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Kinetic analysis of the complexation of aqueous lanthanide(III) ions by arsenazo III†

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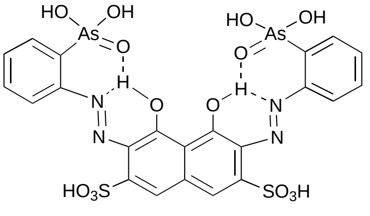
The complexation behavior of Ln^{3+} (aq) (Ln = Eu, Gd or Tb) ions by arsenazo III [3,6-bis(*o*-arsonophenylazo)-4,5-dihydroxynaphthalene-2,7-disulfonic acid] has been investigated by stopped-flow kinetic techniques (ambient and high-pressure). The reaction takes place in three stages. The first kinetic stage differs in pressure dependence for the different metal ions, probably related to a co-ordination number changeover. The second and third kinetic stages were also studied under a variety of conditions. A step by step ring-closure mechanism is suggested to account for the three kinetic stages. The results are discussed with reference to related literature data.

Interest in the co-ordination chemistry, thermodynamics, and kinetics of lanthanide(III) complexes in part arises because of their use as contrast-enhancement agents in magnetic resonance imaging.[1–17] Lanthanide complexes can also simulate some aspects of the clean-up of radioactive actinide wastes such as plutonium because of their chemical similarity; for example, Eu^{3+} is chemically very similar to Pu^{3+}. Complex formation between aqueous lanthanide(III) ions and monodentate or non-cyclic multidentate ligands is usually very fast, so that the kinetics of their complexation can be studied only by relaxation methods.[1–7] The high rate of complex formation is a consequence of the fast water-exchange reactions taking place between the solvation sphere of lanthanide ions and bulk water.[18] Complexation reactions can be significantly slower for protonated, multidentate ligands for which ring closure or proton transfer can be the rate-controlling step.

Arsenazo III [3,6-bis(*o*-arsonophenylazo)-4,5-dihydroxynaphthalene-2,7-disulfonic acid, H_8L] is an often used azo-dye in spectrophotometry, especially for the determination of lanthanide and actinide ions.[19–22] The crystal structure (grown in highly acidic media) of arsenazo III indicates that four intramolecular hydrogen bonds are present within the molecule, including the intramolecular hydrogen bonds between the hydroxyl and arsonate group, in addition to the intramolecular hydrogen bonds between the hydroxyl and azo group.[23]



Arsenazo III

Many studies of the stereochemistry, the complex ion stability and the complexation kinetics of arsenazo III have been reported.[24–38] In particular, several kinetic studies of the reaction between actinide ions and arsenazo III have been published.[39–44] All of the kinetic investigations were carried out under very high acidity conditions and at low concentrations of reactants, which means that the kinetics only covered the first step of the complexation. No subsequent ring-closure steps were observed because arsenazo III existed in the protonated form under such acidic conditions. To our knowledge, no kinetic studies of the complex-formation reactions between aqueous lanthanide ions and arsenazo III have been reported.

In the present paper we describe the results of a detailed study of the formation kinetics of aqueous 1:1 M^{3+}–arsenazo III (M = Eu, Gd or Tb) complexes in the range pH 1.5 to 6.6. The kinetic studies were performed using conventional and high-pressure stopped-flow techniques. The latter is a helpful tool for elucidation of the detailed mechanisms of complex-formation, ligand-exchange and ligand-substitution reactions from measured volumes of activation.[45]

Experimental

Chemicals

Arsenazo III (Aldrich), europium chloride hexahydrate (Strem), gadolinium chloride hexahydrate (Strem), terbium chloride (Alfa), and sodium perchlorate (Aldrich) were used as received.

Acetate buffer solution was prepared by treating acetic acid (J. T. Baker) with sodium hydroxide. Succinate buffer solution was made by mixing succinic acid dipotassium salt (Eastman) with perchloric acid (Fisher Scientific). (2-Morpholinoethanesulfonic acid) (mes) buffer solution was prepared by adjusting the pH of mes (ICN Biomedicals) with NaOH.

Stock solutions of the ligand were prepared by weight. Sodium perchlorate was added to most solutions in order to maintain a constant ionic strength (in most cases $[NaClO_4] = 0.5\ mol\ dm^{-3}$). Bidistilled water was used throughout this study.

All glassware was first treated with an edta solution and then cleaned with successive detergent, ammonia, and distilled water rinses.

Instrumentation

The UV/VIS spectra were recorded on a Hewlett-Packard 8452A diode-array spectrophotometer. pH Measurements were made with an Orion Research 701A Digital Ionanalyzer equipped with glass and calomel electrodes. The desired acidities for the equilibrium measurements and the kinetic runs were obtained by adding to the solutions small amounts of $HClO_4$ or NaOH. Raman spectra were recorded on a Spex-1877 laser Raman spectrometer.

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† *Supplementary data available*: rate constants as a function of pressure, pH and concentration and associated plots, activation volumes. For direct access see http://www.rsc.org/suppdata/dt/1998/967/, otherwise available from BLDSC (No. SUP 57347, 15 pp.) or the RSC Library. See Instructions for Authors, 1998, Issue 1 (http://www.rsc.org/dalton).
Non-SI unit employed: bar = 10^5 Pa.

Table 1 Dissociation constants of arsenazo III *

Constant	Value	Dissociation
pK_1	<1.30	$SO_3H \longrightarrow SO_3^-$
pK_2	<1.30	
pK_3	2.60	$AsO_3H_2 \longrightarrow AsO_3H^-$
pK_4	4.29	
pK_5	6.70	$AsO_3H^- \longrightarrow AsO_3^{2-}$
pK_6	8.79	
pK_7	10.6	$OH \longrightarrow O^-$
pK_8	11.0	

* From ref. 47.

Kinetic measurements

Kinetic measurements were made either at atmospheric pressure on a Durrum stopped-flow spectrophotometer or on a laboratory-made, high-pressure stopped-flow system[46] for pressures up to 1000 bar. *n*-Heptane was used as the pressurizing medium. Transmitted light intensity *versus* time was recorded on a Tektronix (model 7D20) storage oscilloscope and transferred to a personal computer, on which the data were fitted with the On Line Instrument System (OLIS) KINFIT programs (Bogart, GA, 1989). Several experimental records were averaged in the determination of each rate constant. The complexation of M^{3+} (M = Eu, Gd or Tb) by arsenazo III was studied at temperatures between 13.5 and 40.1 °C. Constant temperature was maintained by an external circulating bath (±0.1 °C). All kinetic data were measured after not less than 1 h of temperature equilibration.

Calculations

All experimental runs for the first kinetic stage were best described by a single exponential, whereas all traces for the second and the third stages were fitted best by a sum of two exponentials. Observed pseudo-first-order rate constants were obtained from a least-squares fit of at least 3 half-lives of the reactions. Enthalpies and entropies of activation were determined by a fit of the natural logarithm of the rate constants using the Eyring equation. Volumes of activation were obtained by a fit of the natural logarithm of the observed pseudo-first-order-rate constants using equation (1) where k_0 denotes the

$$\ln k = \ln k_0 - [(\Delta V^\ddagger)P/RT] \qquad (1)$$

rate constant at zero pressure (usually taken as ambient pressure). Errors reported correspond to one standard deviation.

Results and Discussion

Equilibria, spectra and structure

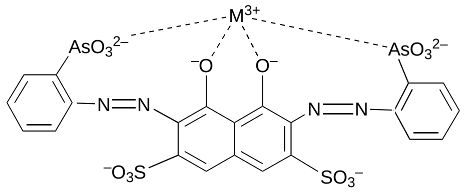
Arsenazo III, H_8L (see the structure above), is a bis(azo) octaprotic weak acid. Its electronic spectrum is very pH dependent. Deprotonation is accompanied by changes from red to reddish purple and finally to deep blue at high pH. Various attempts have been made to describe the behavior of free arsenazo III as a function of pH in terms of protonation equilibria.[19,26,32,47] Table 1 shows the dissociation constants of the several acidic species taken from ref. 47. The most recent report[32] gives the overall pK_a values for H_7L^-, H_6L^{2-}, H_5L^{3-} and H_4L^{4-} as 3.36, 4.32, 7.77 and 10.83, respectively. A typical λ_{max} peak for free arsenazo III is 536 nm.

Complexation of lanthanides by arsenazo III and detection of lanthanides have been extensively investigated spectrophotometrically and thermodynamically because of arsenazo III's high sensitivity and low selectivity and ability to form stable complexes over a wide pH range and in concentrated acid.[19] The studies by Rohwer *et al.*[19] indicated that only the 1 : 1 lanthanide–arsenazo III complex is formed at low arsenazo III concentration and in a dilute acidic medium (pH 3.5) and the conditional formation constants (log $\beta_{1:1}$) and molar absorption coefficients (ε) at 650 nm (pH 3.5 and $[NaNO_3] = 4.9 \times 10^{-3}$ mol dm^{-3}) are ≈7.5 and 8.0×10^4 dm^3 mol^{-1} cm^{-1}, respectively. Rohwer *et al.* resolved the stoichiometry discrepancies of previous workers.[26,48–52] Complete chelation to form the 1 : 1 complex makes the structure much more stable than the 1 : 2 complex. The stability is probably attributable to the metal center being fully chelated by arsenazo III in the 1 : 1 complex and only partially chelated by the ligand in the 1 : 2 complex. Studies on complex formation between the copper(II) ion and ephedrine or norephedrine show the same phenomenon.[53] Recent investigations[32] on complexation of lanthanides by arsenazo III show that the 1 : 1 complex has four protonation states which dominate at pH 3.3, 6.0, 8.3 and >10, respectively, and the maximum wavelength depends to some extent on the ionic strength of the solution.

In order to confirm the structure of the 1 : 1 Eu–arsenazo III complex for the subsequent kinetic studies, Raman spectra of arsenazo III at pH 4.00 and 12.5, and of the 1 : 1 complex at pH 4.00 were obtained. At pH 12.5, arsenazo III showed an aromatic O^- vibration at 1217 cm^{-1} and the N=N stretching vibration at 1400 cm^{-1}. At pH 4.00, no O^- vibration was observed. The complex was formed *in situ* by addition of a 20-fold excess of Eu^{3+} to the arsenazo III solution at pH 4.00. Intense bands at 1221, 1437 and 1480 cm^{-1} were observed. The last two bands have higher frequencies than those of the uncomplexed azo bands,[54] which indicates a higher N=N bond order in the complex.

Meyers *et al.*[54] observed a very similar Raman result when they studied the chelation of nickel(II) by tridentate α-(2-hydrozyphenylazo)acetoacetonitrile and an α-(8-quinolylazo)-acetonitrile dye. They noted that the phenolic OH was ionized at pH 13, the aryl-O stretching vibration appeared at 1246 cm^{-1}, and this vibration was shifted to 1250 cm^{-1} upon complexing at all pH values. The band for N=N stretching at 1411 cm^{-1} has a higher frequency than those of the uncomplexed azo bands, 1370 cm^{-1} at pH 8.3 and 1378 cm^{-1} at pH 11.3.

Based on these pieces of information, we propose the 1 : 1 complex structure shown below. It has been shown that the phenolic OH is deprotonated at a high pH in the absence of metal ion.[47]



General kinetic observations

The reaction of aqueous M^{3+} (M = Eu, Gd or Tb) with arsenazo III occurs in two stages in aqueous buffered or unbuffered acidic solutions at pH < 3.60 when observed by stopped-flow at λ_{max} = 534, 575 (intermediate) or 670 nm. The first more rapid stage corresponds to a decrease in absorbance at 534 nm due to the decrease in dye concentration. The second stage can be followed by either an absorbance increase at 575 nm or an absorbance decrease at 670 nm with a half-life between 500 ms and 10 s depending on pH. The reaction takes place in three stages in aqueous buffered or unbuffered solutions in the range 3.60 < pH < 6.60. The first stage is too fast to be followed by stopped-flow spectrophotometry when pH is larger than 3.60. The two steps of the second stage can be studied by either an absorbance increase at 575 nm or an absorbance decrease at 670 nm with a half-life in the 500–1000 ms range which is independent of pH in this pH range. An oscilloscope trace for these two

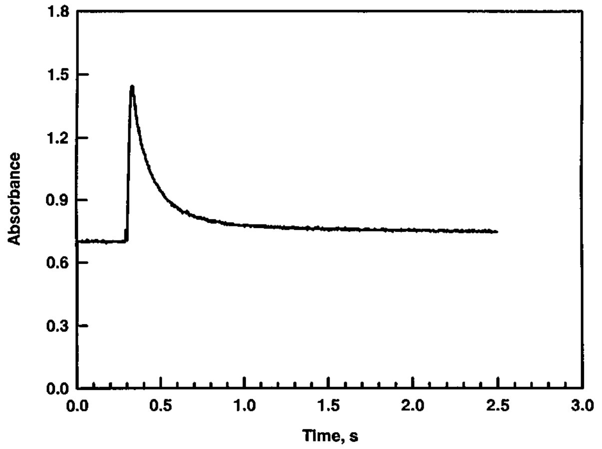


Fig. 1 Typical kinetic trace recorded for the second stage of the reaction of Eu^{3+}(aq) with arsenazo III at pressure of 1 bar and 25.0 °C in 0.1 mol dm^{-3} acetate buffer solution (pH 5.00 and $[NaClO_4] = 0.5$ mol dm^{-3}). $[Eu^{3+}] = 1 \times 10^{-3}$ mol dm^{-3} and [arsenazo III] $= 5 \times 10^{-5}$ mol dm^{-3}, wavelength = 670 nm

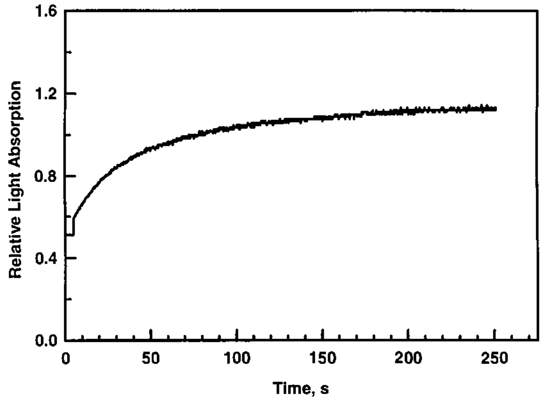


Fig. 2 Typical kinetic trace recorded for the third stage of the reaction of Eu^{3+}(aq) with arsenazo III at pressure of 250 bar and 25.0 °C in 0.1 mol dm^{-3} acetate buffer solution (pH 4.00 and $[NaClO_4] = 0.5$ mol dm^{-3}). Conditions as in Fig. 1

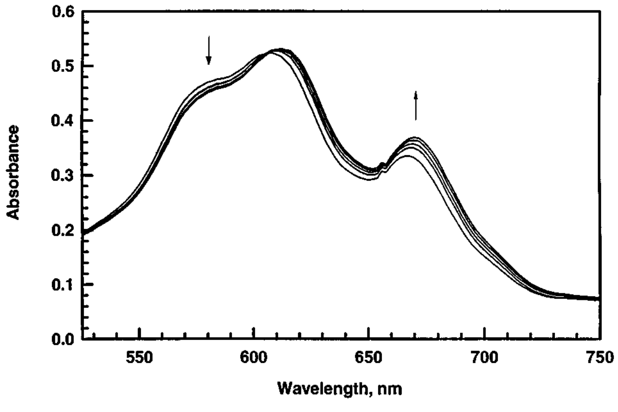


Fig. 3 Repetitive spectral scans for the third stage of the reaction of Eu^{3+}(aq) with arsenazo III with a time interval of 10 s. The reaction conditions are the same as in Fig. 2

steps is shown in Fig. 1. For the slowest two steps of the third stage the absorbance at 670 nm increases with time. These steps are slow enough for monitoring by regular repetitive spectral scans on the HP 8452A diode-array spectrophotometer. Fig. 2 shows a kinetic trace for the slowest step, and a repetitive spectral scan is shown in Fig. 3.

Table 2 Observed rate constants as a function of pressure and activation volumes for the first stage of the reaction of M^{3+} (M = Eu, Gd or Tb) and arsenazo III at 13.5 °C, pH 1.50, $[NaClO_4] = 0.5$ mol dm^{-3}, $[M^{3+}] = 1 \times 10^{-3}$ mol dm^{-3} and [arsenazo III] $= 5 \times 10^{-5}$ mol dm^{-3} in 0.1 mol dm^{-3} succinate buffer solution

	k_1/s^{-1}		
Pressure/bar	M = Eu[a]	M = Gd[b]	M = Tb[c]
1	79.6 ± 9.0	155 ± 7	81.0 ± 7
250	73.6 ± 6.0	142 ± 4	93.5 ± 8
500	69.7 ± 1.2	133 ± 5	114 ± 6
750	63.0 ± 5.0	120 ± 4	142 ± 8
1000	58.4 ± 6.0	111 ± 4	160 ± 9

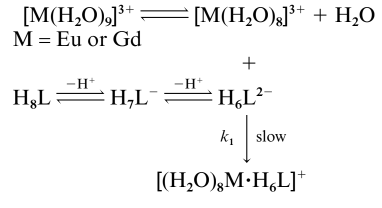
[a] $\Delta V_1^\ddagger = +7.3 \pm 0.4$ cm^3 mol^{-1}. [b] $\Delta V_1^\ddagger = +8.5 \pm 0.4$ cm^3 mol^{-1}. [c] $\Delta V_1^\ddagger = -17.5 \pm 0.9$ cm^3 mol^{-1}.

Kinetics of the first stage

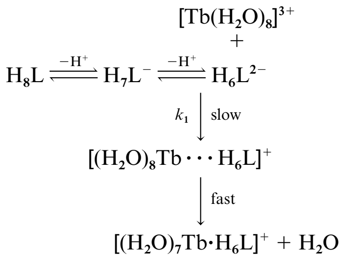
The observed pseudo-first-order rate constants at different pressures for the reaction between $M(H_2O)_9{}^{3+}$ (M = Eu or Gd) or $Tb(H_2O)_8{}^{3+}$ and arsenazo III with M^{3+}(aq) in large excess are given in Table 2. Excellent fits to individual kinetic runs were given by a single exponential.

First of all it should be noted that these reactions are generally much faster than observed for substitution reactions of lanthanide(III) complexes since we are dealing with aquated metal ions in the present study.[55] This is why the first stage of our reaction was studied at 13.5 °C rather than at the standard 25.0 °C and under highly acidic conditions. Difficulties were experienced in studying the concentration dependence since the reactions are too fast for the stopped-flow spectrophotometer if the concentration of M^{3+}(aq) is increased. We also could not investigate the concentration dependence when the concentrations were decreased because the low-amplitude traces were too noisy. Similar kinetic studies of the reactions of actinides with arsenazo III were carried out by others[39–44] at even higher acidities and lower concentrations of reactants.

Knowledge of the co-ordination number of the lanthanide(III) ions in aqueous solution is of primary importance for the interpretation of the thermodynamic and kinetic properties of complexes of these elements. Water-exchange kinetics of lanthanide(III)(aq) determined by a variable-pressure ^{17}O NMR technique indicate that there is a changeover in co-ordination number from nine for the earlier, lighter members of the lanthanide series to eight for the later, heavier members of the series when water is the solvent; Eu and Gd are the border elements for the changeover.[18,56–59] In the present work we selected aqueous Eu^{3+}, Gd^{3+} and Tb^{3+} for kinetic study. From Table 2, we can see that the reaction rate decreases with increasing pressure for the reaction of $M(H_2O)_9{}^{3+}$ (M = Eu or Gd) with arsenazo III, but the rate increases with increasing pressure for the $Tb(H_2O)_8{}^{3+}$ system. The volumes of activation are $+7.43 \pm 0.4$ and $+8.5 \pm 0.4$ cm^3 mol^{-1} for $Eu(H_2O)_9{}^{3+}$ and $Gd(H_2O)_9{}^{3+}$, respectively, whereas $\Delta V^\ddagger$ for the reaction of $Tb(H_2O)_8{}^{3+}$ is -17.5 ± 0.9 cm^3 mol^{-1}. The significantly different pressure dependences observed for complex formation with Eu^{3+}(aq) and Gd^{3+} as compared to Tb^{3+}(aq) clearly indicate a changeover in mechanism.[57] This correlates with the co-ordination number of these complexes, which is nine for the former and eight for the latter.[57] Schemes 1 and 2 are consistent with these data for M = Eu, Gd or Tb, respectively. The final product species in Schemes 1 and 2 is referred to hereafter as

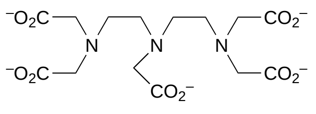


Scheme 1

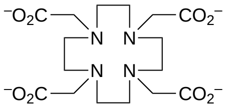


Scheme 2

intermediate I. The positive activation volumes obtained for Eu and Gd indicate a dissociative interchange (I_d) mechanism. Similar results have been reported for water exchange on $Ni(H_2O)_6^{2+}$ ($\Delta V^{\ddagger} = +7.2$ cm^3 mol^{-1}).[60] The activation volumes for water exchange on $[Gd(dtpa)(H_2O)]^{2-}$ ($\Delta V^{\ddagger} = +12.5$ cm^3 mol^{-1}) and $[Gd(dota)(H_2O)]^{-}$ ($\Delta V^{\ddagger} = +10.5$ cm^3 mol^{-1}) are large and positive, indicating a mechanism close to limiting dissociative (D).[12c] The larger volumes of activation are probably the result of steric hindrance caused by the multidentate chelates. In the complex $[Gd(dtpa)(H_2O)]^{2-}$ or $[Gd(dota)(H_2O)]^{-}$ the Gd^{3+} ion is surrounded by the large functional group $dtpa^{5-}$ or $dota^{4-}$ (see the structures below), and there is only enough space for co-ordination of one water molecule. As a consequence, this would limit the operation of an interchange mechanism such that the dissociation of water results in a larger positive activation volume.



$dtpa^{5-}$



$dota^{4-}$

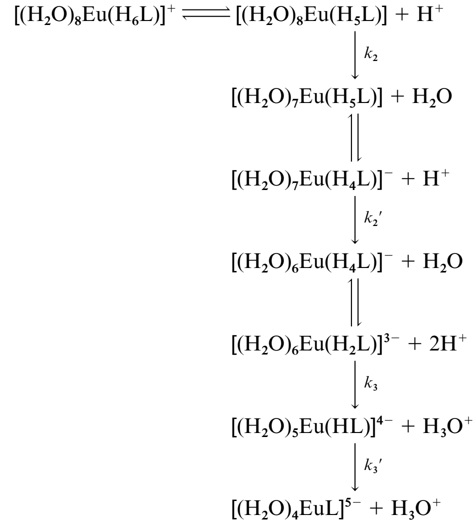
The activation volume (-17.5 cm^3 mol^{-1}) for the reaction of $[Tb(H_2O)_8]^{3+}$ with arsenazo III clearly indicates an associative mechanism. The significant mechanistic difference from the dissociative interchange found for the complexation of $M(H_2O)_9^{3+}$ (M = Eu or Gd) by arsenazo III is probably due to the change-over in co-ordination number as discussed above. It is also interesting to compare the complexation of $[Tb(H_2O)_8]^{3+}$ by arsenazo III with the water exchange for the Tb^{3+} to Tm^{3+} series studied by Merbach and co-workers.[56–58] The activation volumes for the water exchange on the heavy lanthanide ions are all negative and close to -6 cm^3 mol^{-1} indicating a concerted associative interchange (I_a) mechanism. The large and negative activation volume for the complexation of $[Tb(H_2O)_8]^{3+}$ by arsenazo III is attributed to the size of the entering chelate that will cause a more effective overlap of van der Waals radii.

The complexations of aqueous lanthanide(III) ions by other multidentate, weakly basic ligands (such as murexide, xylenol orange, oxalate, anthranilate, methyl red and pyridine-2-carboxylate) have been studied,[1,61–65] and the rates vary by several orders of magnitude from 3×10^6 to 1×10^9 dm^3 mol^{-1} s^{-1} for the same metal with different entering ligands. The ligands do not all have the same charge and size and were not studied at the same pH. Furthermore, the data were not all collected at the same temperature. Our rate constants for the complexation of arsenazo III vary from 0.6×10^5 to 1.60×10^5 dm^3 mol^{-1} s^{-1}, and are lower than those of the systems mentioned above. It is obvious that arsenazo III is larger and a weaker donor ligand than any of the others, which will especially affect the associative reaction mode. We suggest that the first reaction step observed at low pH (where AsO_3H_2 and OH groups are protonated and cannot co-ordinate) involves co-ordination to the deprotonated sulfonate groups.

Subsequent reaction steps

The second and third kinetic stages were either studied at 670 or 575 nm as a function of the concentration of Eu^{3+} (aq) and arsenazo III, pH, temperature and pressure in buffered (succinate, acetate, mes) and unbuffered aqueous solutions; $NaClO_4$ was used to adjust the ionic strength. Under all conditions each reaction stage could be fitted well by two exponentials, these resulting in a total of four subsequent reaction steps, *viz.* k_2, k_2', k_3 and k_3'; k_2 can be determined more accurately than k_2' and k_3 more accurately than k_3'. The two steps (k_3 and k_3') of the third stage are much slower than those of the second stage and the kinetics is slow enough to be followed by a regular repetitive spectral scan technique. Fig. 2 shows a typical kinetic trace for these two steps (k_3 and k_3'), and a repetitive scan is shown in Fig. 3.

Under all studied conditions the concentration of Eu^{3+}(aq) had no effect on the observed rate constants of these steps (see SUP 57347). Since Eu^{3+}(aq) was always used in excess over arsenazo III, these results indicate that the observed reactions must involve intramolecular chelate ring closure as shown in the overall mechanism outlined in Scheme 3. Furthermore, these results argue against the possible formation of higher-order metal complexes or bridged species.



Scheme 3

The kinetic measurements were carried out as a function of pH in unbuffered and buffered (succinate, acetate and mes) solutions over the range 2.0 to 6.6. Kinetic studies at higher pH, such as in Tris [tris(hydroxymethyl)aminomethane] ($pK_a = 8.1$) and ches (2-cyclohexylaminoethanesulfonic acid) ($pK_a = 9.3$) failed because of the precipitation of $Eu(OH)_3$. The results are summarized in Figs. 4 and 5, from which it follows that both k_2(obs.) and k_2'(obs.) exhibit characteristic pH dependences, whereas k_3(obs.) and k_3'(obs.) are independent of pH in the selected range (Fig. 6). The plots of k_2(obs.) and k_2'(obs.) *versus* pH clearly indicate that the second (two) steps may involve pH-dependent intramolecular isomerization of the chelate to bind to AsO_3^{2-}, *i.e.* the ligand 'swings' around and sulfonate co-ordination is replaced by arsenate co-ordination. The first deprotonation step of both AsO_3H_2 groups can account for the observed pH dependence of both k_2 and k_2'. Once AsO_3H^- is co-ordinated the pK_a values will be much lower and spontaneous deprotonation to AsO_3^{2-} will occur.

As discussed above, the deprotonation of the OH groups on arsenazo III is difficult and the pH value must be adjusted to above 11 in the absence of any aquated metal ions.[47] With metal ion, such as lanthanide(III) ion present, its co-ordination by arsenazo III can facilitate deprotonation. Thus the co-ordination of Eu^{3+}(aq) by arsenazo III takes place at pH 4.00.

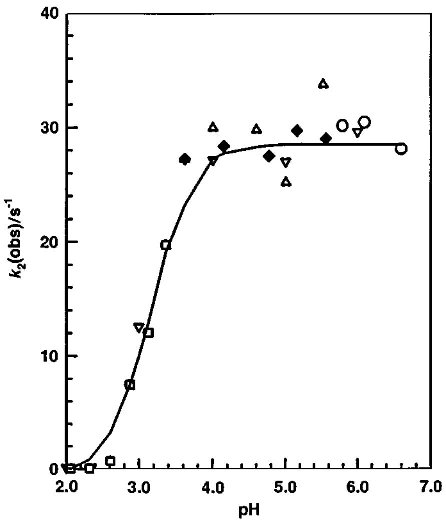


Fig. 4 pH Dependence of k_2(obs.) for the second stage of the reaction of Eu^{3+}(aq) with arsenazo III in buffered (succinate, acetate and mes) or unbuffered aqueous solution ($[Eu^{3+}] = 1 \times 10^{-3}$ mol dm^{-3}; [arsenazo III] $= 5 \times 10^{-5}$ mol dm^{-3}) at 1 bar and 25.0 °C: ▽, no buffer, $[NaClO_4] = 0.5$ mol dm^{-3}; ◆, [acetate] = 0.5 mol dm^{-3}, $[NaClO_4] = 0.5$ mol dm^{-3}; △, [acetate] = 0.1 mol dm^{-3}, no $NaClO_4$; □, [succinate] = 0.01 mol dm^{-3}, $[NaClO_4] = 0.5$ mol dm^{-3}; ○, [mes] = 0.1 mol dm^{-3}, $[NaClO_4] = 0.5$ mol dm^{-3}

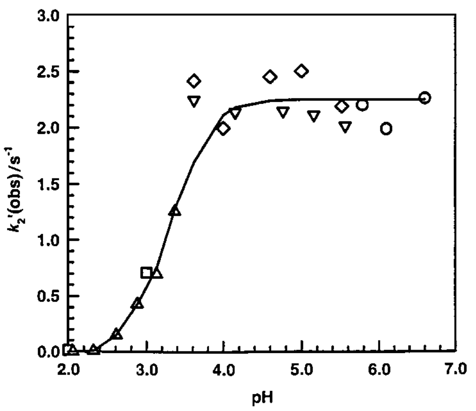


Fig. 5 pH Dependence of k_2'(obs.) for the second stage of the reaction of Eu^{3+}(aq) with arsenazo III in buffered (succinate, acetate and mes) or unbuffered aqueous solution ($[Eu^{3+}] = 1 \times 10^{-3}$ mol dm^{-3}; [arsenazo III] $= 5 \times 10^{-5}$ mol dm^{-3}) at 1 bar and 25.0 °C: □, no buffer, $[NaClO_4] = 0.5$ mol dm^{-3}; ◇, [acetate] = 0.5 mol dm^{-3}, $[NaClO_4] = 0.5$ mol dm^{-3}; △, [succinate] = 0.01 mol dm^{-3}, $[NaClO_4] = 0.5$ mol dm^{-3}; ▽, [acetate] = 0.1 mol dm^{-3}, no $NaClO_4$; ○, [mes] = 0.1 mol dm^{-3}, $[NaClO_4] = 0.5$ mol dm^{-3}

If the pH of the reaction is below 3.60 we cannot observe the two steps of the third stage. This conclusion is supported by the Raman and UV/VIS spectroscopic studies and thermodynamics as discussed above. The two steps of the third stage may involve pH-independent chelation to involve the OH groups. The final k_3 stage is suggested to involve co-ordination (chelation) of the OH groups. These have available donor electrons, such that deprotonation will presumably follow chelation, since these pK_a values will then be significantly lower. No pH dependence was observed for this step, thus deprotonation is not involved in the rate-determining step. This means that the deprotonation of the OH groups will either occur before or after chelation. The pH independence of k_3 and k_3' is quite realistic since two binding sites on arsenazo III are already co-ordinated to Eu^{3+}(aq), which will significantly lower the pK_a values of the remaining sites.

The ligand is finally tetradentately co-ordinated. Therefore, we can summarize the relationship between the reaction step and nature of the coordinated ligand as in Scheme 4 (see Scheme 3).

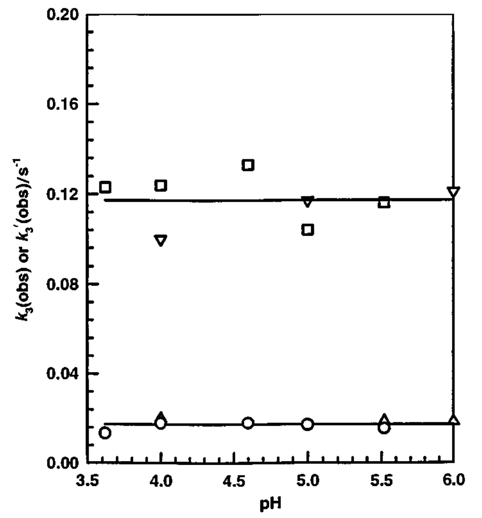


Fig. 6 Plots of k_3(obs.) or k_3'(obs.) *versus* pH for the third stage of the reaction of Eu^{3+}(aq) with arsenazo III in acetate buffer or unbuffered solution ($[Eu^{3+}] = 1 \times 10^{-3}$ mol dm^{-3}; [arsenazo III] $= 5 \times 10^{-5}$ mol dm^{-3}) at 1 bar, pH 4.00 and 25.0 °C: ▽, k_3, $[NaClO_4] = 0.5$ mol dm^{-3}; □, k_3, $[NaClO_4] = 0.5$ mol dm^{-3}, [acetate] = 0.1 mol dm^{-3}; △, k_3', $[NaClO_4] = 0.5$ mol dm^{-3}; ○, k_3', $[NaClO_4] = 0.5$ mol dm^{-3}, [acetate] = 0.1 mol dm^{-3}

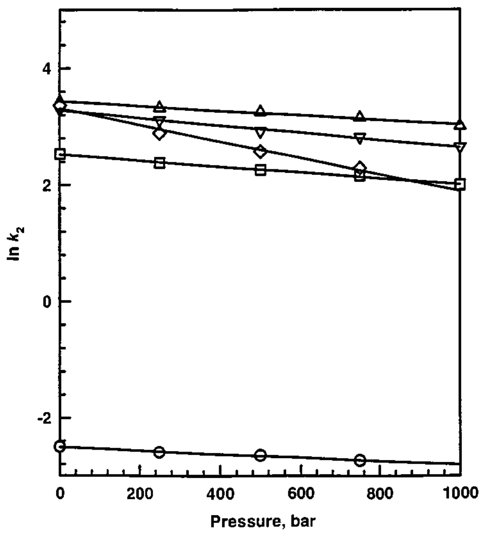


Fig. 7 Plots of ln k_2 *versus* pressure for the second stage of the reaction of Eu^{3+}(aq) with arsenazo III in unbuffered aqueous solution ($[Eu^{3+}] = 1 \times 10^{-3}$ mol dm^{-3}; [arsenazo III] $= 5 \times 10^{-5}$ mol dm^{-3} and $[NaClO_4] = 0.5$ mol dm^{-3}) at different pH values and 25.0 °C: pH 2.00 (○); 3.00; (□), 4.00; (△), 5.00; (▽) or 6.00 (◇)

Reaction	Species
k_1	H_6L^{2-}
k_2/k_2'	$H_6L^{2-} \rightleftharpoons H_5L^{3-} + H^+$
	$H_5L^{3-} \rightleftharpoons H_4L^{4-} + H^+$*
k_3/k_3'	$H_2L^{6-} \rightleftharpoons HL^{7-} + H^+$
	$HL^{7-} \rightleftharpoons L^{8-} + H^+$

Scheme 4 * AsO_3H deprotonates further following binding to the metal center

In order to obtain further insight into the nature of the ligand substitution/chelation mechanism outlined in Scheme 3, the temperature and pressure dependences of the subsequent reaction steps, characterized by k_2, k_2', k_3 and k_3', were investigated. The results along with the calculated activation parameters ($\Delta H^\ddagger$, $\Delta S^\ddagger$ and $\Delta V^\ddagger$) are summarized in Tables 3 to 7 and Figs. 7 and 8 (see also SUP 57347). The experimental conditions for k_2 and k_2' were selected in the pH-independent region (pH 4.0).

Table 3 Reaction rate as a function of temperature and the activation parameters for the second stage of the reaction of Eu^{3+} and arsenazo III at pH 4.00, $p = 1$ bar, $[Eu^{3+}] = 1 \times 10^{-3}$ mol dm^{-3} and [arsenazo III] = 5×10^{-5} mol dm^{-3}

T/K	k_2/s^{-1}	k_2'/s^{-1}
(a) [NaClO$_4$] = 0.5 mol dm^{-3} [a]		
286.1	11.4 ± 0.2	1.17 ± 0.01
291.1	22.1 ± 0.8	2.23 ± 0.05
298.1	30.8 ± 1.1	3.42 ± 0.04
307.0	50.2 ± 4.0	7.31 ± 0.80
313.0	67.0 ± 1.9	9.40 ± 0.01
(b) [NaClO$_4$] = 0.5 mol dm^{-3}, [acetate] = 0.1 mol dm^{-3} [b]		
286.3	17.3 ± 1.5	0.85 ± 0.04
291.1	24.7 ± 0.7	1.29 ± 0.12
298.1	30.1 ± 1.2	2.00 ± 0.08
307.3	40.6 ± 2.1	4.70 ± 0.25
313.2	55.2 ± 1.8	6.90 ± 0.11

[a] For k_2, $\Delta H^‡ = 44 \pm 5$ kJ mol^{-1}, $\Delta S^‡ = -70 \pm 16$ J K^{-1} mol^{-1}; for k_2', $\Delta H^‡ = 55 \pm 4$ kJ mol^{-1}, $\Delta S^‡ = -52 \pm 14$ J K^{-1} mol^{-1}. [b] For k_2, $\Delta H^‡ = 27 \pm 3$ kJ mol^{-1}, $\Delta S^‡ = -125 \pm 8$ J K^{-1} mol^{-1}; for k_2', $\Delta H = 56 \pm 2$ kJ mol^{-1}, $\Delta S^‡ = -50 \pm 8$ J K^{-1} mol^{-1}.

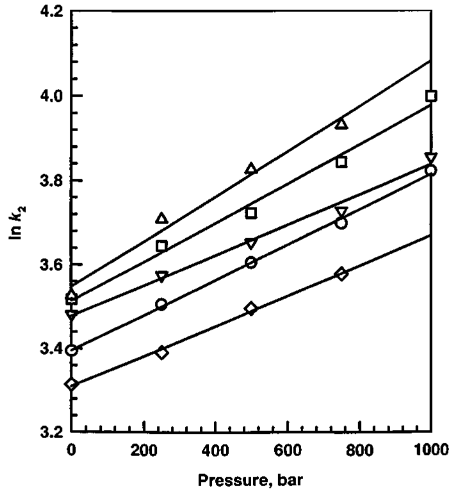


Fig. 8 Plots of ln k_2 *versus* pressure for the second stage of the reaction of Eu^{3+}(aq) with arsenazo III in acetate-buffered aqueous solution ($[Eu^{3+}] = 1 \times 10^{-3}$ mol dm^{-3}; [arsenazo III] = 5×10^{-5} mol dm^{-3}, [NaClO$_4$] = 0.5 mol dm^{-3} or no NaClO$_4$) at different pH values and 25.0 °C: ○, pH 4.60, [acetate] = 0.1 mol dm^{-3}, [NaClO$_4$] = 0.5 mol dm^{-3}; □, pH 5.52, [acetate] = 0.1 mol dm^{-3}, [NaClO$_4$] = 0.5 mol dm^{-3}; △, pH 3.61, [acetate] = 0.1 mol dm^{-3}; ▽, pH 4.15, [acetate] = 0.1 mol dm^{-3}; ◇, pH 5.16, [acetate] = 0.1 mol dm^{-3}

Table 4 Observed rate constants as a function of concentration of Eu^{3+} and pressure and activation volumes for the second stage of the reaction of Eu^{3+} and arsenazo III at 25.0 °C, pH 4.00 and [arsenazo III] = 5×10^{-5} mol dm^{-3}

$10^3[Eu^{3+}]$/mol dm^{-3}	Pressure/bar	k_2/s^{-1}	k_2'/s^{-1}
(a) [NaClO$_4$] = 0.5 mol dm^{-3}			
0.50 [a]	1	30.3 ± 0.8	3.21 ± 0.04
	250	27.1 ± 0.5	2.96 ± 0.03
	500	23.3 ± 0.7	2.45 ± 0.03
	750	21.1 ± 0.7	2.15 ± 0.03
1.00 [b]	1	30.8 ± 1.5	3.40 ± 0.13
	250	27.9 ± 2.5	2.95 ± 0.25
	500	26.0 ± 1.4	2.49 ± 0.11
	750	23.5 ± 1.8	2.14 ± 0.06
	1000	20.3 ± 0.4	1.82 ± 0.04
2.00	1	33.4 ± 0.3	3.48 ± 0.19
5.00	1	32.7 ± 1.4	3.39 ± 0.30
10.0 [c]	1	35.7 ± 1.4	3.40 ± 0.12
	250	32.4 ± 1.9	2.95 ± 0.09
	500	30.1 ± 1.3	2.33 ± 0.07
	750	27.2 ± 1.4	1.92 ± 0.07
	1000	23.5 ± 1.0	1.52 ± 0.06
(b) [NaClO$_4$] = 0.5 mol dm^{-3}, [acetate] = 0.1 mol dm^{-3}			
0.50	1	35.4 ± 1.3	3.05 ± 0.06
1.00	1	35.3 ± 1.7	3.34 ± 0.07
2.00	1	34.2 ± 0.7	3.24 ± 0.07
5.00	1	34.8 ± 1.1	3.36 ± 0.15
10.0	1	35.7 ± 1.5	3.21 ± 0.15

[a] $\Delta V^‡(k_2) = +12.1 \pm 0.7$, $\Delta V^‡(k_2') = +13.6 \pm 1.4$ cm^3 mol^{-1}. [b] $\Delta V^‡(k_2) = +9.9 \pm 0.7$, $\Delta V^‡(k_2') = +15.4 \pm 2.1$ cm^3 mol^{-1}. [c] $\Delta V^‡(k_2) = +9.9 \pm 0.7$, $\Delta V^‡(k_2') = +19.9 \pm 0.9$ cm^3 mol^{-1}.

Table 5 Observed rate constants as a function of pressure and activation volumes for the second stage of the reaction of M^{3+} (M = Eu, Gd or Tb) and arsenazo III at 25.0 °C, pH 4.00, [NaClO$_4$] = 0.5 mol dm^{-3} and [arsenazo III] = 5×10^{-5} mol dm^{-3} in 0.1 mol dm^{-3} acetate buffer aqueous solution. [M] = 1×10^{-3} mol dm^{-3}

Pressure/bar	k_2/s^{-1}	k_2'/s^{-1}
M = Eu [a]		
1	30.1 ± 1.5	2.00 ± 0.07
250	33.8 ± 0.7	1.83 ± 0.04
500	37.3 ± 1.3	1.70 ± 0.06
750	40.6 ± 0.6	1.56 ± 0.03
1000	44.2 ± 1.1	1.42 ± 0.08
M = Gd [b]		
1	30.3 ± 1.8	4.89 ± 0.22
250	33.2 ± 2.5	4.25 ± 0.17
500	38.5 ± 2.0	3.87 ± 0.15
750	41.2 ± 4.0	3.34 ± 0.11
1000	45.4 ± 4.0	3.04 ± 0.10
M = Tb [c]		
1	35.9 ± 0.7	6.21 ± 0.09
250	41.2 ± 1.8	5.85 ± 0.14
500	48.5 ± 1.0	5.58 ± 0.19
750	56.0 ± 1.1	5.20 ± 0.12
1000	68.8 ± 2.3	4.94 ± 0.11

[a] $\Delta V^‡(k_2) = -9.3 \pm 0.4$, $\Delta V^‡(k_2') = +8.3 \pm 1.5$ cm^3 mol^{-1}. [b] $\Delta V^‡(k_2) = -10.0 \pm 0.6$, $\Delta V^‡(k_2') = +11.6 \pm 0.5$ cm^3 mol^{-1}. [c] $\Delta V^‡(k_2) = -15.7 \pm 0.7$, $\Delta V^‡(k_2') = +5.6 \pm 0.2$ cm^3 mol^{-1}.

The results in Table 3 show that k_2 exhibits a significant dependence on the presence of the acetate buffer. This suggests that acetate can induce or assist the intramolecular isomerization from sulfonate to arsenate co-ordination, presumably *via* general acid catalysis. The values of $\Delta S^‡$ and $\Delta V^‡$ for k_2 are significantly more negative in the presence of acetate, which suggests that the induced intramolecular isomerization follows an associative process. In all other cases a positive volume of activation was observed. This result can be attributed to the dissociation of a co-ordinated solvent molecule on the aquated metal center, and/or to charge neutralization that occurs when an anionic donor site chelates the metal center. The latter process will result in decreased electrostriction and an increase in partial molar volume. Activation volumes of *ca.* 15 to 18 cm^3 mol^{-1} are typical for a dissociative mechanism that involves the release of a solvent (water) molecule, whereas values that are significantly more positive must in addition involve a contribution from a decrease in solvent electrostriction. All subsequent chelation reactions (k_2', k_3 and k_3') exhibit significantly positive $\Delta V^‡$ values, which support a dissociative mechanism. The $\Delta S^‡$ values for k_2' are significantly negative and may indicate an effective precursor alignment for this chelation step. The $\Delta S^‡$ value for the final k_3 and k_3' steps are, within the experimental error limits, close to zero.

The observed rate constants as a function of pressure and the activation volumes for the second and third stages of the reaction of M^{3+} (M = Eu, Gd or Tb) and arsenazo III in acetate

Table 6 Reaction rate as a function of temperature and the activation parameters for the third stage of the reaction of Eu^{3+} and arsenazo III at pH 4.00, $p = 1$ bar, $[Eu^{3+}] = 1 \times 10^{-3}$ mol dm^{-3} and [arsenazo III] $= 5 \times 10^{-5}$ mol dm^{-3}

T/K	$10^2\ k_3$/s^{-1}	$10^2\ k_3'$/s^{-1}
(a) $[NaClO_4] = 0.5$ mol dm^{-3} [a]		
286.1	5.3 ± 0.4	1.83 ± 0.04
291.1	9.5 ± 0.5	2.41 ± 0.13
298.1	20 ± 1.7	6.00 ± 0.25
307.0	40 ± 3.5	15.6 ± 0.2
313.0	95 ± 1.2	25.0 ± 0.5
(b) $[NaClO_4] = 0.5$ mol dm^{-3}, [acetate] = 0.1 mol dm^{-3} [b]		
286.3	7.35 ± 0.25	0.53 ± 0.05
291.1	9.00 ± 0.50	0.95 ± 0.04
298.1	12.4 ± 0.7	1.79 ± 0.06
307.3	53.5 ± 5.0	4.50 ± 0.12
313.2	71.0 ± 1.2	7.50 ± 0.12

[a] For k_3, $\Delta H^‡ = 74 \pm 4$ kJ mol^{-1}, $\Delta S^‡ = +28 \pm 14$ J K^{-1} mol^{-1}; for k_3', $\Delta H^‡ = 74 \pm 3$ kJ mol^{-1}, $\Delta S^‡ = +17 \pm 14$ J K^{-1} mol^{-1}. [b] For k_3, $\Delta H^‡ = 66 \pm 10$ kJ mol^{-1}, $\Delta S^‡ = -1 \pm 33$ J K^{-1} mol^{-1}; for k_3', $\Delta H^‡ = 71 \pm 1$ kJ mol^{-1}, $\Delta S^‡ = -3 \pm 4$ J K^{-1} mol^{-1}.

Table 7 Observed rate constants as a function of pressure and activation volumes for the third stage of the reaction of M^{3+} (M = Eu, Gd or Tb) and arsenazo III at 25.0 °C, pH 4.00, $[NaClO_4] = 0.5$ mol dm^{-3} and [arsenazo III] $= 5 \times 10^{-5}$ mol dm^{-3} in 0.1 mol dm^{-3} acetate buffer aqueous solution. $[M] = 1 \times 10^{-3}$ mol dm^{-3}

Pressure/bar	$10\ k_3$/s^{-1}	$10^2\ k_3'$/s^{-1}
M = Eu [a]		
1	1.24 ± 0.06	1.79 ± 0.07
250	0.92 ± 0.06	1.35 ± 0.02
500	0.72 ± 0.07	1.10 ± 0.04
750	0.60 ± 0.03	0.90 ± 0.02
1000	0.50 ± 0.04	0.72 ± 0.02
M = Gd		
1	1.72 ± 0.09	5.00 ± 0.13
M = Tb [b]		
1	2.07 ± 0.13	3.90 ± 0.15
250	1.68 ± 0.16	2.94 ± 0.08
500	1.44 ± 0.06	2.11 ± 0.13
750	1.31 ± 0.08	1.69 ± 0.20
1000	1.20 ± 0.05	1.20 ± 0.10

[a] $\Delta V^‡(k_3) = +22.0 \pm 1.4$, $\Delta V^‡(k_3') = +21.8 \pm 0.8$ cm^3 mol^{-1}. [b] $\Delta V^‡(k_3) = +15.1 \pm 1.0$, $\Delta V^‡(k_3') = +28.5 \pm 0.9$ cm^3 mol^{-1}.

buffer are summarized in Tables 5 and 7, respectively. Rather similar results were observed for all three lanthanide(III) ions investigated, *viz.* k_2 increases with increasing pressure in acetate-buffered systems, and k_2', k_3 and k_3' decrease with increasing pressure. The difference in k_2', k_3 and k_3' among all three lanthanide(III) ions may be related to the size of the latter. The smaller the metal ion the larger is the congestion from the partially co-ordinated arsenazo III ligand and the easier the dissociation of the co-ordinated water molecules. Here steric congestion is the predominant factor, though ions of the same charge but decreasing radius undergo deaquation more slowly because of the greater density and consequent greater attraction for H_2O. Thus, for example, k_2' changes in the order of Eu(2.00 s^{-1}) < Gd(4.89 s^{-1}) < Tb(6.21 s^{-1}).

We conclude that the observed kinetic trends and reported activation parameters can be accounted for in terms of the stepwise chelation mechanism outlined in Scheme 3. The five subsequent reaction steps can be accounted for in terms of binding of the arsenazo III ligand followed by stepwise chelation and deaquation of the metal center. The intimate nature of the mechanism does depend on the metal center, and the observed trends are in good agreement with related findings reported in the literature.[1–18,56–60]

Acknowledgements

This work was supported by the Department of Energy, Office of Basic Energy Sciences (E. M. E.) and by the Volkswagen Foundation (R. v. E.). The authors are indebted to Gabor Konya for help with several computer programs.

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Received 24*th November* 1997; *Paper* 7/08480C