# Complexation of Actinides with Amide Derivatives of Oxydiacetic Acid

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## ABSTRACT

Complexation of Np(V), U(VI) and Nd(III) with dimethyl-3-oxa-glutaramic acid (DMOGA) and tetramethyl-3-oxa-glutaramide (TMOGA) was studied in comparison with the complexation with oxydiacetic acid (ODA). Stability constants and enthalpy of complexation were determined by potentiometry, spectrophotometry and calorimetry. Thermodynamic parameters, in conjunction with structural information of solid compounds, indicate that DMOGA and TMOGA form tridentate complexes with the ether-oxygen participating in bonding with actinide/lanthanide ions. The trends in the stability constants, enthalpy and entropy of complexation are discussed in terms of the difference in the hydration of the amide groups and carboxylate groups and the difference in the charge density of the metal ions.

## INTRODUCTION

Alkyl-substituted amides have been studied in recent years as promising extractants for actinide separation from nuclear wastes. The amide ligands have a few advantages over traditional organophosphorus compounds used in actinide separations (e.g., tributylphosphate, TBP). For example, the products of radiolytic and hydrolytic degradation of amides are less detrimental to separation processes and stripping of actinides from the amide-containing organic solvents is relatively easy. Besides, the amide ligands are completely incinerable so that the amount of secondary wastes generated in nuclear waste treatment could be significantly reduced.

One group of alkyl-substituted oxa-diamides, including the symmetrical tetraoctyl-3-oxa-glutaramide [1] and tetraisobutyl-oxa-glutaramide [2], and asymmetrical N,N'-dimethyl-N,N'-dihexyl-3-oxaglutaramide [3], have been shown to be effective in the solvent extraction of actinides from nuclear wastes. Distribution ratios of actinides under different conditions have been determined in these studies, but the underlying thermodynamic principles governing the complexation of actinides with oxa-diamides remain unrevealed. To improve the efficiency of amides as extractants to separate actinides, systematic studies are needed to obtain thermodynamic and structural information on the complexes. Thermodynamic parameters (e.g., enthalpy and entropy) and structural factors (e.g., denticity and steric hindrance) that affect the binding strength need to be determined. Since the oxa-amide ligands can be considered as derivatives of oxydiacetic acid (ODA) and thermodynamic data on the complexation of ODA with actinides are available in the literature [4,5,6,7], we have chosen to conduct a comparative study between ODA and two methyl-substituted amides, dimethyl-3-oxa-glutaramic acid (DMOGA) and tetramethyl-3-oxa-glutaramide (TMOGA) in aqueous solutions (Figure 1). Using the small methyl groups on the amides gives the ligands substantial solubility in aqueous solutions, so that multiple thermodynamic techniques (potentiometry, spectrophotometry and calorimetry) can be readily applied to this study. By providing insight into the energetics and identifying the driving force of the complexation (e.g., enthalpy, entropy or both), this study helps to design effective extractants for actinide separation from nuclear wastes.

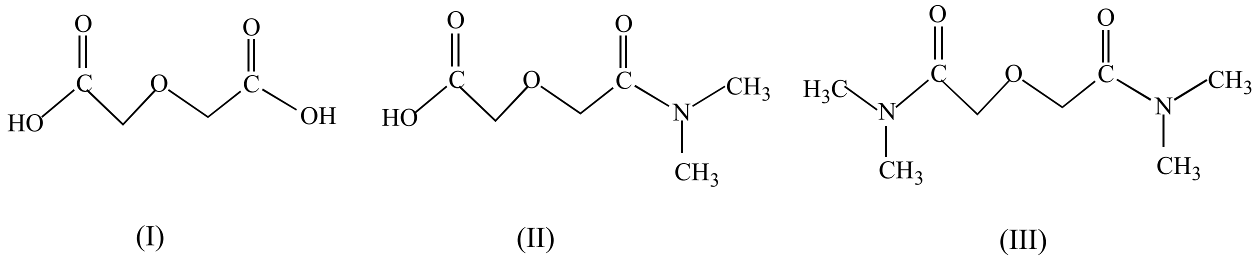


Figure 1. (I) Oxydiacetic acid (ODA); (II) dimethyl-3-oxa-glutaramic acid (DMOGA); (III) tetramethyl-3-oxa-glutaramide (TMOGA).

## EXPERIMENTAL

**Chemicals.** N,N-dimethyl-3-oxa-glutaramic acid (DMOGA) was prepared from diglycolic anhydride and dimethyl ammonia (gas) in 1,4-dioxane with vigorous stirring below 5°C. N,N,N',N'-tetramethyl-3-oxa-gutaramide (TMOGA) was prepared from diglycolyl chloride and dimethyl ammonia (gas) in 1,4-dioxane with vigorous stirring below 5°C. Both products were purified by re-crystallization from water solution and the purity was confirmed by H-NMR and melting point measurements. All other chemicals (Sigma-Aldrich) are of reagent grade or higher. Deionized water from a Milli-Q system was used to prepare all solutions. All thermodynamic measurements were conducted at $I = 1.0$ mol·dm$^{-3}$ ($NaClO_4$) and $t = 25°C$.

**Determination of stability constants.** Spectrophotometry was used to determine the stability constants of the complexes of Np(V), U(VI) and Nd(III) with DMOGA and TMOGA. Sets of absorption spectra of Np(V), U(VI) and Nd(III) in solutions of different concentrations of DMOGA or TMOGA were collected on a Cary-5G spectrophotometer. Potentiometry with a hydrogen electrode was used only to determine the protonation and complexation constants of DMOGA with U(VI). The neutral ligand TMOGA does not have ionizable protons so that direct $H^+$-potentiometry is not applicable to the study of the complexation of TMOGA with actinides. Details of potentiometry are provided elsewhere [6]. Prior to each complexation titration, the electrode was calibrated with a standard acid/base titration in order to calculate the hydrogen ion concentrations from the electrode potential in the subsequent titration. The program Hyperquad 2000 [8] was used to calculate the stability constants from spectrophotometry and potentiometry.

**Determination of enthalpy of complexation.** Calorimetric titrations were conducted with an isothermal microcalorimeter (Model ITC 4200, Calorimetry Sciences Corp). Details of the instrument and the titration procedure have been described elsewhere [9]. The reaction heat was measured after each addition of the ligand solution into the cup that contained the actinides. Multiple titrations with different concentrations of Np(V), U(VI) and Nd(III) were conducted. For each titration, $n$ additions were made (usually $n = 30 - 50$), resulting in $n$ experimental values of the heat generated in the reaction cell ($Q_{ex,j}$, $j = 1$ to $n$). These values were corrected for the heat of dilution of the titrant ($Q_{dil,j}$), which was determined in separate runs. The net reaction heat at the $j$-th point ($Q_{r,j}$) was obtained from the difference: $Q_{r,j} = Q_{ex,j} - Q_{dil,j}$. The value of $Q_{r,j}$, in conjunction with the stability constants of relevant species, is used to calculate the enthalpy of complexation by computer program MQ90 [10].

# RESULTS

## Stability constants determined by spectrophotometry

Np(V), U(VI) and Nd(III) have characteristic absorption bands in the near-IR (around 980 nm), UV (around 420 nm) and visible (around 580 nm) regions, respectively. The positions and intensities of these bands are perturbed by the formation of complexes, which allows the calculation of the stability constants of the complexes. Figure 2 shows a representative set of spectra for the titration of U(VI) with DMOGA. As the concentration of DMOGA increases, three significant changes in the spectra can be observed: 1) the positions of the absorption bands of U(VI) are red-shifted; 2) the intensities of the bands increase; 3) the intensities of the branches from 440 to 480 nm increase more significantly than other branches, indicating that the relative intensities of the branches in the U(VI) complex(es) are quite different from those in free $UO_2^{2+}$. Analysis with the Hyperquad program indicated that the changes in the spectra can be described by successive formation of two U(VI) complexes during the titration, $UO_2L^+$ and $UO_2L_2(aq)$ where L stands for the deprotonated DMOGA anion. The stability constants (log$\beta$) of $UO_2L^+$ and $UO_2L_2(aq)$ were calculated to be 3.90 and 5.88, respectively.

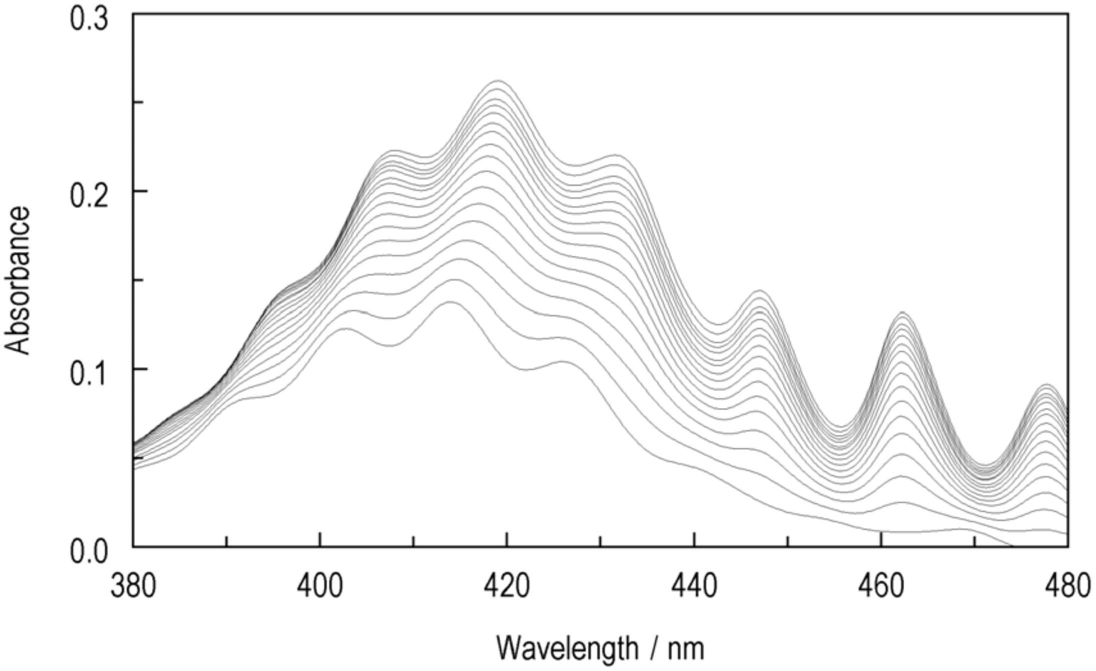


**Figure 2.** Spectrophotometric titration of the U(VI)-DMOGA system, $I = 1.0$ mol·dm$^{-3}$ $NaClO_4$, $t = 25^{o}C$. Initial cuvette solution (2.50 ml): $C_H = 0.0212$ mol·dm$^{-3}$, $C_U = 0.0177$ mol·dm$^{-3}$. Titrant: $C_H = 0.01915$ mol·dm$^{-3}$, $C_{DMOGA} = 0.2192$ mol·dm$^{-3}$. The spectra have been normalized to account for dilution due to volume increase along the titration.

Similar spectrophotometric titrations were performed for other systems including Np(V)/DMOGA, Nd(III)/DMOGA, Np(V)/TMOGA, U(VI)/TMOGA and Nd(III)/TMOGA. Calculated stability constants of corresponding complexes with Hyperquad are listed in Table 1. The spectra of the Np(V)/TMOGA system are particularly interesting because it shows that the symmetry of the complexes governs the intensity of optical absorption that originates from an *f-f* transition. Detailed discussions on the optical properties of the Np(V)/TMOGA complexes are provided elsewhere [11].

**Table 1.** Thermodynamic parameters of the complexation of Np(V), U(VI) and Nd(III) with DMOGA, TMOGA and ODA. $I = 1.0$ mol·dm$^{-3}$ $NaClO_4$, $t = 25^{o}C$. The uncertainties are 3σ.

| Ligand | Ion | Reaction | Method[a] | log $\beta$ | $\Delta H$ kJ·mol$^{-1}$ | $\Delta S$ J·K$^{-1}$·mol$^{-1}$ |
|---|---|---|---|---|---|---|
| DMOGA | $H^+$ | $H^+ + L^- = HL(aq)$ | pot | 3.49(3) | 0.83(1) | 70(1) |
| | Np(V) | $NpO_2^+ + L^- = NpO_2L(aq)$ | sp | 2.99(1) | 5.32(6) | 75(1) |
| | U(VI)[b] | $UO_2^{2+} + L^- = UO_2L^+$ | sp, pot | 3.85(5) | 15.0(1) | 124(1) |
| | | $UO_2^{2+} + 2L^- = UO_2L_2(aq)$ | | 5.88(2) | 21.6(2) | 185(1) |
| | Nd(III) | $Nd^{3+} + L^- = NdL^{2+}$ | sp | 5.13(5) | -6.85(10) | 72(1) |
| | | $Nd^{3+} + 2L^- = NdL_2^+$ | | 8.49(5) | -12.7(1) | 118(1) |
| | | $Nd^{3+} + 3L^- = NdL_3(aq)$ | | 10.9(5) | -14.7(1) | 156(1) |
| TMOGA | Np(V) | $NpO_2^+ + L = NpO_2L^+$ | sp | 1.44(1) | 9.52(80) | 60(3) |
| | | $NpO_2^+ + 2L = NpO_2L_2^+$ | | 2.46(1) | 41.2(15) | 185(3) |
| | U(VI) | $UO_2^{2+} + L = UO_2L^{2+}$ | sp | 1.71(3) | 5.72(9) | 52(1) |
| | | $UO_2^{2+} + 2L = UO_2L_2^{2+}$ | | 2.94(1) | 19.0(2) | 120(1) |
| | Nd(III) | $Nd^{3+} + L = NdL^{3+}$ | sp | 3.15(1) | -10.0(1) | 27(1) |
| | | $Nd^{3+} + 2L = NdL_2^{3+}$ | | 5.14(1) | -17.1(1) | 41(1) |
| | | $Nd^{3+} + 3L = NdL_3^{3+}$ | | 6.12(1) | -16.6(4) | 62(1) |
| ODA | Np(V)[c] | $NpO_2^+ + L^{2-} = NpO_2L^-$ | sp | 3.79(1) | 8.7(4) | 102(1) |
| | U(VI)[d] | $UO_2^{2+} + L^{2-} = UO_2L(aq)$ | pot | 5.01(4) | 16.4(2) | 152(1) |
| | | $UO_2^{2+} + 2L^{2-} = UO_2L_2^{2-}$ | | 7.64(7) | 23.8(1) | 227(2) |
| | Nd(III)[e] | $Nd^{3+} + L^{2-} = NdL^+$ | pot | 5.45(1) | -3.55(6) | 92(1) |
| | | $Nd^{3+} + 2L^{2-} = NdL_2^-$ | | 9.50(1) | -8.80(8) | 151(1) |
| | | $Nd^{3+} + 3L^{2-} = NdL_3^{3-}$ | | 12.16(1) | -12.6(1) | 188(1) |

[a] Method for determination of log $\beta$: pot – potentiometry, sp- spectrophotometry. [b] Values of log $\beta$ for the U(VI)/DMOGA complexes are averaged results from spectrophotometry and potentiometry. [c] Data from [5]. [d] Data from [6]. [e] Data for $20^{o}C$, from [7].

## Stability constants determined by potentiometry

Only the U(VI)/DMOGA system was studied by potentiometry. Results of a representative potentiometric titration are shown in Figure 3. The best fit of the data indicates that two successive complexes form during the titration. The overall complexation reactions are represented by equilibrium (1), where L stands for the DMOGA anion and $j = 1, 2$.

$$UO_2^{2+} + j\,L^- \leftrightarrows UO_2L_j^{(2-j)+} \qquad (1)$$
$$\beta_j = [UO_2L_j^{(2-j)+}]/([UO_2^{2+}][L^-]^j) \qquad (2)$$

The calculated equilibrium constants ($\log\beta$) for $UO_2L^+$ and $UO_2L_2$(aq) are 3.81 and 5.88, respectively, in good agreement with those obtained by spectrophotometry. Therefore, for the U(VI)/DMOGA system, averaged values of stability constants from spectrophotometry and potentiometry are listed in Table 1.

## Enthalpy of complexation

Results of a representative calorimetric titration of U(VI)/DMOGA system are shown in Figure 4. The stepwise heat, as well as the distribution of U(VI) species, is shown as a function of the volume of the titrant added into the cup in Figure 4. Negative values of the heat indicate that the reactions are endothermic. From the results of multiple titrations with different

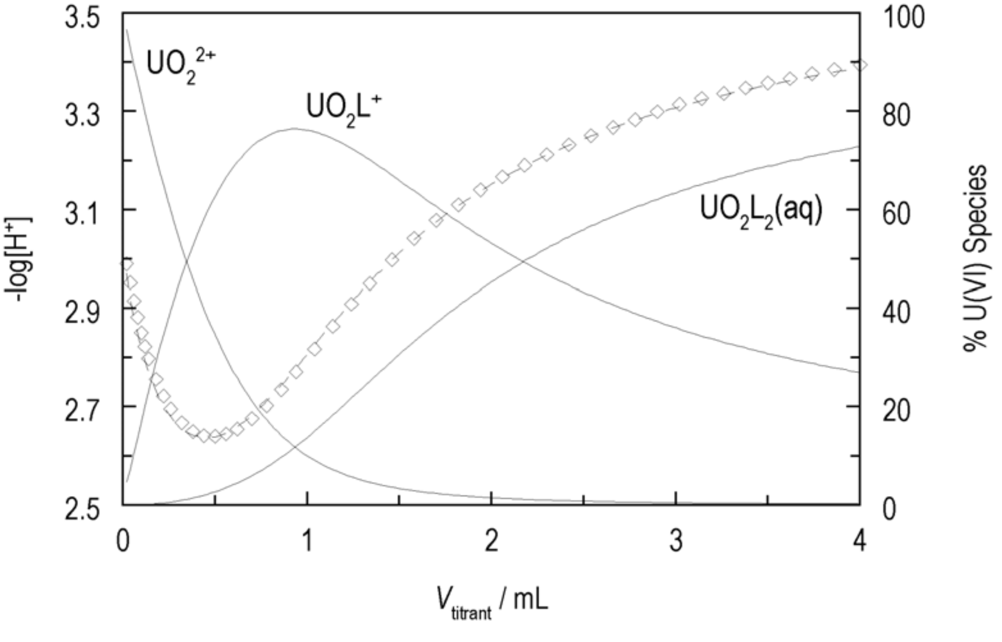


**Figure 3.** A representative potentiometric titration of the U(VI)-DMOGA system, $I = 1.0$ mol·dm$^{-3}$ $NaClO_4$, $t = 25^{o}C$. Initial cup solution (20.0 ml): $C_H = 0.950$ mmol·dm$^{-3}$, $C_U = 8.85$ mmol·dm$^{-3}$. Titrant: $C_H = 0.148$ mol·dm$^{-3}$, $C_{DMOGA} = 0.346$ mol·dm$^{-3}$. Symbols: ◇ - experimental data (-log[H$^+$]); dashed line – fit (-log[H$^+$]); solid lines - percentage of U(VI) species (right y-axis), L stands for the deprotonated DMOGA ligand.

concentrations of U(VI) and acidity, the enthalpies of complexation for $UO_2L^+$ and $UO_2L_2$(aq) are calculated to be 15.0 and 21.6 kJ·mol$^{-1}$, respectively. Similar calorimetric titrations were conducted with the Np(V)/DMOGA, Nd(III)/DMOGA, Np(V)/TMOGA, U(VI)/TMOGA and Nd(III)/TMOGA systems. Calculated enthalpies of complexation are listed in Table 1.

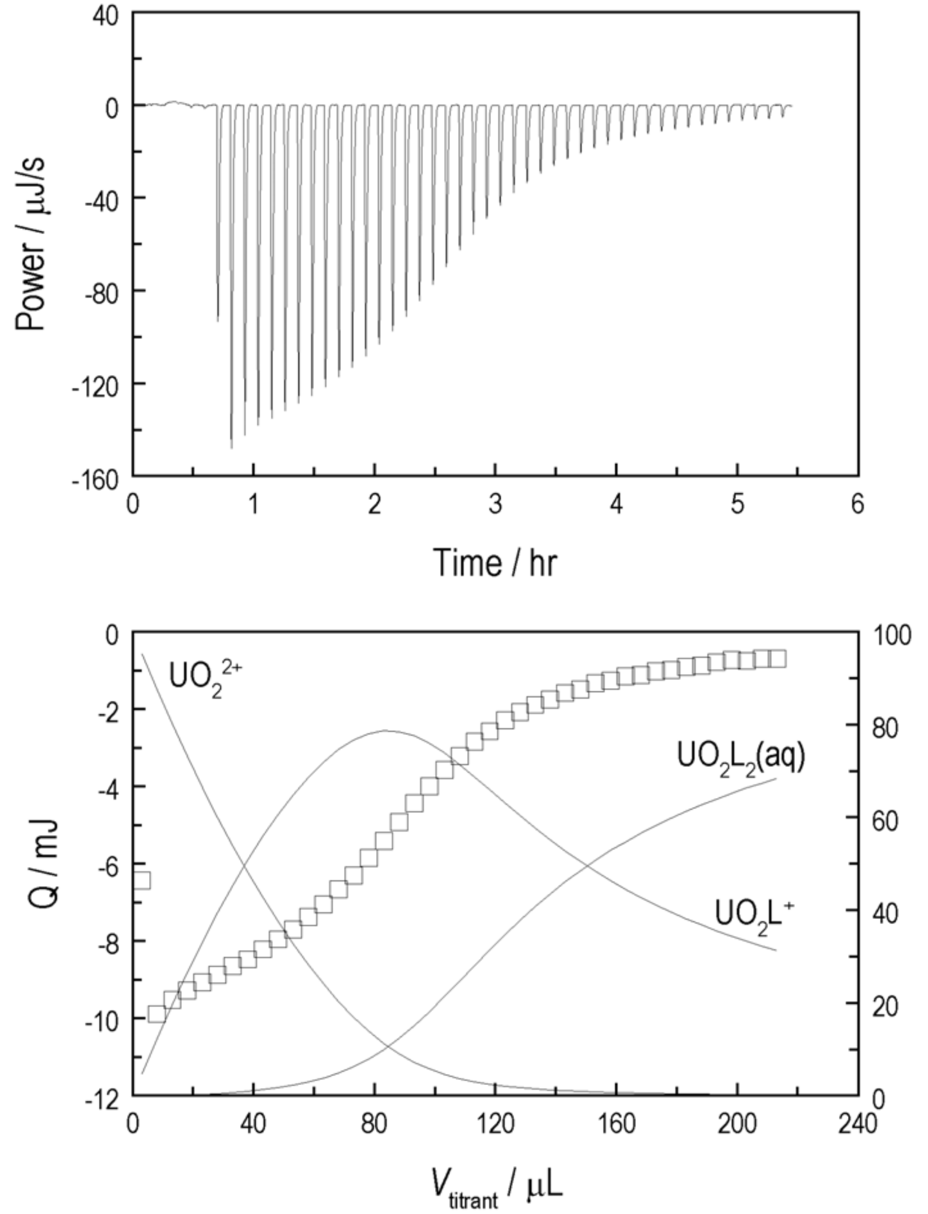


**Figure 4.** Calorimetric titration of the U(VI)-DMOGA system. , $I$ = 1.0 mol·dm$^{-3}$ NaClO$_4$, $t$ = 25$^{o}$C. Initial cup solution (0.900 ml): $C_H$ = 11.78 mmol·dm$^{-3}$, $C_U$ = 9.833 mmol·dm$^{-3}$. Titrant: $C_H$ = 0.0109 mol·dm$^{-3}$, $C_{DMOGA}$ = 0.2282 mol·dm$^{-3}$. (Top) Thermogram; (bottom) Stepwise heat (☐, left y-axis) and speciation of U(VI) (lines, right y-axis) vs. the volume of titrant.

## DISCUSSION

### Thermodynamic trends

The thermodynamic parameters from this work have demonstrated some trends in the complexation of actinides with the three related ligands. The trends for the first complex (ML) are shown in Figure 5 and are discussed in the following with respect to the metal cations and the ligands, respectively.

*Binding strength with different metal ions*. The binding strengths of DMOGA and TMOGA with different metal ions follow the order: Np(V) < U(VI) < Nd(III) (see the values of $-\Delta G$ in Figure 5). This is the same order as observed for the complexation of ODA with these metal ions. Such trend implies that the interactions between the oxa-diamide ligands and actinide/lanthanide ions are dominantly electrostatic and dependent on the electric charge on the cations. This order also agrees with the order of distribution coefficients in the solvent extraction of the metal ions by tetraisobutyl-3-oxa-glutaramide (TiBOGA), where $D_{\mathrm{Np(V)}} < D_{\mathrm{U(VI)}} < D_{\mathrm{Am(III)}}$ [2].

*Binding strength of different ligands*. For each metal ion (Np(V), U(VI) or Nd(III)), the stability constants decrease in the order: ODA > DMOGA > TMOGA (see the trends in $-\Delta G$ in Figure 5). Since the Gibbs Free Energy contains contributions from the enthalpy ($\Delta H$) and the entropy ($T\Delta S$) terms, it is more informative to examine the enthalpy and entropy terms separately. As Figure 5 shows, From ODA to DMOGA and TMOGA, the enthalpy of complexation becomes less endothermic and more favourable to the complexation while the entropy of complexation becomes smaller and less favourable to the complexation. The trend in the enthalpy can be explained by assuming that the amide group is less hydrated than the carboxylate group. When forming complexes with Np(V), U(VI) or Nd(III), less energy is required to dehydrate the amide group than the carboxylate group so that the enthalpy of complexation decreases from ODA to DMOGA, and further to TMOGA. The trend in the entropy supports this assumption. Because the amide group is less hydrated than the carboxylate group, fewer water molecules are released from the hydration sphere of the amide group than the carboxylate group when forming complexes with Np(V), U(VI) or Nd(III). Besides, another mechanism could also contribute to the observed trend in the entropy. As one reviewer has pointed out, the positive charge on the complexes with each metal ion increases in the order ODA < DMOGA < TMOGA. Thus the solvation sphere of the complex probably becomes more ordered from ODA to DMOGA and TMOGA, resulting in smaller entropy gain in the complexation along the series. In summary, the enthalpy and entropy of complexation both decrease in the order: ODA > DMOGA > TMOGA, making opposite contributions to the stability of the complexes. Since the $T\Delta S$ terms are much larger than the $\Delta H$ terms for these systems (Figure 5), the overall effect is that the stability constants decrease from ODA to DMOGA and TMOGA.

The results imply that the replacement of the carboxylate group(s) in ligands such as ODA with the amide group(s) decreases the stability of complexes with actinides due to a less favourable entropy effect. Enlarging the entropy term by using amide ligands with higher denticity could certainly enhance the complexation. For example, a ligand with two properly connected alkyl-3-oxa-glutaramides could behave as a hexa-dentate ligand that is expected to form stronger complexes with actinides due to a larger entropy effect as well as smaller pre-organization energy.

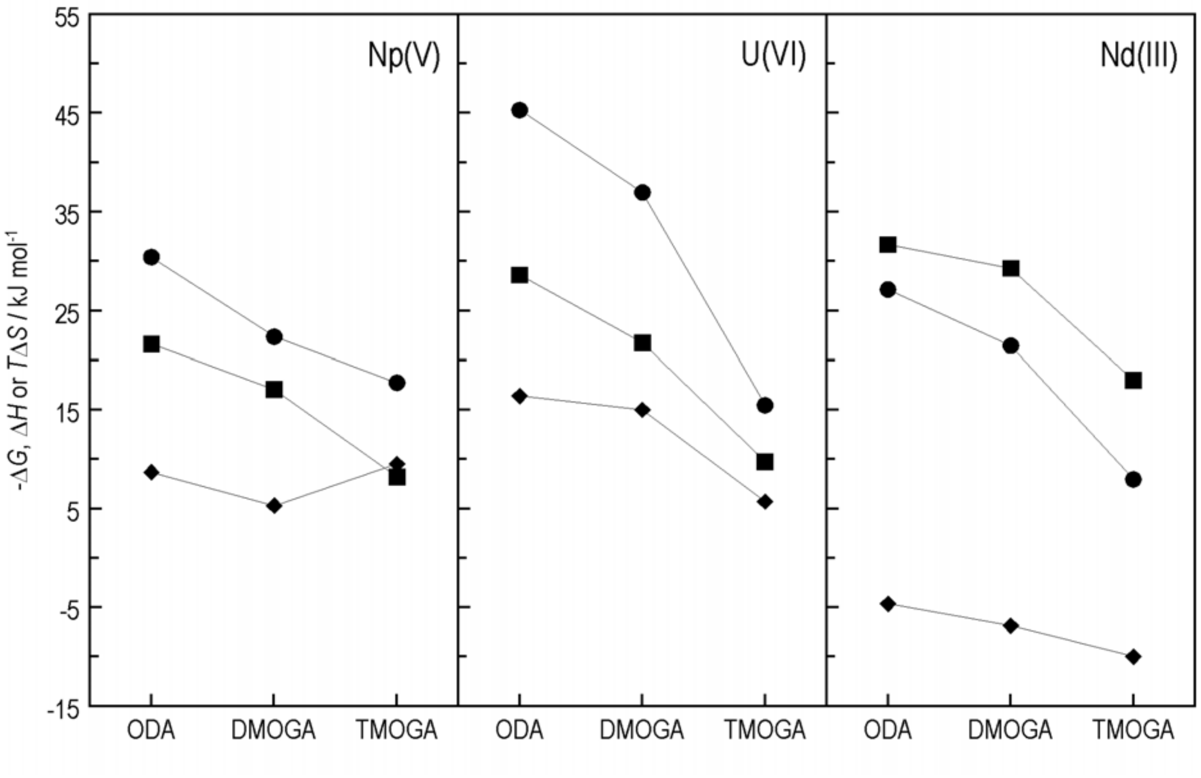
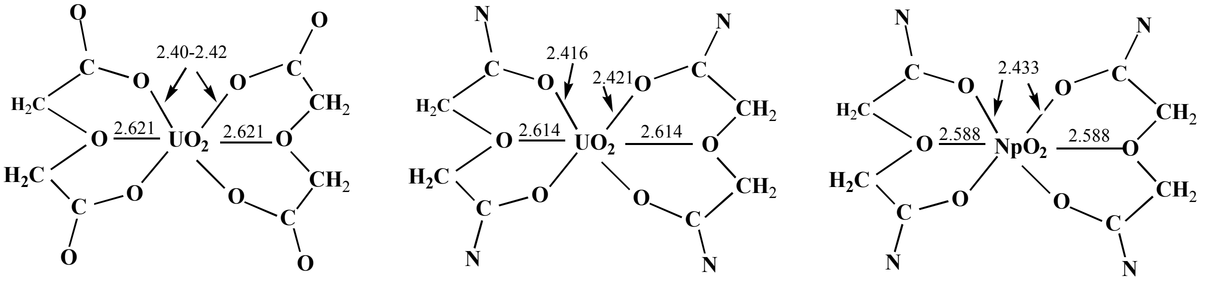


**Figure 5.** Thermodynamic parameters of the complexation (M + L = ML) of Np(V), U(VI) and Nd(III) with ODA, DMOGA and DMOGA. $I = 1.0$ mol·dm$^{-3}$ NaClO$_4$, $t = 25^{\circ}$C. (■) –ΔG, (◆) ΔH, (●) TΔS. Data for Np(V)/ODA, U(VI)/ODA and Nd(III)/ODA are from Ref. [5], [6] and [7], respectively.

## Coordination modes

ODA, DMOGA and TMOGA all have an ether-oxygen that makes the ligands potentially tridentate. Whether the ether-oxygen participates in bonding with metal ions, particularly the dioxo-actinyl ions where steric hindrance may exist, has always been an interesting subject of study. Thermodynamic [6] and structural [4,6] data on the complexation of U(VI) with ODA have revealed that the ether-oxygen of ODA could be in a bonding mode ($R_{\text{U-O}} \sim 2.5 – 2.6$ Å), non-bonding mode ($R_{\text{U-O}} \sim 3.12$ Å), or dynamic mode between bidentate and tridentate configurations ($R_{\text{U-O}} \sim 2.90$ Å) in solution. For the complexes of actinyl ions with DMOGA or TMOGA, we haven't identified the structures in solution. However, solid-state crystal structures of $NpO_2(TMOGA)_2ClO_4$(cr) [11] and $UO_2(TMOGA)_2(ClO_4)_2$(cr) [12] have been obtained, showing the ether-oxygen in TMOGA participates in bonding with Np(V) and U(VI). The M-O distances in these complexes are compared with those in a tridentate $UO_2(ODA)_2^{2-}$ complex [4] in Figure 6. Among the three structures, the $NpO_2(TMOGA)_2ClO_4$(cr) is the most symmetrical: the Np(V) atom is at the inversion center where three mirror planes intersect. It is also interesting to notice that the Np-$O_{\text{carbonyl}}$ distance is the longest (2.433 Å) but the Np-$O_{\text{ether}}$ distance the shortest (2.588 Å) among the three structures.



(I) (II) (III)

**Figure 6.** Solid structures of actinyl complexes. (I) $[C_2H_5NH_2(CH_2)_2NH_2C_2H_5][UO_2(ODA)_2]$(cr) [4]. (II) $UO_2(TMOGA)_2(ClO_4)_2$(cr) [12], (III) $NpO_2(TMOGA)_2ClO_4$(cr) [11]. The cation in (I) and the anion in (II) and (III) are not shown for clarity.

## CONCLUSIONS

Similar to oxydiacetic acid (ODA), dimethyl-3-oxa-glutaramic acid (DMOGA) and tetramethyl-3-oxa-glutaramide (TMOGA) form tridentate complexes with Np(V), U(VI) and Nd(III) in aqueous solutions. The binding strength of the ligands for each metal ion decreases from ODA to DMOGA and further to TMOGA, mainly due to the decrease in the entropy of complexation along the series. For each ligand, the stability constants of the metal complexes follow the order predicted by the electrostatic model: Np(V) < U(VI) < Nd(III). This order also agrees with the order of distribution coefficients in the solvent extraction of the metal ions by using tetraisobutyl-3-oxa-glutaramide (TiBOGA) as the extractant.

## ACKNOWLEDGMENTS

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