

# Some correlations involving the stability of complexes of transuranium metal ions and ligands with negatively charged oxygen donors

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(Received July 2, 1990; revised November 5, 1990)

## Abstract

Established ligand design principles are extended to transuranium elements and were tested out for Pu(IV) complexation by the trihydroxamic acids, desferrioxamine B (DFB) and *N,N',N''*-tris[2-(*N*-hydroxycarbamoyl)ethyl]-1,3,5-benzenetricarboxamide (BAMTPH). Nd(III) was used as a simulant for Am(III) to characterise its complexation with BAMTPH. Log  $K_1$  values for Pu were measured using an optical fibre system coupled to a spectrophotometer and were found to be  $30.8 \pm 0.1$  and  $30.0 \pm 0.2$  for the Pu(IV)-DFB and Pu(IV)-BAMTPH complexes, respectively. The stability constant for the Nd-BAMTPH complex was measured potentiometrically and was found to be  $16.7 \pm 0.01$ . These values were plotted onto existing correlations between  $\log K_1(L)$  versus  $\log K_1(OH^{-1})$  and found to fit very well.

## Introduction

Since the advent of the nuclear industry, effective sequestering agents which selectively remove actinides from the human body have been sought. A review by Raymond and Smith [1] detailed the biological hazards of some transuranium elements and listed sequestering agents used in the therapy of patients exposed to these metals.

At present, the sequestering agent of choice is diethylenetriaminepentaacetic acid (DTPA) which on prompt administration to laboratory animals significantly increases excretion of Pu. Delayed administration also is reasonably effective. DTPA has a major drawback in that it is not selective and promotes excretion of biologically important metal ions such as Zn(II) and Ca(II). The need to develop selective sequestering agents therefore still exists.

Various approaches to ligand design have been used in order to develop actinide sequestering agents. Raymond *et al.* have used a stereochemical approach [2] as well as modifying existing sequestering agents to produce octadentate ligands which satisfy the coordination requirements of Pu [3,4].

In this study, the ligand design approach of Hancock and Martell is employed. The principles developed in this approach are covered in a recent review [5] and are aimed at promoting selectivity in metal ion complexation which is the heart of the problem in actinide sequestering agent design. Hancock and Martell found that linear correlations between  $\log K_1(L)$  versus  $\log K_1(OH^{-1})$  exist for ligands containing negatively charged oxygen donors. Highly charged metal ions such as those of the transuranium elements have great affinity for these ligands. In the present study, it has been found that these correlations may be extended to transuranium elements and thus probably other design principles will hold as well for these actinides. Once a correlation for a particular ligand has been established, it is possible to predict the stability constant of any metal ion with that ligand if its first hydrolysis constant is known. Much may then be learnt about selectivity.

The stability constant for Pu(IV)-desferrioxamine B (DFB) is reported for the first time here as well as for Pu(IV) with the synthetic trihydroxamic acid, *N,N',N''*-tris[2-(*N*-hydroxycarbamoyl)ethyl]-1,3,5-benzenetricarboxamide (BAMTPH). (See Figs. 2 and 4 for the structures of these ligands.) These stability constants were measured spectrophotometrically us-

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ing an optical fibre system connected to a spectrophotometer. The stability constant for Nd-BAMTPH was measured potentiometrically. Characterisation of the system is important in predicting the behaviour of Am with this ligand. Nd(III) is an excellent simulant for Am(III) as it has a similar ionic radius and the same charge. The stability constants were plotted onto existing correlations for DFB and BAMTPH [6].

## Experimental

### Reagents

All chemicals used were reagent grade or better. DFB was obtained from Ciba-Geigy as its methanesulfonate salt (Desferal). BAMTPH was obtained from Professor Martell. Both ligands were pure and so solutions of accurate concentration could be made up by weighing.

Pu stock solutions were standardised for Pu by coulometry and for free acid by the method of Ahmed *et al.* [7]. The tetravalent oxidation state was not stabilised in stock solutions as the Pu-ligand complexes formed strongly stabilise this oxidation state.

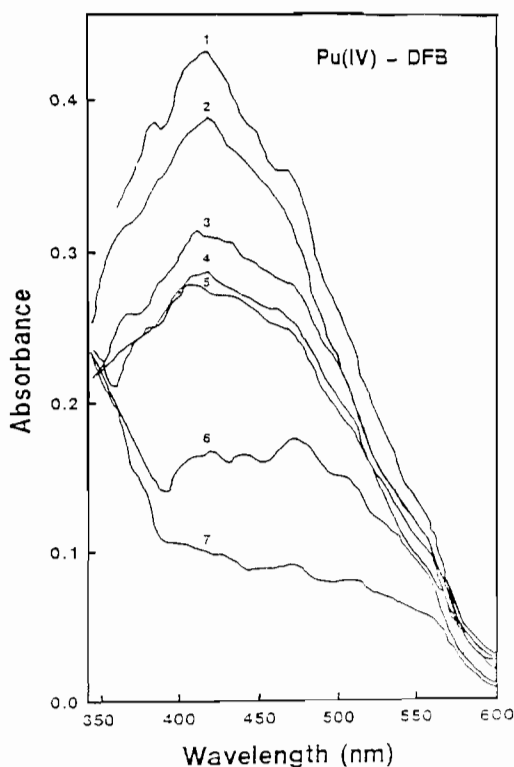


Fig. 1. Spectra of Pu(IV)-DFB complex with varying nitric acid concentration.

### Pu-ligand spectrophotometry

Various solutions of volume 3.000 ml were made up in a quartz cuvette of pathlength 10 mm using micropipettes. The Pu to ligand ratio was maintained at 1:1 while the concentration of nitric acid was varied.  $[Pu] = [ligand] = 1.286 \times 10^{-3}$  M. Ionic strength was not kept constant. This had no effect on  $\log K_1$  as no trends were observed in calculations. It was thus clear that  $\log K_1$  was practically independent of ionic strength in the regions investigated. These were ionic strengths 0.7–2.35 M for DFB and 0.3–1.0 M for BAMTPH. References were solutions without Pu or ligand present. All spectra were recorded at  $22 \pm 2$  °C.

### Nd-BAMTPH potentiometry

Solutions of constant ionic strength (0.1 M NaNO<sub>3</sub>) were made up with ratios Nd:BAMTPH = 1:1, 1:0.75 and 2:1. Titrations with standardised 0.05 M NaOH–0.05 M NaNO<sub>3</sub> were carried out until a precipitate was observed to form. Electrodes used were combined platinum-glass whose electrode constant ( $E_0$ ) and slope had been previously calibrated. All titrations were performed at 25 °C under nitrogen. Initial Nd concentrations were kept in the  $3-4 \times 10^{-3}$  M region.

Data was processed using the ESTA library of programs [8].  $E_0$  was initially kept constant while  $\beta$  values were refined. Once a final model had been obtained, ESTA was allowed to refine  $E_0$  as well to obtain final  $\beta$  values. Data were weighted by the program given in ref. 9. Task 'OBJT' in ESTA2A was used for final refinement.

## Results and discussion

### Pu(IV)-DFB spectrophotometry

Figure 1 shows the spectra obtained. Spectrum 1 is that of the fully formed complex. Addition of base did not increase absorbance at 410 nm which was the wavelength at which absorbance values were taken. Once sufficient base had been added (above pH 7), the solutions turned from orange to green indicating the deprotonation of the amine group. Spectrum 7 is that of the uncomplexed metal ion.

Taking into account the fact that the peak seen in the spectra is due to the MLH complex,  $\log K(ML)$  was calculated as follows.

$$[L]_T = [LH] + [LH_2] + [LH_3] + [L]$$

where

$$\begin{aligned} [L]_T &= \text{apparent total ligand concentration} \\ &= [L] \{ 1 + 10^{pK_{a2}} [H^+] \\ &\quad + 10^{pK_{a2} + pK_{a3}} [H^+]^2 + 10^{pK_{a2} + pK_{a3} + pK_{a4}} [H^+]^3 \} \end{aligned}$$

$$= [L]_T - [MLH]$$

$$= [L]_T - [L]_T(1 - n)$$

Thus  $[L]$  could be calculated and hence

$$\log K_1 = \log [n/1 - n] - \log [L]$$

$pK_{a1}$ s were taken from ref. 6. These were  $pK_{a1} = 10.79$ ,  $pK_{a2} = 9.55$ ,  $pK_{a3} = 8.96$  and  $pK_{a4} = 8.32$ . Results of the calculations are given in Table 1. From these values,  $\log K_1 = 30.8 \pm 0.1$ . Figure 2 shows that Pu(IV) fits the correlation for DFB precisely.

TABLE 1. Results of calculations of the stability constant for the Pu(IV)-DFB complex. Spectra used are in Fig. 1

Spectrum no.	[HNO <sub>3</sub> ] (M)	<i>n</i>	log <i>K</i> <sub>1</sub>
1	Fully formed complex		
2	0.700	0.858	30.10
3	1.50	0.654	30.71
4	2.00	0.560	30.98
5	2.25	0.539	30.71
6	2.35	0.190	30.93
7	Uncomplexed metal ion		

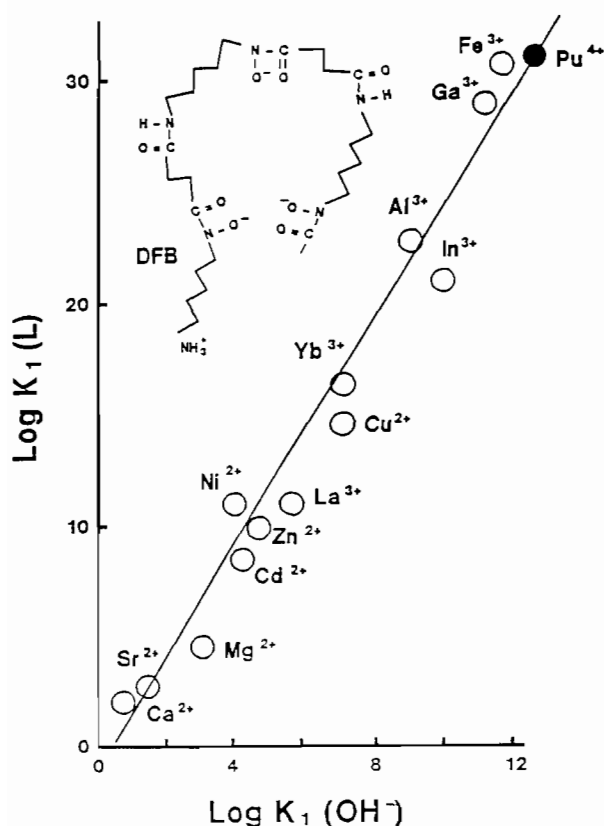


Fig. 2. Correlation between  $\log K_1(L)$  vs.  $\log K_1(OH^-)$  for DFB. Pu(IV) fits correlation perfectly.

#### Pu-BAMTPH spectrophotometry

Figure 3 shows the spectra obtained. Spectrum 1 is that of the fully formed complex. Any addition of base initiates the formation of a precipitate which is probably the MLOH compound. Spectrum 7 is that of the uncomplexed metal ion. As only the ML complex is present,  $[L]_T$  and  $[L]$  are calculated in the normal way.  $pK_{a1}$ s were taken from ref. 10. These were  $pK_{a1} = 10.04$ ,  $pK_{a2} = 9.33$  and  $pK_{a3} = 8.48$ . Results of the calculations are given in Table 2. From these values  $\log K_1 = 30.0 \pm 0.2$ . Figure 4 shows that Pu(IV) fits the correlation for BAMTPH precisely.

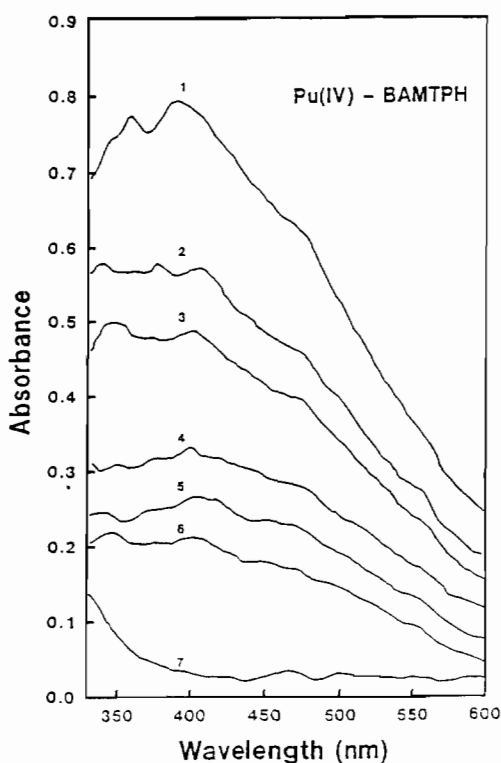


Fig. 3. Spectra of Pu(IV)-BAMTPH complex with varying nitric acid concentration.

TABLE 2. Results of calculations of the stability constant for the Pu(IV)-BAMTPH complex. Spectra used are in Fig. 3

Spectrum no.	[HNO <sub>3</sub> ] (M)	<i>n</i>	log <i>K</i> <sub>1</sub>
1	Fully formed complex		
2	0.300	0.727	30.15
3	0.400	0.607	30.14
4	0.500	0.401	29.88
5	0.600	0.312	29.89
6	1.00	0.239	30.35
7	Uncomplexed metal ion		

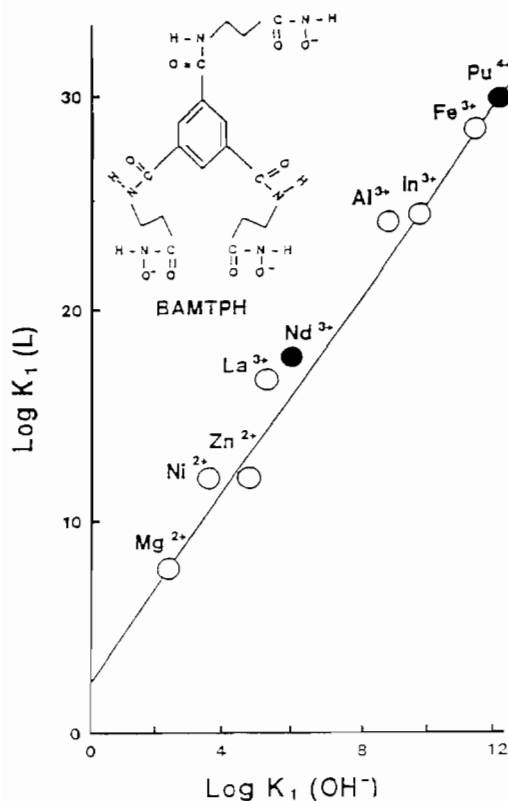


Fig. 4. Correlation between  $\log K_1(L)$  and  $\log K_1(OH^-)$  for BAMTPH. Pu(IV) fits correlation perfectly. Nd(III) fits correlation very well.

#### Nd(III)-BAMTPH potentiometry

A deprotonation function plot generated by task 'QBAR' in program ESTA1 showed that three protons were being liberated on complexation throughout indicating the formation of only a 1:1 Nd-BAMTPH complex. This was confirmed by the final model only containing a 1:1 complex.  $\log K_1$  was found to be  $16.7 \pm 0.01$  (Hamilton  $R$ -factor = 0.00529). Figure 4 shows that Nd(III) fits the correlation for BAMTPH very well.

#### Conclusions

The fact that the correlations for DFB and BAMTPH in Figs. 2 and 4 hold for Pu(IV) is gratifying. The close resemblance of Pu(IV) to Fe(III)

in its behaviour in living systems [3] can be readily understood from these correlations in that the affinity of both metal ions for ligands with negative oxygen donor groups will be very similar on account of the closeness of Pu(IV) to Fe(III) in acidity ( $\log K_1(OH^-) = 11.8$  for Fe(III) and 12.2 for Pu(IV)). Other studies [11] indicate that this similarity to Fe(III) will be enhanced by the fact that both Fe(III), and tetravalent actinide ions such as U(IV) and Pu(IV), will have affinities for nitrogen donor ligands that are similar. Correlations such as those in Figs. 2 and 4 can also be useful for other oxidation states of the actinides. Thus, trivalent actinides should behave like Nd(III), and the oxo cations might behave like  $UO_2^{2+}$ . It is hoped that correlations such as those discussed here will prove useful guides in ligand design for specific complexation of actinides.

#### Acknowledgements

The authors thank Mr W. C. M. H. Meyer and Dr K. S. de Haas for assistance with the optical fibre system, Dr K. Murray for assistance with ESTA, and the AEC for permission to publish these results.

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