom of the trivalent binding site undergoes the largest downfield shift. This result is in agreement with the proposed conformational changes occurring during the complexation process shown in Fig. 4. Similar ^{1}H chemical shift changes have been shown to occur in similar cases of tripodal cationic binding sites [14,15,20].

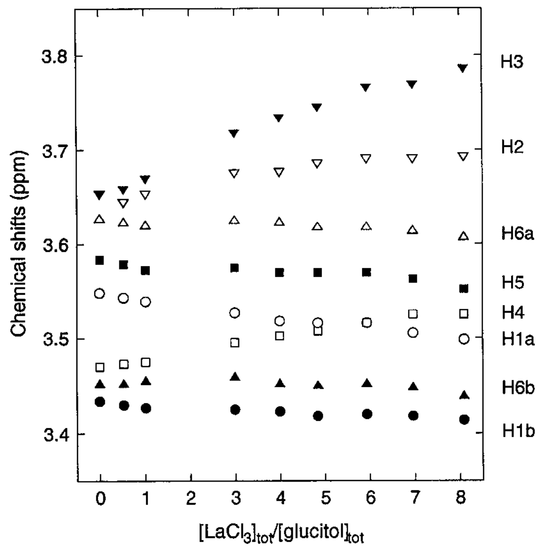

Fig. 5. Variation of the ^{1}H NMR chemical shifts of D-glucitol (2.99×10^{-2} M) as a function of ρ. $T = 300$ K.

The stability constant, K, for the formation of the 1:1 complex, D-glucitol–La(III), can be estimated from a non-linear regression analysis on the observed δ_{H3}, on the basis of Eqs. (4) and (5). A value of 2.1 ± 0.8 was found at 300 K. It is very gratifying that the stability constants determined independently by ^{1}H NMR, ^{13}C NMR, and calorimetry (2.8) [6] are very similar.

A series of ^{139}La NMR spectra were recorded for a total concentration of La(III) of 3.00×10^{-2} M, at 300 K, as a function of the ratio [D-glucitol]$_{tot}$/[$LaCl_3$]$_{tot}$, with the ratio varying from 0 to 15.85. The ^{139}La NMR spectrum of an aqueous solution of $LaCl_3$ (3.00×10^{-2} M) consists of a signal having a linewidth at half-height of 108 Hz, in good agreement with previously reported values [7,22]. Both the chemical shift and the linewidth of the ^{139}La NMR signal vary when increasing amounts of D-glucitol are added to the La(III) aqueous solution. In this range of ratios (0–15.85), the mole fraction of complexed La(III), p_B, as calculated from the calorimetric stability constant, varies from 0 to 54.7%. The presence of a single Lorentzian signal indicates that the exchange between solvated and complexed La(III) is very fast on the ^{139}La NMR timescale. The observed ^{139}La NMR parameters are population averaged over those of free and complexed La(III).

A series of similar experiments were carried out at 300 K on ribitol (**2**). As has previously been shown by calorimetry [6] and chromatography [19], ribitol retains some cation complexing abilities towards the lanthanum cation, albeit to a much smaller degree than does D-glucitol. Upon the addition of ribitol, the ^{139}La signal shifted downfield and its linewidth increased. However, as indicated in Fig. 6a and b, respectively, the downfield shifts and the linewidth increases were both significantly smaller than those observed for D-glucitol.

The ^{139}La NMR chemical shifts of aqueous solutions of $LaCl_3$ as a function of the concentration ratio of D-glucitol over $LaCl_3$ were measured at temperatures ranging from 280 to 340 K. The stability constant, K, for the complexation of La(III) by D-glucitol could then be determined at each temperature on the basis of a 1:1 stoichiometry [7].

For the cases of D-ribose and D-arabinose, a procedure was proposed previously by which the observed ^{139}La linewidth of a non-complexing sugar, D-

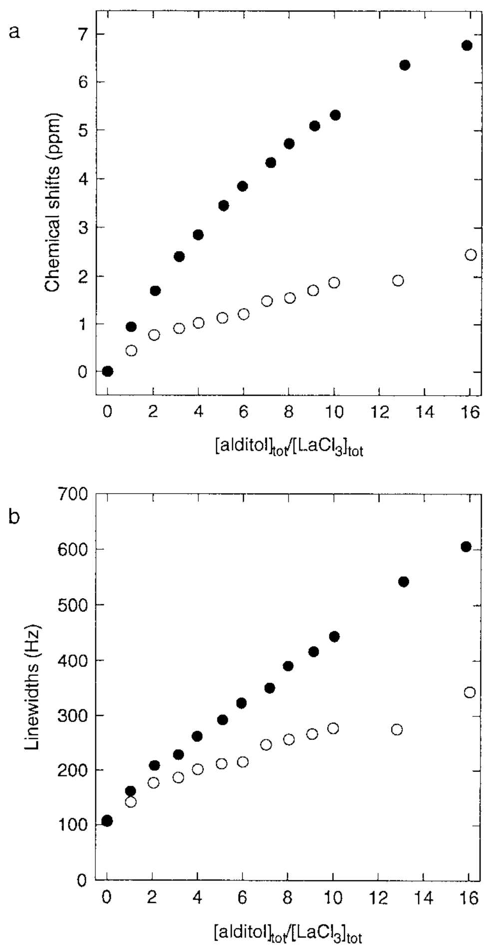

Fig. 6. Variation of ^{139}La NMR parameters as a function of ρ^{-1}. (a) Chemical shifts. (b) Linewidths. (●) D-glucitol, (○) ribitol.

arabinose, was subtracted from that of the complexing sugar, D-ribose, in order to account for the nonspecific effects of the sugar on ^{139}La linewidth, such as a viscosity increase of the solution [7]. Since ribitol cannot be considered an inactive reference for the complexation of La(III) [6] (confirmed by the ^{139}La linewidth variations; see Fig. 6b), this procedure cannot be applied here.

The determination of the equilibrium constant at several temperatures allowed the determination of the enthalpy ($\Delta H°$) and entropy ($\Delta S°$) charges associated with complexation. The values obtained by ^{139}La NMR: ($\Delta H° = -10.3 \pm 1.2$ kJ mol^{-1}, $\Delta S° = -25.7 \pm 3.9$ J K^{-1} mol^{-1}) are in excellent agreement with those obtained by calorimetry ($\Delta H° = -10.2$ kJ mol^{-1}, $\Delta S° = -25.8$ J K^{-1} mol^{-1} [6]), showing that the complexation is enthalpy-driven. The slightly negative entropy value may result from a balance between the losses of conformational entropy of the ligand and translational entropy for the complexing species, combined with the gain of translational entropy for several water molecules liberated from the La(III) coordination sphere during the complexation process.

In conclusion, this multinuclear magnetic resonance (^{1}H, ^{13}C, and ^{139}La) study leads to a complete description of the interactions between D-glucitol and La(III). The ^{1}H and ^{13}C NMR results confirm that the site of complexation involves O_2, O_3, and O_4 [3,14]. A conformational analysis of D-glucitol, based on an analysis of $^{3}J_{H,H}$ values, shows that the complexation of La(III) results from a 120° rotation of the C_2–C_3 bond. As a result, three hydroxyl groups are arranged in a suitable spatial arrangement for the coordination of La(III). Moreover, the parameters characteristic of the equilibrium of complexation (stability constant, enthalpy, and entropy) have been determined, giving values very close to those obtained independently by calorimetry, and showing that the complexation process is enthalpy-driven.

3. Experimental

D-Glucitol (D-sorbitol), ribitol (adonitol), and lanthanum(III) chloride heptahydrate were purchased from Aldrich. Their purity was 99 + %, 99%, and 99.999%, respectively. They were used without further purification.

^{1}H, ^{13}C, and ^{139}La NMR spectra were recorded on a BRUKER AMX-500 spectrometer operating at 500.13, 125.77, and 70.65 MHz, respectively. NMR tubes (5 mm) sealed with parafilm were used, and the solvent was a mixture of water and D_2O (w/w% $D_2O = 5$).

^{1}H-Decoupled ^{13}C NMR spectra were recorded with a 45° pulse angle corresponding to a 5 μs pulse width. Dioxane was used as the internal reference. A value of 67.8 ppm was used for the chemical shift of dioxane at 27 °C. The acquisition time and the delay between two pulses was 1 s. Typically, 1000 transients were collected.

A 45° pulse angle (3 μs) was applied to obtain proton NMR spectra. Pre-saturation of the water signal was carried out at low power for 3 s. Typically, 100 transients were collected. Dioxane ($\delta_H = 3.56$ ppm) was used as the internal reference.

A 90° pulse angle (16 μs) was used to obtain the ^{139}La NMR spectra. All chemical shifts were referenced to a 3×10^{-2} M solution of $LaCl_3$ in water. The acquisition time was 25 ms. Typically, 10,000 transients were collected.

Spectral simulations were done with software developed by G. Hägele, R. Spiske, F. Mistry, and S. Goudetsidis (DSYM-PC ver. 1.0E).

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