Determination of thermodynamic functions and structural parameters of NpO₂⁺ lactate complexes†

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The complexation of NpO₂⁺ with lactate in aqueous solution is studied as a function of the total ligand concentration ([Lac]_{total}), ionic strength (I_m = 0.5–4.0 mol kg⁻¹ Na⁺(Cl / ClO₄⁻)) and temperature (T = 20–85°C) by Vis/NIR absorption spectroscopy. The formation of two NpO₂⁺ lactate species with the stoichiometry NpO₂(Lac)ₙ⁻¹ (n = 1, 2) is observed at the studied experimental conditions. The temperature dependent conditional stability constants logβ_j(0)(T) at different ionic strengths are calculated with the law of mass action. The conditional data are extrapolated to IUPAC reference state conditions (I_m = 0) with the specific ion interaction theory (SIT). With increasing temperature up to 85°C logβ_j(0)(20°C) = 1.92 ± 0.14 decreases by 0.12 and logβ_j(0)(20°C) = 2.10 ± 0.13 decreases by 0.17. The thermodynamic stability constants correlate linearly with the reciprocal temperature according to the integrated Van’t Hoff equation. Thus, linear regression analyses yield the standard reaction enthalpy ΔrH° and entropy ΔrS° for the complexation reactions. In addition, the sum of the SIT specific binary ion ion interaction coefficients Δe_j,(T) of the complexation reactions are determined by variation of the ionic strength. Structural parameters of the formed complex species and the coordination mode of lactate towards the NpO₂⁺ ion are investigated as a function of pH by extended X-ray absorption fine structure spectroscopy (EXAFS) and attenuated total reflection Fourier-transform infrared spectroscopy (ATR-FTIR). The results show, that the coordination mode of lactate changes from end-on (coordination via only the COO group) to side-on (formation of chelate rings involving the OH-group) with increasing pH. The experiments are supported by quantum chemical calculations.

1 Introduction

Deep geological formations are considered for the final disposal of high-level nuclear waste. Suitable host rock formations discussed in several European countries (e.g. Belgium, France, Germany and Switzerland) are rock salt, crystalline formations (e.g. granite) and clay rocks. Due to their long half-lives, the transuranium element plutonium (Pu) and the minor actinides (Np, Am) determine the long-term radiotoxicity of the nuclear waste. Therefore, the actinides are of particular interest for the safety case of a nuclear waste repository. In case of a release of radionuclides from the primary containments, a mechanistic understanding of the most relevant interactions (e.g. dissolution of the waste matrix and solubility of the radionuclides, sorption and complexation processes, etc.) of the radionuclides with the surrounding backfill material, the host rock, and the aquifer components is essential. In particular complexation reactions with naturally occurring inorganic and organic ligands in aqueous solution can significantly affect the mobility and migration of the radionuclides.

Depending on the repository design and host-rock characteristics increased temperatures are expected in the near-field of a nuclear waste repository e.g. up to 100°C for clay rocks and up to 200°C for salt rocks. Additionally, some clay repository sites exhibit high saline conditions, e.g. in Northern Germany the ionic strength of the pore water is above 3.5 mol L⁻¹. It was shown earlier that an increase of the temperature and the ionic strength may have a significant influence on complexation processes with different organic and inorganic components in
natural aquatic systems affecting the retardation efficiency of the host rock.\textsuperscript{6} Low-molecular-weight organic compounds (LMWOC) like formate, acetate, propionate, and lactate make up large fractions of the dissolved organic matter in the pore waters of different clay formations (e.g. Callovo Oxydian (Cox) and Opalinus Clay (OPA)).\textsuperscript{7,10–18} Among the LMWOC lactate is only present in concentrations up to [Lac\textsuperscript{−}] = 1.7 µM. Thus, lactate will have a minor effect on the (geo)chemical speciation of actinides at environmental conditions but is of particular interest as it provides the possibility to coordinate to the metal ion in different coordination modes.\textsuperscript{9,10} This contrasts to mono carboxylic ligands (e.g. acetate, propionate) as the lactate molecule can either coordinate end-on via the carboxyl function or side-on via both the COO\textsuperscript{−} group and the \(\alpha\)-hydroxy group. The coordination mode of lactate might also be affected by the pH value. Thus, lactate can be used as a model ligand to study the effect of \(\alpha\)-OH groups in organic compounds on the complex stability, thermodynamic behaviour and structure of An-LMWOC complexes.

Actinides (An) in the pentavalent oxidation state are known to be highly soluble with low retention by mineral phases.\textsuperscript{11–17} An-LMWOC complexes.

The present work focusses on the determination of thermodynamic data for the complexation of NpO\textsubscript{2}\textsuperscript{3+} with lactate. Thermodynamic data on NpO\textsubscript{2}\textsuperscript{3+} lactate complexes are scarce in the literature and most data are limited to a fixed ionic strength or ambient temperatures. Only one solvent extraction study by Isaac et al. provided thermodynamic functions (\(\Delta H^0\), \(\Delta S^0\), \(\Delta G_{\text{sol}}(T)\)) for the NpO\textsubscript{2}(Lac) complex at IUPAC reference state conditions determined from variation of the ionic strength and temperature.\textsuperscript{18} In this survey the \(\Delta H^0\) and \(\Delta S^0\) values are determined from single SIT extrapolation at one fixed ionic strength. The effect of the ionic strength on the complexation reaction as a function of the temperature has not been investigated.

Concerning the speciation of the NpO\textsubscript{2}\textsuperscript{3+} lactate complexes different studies based on solvent extraction and spectrophotometry report different results.\textsuperscript{19–21} Depending on the experimental approach the formation of only NpO\textsubscript{2}(Lac) or both NpO\textsubscript{2}(Lac) and NpO\textsubscript{2}(Lac\textsuperscript{2−}) was observed. Also, the reported conditional stability constants for NpO\textsubscript{2}(Lac) differ significantly (\(\log \beta' (25 ^\circ \text{C}) = 1.1–1.8\), at \(I_{\text{tot}}(\text{NaClO}_4) = 1\ \text{mol kg}^{-1}\)).

Furthermore, structural investigations are of particular interest as no structural data of An(v)-lactate complexes are available in the literature describing the complexation of An(v) with \(\alpha\)-hydroxy carboxylates on a molecular level.

In the present work the complexation of NpO\textsubscript{2}\textsuperscript{3+} with lactate as a function of the ligand concentration, temperature and ionic strength is studied by Vis/NIR absorption spectroscopy. Structural characterization of the complexes is performed by extended x-ray absorption fine structure spectroscopy (EXAFS) and attenuated total reflection Fourier-transform infrared (ATR FT-IR) spectroscopy. The experimental data are supported by quantum chemical calculations.

2 Experimental

2.1 Sample preparation

Caution: \(^{237}\text{Np}\) is an \(\alpha\)-emitter and must be handled with care in laboratories appropriate for research involving transuranic elements. Health risks caused by radiation exposure or incorporation must be avoided. Higher concentrated Np solutions were handled in glove boxes.

The molal concentration scale (mol kg\textsuperscript{−1} H\textsubscript{2}O\textsuperscript{−1} or mol kg\textsubscript{w}\textsuperscript{−1}) was used for all solutions to avoid changes of the concentration caused by changes of the temperature or the ionic strength. All chemicals except for neptunium were reagent grade or higher and purchased from Merck Millipore. For sample preparation ultrapure water (Milli-Q academic, Millipore, 18.3 MΩ cm) was used.

2.1.1 Absorption spectroscopy. The total initial NpO\textsubscript{2}\textsuperscript{3+} concentration of all samples used for absorption spectroscopy was adjusted to \(2.5 \times 10^{-4}\) mol kg\textsubscript{w}\textsuperscript{−1} in \(2.1 \times 10^{-3}\) mol kg\textsubscript{w}\textsuperscript{−1} HClO\textsubscript{4} by dilution of a \(4.3 \times 10^{-2}\) mol kg\textsubscript{w}\textsuperscript{−1} \(^{237}\text{NpO}_2\textsuperscript{3+}\) stock solution ([HClO\textsubscript{4}]\textsubscript{stock} = \(2.9 \times 10^{-1}\) mol kg\textsubscript{w}\textsuperscript{−1}). The preparation of the stock solution is described in the literature.\textsuperscript{21} The complexation of NpO\textsubscript{2}\textsuperscript{3+} was studied as a function of [Lac\textsuperscript{−}]\textsubscript{eq} at three different ionic strengths (\(I_{\text{tot}} = 0.5, 2.0\) and \(3.6\) mol kg\textsubscript{w}\textsuperscript{−1} NaClO\textsubscript{4}/Lac\textsuperscript{−}) and \(T = 20\ \text{°C}\) ([Lac\textsuperscript{−}]\textsubscript{eq} + [HCl\textsuperscript{−}]\textsubscript{eq}]. The concentration of the Np(v)-lactate complexes is neglectable for the determination of the complex stoichiometry as \([\text{NpO}_2]^+ \ll [\text{Lac}\textsuperscript{−}])\textsuperscript{20}]. The temperature dependence (\(T = 20–85\ \text{°C}\)) of the complexation reactions were determined as a function of [Lac\textsuperscript{−}]\textsubscript{eq} at \(I_{\text{tot}} = 3.6\) mol kg\textsubscript{w}\textsuperscript{−1} NaClO\textsubscript{4}/Lac\textsuperscript{−}]. For preparation of the lactate titration solutions solid sodium lactate was dissolved in water and the ionic strength was adjusted by addition of solid NaClO\textsubscript{4}H\textsubscript{2}O. The ionic strength dependence of the complexation reactions was studied in NaCl and NaClO\textsubscript{4} media at two fixed ligand concentrations ([Lac\textsuperscript{−}]\textsubscript{tot} = \(5.7 \times 10^{-1} \) mol kg\textsubscript{w}\textsuperscript{−1} + \(5.7 \times 10^{-2}\) mol kg\textsubscript{w}\textsuperscript{−1}) between 20 and 85 °C at 8 different ionic strengths between 0.5–4.0 mol kg\textsubscript{w}\textsuperscript{−1} NaCl/NaClO\textsubscript{4}. The concentration of NaClO\textsubscript{4} was increased by successive titration using an aqueous 14.5 mol kg\textsubscript{w}\textsuperscript{−1} NaClO\textsubscript{4} solution. The [Na\textsubscript{Cl}]\textsubscript{tot} was increased by addition of solid NaCl to the samples. All sample and titration solutions were set to a constant total proton concentration \([\text{H}^+]\textsubscript{tot} = 2.3 \times 10^{-5}\) mol kg\textsubscript{w}\textsuperscript{−1} using a 0.01 mol kg\textsubscript{w}\textsuperscript{−1} HClO\textsubscript{4} or HCl ([\text{H}^+]\textsubscript{tot} = [\text{H}^+]\textsubscript{eq} + [\text{HCl}\textsuperscript{−}]\textsubscript{eq}]. As all total proton concentrations are known measurement of the pH values is not necessary. The proton concentrations are calculated using the SIT, integrated Van’ Hoff equation and Henderson–Hasselbalch equation (see section “Peak deconvolution and Speciation”).

2.1.2 EXAFS spectroscopy. For EXAFS measurements samples with a total NpO\textsubscript{2} concentration of \(5.0 \times 10^{-3}\) mol kg\textsubscript{w} and a concentration of [Lac\textsuperscript{−}]\textsubscript{eq} = \(2.5 \times 10^{-1}\) mol kg\textsubscript{w}\textsuperscript{−1} in H\textsubscript{2}O were prepared. The ionic strength of all samples was adjusted to \(I_{\text{tot}}(\text{Na}^+\text{Cl}^-/\text{Cl}^-) = 4.4\) mol kg\textsubscript{w}\textsuperscript{−1} by addition of solid NaCl. The EXAFS experiments were conducted at various proton concentrations. The conditional pH\textsubscript{w} values (pH\textsubscript{w} = 2.6–5.0) were adjusted by addition of small aliquots of 6 mol L\textsuperscript{−1} HCl (Merck, suprapure) or freshly prepared 1 mol L\textsuperscript{−1} NaOH (Merck, Titrisol). The pH was measured by a combination pH
The ionic strength was $I$ measurement and baseline correction samples at the same slit width of 0.7 nm in double beam mode. For reference, weilheim, germany) in H$_2$O. The pH values were corrected calibration was performed using standard pH buffers (WTW, pH-Meter (WTW, Weilheim, Germany) with a Blue Line 16pH electrode (Orion™ PerpHec™ ROSS™), which was calibrated with pH reference buffer solutions (Merck, pH = 7.00, 5.00, 2.00). Details on the definition of the pH and pH$_e$ value are given in the literature. The volume of each sample was 200 μL.

2.1.3 ATR-FT-IR spectroscopy. The characteristic vibrational modes of the NpO$_2^+$ ion in solution are generally observed in the spectral range below 850 cm$^{-1}$ where strong interferences with modes of the bulk water (H$_2$O) occur. Therefore, deuterated water (D$_2$O, Sigma Aldrich, 99.9 atom % D, stored under argon) was used for the samples of the infrared spectroscopic experiments. All samples were prepared under inert gas atmosphere (N$_2$) to reduce the content of H$_2$O. The total NpO$_2^+$ concentration was 1.0 × 10$^{-3}$ mol kg$^{-1}$ and the ionic strength was $I_0 = 1.0$ mol kg$^{-1}$ (Na$^+$,Lac$^-$/Cl$^-$. NaCl was used as background electrolyte as it does not absorb light in the infrared region of interest. The total lactate concentration was [Lac$^-$]$_{tot} = 1.0 × 10^{-3}$ mol kg$^{-1}$. The pH$_c$ between 2.6 and 4.8 was adjusted by addition of small aliquots of 0.2 or 2 mol L$^{-1}$ DCl and 0.2 mol L$^{-1}$ NaOD in D$_2$O. For preparation of the respective acids and bases 35 wt% DCl (Sigma Aldrich, 35 wt% in D$_2$O, ≥99 atom % D) and 40 wt% NaOD (Alfa Aesar, 40 wt% in D$_2$O, 99.5 atom % D) were used. The pH values of the samples were determined and adjusted using an inoLab pH 720 pH-Meter (WTW, Weilheim, Germany) with a Blue Line 16pH microelectrode (Schott Instruments, Mainz, Germany). The calibration was performed using standard pH buffers (WTW, Weilheim, Germany) in H$_2$O. The pH$_c$ values were corrected according to $pD = pH + 0.4$. The NpO$_2^+$ concentration in the samples and the species distribution of the samples was confirmed by Vis/NIR spectroscopy. A Varian Cary 5G UV/Vis/NIR spectrophotometer was connected to the inert gas glove box via optical fibres to enable the characterization of the NpO$_2^+$ samples inside the glove box.

2.2 Vis/NIR absorption spectroscopy

The complexation of NpO$_2^+$ with lactate in aqueous solution was studied by NIR/Vis absorption spectroscopy between 20 and 85 °C using a Varian Cary 5G UV/Vis/NIR spectrophotometer. A Lauda Eco E100 thermostatic system was used to control the temperature of the sample holder. The samples were equilibrated for 15 min at each temperature before measurement to ensure thermodynamic equilibrium. The spectra of the samples placed in quartz glass cuvettes (1 cm path length, Hellma Analytics) were recorded between 950–1050 nm with a data interval of 0.1 nm, a scan rate of 60 nm min$^{-1}$ (average accumulation time 0.1 s) and a slit width of 0.7 nm in double beam mode. For reference measurement and baseline correction samples at the same condition but without NpO$_2^+$ were measured.

The spectra of the single complex species and the stability constants of the Np($v$)-lactate complexes are obtained by peak deconvolution and slope analyses of the mole fractions. The methods of peak deconvolution and slope analysis are described elsewhere.

All uncertainties of the stability constants log $K(n,T)$, enthalpies $\Delta H_m^{n,T}$, entropies $\Delta S_m^{n,T}$ and SIT binary ion–ion interaction coefficients $\Delta_{ij}^{DL}$ determined in the present work are given with a confidence level of 1 $\alpha = 0.95$.

2.3 EXAFS measurements

Np L$_3$-edge-EXAFS spectra were measured in fluorescence mode at an angle of 90° to the incident x-ray beam, using a 4 element Si SDD Vortex (SIINT) detector and an additional 1 element Si Vortex-60EX SDD (SIINT) fluorescence detector. The measurements were performed at the INE-Beamline of the The Karlsruhe Research Accelerator (KARA, Karlsruhe, Germany) which was equipped with a double-crystal monochromator (DCM; Ge(422) crystal pair) and a collimating and focusing mirror system (Rh-coated silicon mirrors). The flux of the incident beam was detuned in the middle of the scan range to 70% peak intensity. An Ar-filled ionization chamber at ambient pressure was used to measure the intensity $I_0$ of the incident X-ray beam. All measurements in the EXAFS range were performed at equidistant k-steps and an increasing integration time following a $\sqrt{k}$ progression. The measurements were performed at $T = 25$ °C. The software packages EXAFSPAK, Athena 0.8.056, and Artemis 0.8.0.012 were used for data evaluation. Theoretical scattering phases and amplitudes were calculated with FEFF8.40, using the crystal structures of UO$_2$ acetate and oxalate after replacement of the U-atom by Np. In all cases the $k^2$- and $k^4$-weighted raw EXAFS spectra were fitted.

2.4 ATR FT-IR spectroscopy

In situ ATR-FT-IR spectroscopic measurements of the formed NpO$_2^+$ lactate complexes were performed in D$_2$O. The spectra were measured on a Bruker Vertex 80/v vacuum spectrometer equipped with a mercury cadmium telluride (MCT) detector. The spectra were recorded between 4000 and 600 cm$^{-1}$ and averaged over 256 scans. The spectral resolution was 4 cm$^{-1}$. The used ATR unit DURA SampIR II (Smiths Inc.), a horizontal diamond crystal with nine internal reflections on the upper surface and an angle of incidence of 45°, was purged with a current of dry air (dew point $< 213$ K). An ATR flow cell with a volume of 200 μL was used to ensure adequate background subtraction without external thermal interference. The measurements were based on the principle of reaction-induced infrared difference spectroscopy. Here, infrared spectra of the solvent, the ligand solution and the samples containing NpO$_2^+$ at equal experimental conditions (pH$_e$, $I_{tot}$, temperature) were recorded in single beam mode. Difference spectra were calculated from spectral data of the NpO$_2^+$ samples subtracting those of the reference samples exhibiting absorption changes caused by the complexation of the NpO$_2^+$ ion. Parts of the spectra which are unaffected by the complexation of NpO$_2^+$, the strong absorbing background from the bulk water as well as contributions from the ATR FT-IR accessory and the instrument were eliminated displaying spectral features even due to minimal absorption changes ($\approx 10^{-3}$ OD).

2.5 Quantum chemical calculations

The TURBOMOLE 7.0 program package was used for quantum chemical calculations and structure optimizations of the NpO$_2^+$...
lactate complexes.\textsuperscript{35} The \( \text{NpO}_2(\text{H}_2\text{O})_3(\text{Lac}) \) (Lac) and \( \text{NpO}_2(\text{H}_2\text{O})(\text{Lac})_2^- \) complexes with different coordination modes (side-on vs. end-on) were optimized on the level of density functional theory (DFT) using the BH-LYP functional due to its better convergence compared to other hybrid-functionals.\textsuperscript{35,36} All N, C, and H atoms were described by triple zeta basis sets (def2-TZVP) and were treated at the all-electron level. The \( \text{Np}(\text{v}) \) ion was represented by a 60-electron core pseudo-potential (Np, ECP60MWB) with corresponding basis sets.\textsuperscript{37} The triplet spin state with two unpaired \( f \)-electrons resulting in a spin multiplicity of \( S(S + 1) = 2 \) was used for all systems. The gas phase energies \( E_g \) were computed on MP2 level. Additionally, thermodynamic corrections \( (G_{\text{corr}} = E_{\text{corr}} + H_0 + T_S) \), \( T_S \), \( E_{\text{corr}} \) being the zero-point energy, \( H_0 \) and \( S \) are the enthalpies and entropies obtained from the calculations of the vibrational modes) and solvation energies \( G_{\text{solv}} \) (obtained using COSMO, \( r(\text{Np}) = 1.72 \) Å) were taken into account to obtain a theoretical approximation of the Gibbs free energies \( G = E_g + G_{\text{corr}} + G_{\text{solv}} \).\textsuperscript{38–40} As the ligands and the \( \text{NpO}_2^- \) ion are charged a second hydration shell consisting of 28 water molecules was added to avoid the charge of the complexes to contact the COSMO cavity. An application of \textit{ab initio} methods to optimize the structures of the \( \text{NpO}_2^- \) complexes was not possible as the size of the systems was too big (\( N > 100 \) atoms) and the computation time was limited.

3 Results and discussion

3.1 Vis/NIR absorption spectroscopy

3.1.1 Absorption spectra. Fig. 1 shows the absorption spectra of \( \text{NpO}_2^- \) as a function of the total lactate concentration \( \text{[Lac]}_{\text{tot}} \) at \( T = 20 \) and \( 85 \) °C and \( I_{\text{osm}} = 3.6 \) mol kg\(^{-1}\) NaClO\(_4\). At \( 20 \) °C the absorption band of the \( \text{NpO}_2^- \) ion is located at \( \lambda_{\text{max}} = 979.4 \) nm (\( \varepsilon = 397 \pm 12 \) L mol\(^{-1}\) cm\(^{-1}\)). With increasing \( \text{[Lac]}_{\text{tot}} \), a bathochromic shift of the absorption spectra is observed. The Full Width at Half Maximum (FWHM) increases from 7.9 to 10.7 nm indicating the formation of \( \text{NpO}_2^- \) lactate complex species.

With increasing temperature the absorption band of the \( \text{NpO}_2^- \) ion shifts bathochromically by 1.2 nm to 978.2 nm while the FWHM is unaffected by the temperature. The extinction coefficient decreases to \( \varepsilon = 362 \pm 15 \) L mol\(^{-1}\) cm\(^{-1}\). This blue shift is in good agreement to literature data. There, hypsochromic shifts by 1.5–1.9 nm are reported.\textsuperscript{41–45} At \( 85 \) °C the bathochromic shift observed at increasing ligand concentration is less pronounced compared to \( 20 \) °C. This is also reflected by a smaller increase of the FWHM from 7.9 to 10.4 nm. This indicates a reduced complex formation according to an exothermic complexation reaction.

The spectral changes and hypsochromic shifts of the \( \text{NpO}_2^- \) ion with increasing temperature are contrary to the bathochromic shift induced by the complexation of \( \text{NpO}_2^- \) at increasing \( \text{[Lac]}_{\text{tot}} \). The effect of the temperature on the position of the absorption band of the \( \text{NpO}_2^- \) ion has been discussed in the literature in detail.\textsuperscript{41,42,44,46} Nevertheless, due to this effect, each series of spectra is evaluated separately and single component spectra must be determined for all experimental conditions.

3.1.2 Peak deconvolution and speciation. The spectra of the formed \( \text{NpO}_2^- \) lactate complexes are derived via subtractive deconvolution of the absorption spectra using the spectrum of the \( \text{NpO}_2^+ \) aquo ion. The spectra derived in NaClO\(_4\) and NaCl media are identical at equal ionic strengths and temperatures. In Fig. 2 the results of the peak deconvolution are presented for 20 and \( 85 \) °C in NaClO\(_4\) (\( I_{\text{osm}} = 3.6 \) mol kg\(^{-1}\)). The absorption band of \( \text{NpO}_2^- \) (Lac) is located at \( \lambda_{\text{max}} = 983.6 \) nm (\( \varepsilon = 356 \pm 12 \) L mol\(^{-1}\) cm\(^{-1}\)), indicating a bathochromic shift of 4.2 nm compared to the absorption band of the \( \text{NpO}_2^+ \) aquo ion. The absorption band of \( \text{NpO}_2^- \) (Lac)\(_2^+ \) is located at \( \lambda_{\text{max}} = 987.1 \) nm (\( \varepsilon = 362 \pm 18 \) L mol\(^{-1}\) cm\(^{-1}\)) and is shifted by 7.7 nm compared to the aquo ion. This shows, that each coordinating lactate ligand induces an average bathochromic shift of approximately 4.0 nm. At \( 85 \) °C all single component spectra are hypsochromically shifted by 1.2 nm whereas the integrated absorption coefficients remain constant. Thus, the absorption spectra of all \( \text{Np}(\text{v}) \) species are affected in the same way by changes of the temperature. Furthermore, at \( 85 \) °C the single component spectrum of the \( \text{NpO}_2^- \) (Lac)\(_2^- \) complex could not be determined due to the low absorption intensity of this species and the unfavourable signal to noise ratio.

The deconvolution of the experimental absorption spectra is performed by principle component analyses using the pure

![Fig. 1. Absorption spectra of \( \text{NpO}_2^- \) with increasing lactate concentration \( \text{[Lac]}_{\text{tot}} \) at \( T = 20 \) °C (left), and \( T = 85 \) °C (right) and \( I_{\text{osm}} \) (NaClO\(_4\)) = 3.6 mol kg\(^{-1}\).]
component spectra. Details on this procedure are given in the literature.26–28

The determined speciation of the NpO$_2^+$ lactate complexation is shown in Fig. 3 (symbols) as a function of the equilibrium lactate concentration [Lac]/[C$_0$]$_{eq}$ at $T = 20$ and $85 \degree$C ($I_m = 3.6$ mol kg$^{-1}$ NaClO$_4$). The calculated speciation according to the derived log $b_n^0$ values are indicated as solid lines for $20 \degree$C and dashed lines for $85 \degree$C. [Lac]/[C$_0$]$_{eq}$ is calculated at each temperature according to the literature procedure using the Henderson–Hasselbalch equation, SIT and the temperature dependence of the p$K_a$(H$^+$ + Lac)/[C$_0$]$_{eq}$ value.47–49 The required standard reaction enthalpies and protonation constants are given in the literature (p$K_a$(Na$^+$, Lac) = 3.88 ± 0.02; $D_{rH}^0$(Lac) = 0.55 ± 0.08 kJ mol$^{-1}$).50 For the protonation reaction of Lac/[C$_0$]$_{eq}$ = 0.01 ± 0.05 is used.48

With increasing ligand concentration, the chemical equilibrium shifts towards the complexed species. For [Lac]/[C$_0$]$_{eq} > 1.6 \times 10^{-2}$ mol kg$^{-1}$ the NpO$_2$(Lac) complex dominates the speciation. The NpO$_2$(Lac)$_2$- complex makes only a minor contribution to the species distribution at the experimental conditions. With increasing temperature the molar fractions of both lactate complexes decrease and the chemical equilibrium shifts towards the NpO$_2^+$ aquo ion. These trends show that the complex formation is repressed at elevated temperatures indicating an exothermic complexation reaction of NpO$_2^+$ with lactate.

#### 3.1.3 Complex stoichiometry

The stoichiometry of the formed complexes is determined by slope analyses at each studied temperature.26,50 The following complexation model of NpO$_2^+$ with lactate is applied (eqn (1)).

$$NpO_2^+ + Lac^- \rightleftharpoons NpO_2(Lac)$$

$$NpO_2(Lac) + Lac^- \rightleftharpoons NpO_2(Lac)_2^-$$

The slope analyses are performed according to the logarithmic form of the law of mass action (eqn (2)).

$$\log K_n = \log \frac{[NpO_2(Lac)]^{1-n}_{al}}{[NpO_2(Lac)$_{n-1}$$^{1-(n-1)}]} - 1 \cdot \log[Lac]_{eq}^{-n};$$

$$b_n^0 = \prod K_n$$

The results of the slope analyses at $I_m = 3.6$ mol kg$^{-1}$ NaClO$_4$ and $T = 20$ and $85 \degree$C are displayed in Fig. 4. The logarithmic molar fractions log([NpO$_2$(Lac)$_{n-1}$$^{1-(n-1)}$]/[NpO$_2$(Lac)$_{n}$$^{1-n}$]) correlate linearly with log[Lac]/[C$_0$]$_{eq}$ and linear regression analyses reveal slopes between 0.9 ± 0.1 and 1.1 ± 0.1 for all experimental conditions. Thus, the formation of two NpO$_2^+$ lactate complexes with a stoichiometry of NpO$_2$(Lac)$_{n}$$^{1-n}$ ($n = 1, 2$) is confirmed.
This result contrasts with solvent extraction studies by Moore et al. reporting the formation of solely NpO₂(Lac) up to [Lac]ₗ = 0.1 mol kg⁻¹ NaCl and T = 25 °C.¹⁹

This was confirmed by recent solvent extraction studies by Vasiliev et al. In contrast to these studies, Inoue et al. reported the formation of NpO₂(Lac)ₙ⁻¹ (n = 1, 2) using absorption spectroscopy and solvent extraction at 1 mol L⁻¹ NaClO₄, T = 25 °C and [Lac]ₗ = 2.0 mol L⁻¹ in the pHₗ range of 5.8 to 7.5. These results are in good agreement with those of the present work concerning the stoichiometry of the identified complex species.

### 3.1.4 Thermodynamic data

Using the experimental speciation data conditional log βₙᵣ(T) values for the formation of NpO₂(Lac)ₙ⁻¹ (n = 1, 2) are determined at different temperatures and are extrapolated to Iₗ = 0 with the specific ion interaction theory (SIT) according to eqn (3). Details on the SIT are given elsewhere.¹¹,¹² The extrapolations are given in the ESI (Fig. S1 and S2).

\[
\log \beta_{n}(T) = \log \beta_{n}(T_0) + \Delta H_{n,m}^{\circ} / (R \ln(10)) \left( 1 / T_0 - 1 / T \right) \tag{4}
\]

R is the universal gas constant and T the absolute temperature. T₀ = 298.15 K is the temperature of the IUPAC reference state. The Van't Hoff equation is only valid for a small temperature range of about ΔT = 100 K assuming ΔCₗ⁰ₙₙₚ = 0 and ΔHₘₙₚ = const.

The obtained ΔHₘₙₚ and ΔSₘₙₚ values are listed in Table 2 and compared to literature data. The formation of both complexes is slightly exothermic in both electrolytes (NaCl and NaClO₄). The averaged standard reaction enthalpies are ΔHₘₙₚ(NpO₂(Lac)) = 4.5 ± 0.5 kJ mol⁻¹ and ΔHₘₙₚ(NpO₂(Lac)₂) = 6.0 ± 0.4 kJ mol⁻¹, the standard reaction entropies are ΔSₘₙₚ(NpO₂(Lac)) = 21.1 ± 4.3 kJ mol⁻¹ K⁻¹ and ΔSₘₙₚ(NpO₂(Lac)₂) = 21.6 ± 6.7 kJ mol⁻¹ K⁻¹.

In the literature only two log β₁(T) values are reported determined by solvent extraction techniques.¹⁹ Moore et al. determined log β₁(T) = 1.70 for the formation of NpO₂(Lac) by application of the SIT and log β₁(T) = 1.97 by application of the Pitzer model. Both values are in very good agreement with the log β₁(T) value in the present work. The formation of higher complex species is not described in this survey. A recent study by Vasiliev et al. provides a stability constant for NpO₂(Lac) of log β₁(T) = 1.96 ± 0.05 as well as ΔH₁ₙₚ(NpO₂(Lac)) = 5.0 ± 1.4 kJ mol⁻¹ and ΔS₁ₙₚ(NpO₂(Lac)) = 19 ± 4 kJ mol⁻¹.¹⁸ These results are in excellent agreement with those of the present work. Nevertheless, due to the lower total lactate concentration the formation of higher complex species was not observed by Vasiliev et al. In addition, conditional stability constants for NpO₂(Lac)ₙ⁻¹ (n = 1, 2) determined by Inoue et al., Vasiliev et al. and Moore et al. at I = 1 mol L⁻¹ NaClO₄ or NaCl and T = 25 °C are compared to the present work in Table 3.¹⁸⁻²⁰,⁵¹ The spectrophotometrically determined log β₁ by Inoue et al. determined from NaClO₄ solution is higher compared to the one of the present work whereas the values determined by both solvent extraction studies are significantly lower.

### Table 1 Thermodynamic stability constants log β₁(T) for the formation of NpO₂(Lac)⁻¹ (n = 1, 2) obtained in NaClO₄ and NaCl media and their mean values "Ω" as a function of temperature. Confidence interval: 1 s = 0.95. Ω: mean values

<table>
<thead>
<tr>
<th>[NpO₂(Lac)]⁻¹</th>
<th>T [°C]</th>
<th>20</th>
<th>30</th>
<th>40</th>
<th>50</th>
<th>60</th>
<th>70</th>
<th>80</th>
<th>90</th>
<th>100</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaClO₄</td>
<td>1.87 ± 0.08</td>
<td>1.88 ± 0.07</td>
<td>1.85 ± 0.09</td>
<td>1.81 ± 0.09</td>
<td>1.76 ± 0.10</td>
<td>1.75 ± 0.05</td>
<td>1.73 ± 0.13</td>
<td>1.73 ± 0.10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaCl</td>
<td>1.96 ± 0.06</td>
<td>1.95 ± 0.09</td>
<td>1.92 ± 0.09</td>
<td>1.90 ± 0.08</td>
<td>1.86 ± 0.08</td>
<td>1.85 ± 0.11</td>
<td>1.81 ± 0.09</td>
<td>1.86 ± 0.13</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ω</td>
<td>1.92 ± 0.10</td>
<td>1.92 ± 0.11</td>
<td>1.88 ± 0.13</td>
<td>1.85±0.12</td>
<td>1.81±0.13</td>
<td>1.80±0.12</td>
<td>1.77±0.16</td>
<td>1.80±0.16</td>
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<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>[NpO₂(Lac)]₂</th>
<th>T [°C]</th>
<th>20</th>
<th>30</th>
<th>40</th>
<th>50</th>
<th>60</th>
<th>70</th>
<th>80</th>
<th>90</th>
<th>100</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaClO₄</td>
<td>2.04 ± 0.08</td>
<td>2.02 ± 0.09</td>
<td>2.00 ± 0.08</td>
<td>1.96 ± 0.09</td>
<td>1.90 ± 0.12</td>
<td>1.89 ± 0.12</td>
<td>1.86 ± 0.15</td>
<td>1.85 ± 0.15</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaCl</td>
<td>2.16 ± 0.06</td>
<td>2.15 ± 0.12</td>
<td>2.10 ± 0.15</td>
<td>2.07 ± 0.09</td>
<td>2.03 ± 0.11</td>
<td>2.03 ± 0.15</td>
<td>1.97 ± 0.09</td>
<td>2.02 ± 0.14</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ω</td>
<td>2.10 ± 0.1</td>
<td>2.09 ± 0.15</td>
<td>2.05 ± 0.17</td>
<td>2.01 ± 0.13</td>
<td>1.96 ± 0.16</td>
<td>1.95 ± 0.19</td>
<td>1.91 ± 0.17</td>
<td>1.93 ± 0.21</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 2 Thermodynamic functions of the formation of NpO2(Lac)n1−n (n = 1, 2) and comparison to literature data. Confidence interval of the present results: 1 ± 0.95. Ø: mean values. p.w.: present work.

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>NpO2(Lac)n1−n</th>
<th>log βn0</th>
<th>ΔH°</th>
<th>ΔS°</th>
<th>Δε</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaClO4</td>
<td>n 1</td>
<td>1.87 ± 0.11</td>
<td>4.2 ± 0.3</td>
<td>19 ± 4</td>
<td>0.09 ± 0.02</td>
<td>p.w.</td>
</tr>
<tr>
<td></td>
<td>n 2</td>
<td>2.03 ± 0.12</td>
<td>5.8 ± 0.5</td>
<td>22 ± 5</td>
<td>0.20 ± 0.03</td>
<td>p.w.</td>
</tr>
<tr>
<td>NaCl</td>
<td>n 1</td>
<td>1.96 ± 0.11</td>
<td>4.8 ± 0.4</td>
<td>21 ± 4</td>
<td>0.12 ± 0.02</td>
<td>p.w.</td>
</tr>
<tr>
<td></td>
<td>n 2</td>
<td>2.13 ± 0.13</td>
<td>6.2 ± 0.3</td>
<td>22 ± 3</td>
<td>0.23 ± 0.02</td>
<td>p.w.</td>
</tr>
<tr>
<td>O</td>
<td>n 1</td>
<td>1.92 ± 0.14</td>
<td>4.5 ± 0.5</td>
<td>22 ± 5</td>
<td>0.20 ± 0.03</td>
<td>p.w.</td>
</tr>
<tr>
<td></td>
<td>n 2</td>
<td>2.10 ± 0.13</td>
<td>6.0 ± 0.4</td>
<td>20 ± 6</td>
<td>0.20 ± 0.03</td>
<td>p.w.</td>
</tr>
<tr>
<td>NaCl</td>
<td>n 1</td>
<td>1.96 ± 0.05</td>
<td>5.4 ± 1.4</td>
<td>19 ± 4</td>
<td>0.13 ± 0.03</td>
<td>18</td>
</tr>
</tbody>
</table>

Table 3 Conditional stability constants for the complexation of NpO2+ with lactate with lΘ = 1.0 mol kg−1 and NaClO4 or NaCl as background electrolyte. T = 25 °C

<table>
<thead>
<tr>
<th>Method</th>
<th>Electrolyte</th>
<th>log β01</th>
<th>log β02</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>NaClO4</td>
<td>1.11 ± 0.08</td>
<td>1.78 ± 0.03</td>
<td>20</td>
</tr>
<tr>
<td>B</td>
<td>NaClO4</td>
<td>1.09</td>
<td>1.60</td>
<td>51</td>
</tr>
<tr>
<td>sp NaClO4</td>
<td>1.75</td>
<td>20</td>
<td></td>
<td></td>
</tr>
<tr>
<td>sp NaClO4</td>
<td>1.48 ± 0.08</td>
<td>1.77 ± 0.09</td>
<td>p.w.</td>
<td></td>
</tr>
<tr>
<td>sp NaClO4</td>
<td>1.43 ± 0.04</td>
<td>19</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A sp NaCl (0.83 mol kg−1)</td>
<td>1.75 ± 0.03</td>
<td>18</td>
<td></td>
<td></td>
</tr>
<tr>
<td>sp NaClO4</td>
<td>1.67 ± 0.10</td>
<td>1.98 ± 0.11</td>
<td>p.w.</td>
<td></td>
</tr>
</tbody>
</table>

Further, different complex species were identified by Inoue et al. within the different experimental approaches.20,31 The solvent extraction experiments reveal the formation of NpO2(Lac)1−n (n = 1, 2), while the spectrosopic study suggests the exclusive formation of NpO2(Lac). This might explain the huge deviations of the log β1 values obtained by Inoue et al. with the two different experimental methods. The log β1 by Vasiliev et al. is in good agreement to the present result obtained from NaCl solution whereas the value reported by Moore et al. is significantly lower.

Furthermore, comparison of the present results with results on the complexation of NpO2+ with the structurally related carboxylate “propionate” reveals the effect of the α-OH group on the thermodynamic functions. Solvent extraction studies by Vasiliev et al. report log βn1(NpO2(Prop), 25 °C) = 1.19–1.26, ΔH°,m (NpO2(Prop)) = 10.9–16.3 kJ mol−1 and ΔS°,m (NpO2(Prop)) = 62–77 J mol−1 K−1.16,22 Comparison with the present results for NpO2(Lac) shows that the additional α-OH group results in an increase of the complex stability accompanied with a lowering of ΔH°,m. This points to significant differences in the coordination mode of both ligands. Propionate coordinates end-on towards NpO2+ whereas lactate can form chelate complexes involving the COO− and OH group. A comparison with other simple carboxylates containing α-OH groups (e.g. malate or tartrate) is not possible as literature data for NpO2+ complexes are not available.

The application of the SIT yields the stoichiometric sum of the binary ion–ion interaction coefficients εj,k of the complex formations. In Fig. 6 the determined Δε01 and Δε02 values are displayed as a function of the temperature for the reaction NpO2+ + nLac− ⇌ NpO2(Lac)n1−n (n = 1, 2) in NaClO4 and NaCl media. No temperature dependence of the Δεj,k values is observed in NaClO4. In NaCl Δε01 increases slightly whereas Δε02 remains constant. However, the temperature dependence is negligible within the error range of the data. Various studies on the ionic strength dependence of complexation reactions of trivalent lanthanides and actinides showed, that the effect of temperature on Δεj,k is rather small and thus negligible in the temperature range of 20 to 90 °C.22,23 Recent studies on the complexation of Np(v) with sulphate, fluoride, formate and acetate support these observations.43,44,45 Thus, temperature independent Δεj,k values are calculated for NaClO4 and NaCl media (see Table 2). The averaged values are Δε01(NaClO4) = 0.09 ± 0.02, Δε01(NaCl) = 0.12 ± 0.02 and Δε02(NaClO4) = 0.20 ± 0.03, Δε02(NaCl) = 0.23 ± 0.02. Comparison with the results by Vasiliev et al. (Δε01(NaCl) = 0.13 ± 0.03) shows an excellent agreement with Δε01(NaCl) of the present work. Thus, the ionic strength dependence as a function of the NaCl concentration is accurately described in both studies.

In order to derive the binary ion–ion interaction coefficients εj,k of the different NpO2+ lactate complexes with both background electrolytes the following parameters stated in the literature are used: ε(Na+, Lac−) = 0.01 ± 0.05, ε(NpO2+, ClO4−) = 0.25 ± 0.05 and ε(NpO2+, Cl−) = 0.09 ± 0.05.11,48 The ε(Na+ + Cl−/ClO4−, NpO2(Lac)) and ε(Na+, NpO2(Lac)−) values are calculated according to eqn (5).

$$Δε = \sum ε_{products} + ε_{educts} \quad (5)$$

The SIT binary ion–ion interaction parameters for NpO2(Lac) are ε(Na+ + ClO4−, NpO2(Lac)) = 0.17 ± 0.05 and ε(Na+ + Cl−, NpO2(Lac)) = 0.02 ± 0.05. For NpO2(Lac)− the parameters are ε(Na+, NpO2(Lac)−) = 0.07 ± 0.05 determined in NaClO4 and ε(Na+, NpO2(Lac)−) = 0.12 ± 0.05 determined in NaCl. The similarity of ε(Na+ + ClO4−, NpO2(Lac)) and ε(Na+, NpO2(Lac)−) determined in NaClO4 as well as of ε(Na+ + Cl−, NpO2(Lac)) and ε(Na+, NpO2(Lac)−) determined in NaCl is expected as the observed ionic strength dependence of the respective log β1 values is weak. According to the SIT it is assumed that εj,k = 0 for uncharged species. Taking into account the error of the εj,k values, this is the case for ε(Na+ + Cl−, NpO2(Lac)). However, ε(Na+ + ClO4−, NpO2(Lac)) deviates significantly from zero and the
discrepancy between these two values accounts for 0.19. Similar deviations were observed for the complexes of NpO$_2$$^+$ with formate, acetate, fluoride and chloride in NaClO$_4$ media.43,45,46,53 Furthermore, a comparable deviation is observed for $\varepsilon$(Na$^+$, NpO$_2$(Lac)$_2$)/C0 determined in NaCl and NaClO$_4$ media which is also 0.19. Thus, we assume that the $\varepsilon$(NpO$_2$$^+$, Cl$^-$)/C0 = 0.25 ± 0.05 given in the NEA-TDB might be defective and should be re-evaluated. Nonetheless, the thermodynamic functions (log $b_0$($^0$T)), $D_{\text{rH}}^0$($^0$T), $m$, $D_{\text{rS}}^0$($^0$T), $m$) obtained for both electrolytes (NaCl and NaClO$_4$) are in excellent agreement and thus the ionic strength dependence of the complex formations is accurately described in the present work.

Comparison of the present $\varepsilon$$_{jk}$ values determined in NaCl with literature data for the acetate and propionate complexes shows that the ion–ion interaction parameters are all close to zero:18,22 $\varepsilon$(Na$^+$ + Cl$^-$, NpO$_2$(Lac)) = 0.05 ± 0.05 $\varepsilon$(Na$^+$, NpO$_2$(Lac)$_2$) = 0.02 ± 0.05 $\varepsilon$(Na$^+$ + Cl$^-$, NpO$_2$(Ac)) = 0.02 ± 0.06 $\varepsilon$(Na$^+$, NpO$_2$(Ac)$_2$) = 0.01 ± 0.06 $\varepsilon$(Na$^+$ + Cl$^-$, NpO$_2$(Prop)) = 0.03 ± 0.04 $\varepsilon$(Na$^+$, NpO$_2$(Prop)) = 0.00 ± 0.04

Thus, the ionic strength dependence of the formation of the NpO$_2$(L) and NpO$_2$(L)$_2^-$ complexes with lactate, acetate and propionate is weak and comparable for all ligands discussed.

3.2 Structural characterization of the NpO$_2$(Lac)$_n$$^+$ complexes

For $\omega$-hydroxy carboxylates two coordination modes towards the NpO$_2$$^+$ ion are possible (see Scheme 1). Information on the structure of the NpO$_2$(Lac)$_n$$^+$ complexes should show if the $\omega$-OH group is involved in the complexation of An($v$) ions and how this might affect the thermodynamic behaviour.

3.2.1 EXAFS spectroscopy. The $k^2$-weighted Np-L$_3$-edge EXAFS spectra of NpO$_2$$^+$ in the presence of lactate, the Fourier transformations and the corresponding fit curves are given in the ESI† as a function of the pH value. The results of the fits and the fit parameters are listed in Table S1 in the ESI.† A summary of the obtained structural parameters is given in Table 4. The spectra are dominated by the axial and equatorial O-atoms (O$_{\text{ax}}$, O$_{\text{eq}}$). The averaged distance of the axial O-atoms (O$_{\text{ax}}$) is 1.84 ± 0.01 Å and of the equatorial O-atoms (O$_{\text{eq}}$) 2.49 ± 0.02 Å. The coordination number of the NpO$_2$$^+$ ion in the equatorial plane varies between 3.1 and 4.9. Both, the coordination numbers and the distances of the O-atoms are not affected by the pH value. Furthermore, the results are in excellent agreement with literature data.54,55

Table 4 Structural parameters for the NpO$_2$(Lac)$_n$$^+$ ($n = 1, 2$) complexes obtained from the fits of the raw $k^2$ weighted Np-L$_3$ edge EXAFS spectra shown in Fig. S3 (ESI)

<table>
<thead>
<tr>
<th>pH</th>
<th>0.8</th>
<th>2.6</th>
<th>3.3</th>
<th>4.0</th>
<th>4.7</th>
<th>5.2</th>
</tr>
</thead>
<tbody>
<tr>
<td>$O_{\text{ax}}$</td>
<td>N</td>
<td>2$^a$</td>
<td>2$^a$</td>
<td>2$^a$</td>
<td>2$^a$</td>
<td>2$^a$</td>
</tr>
<tr>
<td>R/Å</td>
<td>1.83 (1)</td>
<td>1.85 (1)</td>
<td>1.83 (1)</td>
<td>1.84 (1)</td>
<td>1.84 (1)</td>
<td>1.84 (1)</td>
</tr>
<tr>
<td>$O_{\text{eq}}$</td>
<td>N</td>
<td>4.9 (1)</td>
<td>3.1 (1)</td>
<td>4.2 (1)</td>
<td>4.1 (1)</td>
<td>4.2 (1)</td>
</tr>
<tr>
<td>R/Å</td>
<td>2.48 (1)</td>
<td>2.51 (2)</td>
<td>2.49 (1)</td>
<td>2.49 (1)</td>
<td>2.48 (1)</td>
<td>2.48 (1)</td>
</tr>
<tr>
<td>$C_{\text{coord}}$</td>
<td>N</td>
<td>1.3 (1)</td>
<td>1.1 (1)</td>
<td>1.2 (1)</td>
<td>1.3 (1)</td>
<td>2.5 (1)</td>
</tr>
<tr>
<td>R/Å</td>
<td>2.72 (8)</td>
<td>2.81 (4)</td>
<td>3.12 (4)</td>
<td>3.14 (2)</td>
<td>3.23 (2)</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Fixed for fitting.
The coordination mode of the lactate molecules towards the NpO$_2^+$ ion is determined by evaluating the distances of the carbon atoms of the coordinating functional groups (–COO$^-$ and –COH). At pH$_c$ = 0.8 no lactate complexes are formed and the spectrum corresponds to the solvated NpO$_2^+$ ion. At pH$_c$ = 2.6 the evaluation of the EXAFS spectrum reveals 1.3 carbon atoms C$_n$ at 2.72 ± 0.08 Å from the Np(IV) center. With increasing pH$_c$ up to 5.2 both, the number of carbon atoms and the C$_n$ distance increase from 1.3–2.5 and from 2.72 ± 0.08–3.23 ± 0.02 Å, respectively. This indicates a change of the coordination mode of lactate with increasing basicity.

Takao et al. studied the complexation of NpO$_2^+$ with acetate by EXAFS spectroscopy. In this study a C$_n$ distance of 2.91 ± 0.02 Å between the NpO$_2^+$ center and the coordinating COO$^-$ group is reported. In an EXAFS study on Np-propionate complexes by Vassiliev et al., a C$_n$ distance of 2.87 ± 0.03 Å was determined. These distances obtained for monocarboxylic ligands serve as reference for an end-on coordination mode of the COO$^-$ group via the two O-atoms. Furthermore, the C$_n$ distances obtained for NpO$_2^+$ complexes are in good agreement with structural parameters of Am(III)-acetate complexes. There, a C$_n$ distance of 2.82 ± 0.05 Å to the americium ion was determined. Literature data on structural parameters of Am(III) lactate complexes show, that the distal C$_c$ atoms are located at 3.42 ± 0.03 Å. This is distinctly larger compared to the distance in the Am(III) acetate complexes and indicates a side-on coordination of lactate with the formation of a five-membered chelate ring at pH$_c$ ≥ 3.0.

The comparison with the known C$_n$ distances for side-on and end-on coordination indicates that at low pH$_c$ lactate coordinates only via the COO$^-$ group towards NpO$_2^+$. With increasing pH$_c$ the C$_n$ distance increases and the coordination mode changes to a side-on coordination of lactate via the COO$^-$ and COH-group. Thus, the proton concentration has a major effect on the coordination mode of lactate towards the NpO$_2^+$ ion.

3.2.2 ATR FT-IR spectroscopy. The vibrational modes of the coordinated ligand and the NpO$_2^+$ ion provides additional information on the structure of the complexes and the coordination mode of lactate towards the NpO$_2^+$ ion. Prior to the measurement of the NpO$_2^+$ lactate samples, the vibrational spectra of the pure ligand at identical experimental conditions are recorded (Fig. 7, top). All spectra are dominated by bands at 1716, 1587 and 1416 cm$^{-1}$ representing the vibrational modes of the COOD group as well as the symmetric (ν$_s$(COO$^-$)) and anti-symmetric (ν$_a$(COO$^-$)) modes of the COO$^-$ group. The absorption bands at 1462 and 1116 cm$^{-1}$ corresponds to the ν$_{Al}$(OH) and ν$_{Al}$(CO) modes of the COH group. These values are in good agreement with literature data.

The infrared spectra of the NpO$_2^+$ lactate species at various pD$_L$ values (pD$_L$ = 2.6, 4.1, 4.8) are shown in Fig. 7 (bottom) as difference spectra after subtraction of the spectra of the pure ligand. The absorption spectra show a contribution of the free lactic acid which is represented by the negative absorption band at 1716 cm$^{-1}$. Modes of the ligand undergoing alterations upon complexation are detected as positive absorption bands at 1587, 1456, 1416 and 1100 cm$^{-1}$.

The vibrational band of the ν$_s$(NpO$_2^+$) mode is observed in the spectral region below 850 cm$^{-1}$. Its frequency and shape changes slightly as a function of the pD$_L$ value. Thus, a deconvolution of this band was performed, and frequencies of single species were obtained from second derivative spectra (data not shown). At pD$_L$ = 2.6, two bands at 799 and 817 cm$^{-1}$ are observed. The first one represents the OD mode of the free lactate. The band at 817 cm$^{-1}$ is assigned to the free NpO$_2^+$ ion. Thus, at pD$_L$ = 2.6 the NpO$_2^+$ aquo ion is the predominant species. An increasing number of coordinated lactate molecules in the equatorial plane of the NpO$_2^+$ ion lowers the frequency of the antisymmetric stretching vibration. Consequently, upon increasing the pD$_L$ value to 4.1 a vibrational band at 804 cm$^{-1}$ is obtained corresponding to a single species, NpO$_2$Lac. This band remains unchanged in the spectrum obtained at pD$_L$ = 4.8. Thus, the frequency of the ν$_s$(NpO$_2^+$) mode provides information on the number of different complex species but no direct indication of the coordination mode of the ligand.

However, information on the coordination mode of the ligand to the NpO$_2^+$ ion can be derived from the antisymmetric and symmetric stretching modes of the carboxyls groups (ν$_{as}$(COO$^-$) and ν$_{as}$(COO$^-$)). Their spectral splitting (Δν$_{COO}$) allows a differentiation between bidentate and monodentate coordination of the COO$^-$ group to the metal ion. Generally, a bidentate coordination is characterized by a smaller splitting (Δν$_{COO}$ ≤ 100 cm$^{-1}$) whereas a monodentate binding results in a larger spectral splitting (Δν$_{COO}$ ≥ 150 cm$^{-1}$). The vibrational modes of the COO$^-$ group of the lactate ligand have nearly the same frequency values throughout the whole pD$_L$ range investigated, that are 1587 cm$^{-1}$ for the ν$_s$(COO$^-$) and 1416 cm$^{-1}$ for the ν$_a$(COO$^-$) mode. Therefore, the constant value Δν$_{COO}$ of about 171 cm$^{-1}$ suggests a monodentate coordination of the COO$^-$ group in the series of the NpO$_2^+$ lactate spectra excluding an end-on coordination of the ligand towards the
NpO₂⁺ ion (compare Scheme 1). Furthermore, the comparison of the spectral data shown in Fig. 7 (top and bottom) reveals that the impact of replacing the monovalent Na⁺ by NpO₂⁺ on the vibrational modes of the COO⁻ group is not significant. In contrast, a shift of the alcoholic ν_A1(CO) band from 1116 to 1100 cm⁻¹ and of ν_A1(OH) from 1462 to 1456 cm⁻¹ is observed indicating that the COH group is involved in the binding of lactate towards NpO₂⁺. This shift is unaffected by the pH value. According to the EXAFS results with increasing pH/pDc a change of the coordination mode from side-on to end-on is expected. This is not observed by infrared spectroscopy as these results suggest a side-on coordination within the entire pDc range studied. However, the results of the IR measurements at pDc ≥ 4.1, 4.8 are in good agreement with the results obtained by EXAFS for pHc ≥ 4.0 indicating a side-on coordination of lactate towards the NpO₂⁺ ion.

### 3.2.3 Quantum chemical calculations

The molecular structures of different constitution isomers of the NpO₂(Lac) and NpO₂(Lac)_2 complexes (see Scheme 2) are optimized on the DFT level using the BH-LYP functional and def-TZVP basis sets. A detailed visualization of the structures is given in Fig. S5–S7 in the ESI. The cartesian coordinates of the optimized complex structures are also given there. The calculated averaged distances of the coordination shells containing the axial O-atoms O ax, the equatorial O-atoms O eq, and the C-atoms C c of the coordinating COO⁻ and COH group are summarized in Table 5 and compared to the results of the EXAFS evaluation. The data show that the coordination shell distances of the axial and equatorial O-atoms (O ax, O eq) are not affected by the coordination mode of the ligand. Therefore, it is not possible to differentiate between the coordination modes of the lactate molecule using the distances of O ax or O eq towards the NpO₂⁺ center. However, the average distances of the C c coordination shell of the COO⁻ and COH group differ significantly for end-on and side-on coordination. For end-on coordinated lactate a C c distance of 2.91 Å is calculated which is about 0.48 Å shorter compared to the C c distance of the side-on coordinated ligand molecule (C c = 3.39 Å).

The comparison with the experimentally obtained distances shows that the calculated values for O ax and O eq are in excellent agreement with the experimental results. However, the C c distance determined by EXAFS spectroscopy increases with increasing pHc from 2.98 up to 3.38 Å. The distance at low pHc is in good agreement with the calculated distance for the end-on coordinating lactate. The experimentally determined C c distance at pHc = 4.9 agrees with the distance for the side-on coordinating lactate via the COO⁻ and COH group. Unfortunately, the quantum chemical calculations do not account for pHc effects. Nevertheless, the calculations confirm the experimentally observed C c distances for the end-on and the side-on coordination mode of lactate.

Calculations of the Gibb’s free energies ΔG provide additional information on the coordination mode of lactate towards NpO₂⁺. The Gibb’s energies for the isomerisation of NpO₂(Lac)ₙ₋₁⁻ (n = 1, 2) are calculated according to eqn (6a)–(6c).

<table>
<thead>
<tr>
<th>Method</th>
<th>Complex</th>
<th>Coord. mode</th>
<th>O ax [Å]</th>
<th>O eq [Å]</th>
<th>C c [Å]</th>
</tr>
</thead>
<tbody>
<tr>
<td>DFT NpO₂(Lac)</td>
<td>End on</td>
<td>1.83</td>
<td>2.49</td>
<td>2.91</td>
<td></td>
</tr>
<tr>
<td>Side on</td>
<td>1.84</td>
<td>2.46</td>
<td>3.39</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NpO₂(Lac)₂</td>
<td>End on</td>
<td>1.81</td>
<td>2.47</td>
<td>2.92</td>
<td></td>
</tr>
<tr>
<td>Side on</td>
<td>1.84</td>
<td>2.45</td>
<td>3.39</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mixed</td>
<td></td>
<td>1.84</td>
<td>2.47</td>
<td>2.86/3.40</td>
<td></td>
</tr>
<tr>
<td>EXAFS NpO₂(Lac)/NpO₂(Lac)₂</td>
<td></td>
<td>1.84</td>
<td>2.47</td>
<td>2.72/3.32</td>
<td></td>
</tr>
</tbody>
</table>

ΔG is calculated using the difference of the ground state energies ΔEₕ on MP2 level while thermodynamic corrections ΔG vib and solvation effects ΔG COSMO are considered: ΔG = ΔEₕ + ΔG vib + ΔG COSMO. The results show, that in case of the isomerisation of NpO₂(Lac) ΔG is positive, whereas it is negative for NpO₂(Lac)₂⁻ (see Table 6). Thus, for the 1:1 complex the end-on coordination of the ligand is more stable compared to the side-on coordination. In contrast, for the 1:2 complex the formation of chelate complexes is energetically preferred. Furthermore, the 1:2 complex with two lactate molecules forming chelate rings is more stable compared to the mixed structure (see Scheme 2). This is expressed by the more negative ΔG value for the isomerisation according to eqn (6b) in comparison to eqn (6c).

![Scheme 2](image_url)  
Scheme 2 Schematic structures of the different constitution isomers of the NpO₂⁺ lactate complexes. The stoichiometric sum of the complexes in the first coordination sphere is NpO₂(H₂O)(Lac) and NpO₂₂(H₂O)(Lac)₂. The second coordination sphere consists of 28 water molecules. The water molecules are omitted for clarity.
Table 6: Gibbs free energies $\Delta G$ for the isomerisation of NpO$_2$(Lac)$_n$ (n = 1, 2) according to eqn (6a) (6c). Ground state energies calculated on MP2 level.

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\Delta E_g$ [kcal mol$^{-1}$]</th>
<th>$\Delta G_{\text{calc}}$ [kcal mol$^{-1}$]</th>
<th>$\Delta G_{\text{gaseous}}$ [kcal mol$^{-1}$]</th>
<th>$\Delta G$ [kcal mol$^{-1}$]</th>
<th>Eqn.</th>
</tr>
</thead>
<tbody>
<tr>
<td>NpO$_2$(Lac)</td>
<td>4.20</td>
<td>20.15</td>
<td>6.01</td>
<td>39.89</td>
<td>(6a)</td>
</tr>
<tr>
<td>NpO$_2$(Lac)$_2$</td>
<td>28.13</td>
<td>28.26</td>
<td>18.58</td>
<td>18.71</td>
<td>(6b)</td>
</tr>
<tr>
<td></td>
<td>28.90$^a$</td>
<td>1.11$^a$</td>
<td>23.85$^a$</td>
<td>3.93$^a$</td>
<td>(6c)</td>
</tr>
</tbody>
</table>

$^a$ $\Delta E$ = $\Delta E_{\text{side-on}} + \Delta E_{\text{mixed}} + \Delta G_{\text{side-on}} + \Delta G_{\text{mixed}}$.

Table 7: Relative shifts of the calculated vibrational frequencies of the different constitution isomers of the NpO$_2$(Lac) and NpO$_2$(Lac)$_2$ complexes from DFT and comparison with the results by FT-IR spectroscopy. $\nu_\text{lig}(\text{COO}) + \nu_\text{lig}(\text{COO})$

<table>
<thead>
<tr>
<th>Complex</th>
<th>Coordination</th>
<th>$\nu_\text{s}(\text{COO})$ [cm$^{-1}$]</th>
<th>$\nu_\text{s}(\text{COO})$ [cm$^{-1}$]</th>
<th>$\Delta\nu_\text{COO}$ [cm$^{-1}$]</th>
<th>$\Delta\nu_{\text{COO}}$ [cm$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>NpO$_2$(Lac)</td>
<td>End</td>
<td>1686</td>
<td>1598</td>
<td>88</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Side</td>
<td>1730</td>
<td>1457</td>
<td>273</td>
<td></td>
</tr>
<tr>
<td>NpO$_2$(Lac)$_2$</td>
<td>End</td>
<td>1678</td>
<td>1569</td>
<td>107</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Side</td>
<td>1728</td>
<td>1457</td>
<td>271</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Mixed</td>
<td>1679</td>
<td>1587</td>
<td>92</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1702</td>
<td>1478</td>
<td>224</td>
<td></td>
</tr>
<tr>
<td>Exp.</td>
<td>pH 2.6</td>
<td>1587</td>
<td>1449</td>
<td>171</td>
<td></td>
</tr>
</tbody>
</table>

As vibrational frequencies are calculated to estimate $\Delta G_{\text{calc}}$ for the theoretical spectral shifts $\Delta\nu_{\text{lig}}(\text{COO}) = \nu_\text{lig}(\text{COO}) - \nu_\text{lig}(\text{COO})$ for the different constitution isomers of the NpO$_2$(Lac) and NpO$_2$(Lac)$_2$ complexes are compared to the results of the FT-IR spectroscopy in Table 7.

The results of the calculations confirm the interpretation of the FT-IR spectra. For a bidentate coordination of the lactate via both O-atoms (end-on) a spectral splitting of $\Delta\nu_{\text{COO}} \leq 100$ cm$^{-1}$ is expected. The calculations provide $\Delta\nu_{\text{lig}}(\text{COO})$ to be 88–107 cm$^{-1}$ for an end-on coordinating lactate. In case of a side-on coordination of lactate $\Delta\nu_{\text{lig}}(\text{COO}) \geq 150$ cm$^{-1}$ is expected. The calculations reveal $\Delta\nu_{\text{lig}}(\text{COO}) = 224–273$ cm$^{-1}$. In the experiments a value of $\Delta\nu_{\text{lig}}(\text{COO}) = 171$ cm$^{-1}$ is observed indicating a monocentrate coordination of the COO$^-$ group and a side-on coordination of lactate to the NpO$_2^+$ center.

The quantum chemical calculations do not consider effects of the proton concentration on the coordination mode of lactate. Nevertheless, the results confirm the general trend of changing coordination modes with increasing pH$_c$ observed by EXAFS. An increasing pH$_c$ results in a shift of the chemical equilibrium towards the NpO$_2$(Lac)$_2^-$ complex, which is in very good agreement to the experimental results, revealing a preferred side-on coordination at higher pH$_c$ values.

4 Summary

In the present work the thermodynamics and structures of the complexes of NpO$_2^+$ with lactate are investigated by different techniques such as absorption spectroscopy, EXAFS spectroscopy, ATR-FT infrared spectroscopy and quantum chemical calculations. The formation of the NpO$_2^+$ lactate complexes is studied photo metrically as a function of the ligand concentration ([Lac$^{-}$]), ionic strength (NaCl and NaClO$_4$) and temperature (20–85 °C). Two different complex species are observed which are identified as NpO$_2$(Lac) and NpO$_2$(Lac)$_2^-$ . With increasing temperature, the equilibrium of the complex formation shifts towards the NpO$_2^+$ aquo ion. log $\beta_0^0(20 \text{ °C}) = 1.92 \pm 0.09$ decreases by 0.12 and log $\beta_2^0(20 \text{ °C}) = 2.10 \pm 0.06$ decreases by 0.17 in the temperature range of 20–85 °C. Correlation of log $\beta_0^0(T)$ with the reciprocal temperature and fitting according to the integrated Van’t Hoff equation yield the standard reaction enthalpies ($\Delta H_{\text{ag}}$) and entropies ($\Delta S_{\text{ag}}$) of the complexation reactions. Linear regression analyses reveal $\Delta H_{\text{ag}} = 4.5 \pm 0.5$ and $\Delta S_{\text{ag}} = 6.0 \pm 0.4$ confirming slightly exothermic complexation reactions.

The $\Delta G_{\text{aq}}$ and $\Delta G_{\text{aq}}$ values are determined as a function of temperature for two different ionic media (NaCl and NaClO$_4$). No significant temperature dependence of $\Delta G_{\text{aq}}$ and $\Delta G_{\text{aq}}$ is observed and averaged, temperature independent values are used to determine $\varepsilon_{\text{aq}}$ values of the NpO$_2^+$ lactate complexes with the two different electrolytes.

Structural investigations of the formed complexes by EXAFS spectroscopy show a change of the coordination mode of lactate towards the NpO$_2^+$ center when varying the pH$_c$. With increasing pH$_c$, the distance of the C-atom shell increases indicating a change of the coordination mode from end-on to side-on. Quantum chemical calculations confirm the bond distances determined by EXAFS for end-on and side-on coordination. Theoretical approximations of the Gibbs free energies for the isomerisation of end-on to side-on coordinated ligands show the preference of the end-on coordination for NpO$_2$(Lac) and of the side-on coordination for NpO$_2$(Lac)$_2^-$ which agrees to the trend observed by EXAFS spectroscopy as a function of the pH$_c$. In contrast to the EXAFS results, the ATR-FT infrared spectra show no effect of the proton concentration on the coordination mode but indicate a side-on coordination of lactate for pH$_c > 2.6$.

It is expected that different coordination modes of lactate have a strong impact on the thermodynamic functions (log $\beta_0^0(T)$, $\Delta H_{\text{ag}}$, $\Delta S_{\text{ag}}$) of the NpO$_2^+$ complexes. Thus, for the determination of thermodynamic functions detailed information on the structure of the complexes and the coordination mode of the ligand are essential. In the present work the absorption spectroscopic studies were performed at pH$_c = 4.9$. At this pH$_c$ lactate coordinates in the side-on mode forming chelate complexes.

The present work is a detailed study on the complexation of NpO$_2^+$ with lactate providing thermodynamic data and structural information on the formed complexes. The results highlight the effect of the z-hydroxy group on the thermodynamic functions compared to simple monocarboxylates and the effect of the proton concentration on the coordination mode. Furthermore, the here determined data contribute to the thermodynamic database of actinides improving the scientific basis for understanding the chemical behaviour of pentavalent actinides in the presence of multifunctional organic ligands in aqueous solution.

Conflicts of interest

There are no conflicts to declare.
Acknowledgements

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References


28 A. Skerencak, P. J. Panak and T. Fanghänel, Complexation and thermodynamics of Cm(III) at high temperatures: the formation of [Cm(SO₄)₃]²⁻·2n (n = 1, 2, 3) complexes at T = 25 to 200 °C, Dalton Trans., 2013, 42, 542–549.


52 D. Frölich, A. Skerencak-Freh and P. J. Panak, A spectroscopic study on the formation of Cm(III) acetate complexes at elevated temperatures, Dalton Trans., 2014, 43(10), 3958–3965.


54 P. G. Allen, J. J. Bucher, D. K. Shuh, N. M. Edelstein and T. Reich, Investigation of Aquo and Chlro Complexes of


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