Electronic Supporting Information

Formation of mono- and binuclear neodymium(III)-gluconate complexes in aqueous solutions in the pH range of 2–8

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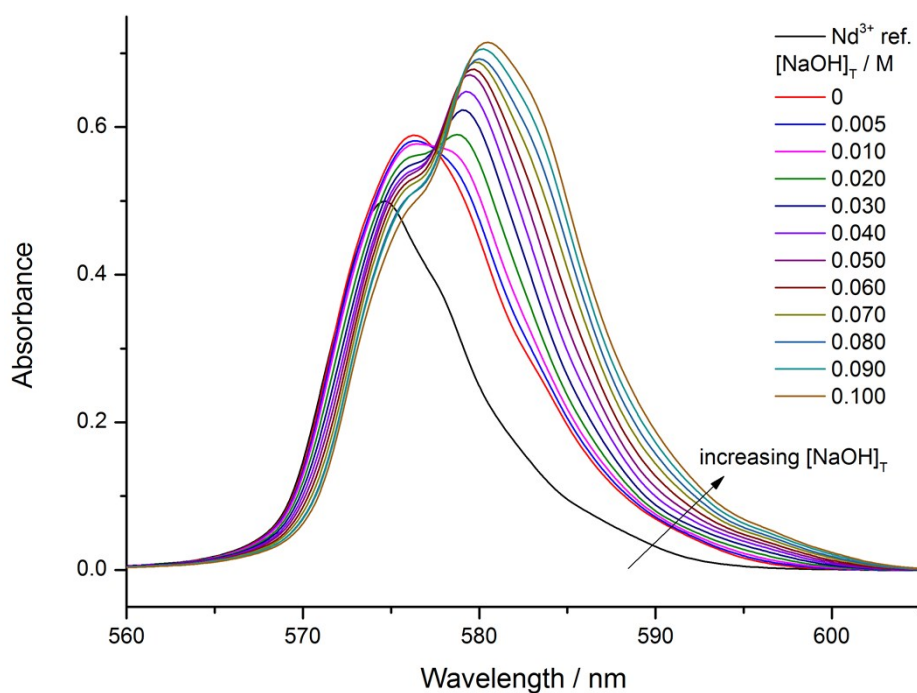
Figure S1. Effect of NaOH on the visible spectra of the Nd(III)–gluconate (Gluc⁻) system at 1:1 ligand to metal ratio. Experimental conditions: T = 25 °C, I = 1 M (NaCl); analytical concentrations: $[NdCl_3]_T = 0.075$ M, $[NaGluc]_T = 0.075$ M, $[NaOH]_T = 0$–0.100 M. The spectrum of 0.075 M NdCl$_3$ (black solid line) as a reference is also plotted.
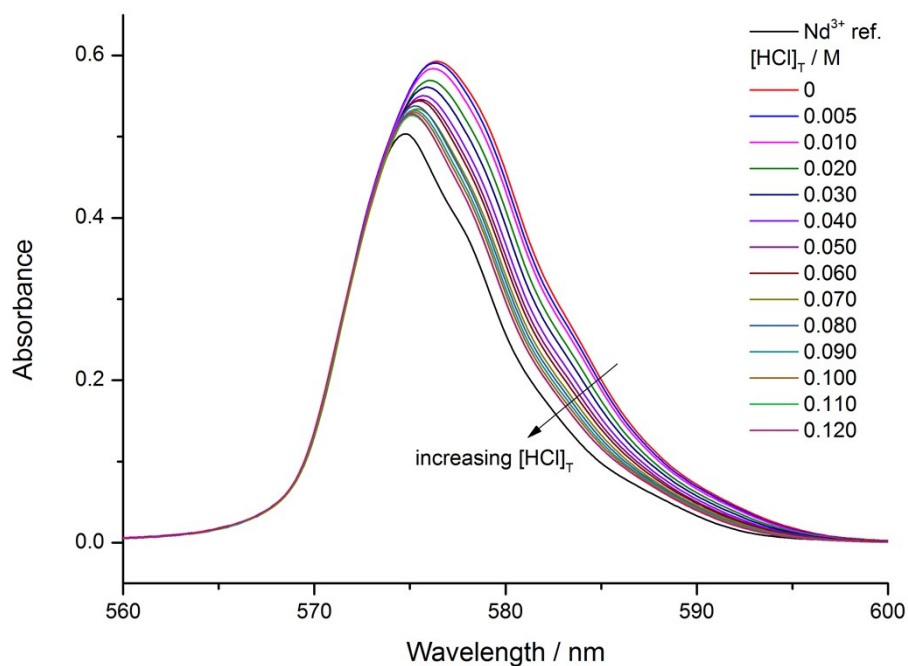
Figure S2. Effect of HCl on the spectra of the Nd(III)–gluconate (Gluc$^-$) system at 1:1 ligand to metal ratio. Experimental conditions: T = 25 °C, I = 1 M (NaCl); analytical concentrations: $[NdCl_3]_T = 0.075$ M, $[NaGluc]_T = 0.075$ M, $[HCl]_T = 0$–0.120 M. The spectrum of 0.075 M NdCl$_3$ (black solid line) as a reference is also plotted.
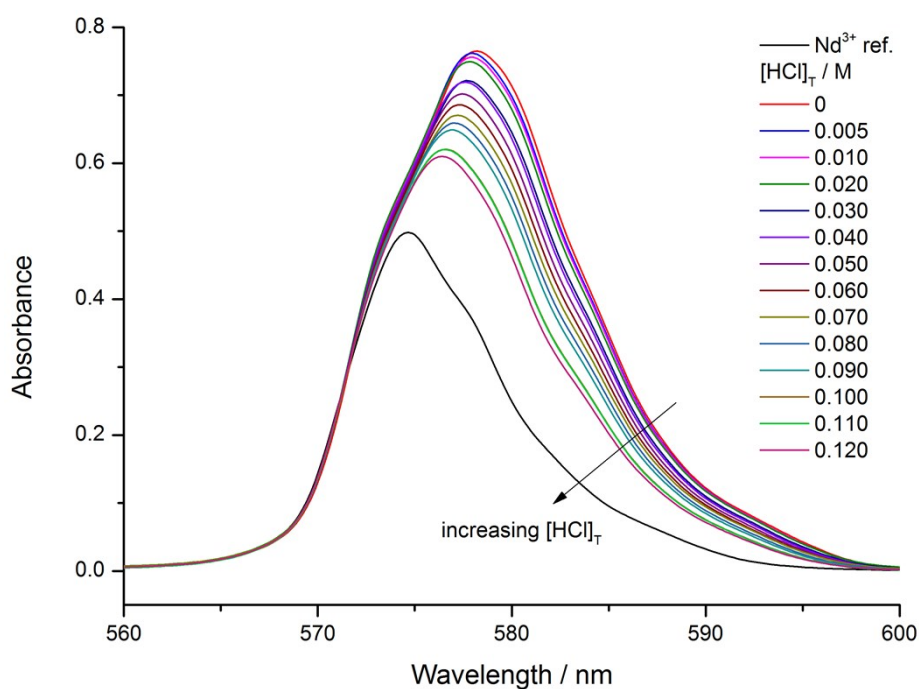

Figure S3. Effect of HCl on the visible spectra of the Nd(III)–gluconate (Gluc$^-$) system at 2.5:1 ligand to metal ratio. Experimental conditions: T = 25 °C, I = 1 M (NaCl); analytical concentrations: $[NdCl_3]_T = 0.075$ M, $[NaGluc]_T = 0.188$ M, $[HCl]_T = 0$–0.120 M. The spectrum of 0.075 M NdCl$_3$ (black solid line) as a reference is also plotted.
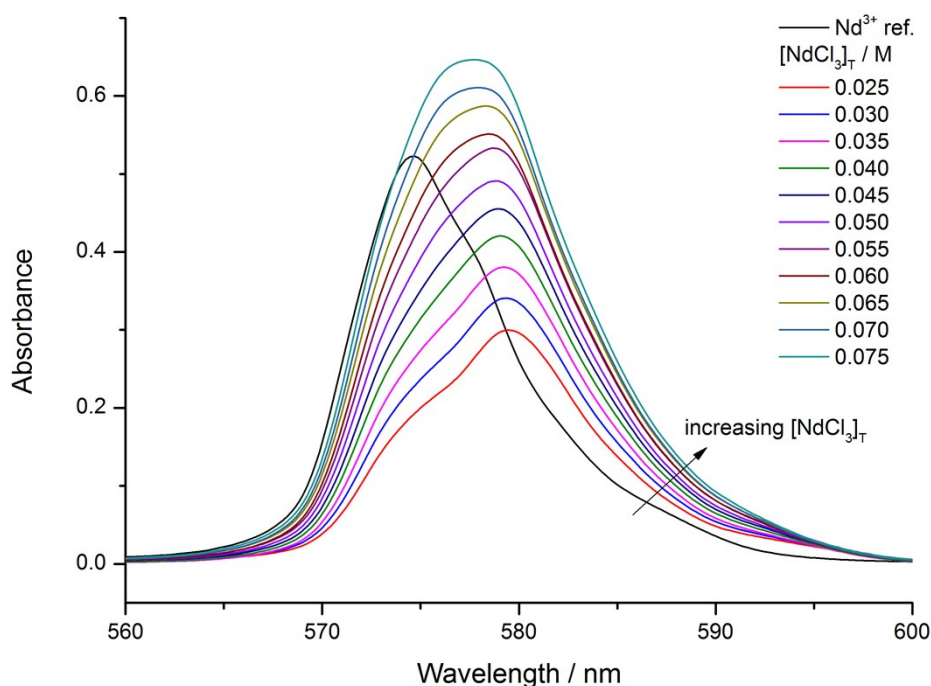
Figure S4. Effect of $NdCl_3$ on the visible spectra of the Nd(III)–gluconate (Gluc⁻) system. Experimental conditions: T = 25 °C, I = 1 M (NaCl); analytical concentrations: $[NaGluc]_T = 0.100$ M, $[NaOH]_T = 0.010$ M, $[NdCl_3]_T = 0.025$–0.075 M. The spectrum of 0.075 M $NdCl_3$ (black solid line) as a reference is also plotted.
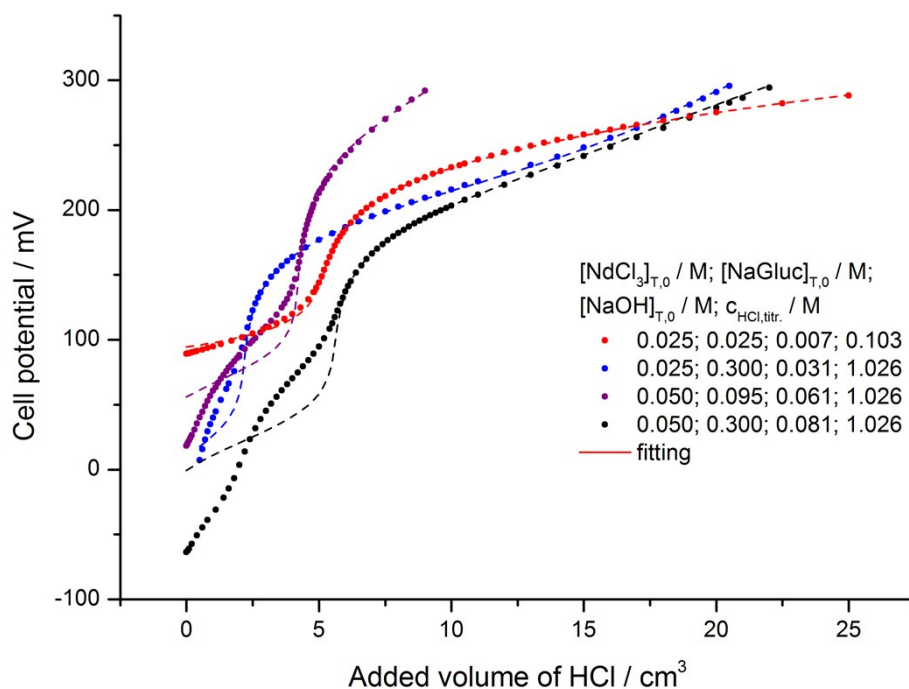

Figure S5. Potentiometric titration curves of the Nd(III)–gluconate (Gluc⁻) system. Experimental conditions: T = 25 °C, I = 1 M (NaCl); initial analytical concentrations, $[X]_{T,0}$, and the concentration of the titrant HCl are listed in the legend. The pH (in terms of $-\log([H^+]/M)$) is varying between 2.0 and 8.1. Symbols: measured, dashed lines: calculated data by neglecting the formation of the $Nd_2Gluc_3H_{-2}^+$ and $Nd_2Gluc_4H_{-2}^0$ species.

According to Figure S6, the 1:1 complex is predominant at $3 < \text{pH} < 5.5$ (the 1:2 species is formed at higher extent as well) Above $\text{pH} = 7.5$, the $NdGlucH_{-2}^0$ is present almost exclusively. Considering the increase for $[NdCl_3]_T$ of one order of magnitude $(3 \cdot 10^{-5}\,M)$ due to this species, the speciation remains the same (even if the formation of the hydroxido complexes is considered).
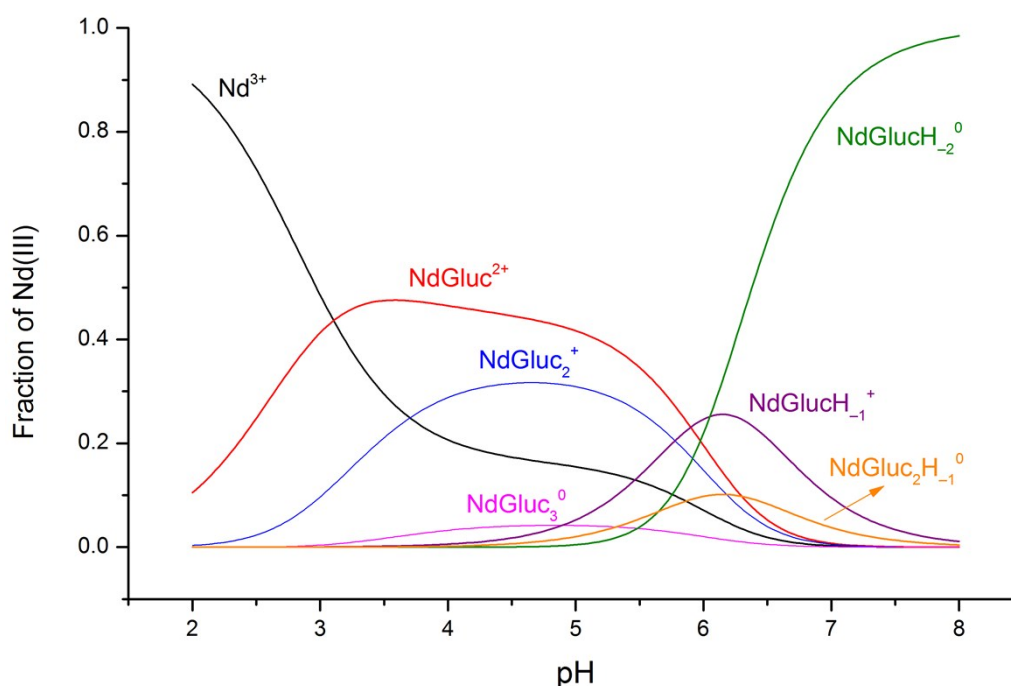

Figure S6. The distribution diagram of neodymium(III) in the Nd(III)–gluconate (Gluc⁻) system. Experimental conditions: $T = 25\,°C$; analytical concentrations: $[NdCl_3]_T = 3 \cdot 10^{-6}\,M$, $[NaGluc]_T = 0.010\,M$. The calculation was based on the formation constants were determined in the present work, except $\log \beta_{11-1}$ and $\log \beta_{12-1}$. These were calculated from our constants with the help of the pK values of refs. 28 and 29.

The conductometric titrations are depicted in Figure S7. Addition of water as 'titrant' to the solutions containing either 0.075 M NdCl₃ or 0.183 M NaGluc, only slight decrease of the conductance was observed due to dilution. Surprisingly, the presence of 0.183 M NaGluc in addition to the NdCl₃ results in nearly the same conductance. Consequently, there is significant extent of association (i.e., complexation) between the Nd^{3+} and Gluc⁻ ions.

When water is 'titrated' with NaOH, the conductance increases significantly due to the addition of OH⁻ ions of high conductivity. It is more surprising that if this solution is titrated with 1.029 M NaOH instead of water, the conductance increases only to 7.1 mS from the starting point to 7.8 cm³, where precipitation occurred. At the same volume, the measured conductance is 27.9 mS, when deionized water is titrated with the same NaOH titrant.

Considering that the conductivity of the OH⁻ ions is the second highest after that of the H⁺, the small increase of 71. mS indicates the consumption of NaOH and the formation of the deprotonated complexes. It has to be noted that these effects can only be elucidated at semi-quantitative level since the molar conductivities of the components are not completely additive in the total concentration range employed.
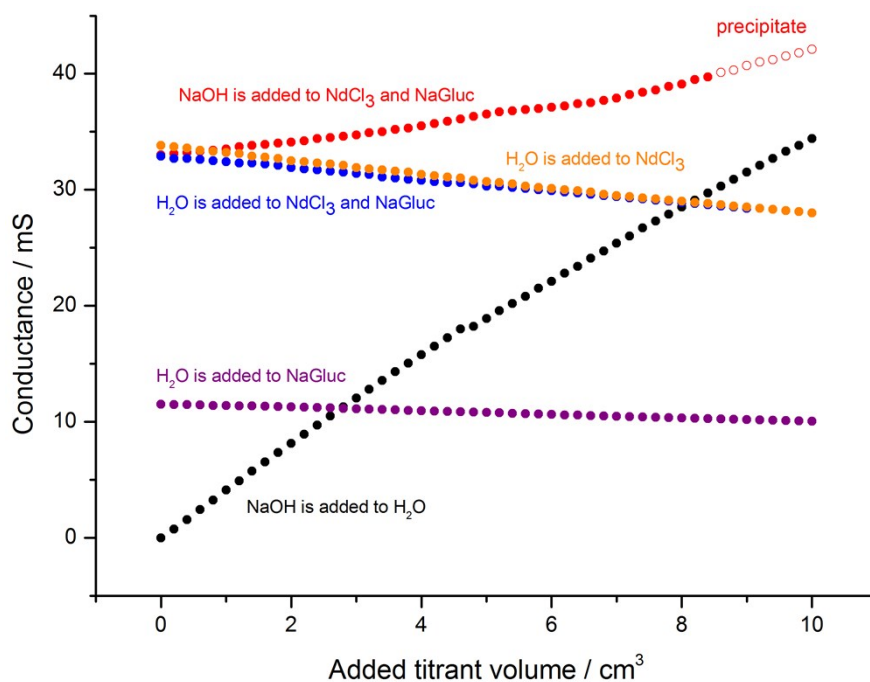
Figure S7. Conductometric titration curves of the Nd(III)–gluconate (Gluc⁻) system. Experimental conditions: T = 25 °C; initial analytical concentrations: $[NdCl_3]_{T,0} = 0.075$ M and $[NaGluc]_{T,0} = 0.183$ M. The titrant is 1.029 M NaOH or deionized water.

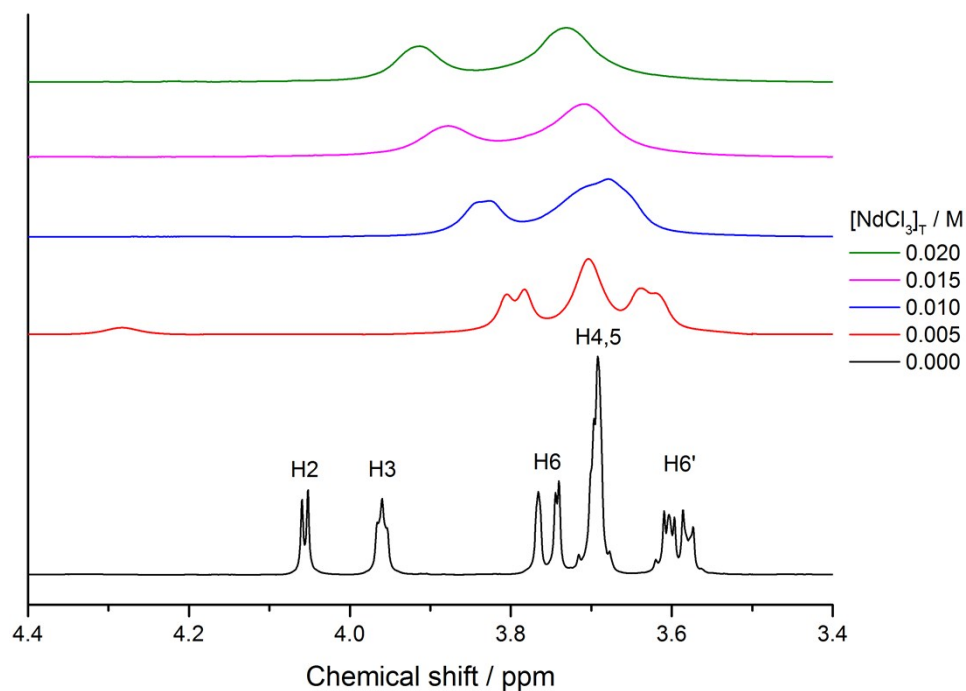**Figure S8.** ¹H NMR spectra of gluconate in the neodymium(III)-gluconate (Gluc⁻) system. Experimental conditions: T = 25 °C; analytical concentrations: $[NaGluc]_T = 0.100$ M, $[NdCl_3]_T = 0$–0.020 M. In parallel, the pH is varying from 6.91 to 4.98.

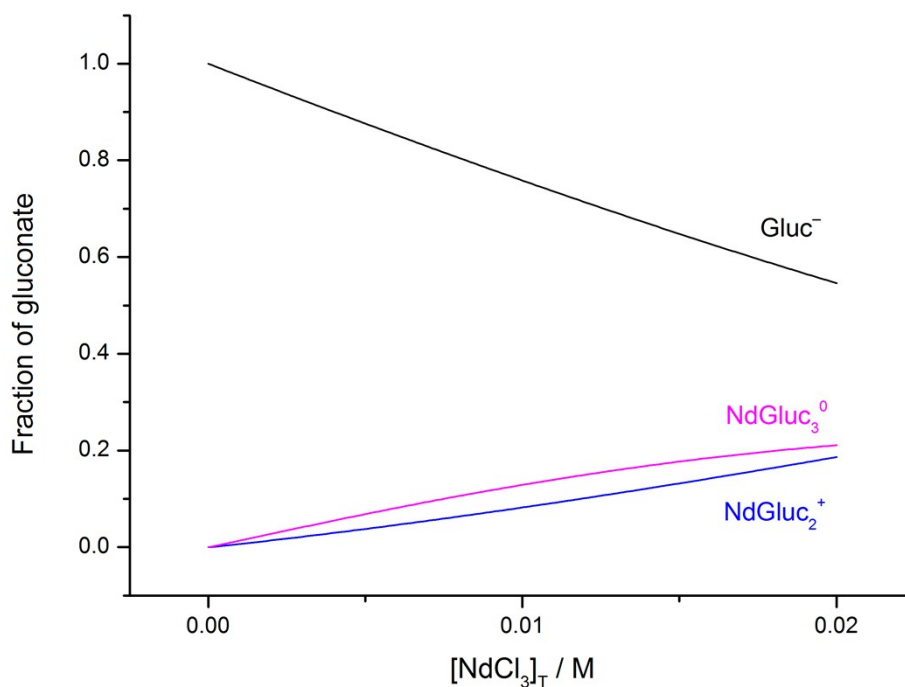**Figure S9.** The distribution diagram of gluconate (Gluc⁻) in the Nd(III)–gluconate system. Experimental conditions: T = 25 °C; analytical concentrations: $[NdCl_3]_T$ = 0–0.020 M, $[NaGluc]_T$ = 0.100 M. The calculation was based on the formation constants were determined in the present work.
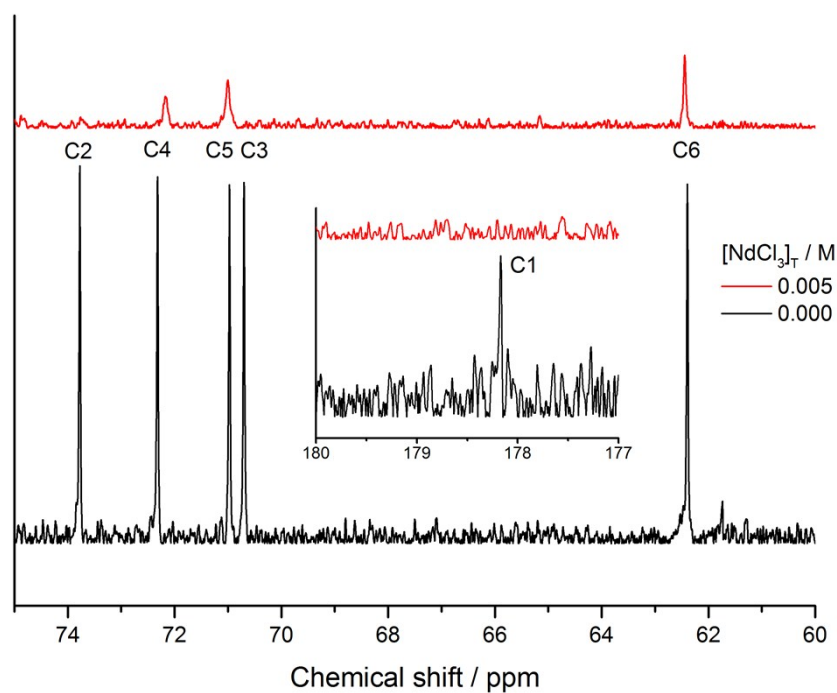

Figure S10. ^{13}C NMR spectra of gluconate in the Nd(III)–gluconate (Gluc⁻) system. Experimental conditions: T = 25 °C; analytical concentrations: $[NaGluc]_T$ = 0.100 M, $[NdCl_3]_T$ = 0–0.005 M.
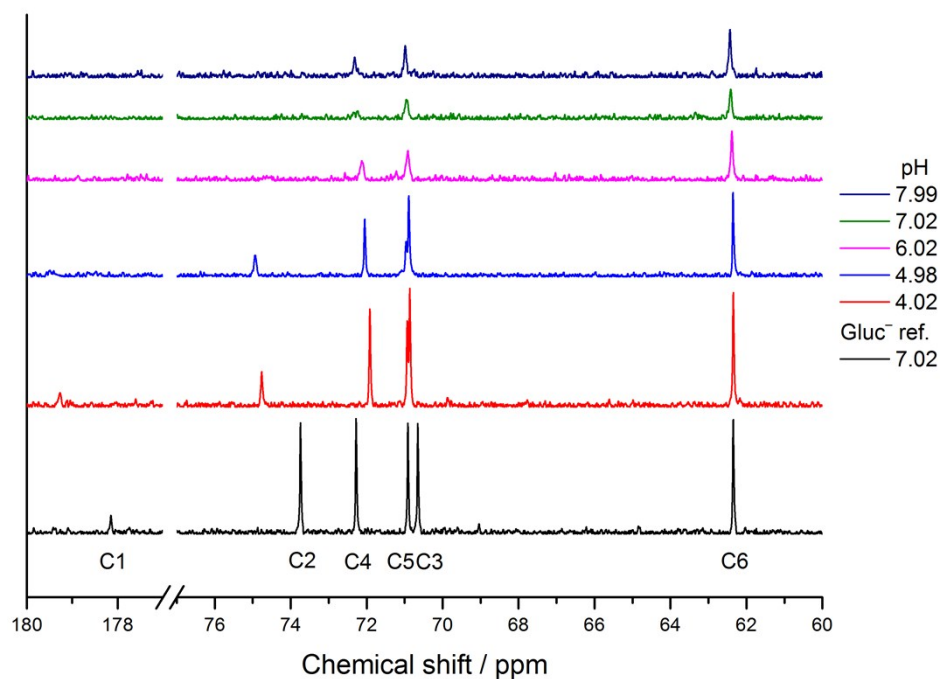
Figure S11. ^{13}C NMR spectra of gluconate in the Nd(III)–gluconate (Gluc$^-$) system. Experimental conditions: T = 25 °C; analytical concentrations: $[NdCl_3]_T$ = 0.005 M, $[NaGluc]_T$ = 0.100 M, pH = 4.02–7.99. The spectrum of 0.100 M NaGluc (black solid line) as a reference is also plotted.
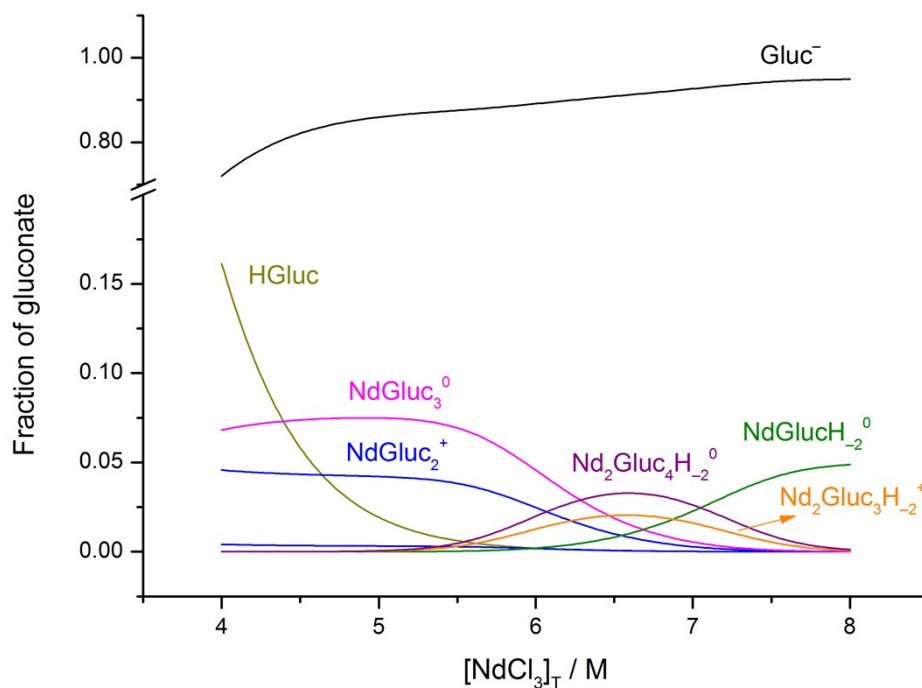

Figure S12. The distribution diagram of gluconate (Gluc$^-$) in the Nd(III)–gluconate system. Experimental conditions: T = 25 °C; analytical concentrations: $[NdCl_3]_T$ = 0.005 M, $[NaGluc]_T$ = 0.100 M. The calculation was based on the formation constants were determined in the present work.

The structure which is of 31.8 kJ/mol higher in energy than the most stable one (see Figure 8 in the article) is seen on Figure S13 (Structure A). The distance between the Nd^{3+} ion and the

carboxylate group is 2.47 Å. Stronger interactions are proposed for the C3–O⁻ alcoholate group (2.27 Å) and a deprotonated water molecule (2.31 Å). The metal-water distances alter between 2.54 Å and 2.68 Å. Interestingly, the incident interaction with the C2–OH group is of same strength, because it is located 2.57 Å from the central metal ion.
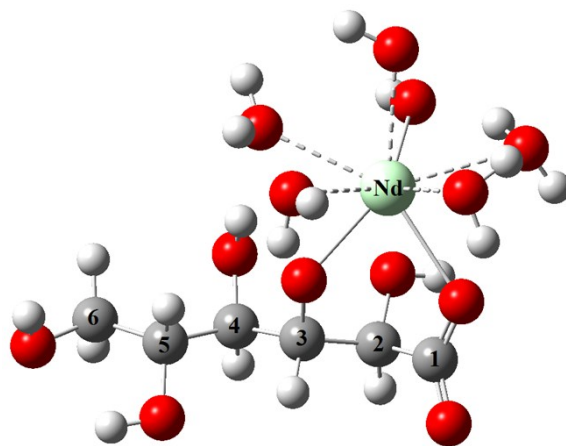

Figure S13. Optimized structure for the NdGlucH$_{-2}$^{0} complex (Structure A) with implicit and explicit water molecules. Calculations were performed at the PBE0 level applying the SDD core potentials for Nd^{3+} and the def2-SVP basis sets for the lighter atoms. The implicit water molecules were taken into account utilizing the COSMO solvation model. The Nd^{3+}–water coordinative interactions are visualized with dashed lines.

The third lowest energy structure (Structure B, Figure S14) for the NdGlucH$_{-2}$^{0} complex was found to be 33 kJ/mol higher in energy suggesting a relatively less stable structure. The Nd^{3+} is at larger distance from the carboxylate (2.53 Å), which is the one possible reason of the higher energy. The metal is bound to the deprotonated C2–OH (2.23 Å) and C3–OH (2.27 Å) groups and it is surrounded with six water molecules (2.56–2.62 Å).
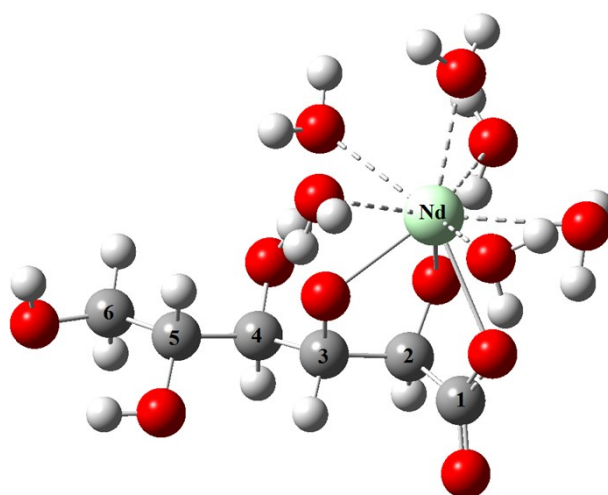

Figure S14. Optimized structure for the NdGlucH$_{-2}$^{0} complex (Structure B) with implicit and explicit water molecules. Calculations were performed at the PBE0 level applying the SDD core potentials for Nd^{3+} and the def2-SVP basis sets for the lighter atoms. The implicit water molecules were taken into

account utilizing the COSMO solvation model. The Nd^{3+}–water coordinative interactions are visualized with dashed lines.