Electronic Supplementary Information for Dalton Transactions
This journal is © The Royal Society of Chemistry 2011

Electronic Supplementary Information (ESI)

Figures 1A_EA and 1B_EA show the stepwise experimental heats, $Q_{exp,,j}$, and the sum of the stepwise experimental heats, $Q_{exp,Tot}$, measured for the five titrations with which β_1 and ΔH_1 for the formation of Th(IV) nitrate complex were obtained. They are exothermic when the nitrate concentration in the cup solution is high, and decrease, becoming endothermic, when the nitrate concentration is lesser.

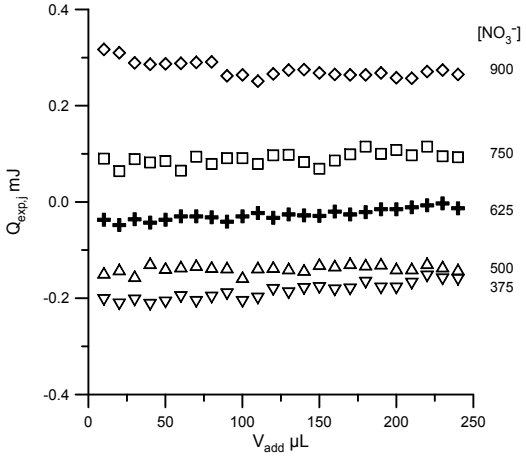


Figure 1A_EA

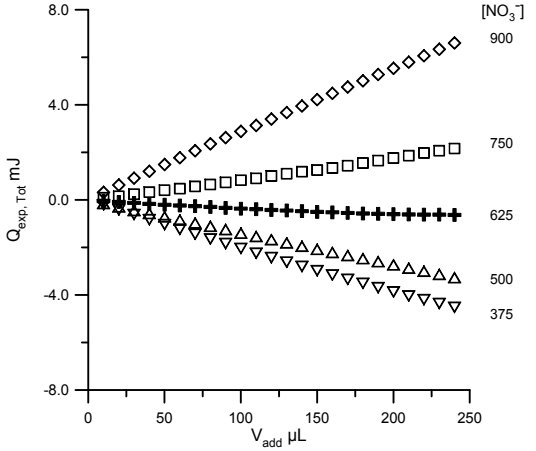


Figure 1B_EA

Figures 1A_EA and 1B_EA. Calorimetric titrations for Th(IV) nitrate systems. I = 1 M and 25 °C. (1A) The stepwise experimental heat ($Q_{exp,j}$) vs. $V_{titrant}$; (1B) The sum of the stepwise experimental heats ($Q_{exp,Tot}$) vs. $V_{titrant}$. Five titrations of solutions with increasing nitrate concentration were carried out: [NO_3^-] ~ 900 (◇); ~750 (□); ~ 625 (✚); ~ 500 (△);~ 375 mmol dm^{-3} (▽).

This trend has no immediate utility because it provides no information (proof) concerning the possible formation of nitrate complexes of Th(IV) in solution. It can only be explained as the result of multiple processes, exo- and endo-thermic, which occur simultaneously when the solution containing the metal cation is added to the solution in the calorimeter cell.

Therefore, in order to rationalize the experimental data, it was necessary to identify each of these different processes.

Electronic Supplementary Information for Dalton Transactions
This journal is © The Royal Society of Chemistry 2011

In this part of the paper we describe how the stepwise experimental heat ($Q_{exp,j}$) was corrected to obtain the stepwise net complexation heat ($Q_{complex,j}$).

In our titrations, beside the heat due to the eventual formation of thorium nitrate complexes ($Q_{complex,j}$), an important part of $Q_{exp,j}$ is due to the mixing of titrant with the cup solutions. In particular, when a definite volume of titrant is added to the cup solutions during metal-ligand titrations, some concentration changes occur which imply heat contributions and necessitate to be considered:

a) the concentration of Na^+ and Th^{4+} passes from ~700 and ~ 50 mM, respectively, in the titrant, to ~900 and ~ < 5 mM, respectively, in the solution cell;

b) the concentration of perchlorate drastically decreases: from 1000 mM in the titrant, to ~100 - ~625 mM in the solution cell;

c) the concentration of nitrate in the titration cell (375, 500, 625, 750 and 900 mM) slightly decreases at each titrant addition.

In addition to the heat contributions due to the above concentration changes, indicated as $Q_{mix1,j}$, $Q_{mix2,j}$ and Q_{cell} (for a), b) and c), respectively), a constant "non chemical" heat (Q_{nc}), which probably arises from the friction of the titrant in the gold capillary tube, has been detected and had also to be taken into account.

Scheme 1 Composition of the solutions employed, either as titrant or in the titration cell, in order to determine the different heat contributions. X = ~ 900, ~ 750, ~625, ~500, ~375 mmol dm^{-3}.

	Q_{exp}		Q_{mix1}		Q_{mix2}		Q_{nc}	
	Titrant	Cell	Titrant	Cell	Titrant	Cell	Titrant	Cell
$[H^+]$	~100	~100	~100	~100	~100	~100	~100	~100
$[Na^+]$	~700	~900	~700	~900	~900	~900	~900	~900
$[Th^{4+}]$	~50	----	~50	----	----	----	----	----
$[ClO_4^-]$	1000	1000 – X	1000	1000	1000	1000 – X	1000	1000
$[NO_3^-]$	----	X				X		

This journal is © The Royal Society of Chemistry 2011

Separate experiments were carried out to determine $Q_{mix1,\,j}$, $Q_{mix2,\,j}$, Q_{cell} and Q_{nc} (See Scheme 1).

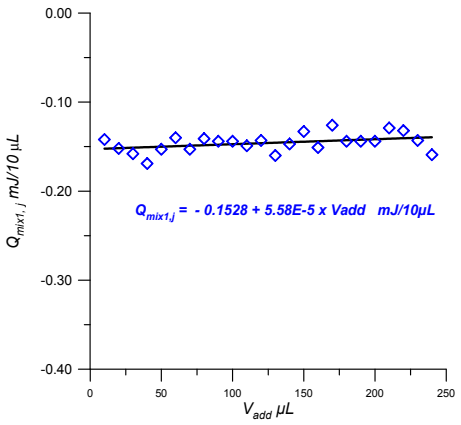


Figure 2_EA. The experimental heats and the corresponding best fit line obtained when 10 µL of a solution of $[Th^{4+}] \sim 50$; $[H^+] \sim 100$; $[Na^+] \sim 700$ and $[ClO_4^-] = 1000$ mmol dm^{-3} are injected into a solution $[H^+] \sim 100$; $[Na^+] \sim 900$ and $[ClO_4^-] = 1000$ mmol dm^{-3} for the determination of $Q_{mix1,j}$.

Measuring $Q_{mix1,j}$ and $Q_{mix2,j}$

$Q_{mix1,j}$ and $Q_{mix2,j}$ are functions of the cup composition and their values were obtained by interpolation of the experimental values.

Figure 2_EA, shows the experimental heats measured to evaluate $Q_{mix1,\,j}$ (see details in Scheme 1) and the best fit line equation used to obtain the contributions of $Q_{mix1,\,j}$ in equation (1).

This journal is © The Royal Society of Chemistry 2011

Figure 3A_EA shows the experimental heats and the linear best fits used to determine $Q_{mix2,j}$ for the five nitrate concentrations used in the experiments. As it can be seen, in a single experiment the experimental heats decrease slightly with the increase of the volume added since nitrate concentrations decrease slightly along the titration. As expected, see Figure 3B_EA, the mixing

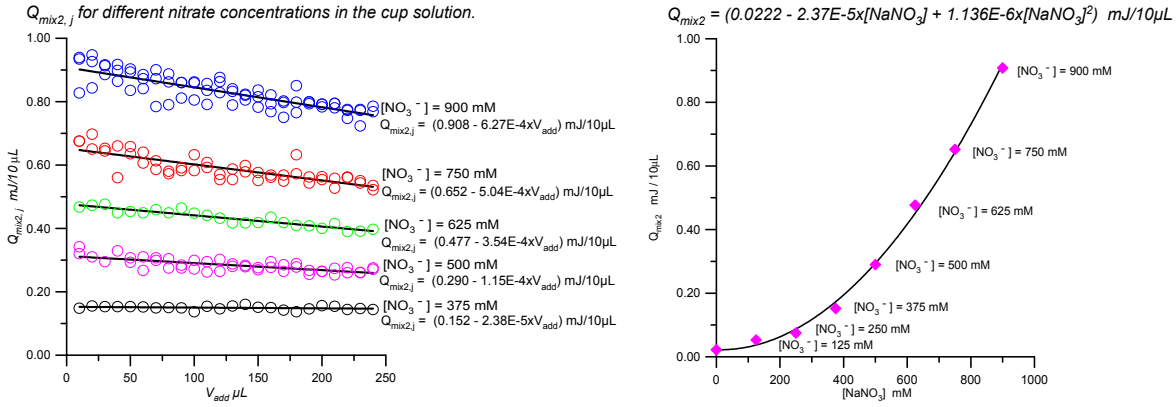


Figure 3A_EA. The experimental heats and the corresponding best fit lines obtained for additions of 10 µL of a solution $[H^+]$ ~ 100 mmol dm^{-3}; $[Na^+]$ ~ 900 mmol dm^{-3} and $[ClO_4^-]$ = 1000 mmol dm^{-3} into solutions with the same cation composition ($[H^+]$ ~ 100 mmol dm^{-3}; $[Na^+]$ ~ 900 mmol dm^{-3}) and increasing nitrate concentration ($[ClO_4^-]$ = 1000 – X mmol dm^{-3}; $[NO_3^-]$ = X mmol dm^{-3}; X = 375, 500, 625, 750, 900) for the determination of $Q_{mix2,j}$.

Figure 3B_EA. $Q_{mix2,j}$ as a function of the nitrate concentration in the cup solution. The symbols in the plot correspond to the intercept of the best fit lines in Figure 3A_EA. $Q_{mix2,j}$. in eq. 1 has been calculated for each nitrate concentration by using the best fit value of Figure 3B_EB and the slope of the best fit line in Figure 3A_EA. Some data are added to this plot concerning the heats of mixing of the titrant in more diluted nitrate solutions: $[NO_3^-]$ ~ 250, ~125 and 0 mmol dm^{-3}, respectively.

effect is larger for the more concentrate nitrate solutions and decreases exponentially with the nitrate concentration.

This journal is © The Royal Society of Chemistry 2011

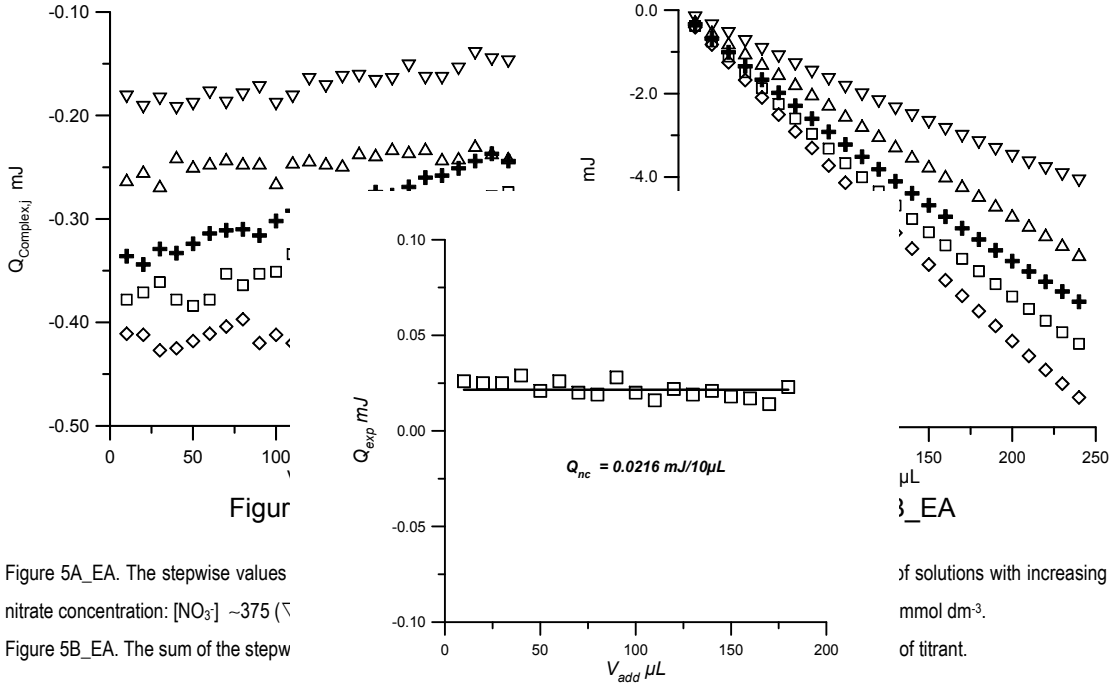
$Q_{nc,}$ has been obtained averaging the values of Q_{exp} for the mixing of two solutions with the same composition. (Scheme 1 and Figure 4_EA).

Q_{cell}, the heat of dilution of nitrate during titrations, is included in $Q_{mix2,\,j}$ and therefore neglected in the following computations.

Having determined the above contributions, it was possible to estimate the heat due to the hypothesized formation of the Th(IV)–nitrate complexes ($Q_{complex,j}$) by the difference in eq. (1):

$$Q_{complex,\,j} = (Q_{exp,\,j} - Q_{nc}) - (Q_{mix1,\,j} - Q_{nc}) - (Q_{mix2,\,j} - Q_{nc}) = Q_{exp,\,j} - Q_{mix1,\,j} - Q_{mix2,\,j} + Q_{nc} \qquad (1)$$

The values of $Q_{complex,\,j}$ so obtained for the five titrations (Figures 5A_EA and 5B_EA) establish that: a) the difference is not zero; which reflects interaction between Th(IV) and nitrate in solution; b) $Q_{complex,j}$ is negative (endothermic) and increase regularly with the concentration of nitrate in the cell, which is in agreement with the increase of complex formation in the more concentrate nitrate solutions.



Figur _EA

Figure 5A_EA. The stepwise values of solutions with increasing nitrate concentration: $[NO_3^-]$ ~375 (? mmol dm^{-3}.

Figure 5B_EA. The sum of the stepw of titrant.

Figure 4_EA. The experimental heats and the corresponding best fit line obtained for additions of 10 µL of a solution $[H^+]$ ~ 100 mmol dm^{-3}; $[Na^+]$ ~ 900 mmol dm^{-3} and $[ClO_4^-]$ = 1000 mmol dm^{-3} into a solution of the same composition.

This journal is © The Royal Society of Chemistry 2011

It is worth noting that the relative weight of thermal contributions which, subtracted to $Q_{exp,j}$, allow the calculation of $Q_{complex,Tot}$ is quite different. In the Figure 6A_EA and 6B_EA we report, for example, the total heats of the different contributions for the titrations with maximum and minimum NO_3^- concentration: 900 and 375 mM, respectively. The figures show clearly that $Q_{complex}$ for the more concentrate solution (red circles) is more negative (more endothermic) than that for the more diluted solution, notwithstanding $Q_{exp,Tot}$ is exothermic for $[NO_3^-]$ ~ 900 and endothermic for $[NO_3^-]$ ~ 375.

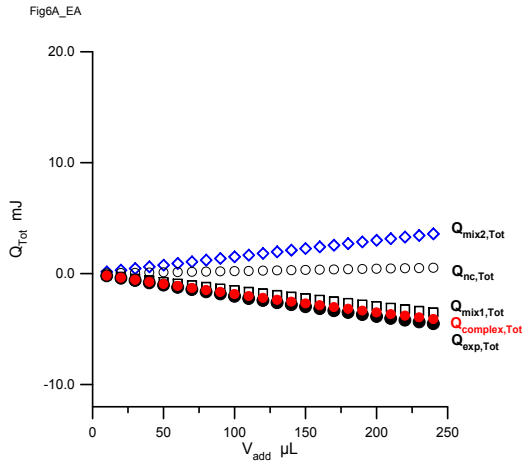


Figure 6A_EA

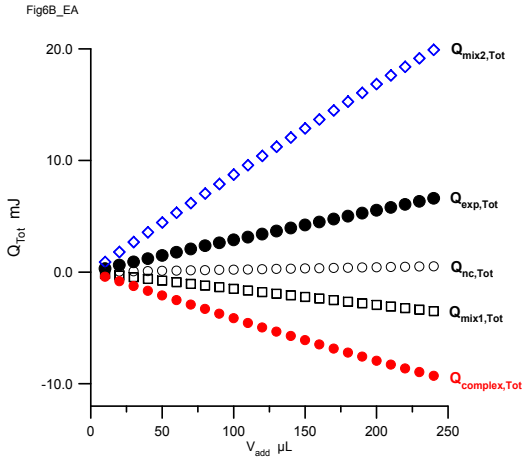


Figure 6B_EA

Figures 6A_EA and 6B_EA. The different thermal contributions used to calculate $Q_{compex,Tot}$ (red circles) for titrations of solutions where the NO_3^- concentration is minimum (6A, $[NO_3^-] \approx 375$ mmol dm^{-3}) and maximum (6B, 6A, $[NO_3^-] \approx 900$ mmol dm^{-3}), respectively. (●) $Q_{exp,Tot}$; (◇) $Q_{mix2,Tot}$; (□) $Q_{mix1,Tot}$; (○) $Q_{nc,Tot}$.

Details on parameter optimization.

In order to ensure that enthalpy and stability constant values reported in table 1 of the work reflect the true minimum, several runs of the minimization program, starting from initial

This journal is © The Royal Society of Chemistry 2011

parameter values far from for the optimization values were made. To reach minimum, the program requires one or more runs but, always, it reaches the same minimum. Sometime the values of β_{final} and ΔH_{final} are insignificantly different (much less than 1σ reported by the program) from the values reported. From the fitting procudere it appears, as expected for very weak complexes, that ΔH and β values are very correlated; the correlation coefficient is -0.9834.

The uncertainties obtained from the minimization program for β (0.04, 3σ) and ΔH (0.9 kJ mol^{-1}, 3σ) do not reflect the possible uncertainties in the heat quantities used to correct Q_{exp} ($Q_{mix,1}$, $Q_{mix,2}$, Q_{nc}) and so they are underestimated. The effect of introducing the uncertainties on $Q_{mix,1}$, $Q_{mix,2}$, and Q_{nc} on the optimization procedure was estimated empirically by applying given perturbations to the heats of input ($Q_{complex}$). First, for each titration set, a value of the dispersion of the experimental heats (Fig. 3_EA) used to obtain $Q_{mix,2}$, the most relevant term in equation (1), was calculated. The estimated values for titrations 1-5 are 29.5, 25.2, 8.8, 13.5 and 5.5 μJ, respectively. Second, all $Q_{complex,j}$ for each data set were corrected in turn by adding or subtracting the corresponding dispersion value (δ). Two new runs of the minimization program with such corrected data points gave the following β and ΔH values:

when δ was added: $\beta = 0.13$; $\Delta H = 8.76$ kJ mol^{-1}

when δ was subctracted: $\beta = 0.34$; $\Delta H = 3.42$ kJ mol^{-1}

From the above values of β and ΔH, the following, more sound, values for the uncertainties on β (0.11) and ΔH (2.7 kJ mol^{-1}) were calculated.