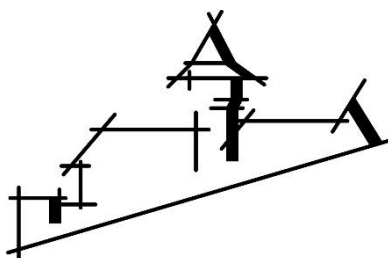


PROGRESSIVE TRENDS IN COORDINATION, BIOINORGANIC, AND APPLIED INORGANIC CHEMISTRY



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The structure and composition of solid complex compounds precipitating from binary Nd(III)–gluconate and ternary Ca(II)–Nd(III)–gluconate solutions

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The chemical equilibria of radioactive waste repositories have been intensively studied in the past decades, since several complexing agents (such as gluconate (Gluc^-) and isosaccharinate) affect the sorption of actinides and lanthanides at contaminated land sites and in waste repositories.

From binary solutions containing Nd(III) and Gluc^- , around $\text{pH} = 8$ a precipitate occurred, which was separated. This precipitate was found to redissolve at $\text{pH} = 12$, but reprecipitated when calcium ions were added to the system. In the present work, an attempt was made to determine the composition and structure of these precipitates *via* using XRD, FT-IR, Raman, SEM-EDAX and UV-DRS. It has been established, formed solid complexes can be characterized by the composition of $\text{NdGlucH}_{-1}(\text{OH})\cdot 2\text{H}_2\text{O}$ and $\text{CaNdGlucH}_{-1}(\text{OH})_3\cdot 4\text{H}_2\text{O}$, in which the chemical environment of the Nd(III) is very similar. Based on spectral analogies, the structure of the solid $\text{NdGlucH}_{-1}(\text{OH})\cdot 2\text{H}_2\text{O}$ is identical to that of the NdGlucH_{-2} solution species.

INTRODUCTION

To get a better knowledge on possible leaching of radioactive compounds, the better understanding of the processes taking place in radioactive waste repositories is essential. As concrete is often used to prevent possible wash-outs, highly alkaline cement pore water has been studied to take into account the complexing agents that are possibly present under these conditions [1,2]. Gluconate (which is a cement additive) and isosaccharinate (a degradation product of cellulose) coordinate various metal ions through their carboxylate group and in several cases, through hydroxyl(ate) group(s). Studies have shown that high pH conditions may facilitate the formation of stable complexes containing lanthanide and actinide ions [3].

In one of our recent studies [4], it has been shown with using a variety of experimental means, that Nd(III) (considered to be a good model for trivalent lanthanide ions) is capable of forming stable mono- and binuclear complexes with gluconate in close-to-neutral solutions. It was observed, that at *ca.* $\text{pH} = 8$ (depending on the metal-to-ligand ratio) a precipitate appeared in the solution, which redissolved at around $\text{pH} = 11-12$. Adding Ca(II) ions to the solution containing this “redissolved” species, the formation of another precipitate was observed.

The aim of the current contribution is the general characterization of these solid compounds (supposedly solid complexes), the determination of their composition and structure and to determine, if there is any correspondence between the structure of the complexes in solution and in the solid state.

EXPERIMENTAL PART

Reagents and solutions

Neodymium(III) chloride hexahydrate (Aldrich, 99.9%) and sodium-D-gluconate (Sigma, $\geq 99\%$) were used in solution. The exact concentration of the NdCl_3 solutions were determined *via* complexometric titrations. The buffer solution was hexamethylenetetramine and methylthymol blue was used as indicator.

During the spectroscopic measurements, Nd_2O_3 (Merck, 99.9%) $\text{Nd}(\text{OH})_3$ (Aldrich, 99.9%) and Ca-D-Gluconate and Na-D-Gluconate (both Sigma, $\geq 99\%$) were used as references.

Apparatus and equipment

X-ray diffractograms were obtained using a Rigaku XRD-6000 diffractometer instrument. Traces were registered in the range of $2\Theta = 5\text{--}80^\circ$, with $4^\circ/\text{min}$ scan speed using $\text{CuK}\alpha$ ($\lambda = 1.5418 \text{ \AA}$) radiation at 40 kV and at 30 mA.

IR spectra with 4 cm^{-1} resolution were recorded with a BIO-RAD Digilab Division FTS-65A/896 FT-IR (Fourier-transform infrared) spectrophotometer. 128 scans were collected for each spectrum in the $4000\text{--}700 \text{ cm}^{-1}$ wavenumber range. The IR instrument was set to ATR (attenuated total reflectance) mode.

To register Raman, a Thermo Scientific™ DXR™ Raman microscope was used at an excitation wavelength of 535 nm in case of “green”, and 720 nm in case of red laser measurements. The applied laser power was 10 mW. Each recorded spectrum is an average of 20 spectra with an exposition time of 6 seconds.

The diffuse reflectance spectra of the solid samples were recorded on an Ocean Optics UV-Vis USB4000 diode array spectrophotometer in the 200 – 890 nm wavelength range (resolution 0.2 nm, integration time 0.5 s). The temperature was $(22 \pm 2 \text{ }^\circ\text{C})$. The incident angle was 45° . As a reference, MgO was employed. For the measurements, an Ocean Optics DH-2000-BAL light source consisting of a deuterium and a halogen lamp was used.

RESULTS AND DISCUSSION

Preparation of the solid compounds

To prepare the solid binary Nd(III)-gluconate complex, a mixture of 6.20 cm^3 0.4764 M NdCl_3 and 6.00 cm^3 0.5000 M Na-D-Gluconate was titrated with 1.0105 M NaOH until a precipitation formed at $\text{pH} \approx 8$. The pH of the solution was monitored with a calibrated glass electrode. To this point 5.80 cm^3 NaOH was necessary to be added to the solution.

In the case of the ternary Ca(II)-Nd(III)-gluconate system, 2.00 cm^3 0.4764 M NdCl_3 and 5.00 cm^3 0.5000 M Na-D-Gluconate was mixed with 4.00 cm^3 1.0105 M NaOH to reach $\text{pH} \approx 12,30$, since the precipitation formed in the binary system at $\text{pH} \approx 8.00$ dissolves again above $\text{pH} \approx 12.00$. Then, the mixture was titrated with 0.4944 M CaCl_2 , until a precipitation formed. For this, the addition of 1.90 cm^3

0.4944 M CaCl_2 was necessary and the $\text{pH} \approx 12$. Note, that at this point the $\text{Ca(II)} : \text{Nd(III)}$ ratio in the solution was equal to *ca.* 1:1.

The precipitations were filtered and washed with cool deionized water, then dried in a desiccator for two days. For XRD and spectroscopic measurement, the glass-like dried precipitates were pulverized in a mortar.

The chemical compositions of precipitations were determined *via* thermogravimetric and ICP-OES measurements.

During the thermogravimetric measurements of the binary precipitation, a well-defined mass of the sample was heated for 24 hours at $1000\text{ }^\circ\text{C}$, until only Nd_2O_3 was left. The Nd^{3+} content of the heated sample was determined by ICP-OES measurements. Based on the thermogravimetric curve of the solid (not shown), some crystalline water is present in the precipitate. From these data, the metal-to-ligand ratio in the complex is 1:1, and the estimated chemical formula of the solid complex is $\text{NdGlucH}_{-1}(\text{OH})\cdot 2\text{H}_2\text{O}$.

The solid obtained from the ternary system was investigated in a manner similar to that of the binary one, but its Ca(II) -content was also determined. A well-defined mass of sample was heated to $1000\text{ }^\circ\text{C}$ until CaO and Nd_2O_3 were left in the system. Based on the ICP-OES measurements, the Ca^{2+} and Nd^{3+} molar ratio of the two metal ions is 1:1. The thermogravimetric curve also shows the presence of crystalline water, therefore, the suggested chemical formula of the ternary system precipitation is $\text{CaNdGlucH}_{-1}(\text{OH})_3\cdot 4\text{H}_2\text{O}$.

Both preparations described above were repeated at another metal to ligand ratio ($\text{Nd(III)}:\text{gluconate} = 1:2.5$), but no significant differences were seen regarding the composition and structure of the complexes.

The powder X-ray diffractograms of the complexes were recorded and were compared with those of Nd(OH)_3 , Ca(OH)_2 , Ca-gluconate (complex constituents) and NaCl (possible side product). The diffractograms obtained (not shown) confirmed that the complexes are X-ray amorphous and neither Nd^{3+} nor Ca^{2+} are present as hydroxide. Furthermore, NaCl salt did not remain in the specimens.

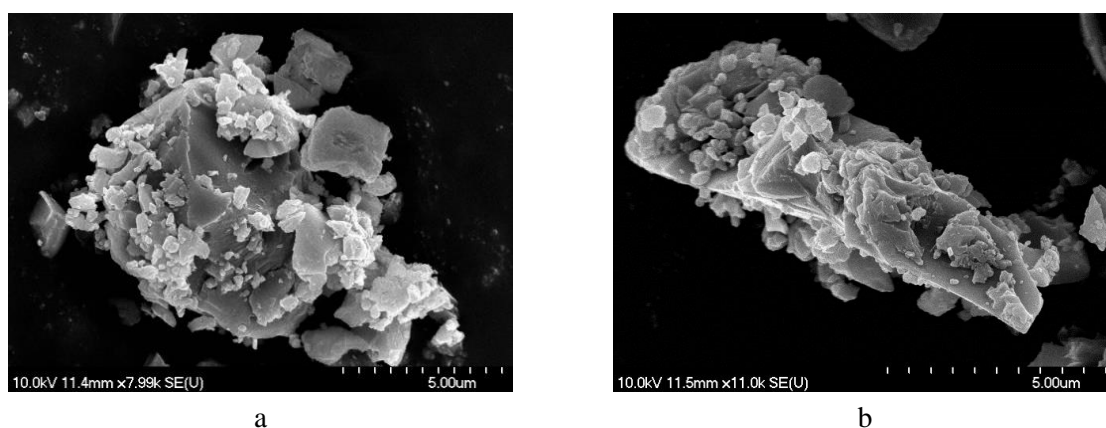


Figure 1. SEM images of the solid $\text{NdGlucH}_{-1}(\text{OH})\cdot 2\text{H}_2\text{O}$ (a) and $\text{CaNdGlucH}_{-1}(\text{OH})_3\cdot 4\text{H}_2\text{O}$ (b) complexes.

The scanning electron micrograph illustrates the similar morphology and particle size of the precipitates of binary and ternary systems (Fig. 1. (a) and (b)). The simultaneously obtained EDAX pictures (not

shown) indicated an even distribution of the various elements (Nd(III) in (a) and Ca(II) and Nd(III) in (b)) in the solid samples.

The FT-IR spectra of the two complexes together with a selected set of references was also recorded (Fig. 2.) The figure demonstrates, that gluconate is present in both complexes, since the asymmetric (1633 cm^{-1}) and symmetric (1398 cm^{-1}) carboxylate peaks of NaGluc can be detected in the binary $\text{NdGlucH}_{-1}(\text{OH})\cdot 2\text{H}_2\text{O}$ (asymmetric peak at 1664 cm^{-1} , symmetric at 1498 cm^{-1}) and ternary $\text{CaNdGlucH}_{-1}(\text{OH})_3\cdot 2\text{H}_2\text{O}$ (c) (asymmetric peak at 1659 cm^{-1} and symmetric at 1500 cm^{-1}) systems. The similarity of the band positions in the two complexes indicate similar binding mode of the carboxylate moiety and most probably coordinative binding to Nd(III).

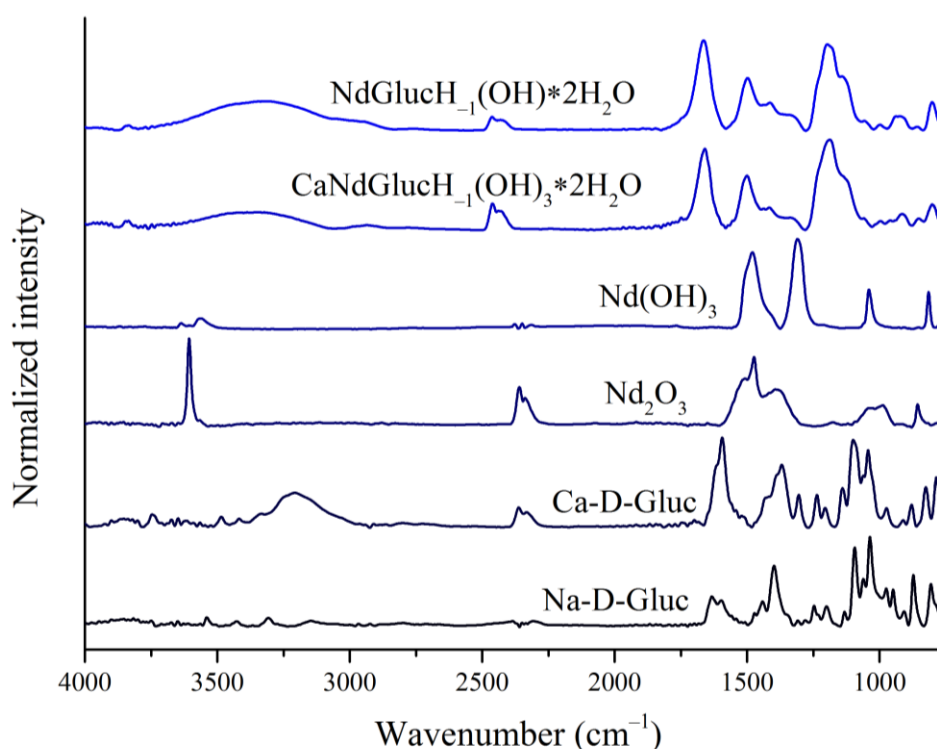


Figure 2. IR spectra of the solid complexes and references

The shift in the position of the asymmetric and symmetric carboxylate vibrations also indicates the coordination between Nd^{3+} and the carboxylate group of the gluconate ligand [5]. The stretching vibrations of hydroxyl groups belonging to excess water present occur on the spectrum as a broad band appearing in the range $3700 - 3000\text{ cm}^{-1}$ with the highest intensity at 3316 cm^{-1} , indicating that the studied solid complexes contain crystalline water.

The Raman spectra (shown in Fig. 3.) of samples present significant differences between the used references and studied solid complexes. The broad band of $\text{Nd}(\text{OH})_3$ appearing in the $2650 - 1750\text{ cm}^{-1}$ interval (highest intensity at 2300 cm^{-1}) shifts to the range of $1900 - 1200\text{ cm}^{-1}$. This can be associated with the formation of a complex, whose structure differs from the salts used as reference during the Raman measurement.

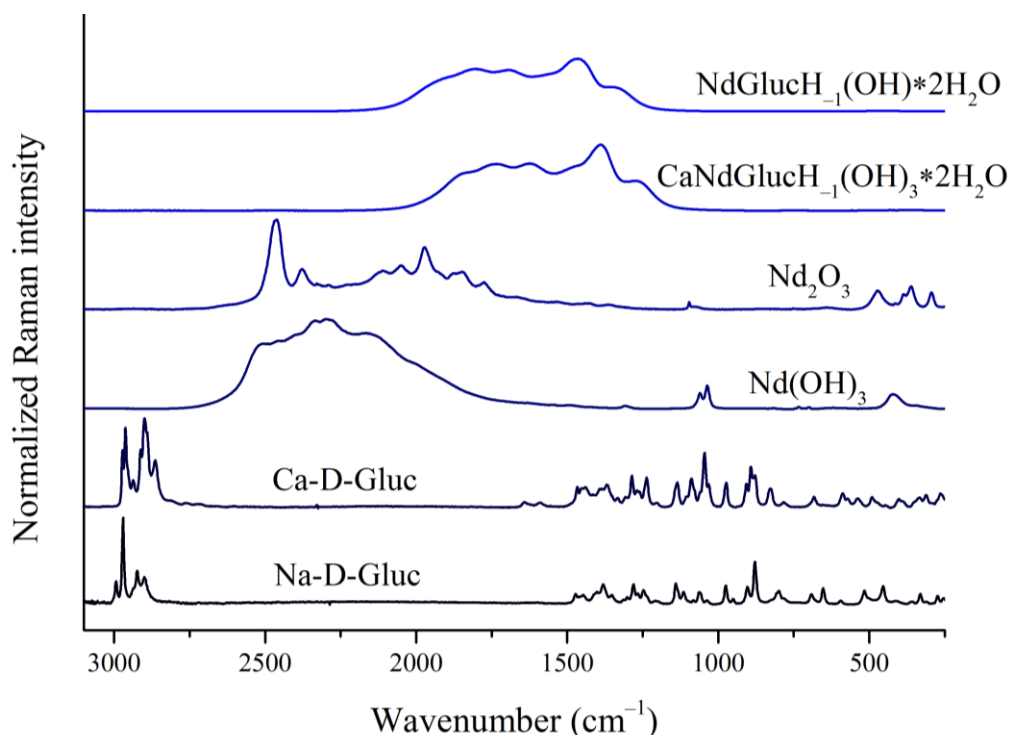


Figure 3. Raman spectra of the solid complexes and references

The diffuse reflectance spectra of the $\text{NdGlucH}_{-1}(\text{OH})\cdot 2\text{H}_2\text{O}$ and $\text{CaNdGlucH}_{-1}(\text{OH})_3\cdot 4\text{H}_2\text{O}$ together with some reference spectra are shown in Fig. 4. The spectra attest, that the chemical environment of Nd(III) (which is the chromophore in this case) is different in the two complexes from that in the $\text{Nd}(\text{OH})_3$ and Nd_2O_3 . On the other hand, the DR spectra of the two complexes are practically identical. This observation, together with the vibration spectroscopic observations attest, that the chemical environment of the Nd(III) is very similar (if not identical) in the binary and ternary complexes.

From our previous studies [4] the molar absorptivity of the *solution* complex species NdGlucH_{-2}^0 has been derived. When one compares the spectra of the solid and this particular solution species (Fig. 5), the similarity between the two spectra is immense. Add to this, that at $\text{pH} = 8$, the predominant complex in these systems (at 1:1 metal-to-ligand ratio) is the charge neutral NdGlucH_{-2}^0 . From this, it seems plausible, that the structure of the solid complex is identical to that of the solution species as described in [4], shown in Fig. 6.

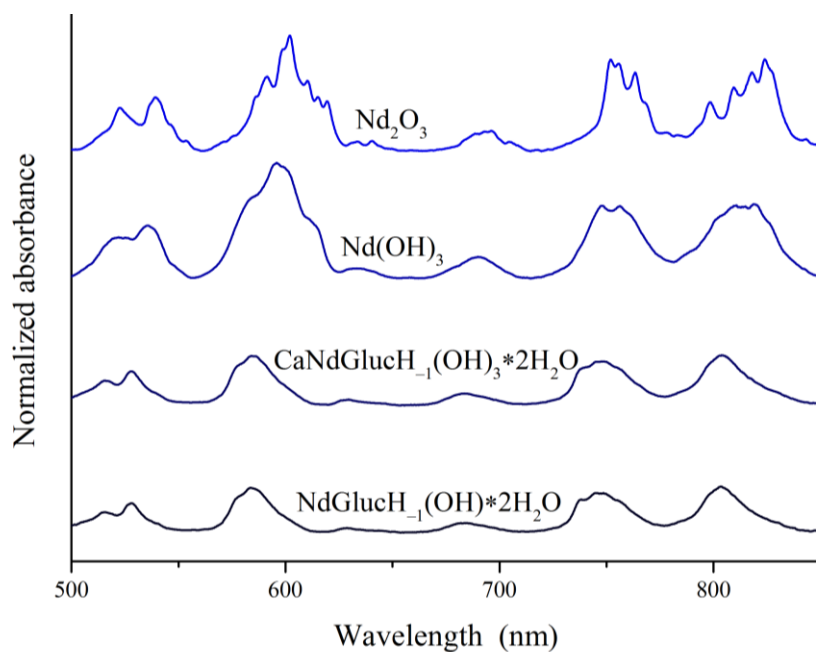


Figure 4. UV-Vis diffuse reflectance spectra of the solid complexes and some selected references.

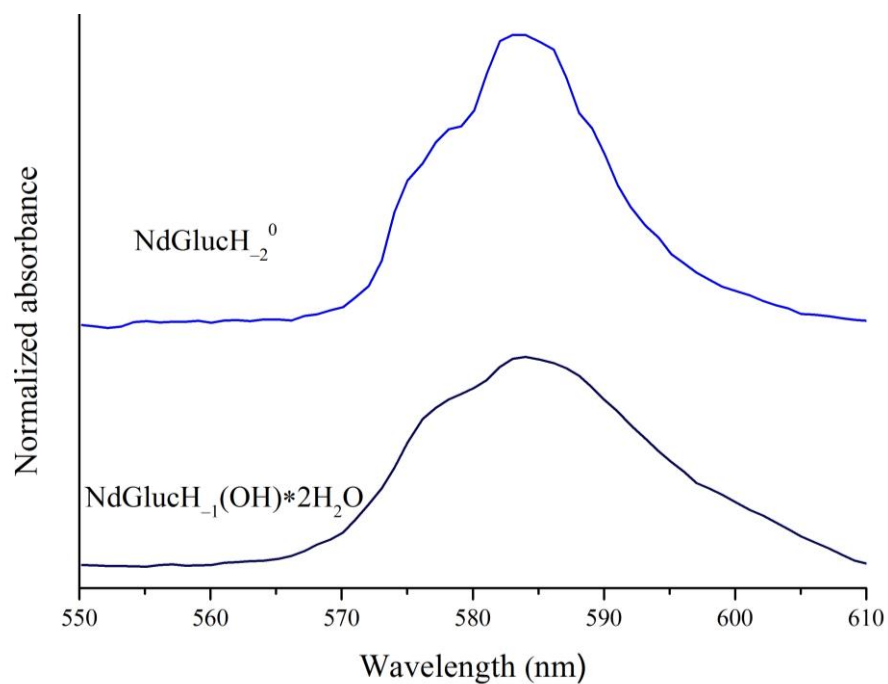


Figure 5. Molar absorbance spectrum of NdGlucH_{-2}^0 complex in solution and the diffuse reflectance spectrum of the solid $\text{NdGlucH}_{-1}(\text{OH}) \cdot 2\text{H}_2\text{O}$ complex.

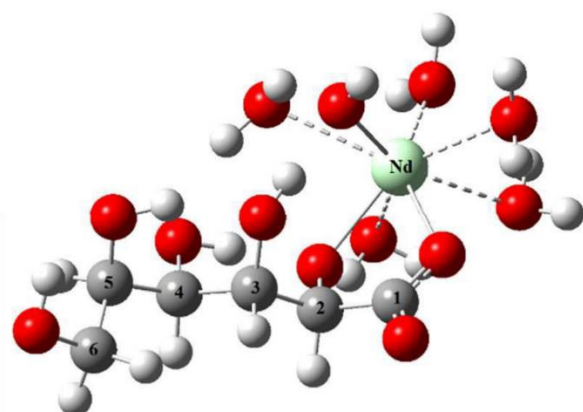


Figure 6. Optimized structure of the NdGlucH₂⁰ solution species, figure taken from ref. [4]

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