1 Introduction

Spent nuclear fuel consists of unspent uranium, fission products, plutonium, and the minor actinides (Np, Am) generated by neutron capture reactions in the reactor. Some of these nuclides have very long half-lives and will determine the long-term radiotoxicity of the nuclear waste. Due to this fact, the high-level radioactive waste has to be isolated efficiently from the living environment for very long time periods. Thus, the emplacement of the radioactive waste in deep geological formations is the worldwide most preferred disposal option.\textsuperscript{1-3} For the safety case of a nuclear waste repository different incident scenarios have to be considered. For instance, the intrusion of water might result in the dissolution of the waste matrix followed by a variety of (geo)chemical reactions (dissolution, sorption, complexation in the aqueous phase, etc.) strongly affecting the migration behaviour of the actinides at repository conditions.\textsuperscript{4} For a detailed description of the chemical behaviour of actinides in natural aquatic systems a comprehensive thermodynamic model based on standard-state stability constants (\(\log K_{\text{eq}}\)) and entropies (\(\Delta S^\circ\)) is required.

For the final storage of high-level nuclear waste different types of host rock formations (clays, salt rocks, and crystalline formations) are discussed.\textsuperscript{1,5-11} Depending on the type of the host rock, different chemical conditions prevail including the presence of organic or inorganic ligands which may affect the geochemical behaviour of the actinides. For example, low molecular weight organic compounds (LMWOC) like formate, acetate, propionate, and lactate as well as macromolecular organic compounds are abundant in clay rocks and different natural systems serving as potential complexation agents.\textsuperscript{12-19} Furthermore, organic polymers, in particular polycarboxylates, used as additives in commercial concrete are another source
of organic macromolecules. Due to their complex structure, the identification of binding sites or specific structural characteristics affecting the complexation properties (log \( \beta_{\text{ns}} \), \( \Delta H^\circ_{\text{ns}} \), \( \Delta S^\circ_{\text{ns}} \)) of these macromolecules is difficult. Furthermore, the decomposition of these organic compounds will lead to the formation of various small carboxylic ligands. Thus, simple and defined carboxylic ligands (e.g. oxalate, malonate, succininate, salicylate, phthalate) are used as reference systems for the organic macromolecules and their degradation products to study the effect of defined structural properties of organic molecules on the complexation properties toward actinides.

The temperature in the near-field of a nuclear waste repository will be increased due to the radioactive decay of the high-level nuclear waste. For example, in clay rock formations temperatures up to 100 °C are expected in the first time-period of post closure. Furthermore, the porewaters of the used host rocks exhibit ionic strength of \( I > 0.1 \) \( \text{mol dm}^{-3} \). For example, in clay rock formations in Northern Germany ionic strengths up to \( I < 3.5 \) \( \text{mol L}^{-1} \) are present. It is known that the temperature and the ionic strength significantly affect the complexation properties of the actinides. Thus, these effects must be considered for an accurate description of the complexation properties of actinides with organic matter and the determination of reliable thermodynamic functions (log \( \beta_{\text{ns}} \), \( \Delta H^\circ_{\text{ns}} \), \( \Delta S^\circ_{\text{ns}} \)).

The actinides U–Am are redox sensitive metal ions and exist as multi valent ions within the thermodynamic stability field of water. The pentavalent actinides (An(V)) are the most soluble actinide ions and thus will show a high mobility in aqueous solution and thus is used as an analogue for other An(V). Furthermore, the Np(V) ion exhibits excellent spectroscopic properties allowing an easy access for the determination of thermodynamic data.

In the literature data on the complexation of Np(V) with oxalate (\( \text{Ox}^2^- \)) are scarce. Different studies by solvent extraction or absorption spectroscopy report log \( \beta_{25^\circ\text{C}} \) (NpO\( _2 \)Ox) values between 3.84 and 4.40 and log \( \beta_{25^\circ\text{C}} \) (NpO\( _2 \)(Ox)) values between 5.8 and 7.36. \( \Delta H^\circ_{298} \) and \( \Delta S^\circ_{298} \) values are missing. There is only one study by Tian et al. using absorption spectroscopy and micro colorimetry on the temperature dependence of the complex formation revealing conditional enthalpy and entropy values at \( I_m(\text{NaClO}_4) = 1.05 \) \( \text{mol kg}^{-1} \), \( \Delta H(\text{NpO}_2\text{Ox}) = -12.2 \pm 0.1 \) \( \text{kJ mol}^{-1} \), \( \Delta S(\text{NpO}_2\text{Ox}) = 27.4 \pm 0.6 \) \( \text{J mol}^{-1} \text{K}^{-1} \), \( \Delta S(\text{NpO}_2\text{Ox}) = 33.7 \pm 0.9 \) \( \text{J mol}^{-1} \text{K}^{-1} \).2

In the present work the complexation of Np(V) with oxalate is systematically studied by near-infrared (Vis/NIR) absorption spectroscopy as a function of the ligand concentration (\( [\text{Ox}^2^-]_{\text{total}} \)), ionic strength \( I_m(\text{NaClO}_4) = 1.05 \) \( \text{mol kg}^{-1} \), and temperature (\( T = 20–85 ^\circ\text{C} \)) revealing thermodynamic data at IUPAC reference state conditions (log \( \beta_{\text{ns}} \), \( \Delta H^\circ_{\text{ns}} \), \( \Delta S^\circ_{\text{ns}} \)) at room temperature and at elevated temperatures. Furthermore, no structural data of the formed complexes and information on the coordination modes of \( \text{Ox}^2^- \) toward Np(V) are available. Thus, extended X-ray absorption fine structure spectroscopy (EXAFS) and quantum chemical calculations are applied to investigate the structure of the Np(V)-\( \text{Ox}^2^- \) complexes on a molecular level.

2 Experimental

2.1 Sample preparation

All solutions were prepared on the molal concentration scale (mol per kg per H\( _2\text{O} \), "m") because this concentration scale is independent of changes in temperature or ionic strength. All chemicals were reagent grade or higher and purchased from Merck Millipore or Alfa Aesar. For sample preparation ultrapure water (Milli-Q academic, Millipore, 18.3 \( \Omega \text{cm} \)) was used.

For speciation studies by absorption spectroscopy an initial Np(V) concentration of \( 2.5 \times 10^{-4} \) \( \text{mol kg}^{-1} \) was used and adjusted by dilution of a \( 6.1 \times 10^{-2} \) \( \text{mol kg}^{-1} \) \( 237\text{Np} \) stock solution in \( 2.9 \times 10^{-3} \) \( \text{mol kg}^{-1} \) HClO\(_4\) provided by the Institute for Nuclear Waste Disposal at the Karlsruhe Institute of Technology (KIT). \( \text{H}_2\text{O} \) total proton concentration (\( [\text{H}^+]_{\text{total}} = [\text{H}^+]_{\text{eq}} + 2[\text{H}_2\text{Ox}]_{\text{eq}} \)) in the samples was adjusted between \( 1.6–2.1 \times 10^{-3} \) \( \text{mol kg}^{-1} \) by addition of a standardized 0.01 \( \text{mol kg}^{-1} \) HClO\(_4\) or HCl solution. Thus, a direct measurement of the pH in the samples is not necessary as all equilibrium conditions are calculated from the known total concentrations in solution (see section 3.1.2).

The complexation of Np(V) with oxalate was studied as a function of the total ligand concentration (\( [\text{Ox}^2^-]_{\text{total}} = 0–1.4 \times 10^{-2} \text{mol kg}^{-1} \)) and temperature (\( T = 20–85 ^\circ\text{C} \)) at a fixed ionic strength \( I_m = 1.0 \) \( \text{mol kg}^{-1} \). The total proton concentration (\( [\text{H}^+]_{\text{total}} = [\text{H}^+]_{\text{eq}} + 2[\text{H}_2\text{Ox}]_{\text{eq}} \)) in the samples was adjusted between \( 1.6–2.1 \times 10^{-3} \) \( \text{mol kg}^{-1} \) by addition of a standardized 0.01 \( \text{mol kg}^{-1} \) HClO\(_4\) or HCl solution. Thus, a direct measurement of the pH in the samples is not necessary as all equilibrium conditions are calculated from the known total concentrations in solution (see section 3.1.2).

The complexation of Np(V) with oxalate was studied as a function of the total ligand concentration (\( [\text{Ox}^2^-]_{\text{total}} = 1.6 \times 10^{-3} \text{mol kg}^{-1} \)) and various concentrations of the background electrolytes (NaClO\(_4\), NaCl). The concentration of NaClO\(_4\) was increased by successive addition of aliquots of an aqueous 14.0 \( \text{mol kg}^{-1} \) NaClO\(_4\) solution. The concentration of NaCl was increased by addition of solid NaCl to the samples. The total proton concentration of all titration solutions was kept constant at \( 2.1 \times 10^{-3} \text{mol kg}^{-1} \) using a standardized 0.01 \( \text{mol kg}^{-1} \) HClO\(_4\) or HCl solution. Details on the experimental conditions are given in the ESI.

For EXAFS measurements a Np(V) concentration of \( 5.0 \times 10^{-3} \text{mol kg}^{-1} \) and an oxalate concentration of 0.1 \( \text{mol kg}^{-1} \) was used. All EXAFS measurements were performed as a function of the conditional pH value (\( \text{pH} = -\log [\text{H}^+]_{\text{eq}} \)). The pH was varied between 1.8 and 5.0 by addition of small aliquots of a 1.0 \( \text{mol kg}^{-1} \) HClO\(_4\) (Merck KGaA, suprapure). The pH was measured with a combination pH electrode (Orion™ PerpHecT™ ROSS™), which was calibrated with pH reference buffer solutions (Merck, \( \text{pH} = 8.00, 5.00, 2.00 \)). Details on the definition of pH are given in the literature. The sample volume was 200 \( \mu\text{L} \). The Np(V) con-
centration in the samples and the species distribution was determined by Vis/NIR absorption spectroscopy before and after the EXAFS measurements to ensure that no redox processes occurred during irradiation of the samples.

All uncertainties of the stability constants log $\beta_i$ (enthalpy $\Delta H_i$, entropy $\Delta S_i$ and SIT binary ion-ion interaction coefficient $\Delta f_{ij}$) are given with a confidence level of 0.95.

2.2 Vis/NIR absorption spectroscopy
Vis/NIR absorption spectra of Np(v) were recorded in the temperature range of 20–85 °C using a Varian Cary 5G UV/Vis/NIR spectrophotometer. The sample holder was temperature controlled using a Lauda Eco E100 thermostatic system (temp. accuracy: ±0.5 °C). The samples (quartz glass cuvettes, 1 cm path length, Hellma Analytics) were equilibrated for 15 minutes at each temperature in a custom-made copper sample holder placed on a heating plate with thermostatic control (VWR Collection VMS-C4 Advanced with IKA (JANKE & KUNKEL) PT 1000 temperature sensor; temp. accuracy: ±0.5 °C) to ensure that the temperature of the aqueous solution inside the cuvettes is correct. The spectra 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.

2.3 EXAFS measurements
Np-L$_3$-EXAFS spectra were measured in fluorescence mode at the INE-Beamline of the Karlsruhe Research Accelerator, KARA, at KIT. For recording of the fluorescence light a 4 element Si SDD Vortex (SIINT) fluorescence detector and a 1 element Si Vortex-60EX SDD (SIINT) fluorescence detector at an angle of 90° were used. The optical components of the beamline consisted of a double-crystal monochromator (DCM) with a Ge(422) crystal pair and a collimating and focusing mirror system (Rh-coated silicon mirrors). The DCM was detuned in the middle of the scan range to 70% peak flux intensity. An Ar-filled ionization chamber was used to measure the intensity $I_0$ of the incident X-ray beam. Within the EXAFS range, the measurements were performed at equidistant $k$-steps and an increasing integration time following a $\sqrt{2}$ progression. The data evaluation was performed with the software packages EXAFSPAK, Athena – Demeter 0.9.26, and Artemis – Iffeffit 8.0.12. The crystal structures of UO$_2$-oxalate were used for calculation of the theoretical scattering phases and amplitudes using FEFF8.40 and replacing U by Np. In all cases, the models were fitted to the $k^2$- and $k^4$-weighted raw EXAFS spectra.

2.4 Quantum chemical calculations
Structure optimizations of the Np(v) oxalate complexes were carried out on density functional theory (DFT) level using the TURBOMOLE 7.0 program package. The BH-LYP functional was chosen for its better convergence compared to other hybrid-functionals. All C, O and H atoms were represented by basis sets of triple zeta basis quality (def-TZVP) and were treated at the all-electron level.$^{45,46}$ The metal ion was represented by a 60-electron core pseudo-potential (Np, ECP60MWB) with corresponding basis sets of triple-zeta quality.$^{49}$ The NpO$_2$(Ox)$^{-}$ and NpO$_2$(Ox)$_2^{3-}$ complexes with different coordination modes (end-on vs. side-on) of the ligand molecules were optimized. The gas phase energies $E_g$ of the triplet ground states were computed on the MP2 level. Additionally, for a theoretical approximation of the Gibbs free energies ($G$) thermodynamic corrections ($E_{\text{corr}} = E_{\text{gibbs}} + H_0 - TS$, $E_{\text{gibbs}}$ being the zero-point energy; $H_0$ and $S$ are the enthalpy and entropy of the complexes obtained from calculations of the vibrational modes) and solvation energies $E_{\text{solv}}$ (obtained using COSMO, $r_{\text{COSMO}} = 1.72$ Å) were taken into account. The Gibbs free energies were calculated as follows: $G = E_g + E_{\text{corr}} + E_{\text{solv}}$. Due to the ionic form of the Np(v) complexes a full second hydration shell was added and optimized to avoid the charge of the complexes to contact the COSMO cavity.

3 Results and discussion

3.1 Vis/NIR absorption spectroscopy
3.1.1 Absorption spectra. The absorption spectra of Np(v) with increasing total oxalate concentration [Ox$^-$]$_{\text{total}}$ at 20 °C and $I_n$([NaClO$_4$] = 1.0 mol kg$^{-1}$) are displayed in Fig. 1. The absorption band of the Np(v) aquo ion is located at 980.1 ± 0.1 nm ($\epsilon_{\text{max}} = 396 \pm 4$ l mol$^{-1}$ cm$^{-1}$). With increasing [Ox$^-$]$_{\text{total}}$ a bathochromic shift of the absorption band and the formation of two additional absorption maxima at about 988 nm and 995 nm are observed. Furthermore, two isosbestic points are located at 984.2 ± 0.2 and 990.9 ± 0.2 nm. At elevated temperatures similar observations are made but the bathochromic shift is less pronounced.

![Fig. 1 Vis/NIR absorption spectra of the Np(v) ion with increasing total oxalate concentration.](image)
The temperature effect on the absorption spectra of Np(\(v\)) at a fixed oxalate concentration (\([\text{Ox}^{-2}]_{\text{total}} = 4.4 \times 10^{-3} \text{ mol kg}^{-1}\)) is shown in Fig. 2. With increasing temperature a hypsochromic shift of the absorption band occurs indicating that the complexation of Np(\(v\)) with oxalate is repressed at elevated temperatures and confirming exothermic complexation reactions.

3.1.2 Peak deconvolution and speciation. The determination of the species distribution requires the single component spectra of the formed Np(\(v\))-oxalate complexes. The spectra are derived via subtractive peak deconvolution using the spectrum of the Np(\(v\)) aquo ion. Details on this method are given in the literature.\(^{53}\) Using this approach the absorption spectra of two different Np(\(v\))-oxalate complexes are deconvoluted at all temperature and ionic strength conditions. The spectra at 20 and 85 °C and \(I_m(\text{NaClO}_4) = 1.0 \text{ mol kg}^{-1}\) are displayed in Fig. 3. At 20 °C the absorption maximum of the first complex species \(\text{NP}_2\text{O}(\text{Ox})_2\) is located at 987.8 ± 0.1 nm and is bathochromically shifted by 7.7 nm compared to the Np (\(v\)) aquo ion. The absorption band of \(\text{NP}_2\text{O}(\text{Ox})_2^{2-}\) is located at 995.4 ± 0.1 nm corresponding to a bathochromic shift of 15.3 nm. Thus, a bathochromic shift of about 7.7 nm occurs for each coordinating oxalate molecule. At 85 °C the spectrum of the Np(\(v\)) aquo ion is hypsochromically shifted by 1.7 nm compared to 20 °C. The spectra of both Np(\(v\))-oxalate complexes are shifted only by 1.3 nm in this temperature interval. Thus, the effect of the temperature on the absorption bands of the Np(\(v\))-oxalate complexes is weaker compared to the Np(\(v\)) aquo ion. According to the literature, the hypsochromic shift of the Np(\(v\)) absorption was contributed to solvatochromic effects or changes of the solvation of the Np(\(v\)) ion in the first and second hydration shell.\(^{24-60}\) As the effect of temperature changes with the complexation of the Np(\(v\)) ion the composition of the first coordination sphere of the Np(\(v\)) ion seems to have a major impact on this temperature effect.

Furthermore, the observed hypsochromic shift of the absorption spectra of the Np(\(v\))-oxalate complexes compared to the Np(\(v\)) aquo ion is in excellent agreement to that of other Np(\(v\)) complexes described in the literature. Yang et al. and Zhang et al. studied the complexation of Np(\(v\)) with benzoate and picolinate by absorption spectroscopy in a temperature range of 10–70 °C.\(^{61,62}\) In comparison to the hypsochromic shift of the Np(\(v\)) aquo ion of 1.8–1.9 nm the hypsochromic shifts of NpO\(_2\)(\(L\)) are 1.5 nm (\(L = \text{picolinate}\)) and 1.7 nm (\(L = \text{benzoate}\)). The spectrum of NpO\(_2\)(\(L\))\(_2\) shifts by 1.6 nm (\(L = \text{picolinate}\)). In the literature this is explained by the more rigid Np(\(v\))-ligand bond compared to the Np(\(v\))-water bond resulting in a hindered thermal expansion of the metal–ligand bonds in the complexes compared to the Np(\(v\)) aquo ion. Nevertheless, the temperature induced hypsochromic shift of the absorption band of the Np(\(v\)) ion is contrary to the bathochromic shift resulting from the complexation reactions and requires the determination of single component spectra for all studied temperature conditions.

The spectroscopic characteristics of the Np(\(v\))-oxalate complexes at 20 and 85 °C are summarized in Table 1.

Deconvolution of the absorption spectra as a function of oxalate concentration by principle component analyses reveals the species distribution of the formed Np(\(v\))-oxalate complexes as a function of the equilibrium concentration of oxalate \([\text{Ox}^{-2}]_\text{eq}\). An
exemplary deconvolution is given in the ESI in Fig. S1† There is no indication for additional chemical species present others than the used ones. Four different chemical species of oxalate can exist in aqueous solution which are H2Ox, HOx−, Ox2− and NaOx−. Thus, the following chemical reactions have to be accounted for in the calculation of [Ox2−]eq:

\[ \log \beta_{A1}^{(25°C)} = 4.25 \pm 0.01 : \text{Ox}^2^- + \text{H}^+ \rightleftharpoons \text{HOx} \]  
\[ \log \beta_{A2}^{(25°C)} = 5.65 \pm 0.06 : \text{Ox}^2^- + 2\text{H}^+ \rightleftharpoons \text{H}_2\text{Ox} \]  
\[ \log \beta_{Na}^{(25°C)} = 1.10 \pm 0.01 : \text{Ox}^2^- + \text{Na}^+ \rightleftharpoons \text{NaOx}^- \]  

The calculations are performed with the software package Hyperquad Hyss2008, Version 4.0.3166 [Ox2−]eq is determined as a function of [Ox2−]extab [H+]extab [I]m and T.63,65 The temperature dependence of the protonation reaction of Ox2− and the formation of NaOx− is well described in the literature.63,65 Thus, log βA1(T), log βA2(T) and log βNa(T) at a given temperature are calculated with the integrated van’t Hoff equation using the thermodynamic data given in the literature (ΔH^°A1,m = 7.3 ± 0.1 kJ mol⁻¹, ΔH^°A2,m = 10.6 ± 0.6 kJ mol⁻¹, ΔH^°Na,m = −5.0 ± 0.7 kJ mol⁻¹). The ionic strength dependence is accounted for by application of the specific ion interaction theory (SIT). The required binary ion-ion interaction coefficients are given in the Nuclear Energy Agency Thermochemical Database (NEA-TDB) (\( \epsilon(\text{Na}^+,\text{Cl}^-) = 0.03 \pm 0.01, \epsilon(\text{Na}^+,\text{OClO}_4^-) = 0.01 \pm 0.01, \epsilon(\text{H}^+,\text{Cl}^-) = 0.12 \pm 0.01, \epsilon(\text{H}^+,\text{OClO}_4^-) = 0.14 \pm 0.02, \epsilon(\text{Na}^+,\text{HOx}^-) = −0.07 \pm 0.01, \epsilon(\text{Na}^+,\text{Ox}^2^-) = −0.08 \pm 0.01, \epsilon(\text{Na}^+,\text{NaOx}^-) \approx \epsilon(\text{Na}^+,\text{HOx}^-) = −0.07 \pm 0.01\)).

In Fig. 4 the speciation (symbols) of the (v)-oxalate complexes is shown as a function of [Ox2−]eq at 20 and 85 °C at I_m = 1.0 mol kg⁻¹ NaClO4. The calculated speciation (lines) using the derived log βA1(T) values (log βA1(20 °C) = 4.12 ± 0.04, log βA1(20 °C) = 6.81 ± 0.05, log βA1(85 °C) = 3.91 ± 0.04, log βA1(85 °C) = 6.46 ± 0.07) is also displayed.

With increasing [Ox2−]eq the complexation equilibrium shifts toward the Np(v)-oxalate species. At 85 °C the species distribution is shifted toward the Np(v) aquo ion confirming exothermic complexation reactions.

3.1.3 Complex stoichiometry. The complex stoichiometry of the oxalate complexes is confirmed by slope analyses using the determined speciation at each studied temperature. The following complexation is applied:

\[ \text{NpO}_2^{+} \text{Ox}^{-} + \text{Ox}^{-} \rightarrow \text{NpO}_2(\text{Ox})_2^{-} \]
\[ \text{NpO}_2(\text{Ox})_2^{-} \rightarrow \text{NpO}_2(\text{Ox})_4^{-} \]
\[ \text{NpO}_2(\text{Ox})_4^{-} \rightarrow \text{NpO}_2(\text{Ox})_6^{-} \]

According to the complexation model the slope analyses are performed using eqn (5):

\[ \log K_n = \log \beta_n - \log \frac{[\text{NpO}_2(\text{Ox})_n^{-}]}{[\text{NpO}_2(\text{Ox})_{n-2}^{-}] [\text{Ox}^{-}]^2} = 1 \times \log ([\text{Ox}^{-}]_{eq})^2 \]  

Thus, slopes of m = 1 indicate that the species \( X_n \) and \( X_{n-1} \) differ by one coordinating oxalate molecule. Details on this procedure are given in the literature.69-71

The slope analyses for 20 and 85 °C at \( I_m = 1.0 \) mol kg⁻¹ are displayed in Fig. 5. The results show a linear correlation of log ([NpO2(Ox)n−1]eq/\([\text{NpO}_2(\text{Ox})_{n-2}] [\text{Ox}^{-}]^2\)) with log([Ox−]eq). Linear regression analyses reveal slopes of 0.9 ± 0.1 to 1.0 ± 0.1 at all experimental conditions. Thus, the formation of two oxalate complexes with the stoichiometry of NpO2(Ox)n−2n and n = 1, 2 is confirmed.

3.1.4 Thermodynamic data. The determination of thermodynamic functions (log βA1(T), ΔH^0m,n, ΔS^0m,n) at IUPAC reference state conditions (I_m = 0, T = 298 K) requires conditional stability constants log βA1(T) at various I_m and T. These data are extrapolated to \( I_m = 0 \) with the SIT according

![Fig. 4](image1.png)  
Fig. 4 Experimentally determined (symbols) and calculated species distribution of NpO2(Ox)n−2n (n = 0, 1, 2) complexes as a function of the equilibrium ligand concentration in aqueous solution. \( I_m(\text{NaClO}_4) = 1.0 \) mol kg⁻¹, T = 20 °C (solid lines) and 85 °C (dashed lines).

![Fig. 5](image2.png)  
Fig. 5 Plots of log ([NpO2(Ox)n−1]eq/\([\text{NpO}_2(\text{Ox})_{n-2}] [\text{Ox}^{-}]^2\)) vs. log([Ox−]eq) and linear regression analyses at T = 20, 85 °C and \( I_m(\text{NaClO}_4) = 1.0 \) mol kg⁻¹.
to eqn (6) yielding the thermodynamic stability constants log $\beta_i^m(T)$.\(^{5,8}\)

$$\log \beta_i(T) = \Delta z^i D = \log \beta_i^m(T) + \Delta \varepsilon_{m}$$  \hspace{1cm} (6)

$D$ is the Deby–Hückel term, $\Delta z^i$ is the sum of the charges $z$ of the chemical species and $\Delta \varepsilon$ is the sum of the binary ion–ion interaction coefficients $\varepsilon_{(j,k)}$ of the educts and products. A linear correlation of $\log \beta_i^m(T) - \Delta z^i D$ with $I_m$ is observed for all studied temperatures in both studied electrolytes (NaCl and NaClO₄). In Fig. 6 the SIT plots for $T = 20$ and 85 °C and NaClO₄ media are displayed as examples.

The calculated log $\beta_i^m(T)$ are listed in Table 2. For both electrolytes the obtained log $\beta_i^m(T)$ values are in excellent agreement and averaged (“Ø”) log $\beta_i^m(T)$ values are calculated. In case of the first stability constant log $\beta_i^m(T)$ only a weak temperature dependence is observed. In contrast, log $\beta_i^m(T)$ decreases significantly with increasing temperature. Thus, the formation of NpO₂(Ox)₃⁻ is clearly exothermic.

In Fig. 7 the temperature dependence of the averaged log $\beta_i^m(T)$ is displayed as a function of the reciprocal temperature $T^{-1}$. The data correlate linearly with $T^4$ indicating that the reaction enthalpies $\Delta_r H_{n,m}^0$ for both complexation steps are constant in the studied temperature interval. Thus, the temperature dependence can be described by the integrated van’t Hoff equation (eqn (7)).

$$\log \beta_i^m(T) = \log \beta_i^m(T_0) + \frac{\Delta_r H_{n,m}^0(T_0)}{R \ln(10)} \left( \frac{1}{T} \right) \left( \frac{1}{T_0} \right)$$  \hspace{1cm} (7)

With $R$ being the universal gas constant and $T_0 = 298.15$ K. Linear regression analyses according to eqn (7) yield the standard reaction enthalpy $\Delta_r H_{n,m}^0$ of the complexation reactions. The standard reaction entropy $\Delta_r S_{n,m}^{0}$ is calculated using eqn (8).

$$\Delta_r S_{n,m}^{0} = \Delta_r H_{n,m}^{0} - T \times \Delta_r S_{n,m}^{0} = RT \ln \beta_i^m$$  \hspace{1cm} (8)

This approach is valid for small temperature intervals ($\Delta T = 100$ K) assuming $\Delta_n C_{m,p}^0 = 0$ and $\Delta_r H_{n,m}^0 = \text{const}$. The deter-

![Fig. 6](image)

**Fig. 6** Ionic strength dependence of $\log \beta_i^m(T)$ $\Delta z^i D$ and linear fitting of the data according to the SIT for the complexation reactions NpO₂⁺ + $\text{nOx}^2$ $\rightarrow$ NpO₂(Ox)₃⁻ $\text{2n}$ ($n = 1, 2$) in NaClO₄, $T = 20, 85$ °C.

![Fig. 7](image)

**Fig. 7** Plot of $\log \beta_i^m(T)$ ($n = 1, 2$) as a function of the reciprocal temperature and fitting according to the integrated van’t Hoff equation.

### Table 2

<table>
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<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>85</th>
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<td>NpO₂(Ox)⁻</td>
<td>NaClO₄</td>
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<td>4.49 ± 0.08</td>
<td>4.48 ± 0.07</td>
<td>4.48 ± 0.06</td>
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<td>4.53 ± 0.04</td>
<td>4.59 ± 0.05</td>
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<tr>
<td>NpO₂(Ox)₂⁻</td>
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<td>6.23 ± 0.06</td>
<td>6.18 ± 0.05</td>
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<tr>
<td></td>
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<td>5.99 ± 0.03</td>
<td>6.11 ± 0.04</td>
<td>5.95 ± 0.05</td>
<td>5.94 ± 0.06</td>
<td>5.94 ± 0.08</td>
</tr>
<tr>
<td></td>
<td>Ø</td>
<td>6.28 ± 0.07</td>
<td>6.18 ± 0.07</td>
<td>6.09 ± 0.06</td>
<td>6.13 ± 0.06</td>
<td>6.03 ± 0.09</td>
<td>6.00 ± 0.09</td>
<td>5.98 ± 0.11</td>
</tr>
</tbody>
</table>
minded $\Delta H_{m}^0$ and $\Delta S_{m}^0$ values are summarized in Table 3. The obtained data reveal that both complexation steps are exothermic and entropy driven.

In the literature no temperature dependent log $\beta_0^n(T)$ values are reported. The available data were determined by different experimental techniques like spectrophotometry or solvent extraction and are mostly limited to 25 °C. In our work conditional log $\beta_0^n$ values in the literature vary between 3.84 and 4.40 and are lower than the present result. The log $\beta_0^n(T)$ values of NpO$_2$(Ox)$_2$ range between 5.8 and 7.36 in the literature. The value of the present work fits perfectly within this interval. Definite reasons for the discrepancy between 5.8 and 7.36 in the literature. The value of the present work

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>NpO$<em>2$(Ox)$</em>{n-2}$</th>
<th>log $\beta_0^n(25 , ^\circ C)$</th>
<th>$\Delta H_{m}^0$ [kJ mol$^{-1}$]</th>
<th>$\Delta S_{m}^0$ [J mol$^{-1}$K$^{-1}$]</th>
<th>$\Delta x$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaClO$_4$</td>
<td>n 1</td>
<td>4.49 ± 0.08</td>
<td>0.6 ± 0.6</td>
<td>84 ± 4</td>
<td>0.39 ± 0.04</td>
</tr>
<tr>
<td></td>
<td>n 2</td>
<td>6.24 ± 0.11</td>
<td>7.3 ± 0.7</td>
<td>95 ± 9</td>
<td>0.52 ± 0.04</td>
</tr>
<tr>
<td>NaCl</td>
<td>n 1</td>
<td>4.58 ± 0.14</td>
<td>1.9 ± 0.4</td>
<td>79 ± 16</td>
<td>0.18 ± 0.03</td>
</tr>
<tr>
<td></td>
<td>n 2</td>
<td>6.20 ± 0.09</td>
<td>10.0 ± 1.8</td>
<td>85 ± 11</td>
<td>0.20 ± 0.06</td>
</tr>
<tr>
<td>$\Theta$</td>
<td>n 1</td>
<td>4.53 ± 0.12</td>
<td>1.3 ± 0.7</td>
<td>82 ± 2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>n 2</td>
<td>6.22 ± 0.24</td>
<td>8.7 ± 1.4</td>
<td>90 ± 5</td>
<td></td>
</tr>
</tbody>
</table>

In the literature $\Delta H_{m}^0$ and $\Delta S_{m}^0$ values are not available in the literature. Only one study by Tian et al. provides conditional $\Delta H_{m}^0$ and $\Delta S_{m}^0$ values determined by spectrophotometry and micro calorimetry at $I_m$(NaClO$_4$) = 1.05. 15 A comparison of these values with the results of the present work at equal experimental conditions is given in Table 5. First of all, the log $\beta_0^n(25 \, ^\circ C)$ values of the present work are by approximately 0.5–0.6 logarithmic units higher compared to the literature. Nevertheless, the reported $\Delta H_{m}^0$ is in very good agreement with the present value whereas the $\Delta S_{m}^0$ values show significant deviations. The literature reports more exothermic formation of NpO$_2$(Ox)$_2$ 15. Comparison of the literature data with the present work shows that the results of the present work are higher compared to the literature. This deviation might originate from the discrepancies in the log $\beta_0^n(25 \, ^\circ C)$ values.

### 3.1.5 Ionic strength dependence
In addition to the thermodynamic functions (log $\beta_0^n(T)$, $\Delta H_{m}^0$, $\Delta S_{m}^0$) at IUPAC reference state conditions, application of the SIT yields the stoichiometric sum of the binary ion–ion interaction coefficients of the complexation reactions ($\Delta H_{m}^0(T)$ and $\Delta S_{m}^0(T)$) as a function of the temperature. The $\Delta H_{m}^0(T)$ and $\Delta S_{m}^0(T)$ values for the formation of NpO$_2$(Ox)$_{n-2}$ (n = 1, 2) in NaClO$_4$ and NaCl

### Table 4 Thermodynamic stability constants the formation of NpO$_2$(Ox)$_{n-2}$ (n = 1, 2) and comparison with literature data

<table>
<thead>
<tr>
<th>Complex</th>
<th>Method/data base</th>
<th>log $\beta_0^n(25 , ^\circ C)$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>NpO$_2$(Ox)$^-$</td>
<td>sp</td>
<td>4.53 ± 0.12</td>
<td>p.w.</td>
</tr>
<tr>
<td></td>
<td>cix</td>
<td>4.40</td>
<td>31</td>
</tr>
<tr>
<td></td>
<td>sp</td>
<td>3.93</td>
<td>31</td>
</tr>
<tr>
<td></td>
<td>sx</td>
<td>4.08 ± 0.11</td>
<td>32</td>
</tr>
<tr>
<td></td>
<td>NEA TDB</td>
<td>3.84</td>
<td>33</td>
</tr>
<tr>
<td></td>
<td>NIST</td>
<td>3.9</td>
<td>68</td>
</tr>
<tr>
<td>NpO$_2$(Ox)$_2$</td>
<td>sp</td>
<td>6.22 ± 0.24</td>
<td>p.w.</td>
</tr>
<tr>
<td></td>
<td>cix</td>
<td>7.36</td>
<td>31</td>
</tr>
<tr>
<td></td>
<td>sp</td>
<td>7.06</td>
<td>31</td>
</tr>
<tr>
<td></td>
<td>sp</td>
<td>6.12 ± 0.21</td>
<td>32</td>
</tr>
<tr>
<td></td>
<td>NEA TDB</td>
<td>5.8 ± 0.2</td>
<td>68</td>
</tr>
<tr>
<td></td>
<td>NIST</td>
<td>5.8</td>
<td>72</td>
</tr>
</tbody>
</table>

Methods: sp: spectrophotometry; sx: solvent extraction; cix: cation exchange.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Method/data base</th>
<th>log $\beta_0^n(25 , ^\circ C)$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>NpO$_2$(Ox)$^-$</td>
<td>sp</td>
<td>4.12 ± 0.10</td>
<td>p.w.</td>
</tr>
<tr>
<td></td>
<td>sp</td>
<td>3.57 ± 0.02</td>
<td>32</td>
</tr>
<tr>
<td>NpO$_2$(Ox)$_2$</td>
<td>sp</td>
<td>6.81 ± 0.31</td>
<td>32</td>
</tr>
<tr>
<td></td>
<td>sp</td>
<td>6.23 ± 0.02</td>
<td>32</td>
</tr>
</tbody>
</table>

Methods: sp: spectrophotometry; cal: micro calorimetry.

### Table 5 Conditional stability constants log $\beta_0^n(25 \, ^\circ C)$ and thermodynamic functions $\Delta H_{m}^0$, $\Delta S_{m}^0$ and comparison with literature data at $I_m = 1.0$ mol kg$^{-1}$

<table>
<thead>
<tr>
<th>Complex</th>
<th>Method/data base</th>
<th>log $\beta_0^n(25 , ^\circ C)$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>NpO$_2$(Ox)$^-$</td>
<td>sp</td>
<td>4.12 ± 0.10</td>
<td>p.w.</td>
</tr>
<tr>
<td></td>
<td>sp</td>
<td>3.57 ± 0.02</td>
<td>32</td>
</tr>
<tr>
<td>NpO$_2$(Ox)$_2$</td>
<td>sp</td>
<td>6.81 ± 0.31</td>
<td>32</td>
</tr>
<tr>
<td></td>
<td>sp</td>
<td>6.23 ± 0.02</td>
<td>32</td>
</tr>
</tbody>
</table>

Methods: sp: spectrophotometry; cal: micro calorimetry.
media are displayed in Fig. 8. Within the error, the scattering of the $\Delta \varepsilon_j^\prime(T)$ values observed for both electrolytes agrees with various studies on the ionic strength dependence of the complexation of Np(v) or trivalent lanthanides and actinides and only a marginal temperature dependence between 20–85 °C is observed.4,16,69,71,73,74 Thus, averaged temperature-independent $\Delta \varepsilon_j,k$ values are calculated for both background electrolytes (NaCl, NaClO4). The averaged values are given in Table 3. According to the SIT the temperature independent binary ion–ion interaction coefficients $\varepsilon_{j,k}$ of the different Np(v)–oxalate complexes with Na$^+$ are calculated (eqn (9)).

$$\Delta \varepsilon = \sum \varepsilon_{\text{products}} - \sum \varepsilon_{\text{educt}}$$

The binary ion–ion interaction coefficients $\varepsilon(\text{Na}^+,\text{Ox}^{2-}) = 0.03 \pm 0.01$, $\varepsilon(\text{Na}^+,\text{ClO}_4^{-}) = 0.25 \pm 0.05$, and $\varepsilon(\text{Na}^+,\text{Cl}^-) = 0.09 \pm 0.05$ reported in the NEA-TDB are used for this purpose.27 The calculated values are listed below:

$$\varepsilon_{\text{NaCl}}(\text{Na}^+,\text{NpO}_2(\text{Ox})\text{)} = 0.17 \pm 0.06,$$

$$\varepsilon_{\text{NaClO}_4}(\text{Na}^+,\text{NpO}_2(\text{Ox})\text{)} = 0.22 \pm 0.06,$$

$$\varepsilon_{\text{NaCl}}(\text{Na}^+,\text{NpO}_2(\text{Ox})_2\text{)} = 0.27 \pm 0.08,$$

$$\varepsilon_{\text{NaClO}_4}(\text{Na}^+,\text{NpO}_2(\text{Ox})_2\text{)} = 0.43 \pm 0.09$$

Comparison of the $\varepsilon_{j,k}$ values for the two complex species shows slight deviations between the values obtained in NaCl and NaClO4 media. In case of the 1:1 complex the deviation is 0.05 which is within the error range of the $\varepsilon_{j,k}$ values. In case of the 1:2 complex a deviation of 0.16 is observed. This discrepancy can be explained by a defective $\varepsilon(\text{NpO}_2^-,\text{ClO}_4^-) = 0.25 \pm 0.05$ reported in the NEA-TDB.27 This assumption is based on similar observations for the complexation of Np(v) with formate, acetate, chloride and fluoride.55,70,71,75 Nonetheless, the obtained log $\beta_j^\prime(T)$ values and thermodynamic functions for the formation of the Np(v)–oxalate complexes determined in NaCl and NaClO4 media are in excellent agreement. This confirms that the ionic strength dependency of the complex formation is accurately described in both background electrolytes using the determined $\Delta \varepsilon_j,k$ values.

Within the NEA-TDB review conditional stability constants at various ionic strengths and 20–25 °C from different studies were compared and extrapolated to $I_m = 0$ yielding an $\varepsilon(\text{Na}^+,\text{NpO}_2(\text{Ox})\text{)} = -0.4 \pm 0.1$ and $\varepsilon(\text{Na}^+,\text{NpO}_2(\text{Ox})_2\text{)} = -0.3 \pm 0.2$.18 These $\varepsilon_{j,k}$ values deviate significantly from the values determined in the present work. This discrepancy most likely originates from the wide scattering of the log $\beta_j^\prime$ values used in the NEA-TDB for the SIT extrapolation and the resulting poor linearity of the log $\beta_j^\prime$ – $\Delta Z^2$ vs. $I_m$ plots. In contrast, the $\varepsilon_{j,k}$ values determined in the present work are based on a consistent data set resulting in fits with superior quality and more reliable data.

3.2 Structural investigation

Oxalate is the simplest dicarboxylate available and can either coordinate only via one COO$^-$ group (end-on mode) or via both COO$^-$ groups toward the metal ion forming chelate complexes (side-on mode) In Fig. 9 the structures of the complexes with the two coordination modes are sketched. The equatorial coordination number accounts for 5. Free coordination places in the equatorial plane are occupied by water molecules. These are omitted for clarity in Fig. 9. Valuable structural data of the complexes and information on the coordination mode of oxalate can be obtained by EXAFS analysis.

3.2.1 EXAFS data analysis. In Fig. 10 the $k^2$-weighted Np-L$_3$-edge EXAFS spectra of the Np(v)–oxalate complexes, their
Fourier transformations and the corresponding fit curves are displayed as a function of the pHc value. The results of the fits and the fit parameters are listed in Table 6. The spectra are dominated by the axial and equatorial O-atoms (Oax, Oeq) which are located at 1.83 ± 0.02 Å (Oax) and 2.45 ± 0.02 Å (Oeq). These results are in excellent agreement with literature data.36,76,77 The coordination number of the Np(v) ion is in good accordance with the expected value of 5 within the studied pH range.77,78 With increasing pHc the coordination number and the Oax and Oeq distances remain constant. The coordination mode of the oxalate molecules toward the Np(v) centre is determined using the distances of the carboxylic carbon atoms (Cc). An averaged value of 3.32 ± 0.06 Å is obtained within the studied pH range. Their coordination number increases with increasing pHc which is in excellent agreement with the results of the speciation studies by Vis/NIR. EXAFS studies by Takao et al. and Vasiliev et al. on the complexation of Np(V) with acetate and propionate show Cc distances of 2.91 ± 0.02 Å and 2.87 ± 0.03 Å.36,76 As acetate and propionate are monocarboxylates these distances correspond to a bidentate coordinating COO\(^{-}\) group (end-on coordination). The Cc distances determined herein for the NpO\(_2\)(Ox)\(_n\) complexes are about 0.4–0.5 Å longer compared to the Cc distances of the acetate and propionate complexes indicating a different coordination mode of oxalate. Recently, we investigated the complexation of Np(v) with formate by EXAFS.75 In this study an averaged Cc distance of 3.39 ± 0.07 Å was determined. This distance was attributed to a monodentate coordination of formate with only one O-atom of the carboxylic group. This distance is in good agreement with the results for the oxalate complexes in the present work. Thus, the oxalate molecules coordinate via one O-atom of each COO\(^{-}\) group toward the Np(v) centre forming five membered chelate rings. The coordination mode is not affected by the pH.

### 3.2.2 Quantum chemical calculations

The interpretation of the EXAFS results is verified by quantum chemical calculations. The determined bond distances of the optimized molecular structures of the five-fold coordinated NpO\(_2\)(Ox)\(^{-}\) complexes are shown in Fig. 8.

**Table 6** Fit parameters of the \(k^2\) weighted Np L\(_3\) edge EXAFS spectra shown in Fig. 8

<table>
<thead>
<tr>
<th>pH</th>
<th>1.8</th>
<th>2.7</th>
<th>3.7</th>
<th>5.0</th>
<th>8.8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oax</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<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 ± 0.01</td>
<td>1.82 ± 0.1</td>
<td>1.82 ± 0.01</td>
<td>1.84 ± 0.01</td>
<td>1.84 ± 0.01</td>
</tr>
<tr>
<td>σ(^2)/Å(^2)</td>
<td>0.0019 ± 0.0001</td>
<td>0.0007 ± 0.0002</td>
<td>0.0017 ± 0.0004</td>
<td>0.0002 ± 0.0004</td>
<td>0.0002 ± 0.0004</td>
</tr>
<tr>
<td>Oeq</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N</td>
<td>4.5 ± 1.0</td>
<td>3.6 ± 1.0</td>
<td>4.5 ± 1.0</td>
<td>5.3 ± 1.0</td>
<td>4.1 ± 1.0</td>
</tr>
<tr>
<td>R/Å</td>
<td>2.47 ± 0.01</td>
<td>2.48 ± 0.01</td>
<td>2.44 ± 0.01</td>
<td>2.43 ± 0.01</td>
<td>2.45 ± 0.01</td>
</tr>
<tr>
<td>σ(^2)/Å(^2)</td>
<td>0.0062 ± 0.0015</td>
<td>0.0044 ± 0.0019</td>
<td>0.0061 ± 0.0013</td>
<td>0.0085 ± 0.0020</td>
<td>0.0045 ± 0.0008</td>
</tr>
<tr>
<td>Cc</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N</td>
<td>0.9 ± 1.0</td>
<td>1.5 ± 1.0</td>
<td>2.2 ± 1.0</td>
<td>3.3 ± 1.0</td>
<td>3.3 ± 1.0</td>
</tr>
<tr>
<td>R/Å</td>
<td>3.47 ± 0.03</td>
<td>3.47 ± 0.03</td>
<td>3.30 ± 0.03</td>
<td>3.32 ± 0.03</td>
<td>3.39 ± 0.02</td>
</tr>
<tr>
<td>σ(^2)/Å(^2)</td>
<td>0.004(^a)</td>
<td>0.004(^a)</td>
<td>0.004(^a)</td>
<td>0.004(^a)</td>
<td>0.004(^a)</td>
</tr>
<tr>
<td>Δ(E_0)/eV</td>
<td>10.5 ± 0.7</td>
<td>12.9 ± 0.3</td>
<td>10.7 ± 0.5</td>
<td>10.8 ± 0.7</td>
<td>10.7 ± 0.4</td>
</tr>
<tr>
<td>Red error</td>
<td>0.0207544</td>
<td>0.00722427</td>
<td>0.0167346</td>
<td>0.0261492</td>
<td>0.0101572</td>
</tr>
</tbody>
</table>

\(\text{a}\) Parameter fixed; Oax axial O atoms, Oeq equatorial O atoms, Cc C atoms of coordinating COO\(^{-}\) groups.

---

**Fig. 10** Raw \(k^2\) weighted Np L\(_3\) edge EXAFS spectra (left) and Fourier transforms (right) of Np(v) in the presence of oxalate as a function of pHc (black) together with the best fit from EXAFSPAK (red circles).
and NpO$_2$(Ox)$_2$$^{3-}$ complexes with end-on and side-on coordinating oxalate molecules (see Fig. 9) are summarized in Table 7 and compared to the EXAFS results. The experimentally obtained distances for O$_{ax}$ and O$_{eq}$ are in excellent accordance with the results of the structure optimizations. The distances are 1.83 ± 0.01 Å (O$_{ax}$) and 2.46 ± 0.01 Å (O$_{eq}$). The calculated C$_c$ distances for end-on and side-on coordination of oxalate are 2.85 ± 0.01 Å and 3.28 ± 0.02 Å, respectively. Thus, the structure optimizations confirm the interpretation of the EXAFS data that oxalate coordinates in a side-on mode forming five membered chelate rings in the equatorial plane with Np(V).

Additionally, calculations on isomerisation reactions for an end-on into a side-on coordinated oxalate according to eqn (10) are performed.

$$
\text{NpO}_2\text{(Ox)}^{−}\text{ (end-on)} \rightleftharpoons \text{NpO}_2\text{(Ox)}^{−}\text{ (side-on)}
$$

The theoretical approximation of the Gibbs free energies $\Delta G$ for the isomerisation reactions according to eqn (10) are listed in Table 8. The $\Delta G$ values are calculated using the difference of the ground state energies $\Delta E_g$ on MP2 level with thermodynamic corrections $\Delta E_{th}$ and solvation effects $\Delta E_{solv}$ taken into account: $\Delta G = \Delta E_g + \Delta E_{th} + \Delta E_{solv}$ ($\Delta G = \Delta E_{\text{end-on}} - \Delta E_{\text{side-on}}$) (see eqn [11]):

$$
DG = G_{\text{end-on}} - G_{\text{side-on}} = E_{g(\text{end-on})} - E_{g(\text{side-on})} + E_{th(\text{end-on})} - E_{th(\text{side-on})} + E_{solv(\text{end-on})} - E_{solv(\text{side-on})}
$$

The results show negative $\Delta G$ values (NpO$_2$(Ox)$^{−}$: −32.93 kJ mol$^{-1}$; NpO$_2$(Ox)$_2$$^{3−}$: −84.34 kJ mol$^{-1}$) for both isomerisation reactions. Thus, the formation of the oxalate coordinating in a side-on mode toward the Np(v) ion is energetically preferred compared to an end-on coordination via only one COO$^-$ group of the ligand. This is again in excellent agreement with the EXAFS results.

The determined coordination mode of oxalate by EXAFS and the quantum chemical calculations provides an excellent explanation for the observed thermodynamic behaviour of the complexation reactions. The formation of chelate complexes is usually directed by significantly lower $\Delta H_{n,m}$ values.$^{79}$

4 Summary and conclusion

In the present work stability constants and thermodynamic functions for the complex formation of Np(v) with oxalate are determined. The complexation is studied systematically as a function of the ligand concentration ([Ox$^2$]$_{\text{total}}$), ionic strength (NaCl and NaClO$_4$) and temperature (20–85 °C) by absorption spectroscopy in the near infrared region. The formation of exclusively different Np(v) oxalate complexes with a stoichiometry of NpO$_2$(Ox)$_n$$^{1−2n}$ ($n = 1, 2)$ is observed at the studied experimental conditions. The stoichiometry of the formed complexes is confirmed by slope analyses according to the law of mass action. With increasing temperature the equilibrium of the complexation reaction shifts toward the Np(v) aquo ion and the formation of NpO$_2$(Ox)$_n$$^{1−2n}$ is repressed at elevated temperatures. This is reflected by a decrease of the stability constants. The log $\beta_2(25 °C) = 4.53 ± 0.12$ decreases by about 0.1 and log $\beta_2^0(25 °C) = 6.22 ± 0.24$ decreases by about 0.3. The thermodynamic stability constants correlate linearly with $T^{-1}$ and the reactions enthalpies and entropies are calculated with the integrated van’t Hoff equation. The results show that the complexation reactions are exothermic with $\Delta H_{0,m}^n = −9.7 ± 3.4$ kJ mol$^{-1}$ and $\Delta H_{0,m}^2 = −14.1 ± 2.6$ kJ mol$^{-1}$. Furthermore, the $\Delta \epsilon_1^n$ and $\Delta \epsilon_2^n$ values are determined as a function of temperature for two different ionic media (NaCl and NaClO$_4$) using the SIT. No significant temperature dependence of $\Delta \epsilon_1^n$ and $\Delta \epsilon_2^n$ is observed and the respective binary ion-ion interaction coefficients $\epsilon_{ij,k}$ are calculated.

Structural investigations by EXAFS spectroscopy and quantum chemical calculations provide information on the coordination mode of oxalate toward the Np(v) ion. The experiments and calculations confirm a side-on coordination of

<table>
<thead>
<tr>
<th>Method</th>
<th>Complex</th>
<th>Coord. mod.</th>
<th>O$_{ax}$ [Å]</th>
<th>O$_{eq}$ [Å]</th>
<th>C$_c$ [Å]</th>
</tr>
</thead>
<tbody>
<tr>
<td>DFT</td>
<td>NpO$_2$(Ox)$^{−}$</td>
<td>End on</td>
<td>1.84</td>
<td>2.47</td>
<td>2.84</td>
</tr>
<tr>
<td></td>
<td>NpO$_2$(Ox)$_2$$^{3−}$</td>
<td>End on</td>
<td>1.83</td>
<td>2.46</td>
<td>3.26</td>
</tr>
<tr>
<td></td>
<td>NpO$_2$(Ox)$^{−}$/NpO$_2$(Ox)$_2$$^{3−}$</td>
<td>End on</td>
<td>1.83</td>
<td>2.47</td>
<td>2.86</td>
</tr>
<tr>
<td></td>
<td>NpO$_2$(Ox)$_2$$^{3−}$</td>
<td>Side on</td>
<td>1.83 ± 0.02</td>
<td>2.45 ± 0.02</td>
<td>3.39 ± 0.07</td>
</tr>
</tbody>
</table>

Table 7 Distances of the ligands atoms toward the metal centre. Results of the quantum chemical calculations compared to EXAFS data

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\Delta E_g$ [kJ mol$^{-1}$]</th>
<th>$\Delta E_{th}$ [kJ mol$^{-1}$]</th>
<th>$\Delta E_{solv}$ [kJ mol$^{-1}$]</th>
<th>$\Delta G$ [kJ mol$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>NpO$_2$(Ox)$^{−}$</td>
<td>34.35</td>
<td>6.13</td>
<td>4.71</td>
<td>32.93</td>
</tr>
<tr>
<td>NpO$_2$(Ox)$_2$$^{3−}$</td>
<td>170.71</td>
<td>44.74</td>
<td>41.64</td>
<td>84.34</td>
</tr>
</tbody>
</table>

Table 8 Gibbs free energies for the isomerisation reactions according to eqn (10) and (11). Ground state energies $E_g$ calculated on MP2 level
oxalate toward the Np(V) ion and the formation of five membered chelate rings.

The present work is a detailed spectroscopic and quantum chemical study focusing on thermodynamic functions for the complexation reactions of Np(V) with oxalate and the structures of the formed complex species. The studied ligand system serves as model for macromolecular organic compounds and the derived data improve the knowledge of the complexation properties of An(V) with polyfunctional macromolecular organic compounds on a molecular level. Furthermore, the present results are a valuable contribution to the thermodynamic database of actinides improving the scientific basis for describing the aquatic chemistry of actinide ions at conditions relevant for nuclear waste disposal.

Conflicts of interest

There are no conflicts to declare.

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