Magnesium(II) d-Gluconate Complexes Relevant to Radioactive Waste Disposals: Metal-Ion-Induced Ligand Deprotonation or Ligand-Promoted Metal-Ion Hydrolysis?

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ABSTRACT: The complexation equilibria between Mg2+ and d-gluconate (Gluc−) ions are of particular importance in modeling the chemical speciation in low- and intermediate-level radioactive waste repositories. NMR measurements and potentiometric titrations conducted at 25 °C and 4 M ionic strength revealed the formation of the MgGluc+, MgGlucOH0, MgGluc(−)(OH)2−, and Mg3Gluc2(OH)40 complexes. The trinuclear species provides indirect evidence for the existence of multinuclear magnesium(II) hydroxido complexes, whose formation was proposed earlier but has not been confirmed yet. Additionally, speciation calculations demonstrated that MgCl2 can markedly decrease the solubility of thorium(IV) at low ligand concentrations. Regarding the structure of MgGluc+, both IR spectra and density functional theory (DFT) calculations indicate the monodentate coordination of Gluc−.

By the potentiometric data, the acidity of the water molecules is higher in the MgGluc+ and MgGlucOH0 species than in the Mg(H2O)62+ aqua ion. On the basis of DFT calculations, this ligand-promoted hydrolysis is caused by strong hydrogen bonds forming between Gluc− and Mg(H2O)62+. Conversely, metal-ion-induced ligand deprotonation takes place in the case of calcium(II) complexes, giving rise to salient variations on the NMR spectra in a strongly alkaline medium.

INTRODUCTION

The chemical behavior of actinides in aqueous solutions is of general importance for the disposal of nuclear waste in underground salt mines. The solubility of actinide hydroxides in the so-called pore water is determined by various factors, such as the pH, ionic strength, presence of complexing agents, etc. Portland cement, used for the formulation of cementitious materials, has a large impact on the solution pH. The pH of the pore water is known to increase from neutral to ca. 12.5 because of the dissolution of Ca(OH)2(s). In underground salt mines, concentrated MgCl2- or NaCl-containing salt brines are supposed to form as a result of the incidental intrusion of water. Bube and co-workers reported that, for brines containing ≈3.8 M MgCl2, the pH increases to ≈12, while most of the Mg2+ ions are replaced by Ca2+ ions.3 In leachant solutions containing ≈5-4 M NaCl, the pH becomes as high as 13.

In principle, a highly caustic medium leads to the precipitation of radionuclides, thereby lowers their mobility as well as their release to the geosphere. The presence of various organic molecules, however, may result in an increase of the solubility through the formation of stable metal complexes. d-Gluconate (Gluc−; Scheme 1), being used as an additive in cement, is likely to be present in underground repositories; thus, it is regarded as a general model compound for organic contaminants. Gluc− is known to chelate thorium(IV), uranium(IV), uranium(VI), neptunium(IV), plutonium(IV), and americium(III) in an alkaline medium.

In a caustic medium, one of the OH groups of Gluc− undergoes deprotonation:

$$\text{Gluc}^- = \text{GlucH}_2^- + \text{H}^+$$  (1)

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The corresponding concentration stability constant, \( K_\alpha \), reads as
\[
K_\alpha = \frac{[\text{GlucH}_\alpha^2\text{+}] [\text{H}^+] \cdot e^\alpha}{[\text{Gluc}^-]^2} \tag{2}
\]
where \( e^\alpha \) is the standard molar concentration, 1 mol·dm\(^{-3}\). In concentrated electrolyte solutions, the \( pK \) was found to be 13.7 \((I = 1 \text{ M})^{14,15}\) and 14.1 \((I = 4 \text{ M})^{16}\). Additionally, the deprotonation reaction was invoked to explain the solubility curve of \( \text{UO}_2(\text{OH})_2(\text{s})^5 \) as well as \( \text{Th}([\text{OH}]_2(\text{s})^{5,17} \) in the presence of \( \text{Gluc}^- \). The \( pK \) of the \( \text{ThGluc(OH)}_4^- \) aqueous species was calculated to be 9.2 (at infinite dilution).\(^{17}\) In conclusion, deprotonation of \( \text{Gluc}^- \) occurs more readily in its metal-bound form compared to the free ligand.

The solubility of actinides can be affected by \( \text{CaCl}_2 \) and/or \( \text{MgCl}_2 \); both salts are expected to be present at high concentrations.\(^3\) First, stable binary complexes forming between \( \text{Ca}^{2+} \) or \( \text{Mg}^{2+} \) and \( \text{Gluc}^- \) ions may suppress the formation of actinide gluconate species, resulting in a decrease of the solubility. For calcium(II), the formation of \( \text{CaGlucOH} \)\(^0\) was detected above \( pH \approx 11 \), while the multinuclear \( \text{Ca}_2\text{Gluc(OH)}(\text{s})^0 \) and \( \text{Ca}_3\text{Gluc(OH)}(\text{s})^0 \) complexes are the predominant ones at higher \( \text{CaCl}_2 \) and ligand concentrations.\(^{15}\)

Second, the formation of ternary species consisting of calcium(II), actinide(IV), and gluconate ions increases the solubility. For thorium(IV), the \( \text{CaThGluc}_4(\text{OH})_4 \)\(^0\) complex was proposed to elucidate the sorption properties of thorium(IV) onto calcite at \( pH = 13.3 \).\(^{13}\) The formation of this ternary species can be promoted via the mononuclear \( \text{CaGlucOH} \)\(^0\):
\[
\text{Th(OH)}_4(\text{s}) + 2\text{CaGlucOH}^0 = \text{CaThGluc}_4(\text{OH})_4^0 + \text{Ca}^{2+} + 2\text{OH}^- \tag{3}
\]
Ternary complexes with similar stoichiometry and stability might be formed with \( \text{Mg}^{2+} \) ions as well. Contrary to \( \text{Ca}^{2+} / \text{Glu}^- \) complexes, the literature concerning \( \text{Mg}^{2+}/\text{Glu}^- \) interactions is sporadic. In an early paper, the \( \text{MgGluc}^- \) species was reported to form at neutral \( pH \).\(^{18}\) Using IR and \(^1H\) NMR spectroscopic means at 25 °C, it was found that the interaction with \( \text{Mg}^{2+} \) mainly localizes to the carboxylate group of \( \text{Gluc}^- \).\(^{19}\) Above \( \approx 35^\circ \text{C} \), \(^{13}\text{C} \) NMR relaxation studies indicated the additional participation of the terminal hydroxymethyl group (C6-OH; Scheme 1).\(^{20}\) Alteration of the coordination mode was interpreted in terms of conformational changes: at \( T < 30 \text{ °C} \), \( \text{Gluc}^- \) exists in solution as a mixture of the planar (zigzag) and bent-chain forms. With increasing temperature, however, the bent-chain conformer becomes predominant,\(^{20-25}\) rendering the simultaneous coordination of \( \text{CO}^- \) and C6-OH possible.

In contrast to \( \text{Ca}^{2+} \), the complexation equilibria between \( \text{Mg}^{2+} \) and \( \text{Gluc}^- \) ions in the alkaline \( pH \) regime were not studied. The formation of such coordination compounds may have a marked influence on the solubility of actinides in the presence of \( \text{Gluc}^- \). Thus, for modeling the solubility and aqueous speciation of these metal ions in \( \text{MgCl}_2 \)-containing solutions, a quantitative description of the \( \text{Mg}^{2+}/\text{Glu}^-/\text{OH}^- \) system is indispensable. Furthermore, to reveal the binding sites of the ligand and to make reliable comparisons with the calcium(II) complexes, structural analysis of the magnesium(II) species is necessary.

In this Article, we report on the solution equilibria of magnesium(II) gluconate complexes forming in a neutral-to-alkaline medium. The complexation reactions were studied by potentiometry, IR as well as \(^1H\) and \(^{13}\text{C} \) NMR spectroscopies. Additionally, the experiments were augmented with quantum-chemical computations. The results are discussed with respect to (1) the effect of \( \text{MgCl}_2 \) on the solubility of thorium(IV) and (2) the possible structures of the magnesium(II) gluconate complexes in comparison with the calcium(II) ones.

### Experimental Section

**Reagents and Solutions.** \( \text{NaGluc} \) (≥98%, Acros Organics), \( \text{MgCl}_2 \cdot 6\text{H}_2\text{O} \) (ACS grade, VWR Chemicals), \( \text{CaCl}_2 \cdot 2\text{H}_2\text{O} \) (ACS grade, VWR Chemicals), and \( \text{NaCl} \) (analytical reagent grade, VWR Chemicals) were used without further purification. Stock solutions of \( \text{NaGluc}, \text{MgCl}_2 \), and \( \text{CaCl}_2 \) were prepared by dissolving the salts in Milli-Q Millipore water. The exact concentration of the \( \text{Mg}^{2+} \) or \( \text{Ca}^{2+} \) ions was determined by ethylenediaminetetraacetic acid titration.

A 1 M stock solution of \( \text{NaOH} \) was prepared by diluting a carbonate-free 50% (w/w) \( \text{NaOH} \) prepared by the procedure reported in ref 24. The \( \text{NaOH} \) solution was then standardized against \( \text{HCl} \). The 1 M stock solution of \( \text{HCl} \) was made by volumetric dilution of \( \approx 37% \) (w/w) \( \text{HCl} \) (analytical reagent grade, VWR Chemicals), and its concentration was determined via titration of a \( \text{KHCO}_3 \) solution.

**Potentiometric Titrations.** The potentiometric titrations were carried out using a Metrohm Titrrando 888 titration instrument in a double-jacketed glass cell. Each solution was stirred continuously, while the temperature was kept at 25.0 ± 0.1 °C by a Julabo F12-MB thermostat. The equilibrium cell potentials were measured by a Jenway 3540 Bench \( \text{pH} \) and conductivity meter using a SenTiX-62 combined glass electrode (from WTW). The ionic strength was adjusted to 4 M with \( \text{NaCl} \).

During the course of electrode calibration, a weak acid (0.200 M malonic acid) and, subsequently, a strong acid (0.196 M HCl) were combined with each other. As a result, the electrode response was found to be linear in the range of \( 1.8 < \text{pHc} < 12.2 \), where \( \text{pHc} \) is defined as \( \log([\text{H}^+]/[\text{OH}^-]) \).

**NMR Spectroscopic Measurements.** \(^1H\) and \(^{13}\text{C} \) NMR spectra were recorded with a Bruker Ascend 500 MHz NMR spectrometer equipped with a 5 mm inverse broadband probe head furnished with...
z-oriented magnetic-field-gradient capability. The magnetic field was stabilized by locking it to the $^1$D signal of the solvent prior to spectral acquisition. The sample temperature was set to $25 \pm 1$ °C for measurements at a constant temperature and to $7$–$47$ °C during the temperature-dependent experiments. $10\% (v/v)$ D$_2$O was added to each sample, and 32 or 256 interferograms were collected to obtain the $^1$H or $^{13}$C NMR spectra. For comparison, the spectra were baseline-corrected and normalized.

The pH values of the solutions were set using the SenTix-62 electrode, which was calibrated with buffers (obtained from WTW). Conversely, the activity coefficient of H$^+$ in the buffers is considerably different from that in the samples because of the more concentrated ionic media and use of D$_2$O in the latter. Thus, the nominal pH adjusted in the solutions is referred to as pH$^*_H$ hereafter, and its deviation from the real pH can be estimated as ±0.2 units. Nevertheless, this difference is acceptable for qualitative purposes.

To study the complex formation between Mg$^{2+}$ and Gluca$^−$ at neutral pH, solutions with [Gluca]$^−_T = 0.200$ M and [Mg$^{2+}$]$^+_T = 0.000$–0.492 M were prepared. The ionic strength was adjusted to 4 $\text{Mg}^{2+}$/Gluc$^−$ solution. The ionic strength was adjusted to 4.000–4.492 M was prepared at pH$^*_H = 6$–13. The temperature dependence of a solution containing [Gluca]$^−_T = 0.200$ M and [Mg$^{2+}$]$^+_T = 0.1$ M was studied in the range of $7$–$47$ °C, and the pH$^*_H$ was adjusted to 10.0 at $T = 22$ °C. In each case, the pH$^*_H$ was set by HCl or NaOH solutions (right before the measurements), and the ionic strength was not adjusted.

**IR Spectroscopic Measurements.** The IR spectra were recorded at room temperature, using a Bio-Rad Digital Division FTS-65 A/896 Fourier transform infrared instrument with a spectral resolution of 4 cm$^{-1}$. The measurements were performed in transmission mode in the 750–$4000$ cm$^{-1}$ range, and 256 scans were collected for each sample. The spectra were baseline-corrected and normalized.

To investigate the effect of Mg$^{2+}$ ions on the IR absorption of gluconate, a series with [Gluca]$^−_T = 0.2$ M as well as [Gluca]$^−_T = 0.2$ M and [Mg$^{2+}$]$^+_T = 0.000$–1.0 M was prepared by applying D$_2$O as the solvent. The pH$^*_H$ values of the solutions were checked and found to be neutral.

**Computations**

**Data Evaluation and Speciation Calculations.** The potentiometric and NMR spectroscopic data were evaluated with the aid of PSEQUAD.$^{27}$ The general complexation reaction and corresponding conditional stability product, $\beta_{pq}$, read as

$$p\text{Mg}^{2+} + q\text{Gluca}^- + r\text{H}_2\text{O} = \text{Mg}_p\text{Gluca}_q(\text{OH})_{r(2p-q-r)+} + r\text{H}^+ \quad (4)$$

$$\beta_{pq} = \frac{[\text{Mg}_p\text{Gluca}_q(\text{OH})_{r(2p-q-r)+}][\text{H}^+]^r}{[\text{Mg}^{2+}]^p[\text{Gluca}^-]^q(\text{H}_2\text{O})^{r-p-q}} \quad (5)$$

During fitting, the stability product, log $\beta_{pq}$, was refined by minimizing the so-called fitting parameter, FP, which reads as

$$FP = \sqrt{\frac{\sum_{i=1}^{n}(Y_{i,\text{calc}} - Y_{i,\text{meas}})^2}{n - k}} \quad (6)$$

where $Y_{i,\text{calc}}$ and $Y_{i,\text{meas}}$ pertain to the calculated and measured data (pH, or chemical shift), while $n$ and $k$ represent the number of the measured data and fitted parameters, respectively. The log $K_{ij}$ value was set to $-14.26^{16}$ throughout the calculations.

For homogeneous systems, speciation calculations were carried out utilizing the MEDUSA$^{28}$ program. For heterogeneous systems, where the solubility is controlled by Th-(OH)$_4$($s$), PSEQUAD$^{27}$ was applied by setting the Th-(OH)$_4$($aq$) complex as the primary species. The stability product of Th(OH)$_4$($s$) and those of the various hydrolysis species, Th(OH)$_{4n}$($aq$), were taken from the respective NEA-TDB review.$^{29}$ No formation constant was selected for the Th(OH)$_4$($s$) complex; hence, it was taken from ref 30. Concerning the gluconate complexes of thorium(IV).$^{5,6}$ the equilibrium constants were taken from ref 17. All of these values are presented in Table S1.

In order to perform speciation calculations for the Th$^{4+}$/Mg$^{2+}$/Gluca$^-$/OH$^-$ system, the literature data of the thorium-(IV)-containing species were converted to $I = 4$ M. For this purpose, the specific-ion-interaction theory (SIT)$^{31–34}$ was applied. The SIT introduces ion-interaction parameters ($\epsilon_{ij}$) to describe short-range ion interactions and the ionic strength dependence of the mean activity coefficient. It is worth mentioning that, in general, the Pitzer approach$^{35}$ or the modified SIT$^{36}$ is known to be more accurate at higher ionic strength. The literature data, however, are insufficient (especially for the gluconate complexes) to perform accurate calculations with these models. Nonetheless, the SIT approach was found to be applicable at $I > 4$ M in numerous cases, a also for different background electrolytes,$^{37–39}$ including NaCl.$^{40,41}$ Hence, we used this model following the approach of the standard NEA-TDB review.$^{29}$

The respective $\epsilon_{ij}$ coefficients (Table S2) were taken from refs 29 and 42. The stability constants calculated using the SIT equation are listed in Table S1. For further details, the reader is referred to the Supporting Information and to refs 29–34.

**Quantum-Chemical Calculations.** To model the structure of the complexes, in vacuo calculations were performed using the M11 range-separated hybrid meta-generalized gradient approximation density functional theory (DFT) functional$^{44}$ coupled with the cc-pVQZ basis set. The recently developed M11 functional was shown to provide excellent performance for main-group energies, proton and electron affinities, barrier heights, bond dissociation, and noncovalent interaction energies. The computations were coupled with conformational analysis by varying the freely rotating HCCH dihedral angles of Gluca$^-$. Subsequent geometry optimizations of all structures were carried out utilizing the same functional and the aug-cc-pVTZ basis set. These calculations with the higher basis set were undertaken by taking solvent effects into account with the aid of the conductor-like polarizable continuum model (CPCM)$^{44}$ (where water was considered to be the solvent). All calculations were carried out using the Gaussian09$^{45}$ software package.

**Results and Discussion**

**Complexation between Mg$^{2+}$ and Gluca$^-$.** With increasing [MgCl$_2$]$_T$ in solutions containing [Gluca]$^-_T = 0.2$ M, the H2 and H3 NMR signals of Gluca$^-$ show a gradual downfield shift (Figure 1). Simultaneously, the position of the C1 signal shifts upfield. Such variations indicate complex formation as in the case of Ca$^{2+}$ binding, which was confirmed by 2D $^1$H–$^{13}$C NMR measurements.$^{46}$ Moreover, no additional peaks appear on the spectra, which stems from...
fast ligand-exchange processes between free and complexed Gluc$^\text{−}$.

The experimentally obtained chemical shifts were fitted as a function of [Mg$^{2+}$]$_T$, assuming formation of the 1:1 complex. The relationship between the observed chemical shift ($\delta_{\text{obs}}$) and the equilibrium concentrations of Gluc$^\text{−}$ and MgGluc$^+$ is as follows:

$$\delta_{\text{obs}} = \delta_{\text{Gluc}}[\text{Gluc}^\text{−}] + \delta_{\text{MgGluc}}[\text{MgGluc}^+]$$

(7)

where $\delta_{\text{Gluc}}$ and $\delta_{\text{MgGluc}}$ are the limiting chemical shifts of Gluc$^\text{−}$ and MgGluc$^+$, respectively.

When solely the $^{13}$C chemical shifts are fitted, log $\beta_{110}$ was determined to be 0.25±0.33, with FP (eq 6) being 0.002–0.006 ppm. When only the $^1$H chemical shifts are fitted, log $\beta_{110}$ ranged from 0.46 to 0.60 (FP = 0.0006–0.0012 ppm). When both the $^1$H and $^{13}$C shifts were taken into account, log $\beta_{110}$ was found to be 0.25 on average (FP = 0.002 ppm). The best fitting from each set is shown in Table 1, while the calculations considering all chemical shifts are depicted in Figure 1.

The difference in the formation constants obtained by $^1$H and $^{13}$C nuclei is not unusual for weak complexes because $β_{110}$ and the actual limiting chemical shifts are highly correlated. Hence, on the basis of the NMR results, we suggest 0.4±0.2 for log $\beta_{110}$; this value is in reasonable agreement with log $\beta_{110}$; this value is in reasonable agreement with log $\beta_{110}$ for MgGluc$^+$ and 1.21 for Ca$^{2+}$ + Gluc$^−$.

Moreover, if dehydration occurs in both cases, it is again dehydration, yielding more stable calcium(II) complexes.

Table 1. Stability Products, log $\beta_{pp}$, for Equilibria Taking Place in the Mg$^{2+}$/Gluc$^−$/H$_2$O$^+/$/OH$^−$ System

| reaction | log $\beta_{pp}$ | method$^b$ | ref |
|----------|-----------------|-------------|-----|
| H$_2$O = H$^+$ + OH$^−$ | −14.26 | H$_2$-Pt POT | 16 |
| HGluc = Gluc$^−$ + H$^+$ | −3.73 ± 0.05 | GLE POT | p.w. |
| Gluc$^−$ = GlucH$^−$ + H$^+$ | −13.92 ± 0.06 | GLE POT | p.w. |
| Mg$^{2+}$ + H$_2$O = MgOH$^+$ + H$^+$ | −13.92 ± 0.03 | H$_2$-Pt POT | 16 |
| Mg$^{2+}$ + H$_2$O = MgOH$^+$ + H$^+$ | −13.90 ± 0.03 | 13C NMR | 16 |
| Mg$^{2+}$ + Gluc$^−$ = MgGluc$^+$ | −0.70 | 0.33 ± 0.04 | 13C NMR | p.w. |
| Mg$^{2+}$ + Gluc$^−$ = MgGluc$^+$ | 0.47 ± 0.05 | 1H NMR | p.w. |
| Mg$^{2+}$ + Gluc$^−$ = MgGluc$^+$ | 0.25 ± 0.02 | 13C NMR | p.w. |
| Ca$^{2+}$ + Gluc$^−$ = CaGluc$^+$ | 0.70$^{1d}$ | 0.25 ± 0.05 | 1H/13C NMR | p.w. |
| Ca$^{2+}$ + Gluc$^−$ = CaGluc$^+$ | 0.70$^{1d}$ | 0.4 ± 0.2$^{1d}$ | GLE POT | p.w. |
| Ca$^{2+}$ + Gluc$^−$ = CaGluc$^+$ | 0.85 ± 0.15 | 1H/13C NMR | 46 |
| Ca$^{2+}$ + Gluc$^−$ = CaGluc$^+$ | 1.12$^{1d}$ | GLE POT | p.w. |

$^{1d}$ For comparison, analogous constants for the Ca$^{2+}$/Gluc$^−$/H$_2$O$^+/$/OH$^−$ system are presented. The constants correspond to T = 25 °C and I = 4 M (NaCl), unless indicated differently. $^H_2$-Pt, GLE, ISE POT: potentiometry applying hydrogen (platinized platinum), glass or calcium ion-selective electrode. $^1$H and $^{13}$C NMR: nuclear magnetic resonance spectroscopy. SOL/ICP-OES: solubility determined with inductively coupled plasma optical emission spectroscopy.

$^a$ Here the solubility product (log $K_{sp}$) is given. $^b$ The experiments were performed at T = 22.5 °C in ref 49 and at I = 0.2 M (KCl) in ref 18.

$^c$ Recommended value for log $\beta_{110}$ (see the text for discussion).

Conversely, other thermodynamic factors may play important roles in the complex formation reactions of Mg$^{2+}$.

First, Mg$^{2+}$ prefers 6-fold coordination, while the first coordination sphere of Ca$^{2+}$ is rather flexible, with the hydration number being 6–8.$^{52–59}$ As a result, binding of the COO$^\text{−}$ group requires the loss of (at least) one solvent molecule for Mg$^{2+}$, while Ca$^{2+}$ can accommodate it without dehydration, yielding more stable calcium(II) complexes. Moreover, if dehydration occurs in both cases, it is again more favorable for Ca$^{2+}$: the enthalpy of dehydration was found to be 16.8–17.7 kJ·mol$^{-1}$ for Ca(H$_2$O)$_2$$^{2+}$, while 23.4–24.2 kJ·mol$^{-1}$ was determined for Mg(H$_2$O)$_2$$^{2+}$.$^{60}$

It is important to note that the release of water molecules would result in higher disorder, thereby favoring the formation of MgGluc$^+$. The higher stability constant of CaGluc$^+$, however, indicates that enthalpy effects dominate the formation of 1:1 complexes.

Coordinating Mode of Gluc$^−$ in the MgGluc$^+$ Complex. The variations of the NMR chemical shifts do not allow one to decide whether Gluc$^−$ is bound in a mono-

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Figure 1. $^1$H and $^{13}$C NMR chemical shifts as a function of [Mg$^{2+}$]$_T$. Experimental conditions: I = 4 M (NaCl) and $T = 25 \pm 1$ °C; [Gluc$^−$]$_T$ = 0.200 M. Symbols represent measured data, while solid lines were calculated assuming the formation of MgGluc$^+$.

The chemical shifts were normalized to the neat Gluc$^−$ ion for better visualization.

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| Mg$^{2+}$ + H$_2$O = MgOH$^+$ + H$^+$ | −13.92 ± 0.03 | H$_2$-Pt POT | 16 |
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| Mg$^{2+}$ + Gluc$^−$ = MgGluc$^+$ | 0.25 ± 0.05 | 1H/13C NMR | p.w. |
| Ca$^{2+}$ + Gluc$^−$ = CaGluc$^+$ | 0.70$^{1d}$ | 0.4 ± 0.2$^{1d}$ | GLE POT | p.w. |
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$^{1d}$ For comparison, analogous constants for the Ca$^{2+}$/Gluc$^−$/H$_2$O$^+$/$$/OH^−$ system are presented. The constants correspond to T = 25 °C and I = 4 M (NaCl), unless indicated differently. $^H_2$-Pt, GLE, ISE POT: potentiometry applying hydrogen (platinized platinum), glass or calcium ion-selective electrode. $^1$H and $^{13}$C NMR: nuclear magnetic resonance spectroscopy. SOL/ICP-OES: solubility determined with inductively coupled plasma optical emission spectroscopy.

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$^c$ Recommended value for log $\beta_{110}$ (see the text for discussion).
A bidentate manner to the metal ion. To unravel the coordination mode in the 1:1 complex, a solution series of \([\text{Gluc}]_T = 0.2 \text{ M}\) and \([\text{Mg}^{2+}]_T = 0–1 \text{ M}\) was studied via IR spectroscopy, applying D\(_2\)O as the solvent.

Upon the addition of Mg\(^{2+}\) ions, the region of –O–H stretching vibrations (3000–3700 cm\(^{-1}\)) does not exhibit any significant changes upon metal-ion coordination. In conclusion, the metal–ligand interactions are localized to the region of carboxylate stretching vibrations, in agreement with a previous IR study.\(^{19}\) Therefore, only this region is presented (Figure 2) and discussed.

![Figure 2. Traces of IR spectra of a solution series of [NaGluc]\(_T\) = 0.2 M and [MgCl\(_2\)]\(_T\) = 0–1 M at room temperature.](image-url)

Assignment of the symmetric and asymmetric stretching vibrations of Gluc\(^{-}\) is rather difficult. The asymmetric vibration mode is obviously split into two components (1599 and 1653 cm\(^{-1}\)), which was also previously observed on the spectrum of the solid NaGluc salt.\(^{16}\) Such a splitting is an indicative of two different coordination modes between the metal ion and ligand, as was proposed for the cobalt(II) acetate dihydrate complex formation. At [MgCl\(_2\)]\(_T\) = 1 M, ca. 70% of the ligand is bound in the 1:1 complex, where the distance is 180 cm\(^{-1}\). On the basis of IR analysis of numerous solid complexes,\(^{64,65}\) such a difference refers to the so-called pseudobridged monodentate coordination, where one oxygen atom of the COO\(^{-}\) group is bound to the metal ion, while the other establishes hydrogen bonding of a neighboring OH group.

Solely on the basis of the IR spectra, participation of the OH groups in ligand coordination is still uncertain. To address this problem, quantum-chemical computations were undertaken. The following scenarios were taken into consideration: (1) monodentate binding, (2) bidentate coordination of COO\(^{-}\), and (3) monodentate binding of COO\(^{-}\) and the adjacent OH group. During calculations, octahedral geometry around Mg\(^{2+}\) was assumed.

For bidentate coordination modes, the binding of both oxygen atoms of the COO\(^{-}\) group (Figure S4) yields a less stable complex than monodentate coordination of both the COO\(^{-}\) and OH groups (Figure S5). The difference in energy is 13.5 kJ mol\(^{-1}\), significantly higher than the energy of thermal motion (≈2.5 kJ mol\(^{-1}\) at 25 °C). Thus, bidentate coordination of COO\(^{-}\) can be excluded, in agreement with the outcome of the IR experiments.

To compare the stabilities of the chelate (Figure S5) and monodentate species, the number of water molecules must match. Hence, a water molecule was added to the chelate complex, and its position was varied around the metal ion and along the gluconate backbone. The most stable structure is depicted in Figure S6. Alternatively, this complex represents the product of the reaction

\[
\text{Mg(H}_2\text{O)}_4\text{Gluc}^+ = \text{Mg(H}_2\text{O})_4\text{Gluc}^+ + \text{H}_2\text{O} \quad (8)
\]

Its energy, however, is higher by 6.2 kJ mol\(^{-1}\) than that of Mg(H\(_2\)O)\(_4\)Gluc\(^+\) (Figure S7). In conclusion, the bidentate coordination of Gluc\(^{-}\) is not favored because of the strong hydration of Mg\(^{2+}\). Additionally, one oxygen atom of COO\(^{-}\) establishes strong hydrogen bonding with an axial metal-bound water molecule (dashed line in Figure S7), resulting in pseudobridged monodentate coordination.\(^{64,65}\) The discussion of the role of hydrogen bonding is deferred to the Role of Hydrogen Bonds in the MgGluc\(^+\) and MgGlucOH\(^\circ\) Complexes section.

In summary, both IR measurements and structure computations suggest that Gluc\(^{-}\) acts as a monodentate ligand in the MgGluc\(^+\) complex. Conversely, chelate formation is preferred for CaGluc\(^+\).\(^{36}\)

**Effect of the pH on the Complexation between Mg\(^{2+}\) and Gluc\(^{-}\) Ions.** In order to examine the complex formation between Mg\(^{2+}\) and Gluc\(^{-}\) as well as protonation of the ligand, a series of potentiometric titrations were performed in the pH\(_c\) range of 1.9–12.1. To demonstrate the pH changes caused by complex formation, several comparative titration curves are shown in Figure 3.

The red curve depicts the pH\(_c\) values of a slightly acidic solution of 0.2 M NaGluc titrated with NaOH. Upon the addition of MgCl\(_2\) (0–0.2 M), the shapes of the curves resemble that of 0.2 M NaGluc. The pH\(_c\) however, is much lower after the equivalence point, indicating complex formation.

Furthermore, the titration curves of solutions with [Gluc\(^{-}\)]\(_T\) = 0.1 M and [Mg\(^{2+}\)]\(_T\) = 0.1 M (orange curve) and [Gluc\(^{-}\)]\(_T\) = 0.2 M and [Mg\(^{2+}\)]\(_T\) = 0.05 M (blue curve) are essentially the same in the alkaline region. According to the Goldberg–Waage mass action law, the equilibrium concentration of the complex(es) formation must be proportional to the product of the reaction

\[
\text{Mg(H}_2\text{O)}_4\text{Gluc}^+ + \text{H}_2\text{O} = \text{Mg(H}_2\text{O})_4(\text{GlucOH})^+ \quad (9)
\]
that of \([\text{Mg}^{2+}]_0[\text{Gluc}^-]^0\) and, hence, to that of \([\text{Mg}^{2+}]_0[\text{Gluc}^-]^0\). Because in both cases \([\text{Mg}^{2+}]_0[\text{Gluc}^-]^0\), the similar values of \(pH_1\) imply that \(\alpha = \beta = 1\), i.e., the formation of 1:1 species. It is also worth mentioning that, with increasing \([\text{Mg}^{2+}]_0\), a small but significant decrease in \(pH_1\) is discernible in the acidic region, which follows from the reaction

\[
\text{Mg}^{2+} + \text{HGluc} = \text{MgGluc}^+ + \text{H}^+ \tag{9}
\]

When the titration curve of the solution containing only 0.1 M MgCl\(_2\) (black curve) is compared to those containing Gluc\(^-\), it is seen that the increase of \(pH_1\) is less steep for the latter, indicating a stronger buffering capacity and, thus, complexion between the \(\text{Mg}^{2+}\) and Gluc\(^-\) ions in the alkaline regime. This is strongly supported by the fact that, in contrast to the solution with 0.1 M MgCl\(_2\), precipitation of Mg(OH)\(_2\)(s) cannot be observed in the presence of Gluc\(^-\).

Expectedly, titrations performed with 1 M MgCl\(_2\) as the titrant (Figure S8) exhibit a remarkable \(pH_1\) decrease (\(\Delta pH = 2\)) upon the addition of 5 mL of titrant. Starting with the titrations from the acidic region ([HCl]\(_T,0\) = 0.1 M), a lower but still pronounced \(pH_1\) decrease (\(\Delta pH \approx 0.3\)) is seen as a token of the formation of MgGluc\(^-\) (eq 9).

During data evaluation, the \(pH_1\) and MgCl\(_2\)-dependent titrations as well as the protonation measurements of Gluc\(^-\) were fitted simultaneously. Assuming the formation of HGluc, GlucH\(_{12}\), MgGluc\(^-\), and its two deprotonated forms, MgGluc(OH)\(^0\) and MgGluc(OH)\(^-\), the FP was found to be 0.024 (in \(pH_1\) units).

Further improvement of the FP (0.017) could be achieved by taking the formation of MgGluc\(_2\)(OH)\(^0\) into consideration. Expectedly, the two curves, starting from the alkaline region and with MgCl\(_2\) as the titrant, are the most affected ones. That is, the individual FP decreased from 0.034 to 0.021 (Figure S8, red curve) as well as from 0.040 to 0.015 (Figure S8, blue curve). Given that the calcium(II) analogues were detected in the presence of Gluc\(^-\), the presence of such a trinuclear magnesium(II) complex seems to be realistic.

In conclusion, the proposed chemical model for the Mg\(^{2+}\)/Gluc\(^-\)/OH\(^-\)/H\(^+\) system consists of HGluc, GlucH\(_{12}\), MgGluc\(^-\), MgGluc(OH)\(^0\), MgGluc(OH)\(^-\), and MgGluc\(_2\)(OH)\(^0\). The calculated potentials are depicted in Figures S8–S10, while the respective stability products are listed in Table 1. To the best of our knowledge, the deprotonation constant of HGluc (at \(I = 4\) M NaCl) is the only one to date. Regarding GlucH\(_{12}\), the reliability of its stability constant (\(-13.92\)) is justified by the excellent agreement with that (\(-13.90\)) determined previously via \(^{13}\)C NMR at the same ionic strength. As for MgGluc\(^-\), \(\log \beta_{110} = 0.33\) agrees well with that proposed from the NMR results (0.4 ± 0.2).

Comparing the stability products of the calcium(II) and magnesium(II) analogues (i.e., the 1:1 and 3:2:4 species), it is evident that more stable complexes are formed with Mg\(^{2+}\). This striking difference can be explained by the fact that Mg\(^{2+}\) ions undergo hydrolysis more readily. In fact, the stability of MgOH\(^+\) is higher by roughly 1.5 orders of magnitude than that of CaOH\(^+\). Similarly, the solubility product of Mg(OH)\(_2\)(s) is smaller by more than 6 orders of magnitude than that of Ca(OH)\(_2\)(s).

Figure 4 shows the concentration distribution diagram of magnesium(II) for the most concentrated solution used in our studies (\([\text{Gluc}^-] = 0.2\) M and \([\text{Mg}^{2+}] = 0.1\) M). It is seen that the Mg\(_3\)Gluc\(_2\)(OH)\(_4\)\(^0\) species is the predominant one in the \(pH_1\) range of 10.5–12.0. As for the stoichiometry of MgGluc\(_2\)(OH)\(^0\), it shows a pronounced similarity with both the Mg\(_3\)Gluc\(_2\)(OH)\(_4\)\(^0\) and Mg\(_4\)Gluc\(_4\)(OH)\(_4\)\(^0\) polynuclear species that were invoked in previous studies. Because their formation coincides with the onset of the precipitation of Mg(OH)\(_2\)(s). Nevertheless, the formation of Mg\(_3\)Gluc\(_2\)(OH)\(_4\)\(^0\) can be indirect evidence of the existence of these hydroxido complexes because they might be stabilized by Gluc\(^-\) through the following reactions:

\[
\text{Mg}_{3}(\text{OH})_{4}^{2+} + 2\text{Gluc}^- = \text{Mg}_{3}\text{Gluc}_{2}(\text{OH})_{4}^{0} \tag{10}
\]
The impact of MgCl₂ on the solubility of thorium(IV) hydroxide as a function of pHc. The calculations were based on equilibrium constants corresponding to T = 25 °C and I = 4 M (NaCl). Total concentrations: [Gluc⁻]T = 0 M (black line) and 0.01 M (colored lines). [Mg²⁺]T: listed in the legend. In the pH ranges depicted with dashed lines, Mg(OH)₂(s) is expected to precipitate.
Effect of the pH and Temperature on the NMR Spectra of Gluc$^-$ in the Presence of MgCl$_2$. To gain further insights concerning the structures of the complexes formed, a series of NMR spectra were recorded. Figure 7

![Normalized intensity](image

Figure 7. $^1$H NMR spectra of solutions containing [Gluc$^-$]$_T$ = 0.200 M and [Mg$^{2+}$]$_T$ = 0.100 M as a function of the nominal pH$^*$ at $T$ = 25 ± 1 °C.

shows the pH dependence of the $^1$H spectra of Gluc$^-$ in solutions containing [Gluc$^-$]$_T$ = 0.2 M and [Mg$^{2+}$]$_T$ = 0.1 M. At pH$^*$ = 6, ca. 14% of [Gluc$^-$]$_T$ is bound in the MgGluc$^-$ complex. [It has to be noted that only a semiquantitative comparison is possible because the formation constants of the present samples are somewhat different (I < 1 M) from those used for the speciation calculations (I = 4 M).]

At pH$^*$ = 6−9, the spectra remain unchanged, while at pH$^*$ = 9.5−10, the H2 peak is shifted slightly downfield; furthermore, the H4−H5 signals become more resolved. These minor variations result from the formation of MgGlucOH$^0$, which is supported by the speciation diagram (Figure 8): the formation of this species starts at pH$_c$ = 9.

Interestingly, the shape of the spectra above pH$^*$ = 10 returns to those observed at pH$^*$ < 9. This is a hint that another complex is formed that suppresses the formation of MgGlucOH$^0$. Indeed, these reverse spectral changes coincide well with the Mg$_6$Gluc$_4$(OH)$_8$ species, which appears at pH$_c$ = 10 and becomes the dominant one up to pH$_c$ = 12 (Figure 8).

In parallel, the amount of free ligand drops to approximately 60%, yet the spectra resemble those of the free ligand (at pH$^*$ = 6). This similarity implies that the interactions between Mg$^{2+}$ and Gluc$^-$ are weaker in the trinuclear complex than in MgGlucOH$^0$; hence, Mg$_6$Gluc$_4$(OH)$_8$ might be the ligand-stabilized form of the Mg$_4$(OH)$_2$ species.

Above pH$^*$ ≈ 13, the H3−H6′ peaks are slightly shifted upfield because of the formation of GluCH$_2$H$_2$.$^2^-$ Conversely, the same downfield shift is seen on the H2 signal, indicating that the structures of the MgGlucOH$^0$ and the newly-formed MgGluc(OH)$_2$ species are similar. This conclusion is corroborated by the $^{13}$C NMR spectra as well (Figure S13), on which the same trend is seen. Additionally, the C1 signal (Figure S14) exhibits the highest variation: its chemical shift increases by 0.8 ppm at pH$^*$ = 10, while it merges to the baseline at pH$^*$ = 13. Hence, the COO$^-$ group is likely to be bound to Mg$^{2+}$ in these complexes, similarly to MgGluc$^-$.

On the other hand, it is not obvious where the deprotonation takes place: on an alcoholic OH group of the ligand or on a coordinated water molecule. Although potentiometry is in general not suitable to distinguish between these processes, comparing pK values of the ligand and aqua complexes of a given metal ion might help. In this respect, Van Duin and co-workers proposed a general ionization scheme for the complexation reactions occurring between metal ions and poly(hydroxycarboxylates). Accordingly, deprotonation of MgGluc$^-$ can be attributed to ionization of the C2−OH group because the respective pK is lower by ≈2 units than that of the first hydrolytic step of the aqua complex (pK$_{a1}$). The same conclusion was drawn by analyzing the formation constants of the gluconate complexes of aluminum(III) and praseodymium(III), respectively. This so-called metal-induced ligand deprotonation is driven by the formation of very stable, five-membered chelate complexes.

The pK$_{a0}$ of the Mg$^{2+}$ aqua ion (i.e., $-\log \beta_{100}$) was reported to be 12.33. For MgGluc$^-$, using $\log \beta_{110} = 0.33$, pK$_2$ is 10.53 (i.e., $\log \beta_{110} - \log \beta_{111}$), while pK$_2$ is 11.46 (i.e., $\log \beta_{111} - \log \beta_{112}$). Given that pK$_{a1}$ < pK$_{a2}$ < pK$_{a0}$, even the second deprotonation of the 1:1 complex can occur on the alcoholic OH groups of Gluc$^-$.

Because displacement of an alcoholic proton has already been established for the calcium(II) gluconate complexes, comparative NMR measurements were undertaken for the Gluc$^-$, Mg$^{2+}$/Gluc$^-$, and Ca$^{2+}$/Gluc$^-$ systems. The $^1$H NMR spectra are displayed in Figure 9, while the $^{13}$C NMR spectra are depicted in Figures S15 and S16.

From pH$^*$ = 6 to 10, only small spectral variations are discernible for both metal-ion-containing solutions compared to the spectra of free Gluc$^-$.. These changes are caused by formation of the mononuclear species, discussed in detail in the previous sections as well as in ref 46. Conversely, the spectrum of the Ca$^{2+}$/Gluc$^-$ system exhibits salient changes at pH$^*$ = 12. That is, the $^1$H peaks are broadened, especially the H2 and H3 ones, indicating their substantial role in the formation of two deprotonated complexes, CaGlucOH$^0$ and Ca$_2$Gluc(OH)$_2$ species, which is visualized on the distribution diagram of this system (Figure S17).

To calculate the species...
distribution, formation constants were obtained from refs 16, 46, and 48. The dramatic changes seen on the $^1$H NMR spectra appear on the $^{13}$C NMR spectra as well: the peaks of C1–C4 are merged to the baseline, while those of C5 and C6 are widened (Figures S15 and S16).

Such marked changes can be interpreted in terms of metal-ion-induced ligand deprotonation. Namely, the simultaneous coordination of Ca$^{2+}$ and deprotonation of the OH group(s) lead to the formation of alcolohate binding site(s) and therefore much stronger coordinative bonds than those present in the CaGluc$^-$ species. As a result, the rate of ligand exchange between bound and free Gluc$^-$ slows down, becoming commensurate to the NMR relaxation rates. This, in turn, results in an increase of the signal half-widths, especially of those belonging to the coordination sites. Such a spectral feature was detected for the Ca$^{2+}$/Gluc$^-$ system, and the shift from slow to fast complexation dynamics was attested by temperature-dependent measurements.15

Conversely, only marginal changes can be observed for Mg$^{2+}$ at the same pH$^*$. Given that the concentrations of the magnesium(II) gluconate complexes are higher than those of the calcium(II) complexes (Figure 8 vs Figure S17), this difference is striking. Obviously, there is no sign of metal-ion-promoted deprotonation of Gluc$^-$, indicating that, similarly to MgGluc$^-$, the alcoholic OH groups are not directly bound to the metal ion. The lack of ligand deprotonation is also supported by the temperature-dependent $^1$H and $^{13}$C NMR experiments (Figures S18–S20). At pH$^* = 10$ (at T = 22 °C), where the concentration of MgGlucOH$^0$ is the highest, the characteristic transition between the slow and fast exchange rates is absent. Furthermore, the monotonous shift of the C6 peak position provides no sound evidence of coordination of the C6–OH group, which was proposed in a previous $^{13}$C NMR relaxation study.20 A possible reason is that the chemical shift is a less sensitive quantity compared to the relaxation time.

In conclusion, deprotonation in the magnesium(II) gluconate species takes place not on the ligand side but on one of the coordinated water molecules. Still, proton displacement occurs more readily in the MgGluc$^-$ complex (pK$\text{a} \approx 10.5$) than in the Mg(H$_2$O)$_2^{2+}$ aqua ion (pK$\text{a} \approx 12.3$).47 Hence, this apparent ligand-promoted hydrolysis of Mg$^{2+}$ in the 1:1 species probably arises from other structural features that are invisible for NMR spectroscopy.

**Role of Hydrogen Bonds in the MgGluc$^+$ and MgGlucOH$^0$ Complexes.** The structure of MgGluc$^-$ was optimized by assuming octahedral coordination geometry around Mg$^{2+}$ and monodentate binding of the COO$^-$ group. The optimum geometry is depicted in Figure 10, while the metal–oxygen distances and hydrogen bonds are listed in Table 2.

First, it is seen that the Mg–O1B distance (2.04 Å) is lower only by 0.03–0.05 Å than the respective Mg–O1W bond lengths, implying that the Mg$^{2+}$–OOC and Mg$^{2+}$–OH$_2$ interactions are of similar strengths. Second, two OH groups of Gluc$^-$ interact with the hydrating water molecules; namely, very strong hydrogen bonds are established between O1A and O1W (1.69 Å) as well as O3 and O3W (1.75 Å). (In general, strong hydrogen bonds are considered when d < 2.5 Å.)73) Meanwhile, the respective O1W–H and O3W–H covalent bond lengths are more elongated (0.99–1.00 Å) than those for the other water molecules (≈0.96 Å). Interestingly, those structures that are less stable but whose differences in energy are lower than the energy of thermal motion (≈2.5 kJ·mol$^{-1}$ at 25 °C) exhibit the same coordination motif.

Structure optimization of the MgGlucOH$^0$ species was based on the most stable geometry of MgGluc$^-$ as the input, and the site of deprotonation was varied from O1A to O5W. The lowest-energy complex is shown in Figure 11, and the corresponding bond distances are listed in Table 2.

Deprotonation on the equatorial 4W water molecule results in slight weakening of the Mg–O1B (2.08 Å) and of the Mg–OH$_2$ (2.10–2.18 Å) bonds, while the formation of a hydroxide ion establishes strong interaction with the metal ion (1.97 Å) as well as a hydrogen bond with O2W (1.76 Å). (It is worth mentioning that a complex hydrogen-bonding network is present in MgGluc$^-$ and MgGlucOH$^0$, respectively. Such intramolecular interactions were found in the NaGluc and CaGluc$^-$ solid complexes as well.47,48) More importantly, strong hydrogen bonding is seen between O1A and O1W as well as O3 and O3W, as for MgGluc$^-$.

Concerning the hydrogen bonding in these species, this unique feature at the macroscopic level can be related to our macroscopic findings. That is, elongation of the water O–H...
MgGluc(H2O)4(OH)0 Complexes also possible in the MgAc+ species, the diin metal complexes are dielucidated qualitatively. Additionally, such hydrogen bonds because it has no OH groups, and the stability of MgAc+ 18,50 is compared to those in the Mg(H2O)6 coordination of Gluc− Mg(OH)2(s) was not observed. Conversely, the precipitate similar to that of MgGluc+. For Gluc− gluconate or acetate (Ac−) was detected right after the addition of NaOH in the case of NMR measurements.

- The complex formation between Mg2+ and Gluc− was studied in neutral-to-alkaline aqueous solutions at 25 °C and 4 M ionic strength. The formation of the MgGluc− complex was observed and quantitatively described via 1H and 13C NMR spectroscopic measurements. It was proven by additional IR measurements and quantum-chemical computations that the preferred coordination mode is a pseudobridged monodentate, where one oxygen atom of COO− is bound to the metal ion, while the other is in hydrogen-bonding interaction with an adjacent OH group.

- Because concentrated MgCl2 salt brines might contact with underground radioactive waste disposals, the effect of Mg2+ ions on the solubility of actinides is a key factor in the long-term stability assessment of these repositories. Using the stability products obtained in the present work, we calculated the solubility curve of thorium(IV) as a function of pHc by term stability assessment of these repositories. Using the stability products obtained in the present work, we calculated the solubility curve of thorium(IV) as a function of pHc by varying the concentrations of Gluc− and MgCl2. It was found that, with an increase in the concentration of MgCl2, the solubility of thorium(IV) decreases, which stems from binary complexes forming between the Mg2+ and Gluc− ions. These processes can effectively suppress complexation between Th(OH)4(s) and Gluc− at low ligand concentrations.

- Additional pH-dependent 1H and 13C NMR experiments showed that deprotonation does not significantly affect the spectrum of Gluc−. Comparing these spectra with those of the Ca2+/Gluc− system revealed that, for the magnesium(II) complexes, deprotonation takes place on the coordinated water molecules rather than on the OH groups of the ligand. The main reason for the difference between the two metal complexes is that, in contrast to Ca2+, the OH groups are not directly attached to Mg2+. On the basis of the titration data, hydrolysis of Mg2+ is facilitated by the coordination of Gluc−; this phenomenon can

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### Table 2. Selected Bond Lengths and Hydrogen Bond Distances (in Å) in the Optimized Structures of the Mg(H2O)5Gluc+ and MgGluc(H2O)4(OH)0 Complexes

|     | d(Mg−O) | D | H   | A   | d(D−H) | d(H−A) |
|-----|---------|---|-----|-----|--------|--------|
| Mg  | O1B     | 2.044 | O1W | H(O1W) | O1A    | 0.995  | 1.687  |
| Mg  | O1W     | 2.069 | O3W | H(O3W) | O3     | 0.986  | 1.746  |
| Mg  | O2W     | 2.094 | O3  | H(O3)  | O4     | 0.969  | 2.172  |
| Mg  | O3W     | 2.083 | O2  | H(O2)  | O1A    | 0.974  | 1.951  |
| Mg  | O4W     | 2.071 | O4  | H(O4)  | O2     | 0.972  | 1.920  |
| Mg  | O5W     | 2.093 | O6  | H(O6)  | O4     | 0.968  | 1.961  |

The calculations were performed at the M11/aug-cc-pVTZ level of theory, while solvation effects were considered by applying the CPCM. aD: donor oxygen atom. A: acceptor oxygen atom.

**CONCLUSIONS**

The complex formation between Mg2+ and Gluc− is bound to the metal ion, while the other is in hydrogen-bonding interaction with an adjacent OH group.

- Because concentrated MgCl2 salt brines might contact with underground radioactive waste disposals, the effect of Mg2+ ions on the solubility of actinides is a key factor in the long-term stability assessment of these repositories. Using the stability products obtained in the present work, we calculated the solubility curve of thorium(IV) as a function of pHc by varying the concentrations of Gluc− and MgCl2. It was found that, with an increase in the concentration of MgCl2, the solubility of thorium(IV) decreases, which stems from binary complexes forming between the Mg2+ and Gluc− ions. These processes can effectively suppress complexation between Th(OH)4(s) and Gluc− at low ligand concentrations.

- Additional pH-dependent 1H and 13C NMR experiments showed that deprotonation does not significantly affect the spectrum of Gluc−. Comparing these spectra with those of the Ca2+/Gluc− system revealed that, for the magnesium(II) complexes, deprotonation takes place on the coordinated water molecules rather than on the OH groups of the ligand. The main reason for the difference between the two metal complexes is that, in contrast to Ca2+, the OH groups are not directly attached to Mg2+.

- On the basis of the titration data, hydrolysis of Mg2+ is facilitated by the coordination of Gluc−; this phenomenon can

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**Figure 11.** Optimized structure of the Mg(H2O)5Gluc+ complex at the M11 level, applying the aug-cc-pVTZ basis set. The solvation effects were taken into account by utilizing the CPCM. Dashed lines indicate the hydrogen-bonding system.
be interpreted on the basis of molecular structures of the MgGluc\(^{−}\) and MgGlucoH\(^{0}\) complexes. DFT calculations showed that, in parallel to ligand binding, two strong hydrogen bonds are established between the COO\(^{−}\) and C3−OH groups of Gluc\(^{−}\) and two metal-bound water molecules, leading to increased acidity of these O−H bonds. Macroscopically, this yields lower pK values for the complexes compared to the aqua ion.

In conclusion, ligand-promoted metal-ion hydrolysis appears to be the result of strong hydrogen bonding between the ligand and hydrating water molecules, while the direct binding of ligand OH groups gives rise to metal-ion-induced ligand deprotonation.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.9b00289.

Detailed description about conversion of the stability/solubility products of the Th\(_2\)Gluc\(_{(OH)}\)\(^{(4−q−)}\) species applying the SIT model, tables listing the converted equilibrium constants and ion interaction parameters, graphical representation of the electrode calibration curves and fitted titration data, optimized structures for the MgGluc\(^{−}\) complex with varying coordination modes, additional speciation diagrams for the Mg\(^{2+}\)/Gluc\(^{−}\) and Ca\(^{2+}\)/Gluc\(^{−}\) systems, additional solubility curves of thorium(IV), pH-dependent \(^{13}\)C NMR, and temperature-dependent \(^{1}\)H and \(^{13}\)C NMR spectra (PDF)

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Notes
The authors declare no competing financial interest.

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