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LETTER

Complexation of Actinides with Ionisable Macrocyclic Ligands

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Because of the large cation solvation energy, the interactions of lanthanide and actinide ions (in their high oxidation states) with neutral cyclic polyethers in aqueous solution are too weak to be measured experimentally [1]. On the other hand, strong complexation of uranyl ions [2] as well as of lanthanide ions [3] with ionisable macrocyclic ligands has been reported in the literature. No systematic study has been carried out so far to investigate the effect of size on the complexation of transuranium elements with neutral or ionisable macrocyclic ligands. An attempt at this has been made in the present work for the first time. The complexation behaviour of Th(IV), Pu(IV), Am(III) and Eu(III) with the ionisable macrocyclic ligands 1,7-diaza-4,10,13-trioxacyclopentadecane-*N*,*N*′-diacetic acid (K21DA) and 1,10-diaza-4,7,13,16-tetraoxacyclooctadecane-*N*,*N*′-diacetic acid (K22DA) has been investigated by potentiometric and solvent extraction tracer techniques.

Experimental

K21DA and K22DA were synthesized and standardized by the method described earlier [4]. ^{241}Am and ^{239}Pu purified by an ion-exchange technique and ^{152,154}Eu, obtained by irradiating spectroscopically pure Eu_2O_3, were used as tracers in the solvent extraction experiments. Potentiometric titrations were carried out at 25 ± 0.1 °C on a mixture of the ligand and the Th(IV) salt (1.2×10^{-3} M solution in both) keeping the ionic strength at 0.1 M $(CH_3)_4NCl$. Calculations were made using the computer program described earlier [5].

Proanalysi grade thenoyltrifluoroacetone (TTA; Merck) was used for the extraction experiments, which were performed at 25 ± 0.1 °C, keeping the ionic strength as 0.1 M. The concentration of the ligand was in large excess (~1000 times) compared to the metal ion concentration. Concentrated organic extracts required for Am(III)/Eu(III) back-extraction experiments were prepared by equilibrating 0.4 M TTA (0.04 M for Pu(IV)) in xylene as the organic phase with an aqueous phase comprising 10^{-5} to 10^{-6} M of radiotracer at pH 3.0 ($[H^+] = 1$ M for Pu(IV)). Experiments were carried out with various [TTA] and $[H^+]$ to ascertain the nature of the extracted species [6]. The ligand variation experiments were performed to obtain the aqueous phase complex formation constants. Proton ligand dissociation constants as well as the hydroxy, acetate, chloride and TTA complexes in the aqueous phase required for the calculations were obtained from the literature [7, 8].

Results and Discussion

Potentiometric titration curves for the ligands in the presence and absence of Th(IV) suggest that the complex formation reactions start even before the complete removal of the first proton attached to the acetate group, suggesting a contribution of the following equilibrium

$$Th^{4+} + H_4L^{2+} \rightleftharpoons ThL^{2+} + 4H^+$$

(H_2L = K21DA/K22DA)

This observation is in contrast to the behaviour of trivalent lanthanides [9, 10] which were found to interact principally with the H_2L species. Unlike the results obtained for lanthanides, a gradual decrease was observed in the log *K* values for the Th(IV)–K21DA as well as the Th(IV)–K22DA systems. A steady value was obtained in each case when a slight modification of the program (used for calculations) was carried out by incorporating the possibility of hydrolysis of the Th(IV) ion. Data points with pH greater than 3.5 were not included in the calculations to avoid the possibility of the formation of hydroxo-bridged polynuclear species.

As reported earlier [11, 12], the forward extraction rate of the Ln(III) ion in the system Ln(III)–K21DA/K22DA–TTA–$CHCl_3$ varied significantly with the pH of the aqueous phase. This has been explained on the basis of the slow dissociation kinetics of the macrocyclic complexes in the aqueous phase [13]. Similar observations were made during the solvent extraction experiments involving Am(III) and Pu(IV) ions. Whereas several hours were required to attain equilibrium in the forward direction, it took only 30 min if approached from the backward direction under identical experimental conditions [6].

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TABLE 1. Complex formation constants and ionic radii[a] of metal ions with K21DA, K22DA and EDDA

Metal ion	Internal radius (Å)	Method	K21DA	K22DA	EDDA
Am(III)	1.09	Solv. extr.	12.86 ± 0.03	13.33 ± 0.11	
Eu(III)	1.07	Solv. extr.	12.23 ± 0.08	12.33 ± 0.12	
		Potentiometric[b]	11.85 ± 0.11	12.02 ± 0.11	8.38
Th(IV)	1.06	Potentiometric	16.26 ± 0.14	13.98 ± 0.07	
Pu(IV)	0.96	Solv. extr.	21.52 ± 0.31	19.11 ± 0.05	18.90

[a] Taken from ref. 18. [b] Refs. 9 and 10.

Table 1 shows the complex formation constants of the metal ions together with their ionic radii (CN 8) investigated in the present work. The cavity sizes of K21DA and K22DA appear to be 0.97 ± 0.13 Å (typical of 15-membered ligands) and 1.45 ± 0.15 Å (typical of 18-membered ligands) respectively [14]. In view of the empirical guest–host size correlation derived by Christensen *et al.* [15], it is probable that whereas Am(III) and Eu(III) may be loosely held in the K22DA cavity, no such encapsulation is possible in the K21DA cavity. Extensive X-ray work carried out by Rogers *et al.* [16] on the lanthanide macrocyclic complexes provides support for this suggestion. Whereas all the 15C5 complexes of lanthanides investigated were hydrogen bonded, encapsulation was indeed observed in certain 18C6 complexes.

It appears that, apart from the size effect, stereochemical constraints imposed by the coordination of acetate groups to the central cation also play a role in the complex formation. A recent publication [17] mentions that the steric constraints increase significantly on substituting an acetate group with a propionate group. Chang *et al.* [9, 10] found that $\log K$ values of Cu(II) (ionic radius = 0.73 Å) and Ni(II) (0.69 Å) for their complexes with different ligands follow the trend EDDA > K21DA > K22DA. This is in sharp contrast to the observed trend (K22DA > K21DA > EDDA) for trivalent lanthanides and for Am(III) (radius = 1.09 Å), as observed in the present work. These trends could be rationalized if one considers that steric constraints increase with a decrease of metal ion radius as well as with an increase of ring size. The close $\log K$ values of Am(III)–K22DA and Am(III)–K21DA may be due to the fact that the favourable size effect of K22DA is offset to a large extent by its unfavourable stereochemical constraints. It is postulated that the formation constant for the Am(III)–K22 (or 18C6) complex would be significantly larger compared to that of the Am(III)–K21 (or 15C5) complex.

Table 1 also shows that the $\log K$ values are larger for the Pu(IV)–K21DA and Pu(IV)–K22DA complexes compared to that of the Pu(IV)–EDDA complex. On the basis of the reported ionic radius of Pu(IV) (0.96 Å) [18], it is expected that K21DA may offer a cavity of compatible size. On the other hand, K22DA may offer a larger cavity as well as increased stereochemical strain for the coordination of pendent acetate groups. It should be noted that the larger complex formation constants of Pu(IV) and Th(IV) with K21DA compared to those with K22DA are in sharp contrast to the observed behaviour of Am(III) and Eu(III). The energy of stabilization (as represented by the difference in their $\log K$ values) for Pu(IV) over Am(III) in the presence of K21DA is 8.66 units, whereas in the presence of K22DA it is 5.78 units. In this respect K21DA could be compared with EDTA (non-cyclic tetraacetate anion) where the difference in the stability constants of the two ions reportedly varies by 8–9 log units.

The present work suggests a possible use of ionisable macrocyclic ligands for the stabilization of unusual tetravalent states of some transplutonium elements. In particular, 15-membered macrocyclic ligands with pendent acetate groups appear to be promising for the stabilization of Am(IV) over Am(III).

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