

Complexing tendencies of UO_2^{2+} and Th^{4+} in their mixed ligand complexes with aminopolycarboxylates and resorcinol or its derivatives

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Abstract. Formation constants ($\log K_{MAL}^{MA}$) of mixed ligand complexes MAL, where M = UO_2^{2+} or Th^{4+} , A = IMDA, NTA, HEDTA, EDTA, CDTA or DTPA, and L = resorcinol (res), 2-methyl resorcinol (2-Me-res), 5-methyl resorcinol (5-Me-res) or 4-chloro resorcinol (4-Cl-res), have been determined pH-metrically by the Irving–Rossotti approach at 25°C and at an ionic strength, $I = 0.2(\text{mol dm}^{-3} \text{KNO}_3)$. The observed stability sequences are $\text{IMDA} > \text{NTA} > \text{HEDTA} > \text{EDTA} > \text{CDTA} > \text{DTPA}$, and $4\text{-Cl-res} > 5\text{-Me-res} > 2\text{-Me-res} > \text{res}$ with respect to primary and secondary ligands, respectively. Th^{4+} forms more stable mixed complexes than UO_2^{2+} . The $\Delta \log K$ values are negative due mainly to the charge repulsion involved in the complexation $\text{MA} + \text{L} \rightleftharpoons \text{MAL}$.

Keywords. $\text{UO}_2^{2+}/\text{Th}^{4+}$ mixed ligand complexes; aminopolycarboxylate; resorcinol; formation constants.

1. Introduction

The actinide metal ions uranium and thorium exhibit class-A or ‘hard acid’ behaviour in complex formation. A sequence $\text{U}^{4+} > \text{Th}^{4+}$ has been reported (Ramamoorthy and Santappa 1972; Cotton and Wilkinson 1980) for the stability of their metal complexes. This sequence appears to be a consequence of their charge-size relationship. In the uranyl, UO_2^{2+} ion, however, two axial coordination positions of uranium are occupied by oxygens, and the $\text{O}=\text{U}=\text{O}$ arrangement has been shown (Bagnall 1975) to be linear. On going from U^{4+} to UO_2^{2+} the charge-size ratio should become relatively less favourable; the linearity of $\text{O}=\text{U}=\text{O}$ moiety may cause some steric hindrance during chelation. The earlier work suggests that four unidentate coordinating groups may be arranged around uranium in equatorial positions in the UO_2^{2+} ion, but recent studies indicate (Bagnall 1975; Carey *et al* 1964; Carey and Martell 1967) that higher coordination numbers are more frequent with actinides including UO_2^{2+} , and expansion of the coordination sphere may also occur.

The present studies report complexing tendencies of UO_2^{2+} and Th^{4+} in their mixed ligand complexes of the type MAL, where M = UO_2^{2+} or Th^{4+} , A = iminodiacetic acid (IMDA), nitrilotriacetic acid (NTA), 2-hydroxyethyl-ethylenediaminetriacetic acid (HEDTA), ethylenediaminetetraacetic acid (EDTA), 1,2-diaminocyclohexane tetraacetic acid (CDTA), or diethylenetriaminepentaacetic acid (DTPA) and L = resorcinol (res),

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2-methyl resorcinol (2-Me-res), 5-methyl resorcinol (5-Me-res) or 4-chloro resorcinol (4-Cl-res).

2. Experimental

All standard grade (BDH-Analar, Merck - GR, Fluka, Loba-AR) chemicals were used. The solutions were prepared in double distilled water. UO_2^{2+} and Th^{4+} solutions (nitrates) were standardised by EDTA complexometric titrations (West 1969). The formation constants ($\log K_{\text{MAL}}^{\text{MA}}$) were determined by potentiometric pH titrations using the Irving-Rossotti approach (Irving and Rossotti 1953, 1954; Chidambaram and Bhattacharya 1970) at 25°C and at an ionic strength, $I = 0.2$ (mol dm^{-3} , KNO_3). The final concentrations of metal ion and primary ligand (A) were kept at $1.0 \times 10^{-3} \text{ mol dm}^{-3}$, and the secondary ligand (L) was taken in five-fold excess. A

Table 1. Formation constants of binary ($\log K_{\text{ML}}^{\text{M}}$ and $\log K_{\text{ML}_2}^{\text{ML}}$) and ternary ($\log K_{\text{MAL}}^{\text{MA}}$) complexes of UO_2^{2+} and Th^{4+} with complexones and resorcinol (res) or its derivatives (2-Me-res, 5-Me-res, 4-Cl-res) and $\Delta \log K$ values.

Temperature = 25°C ; Ionic strength (I) = 0.2 (mol dm^{-3} , KNO_3)

Metal ion	Formation constant				
		res	2-Me-res	5-Me-res	4-Cl-res
UO_2^{2+}	$\log K_{\text{ML}}^{\text{M}}$	8.41	8.48	8.55	8.80
	$\log K_{\text{ML}_2}^{\text{ML}}$	7.58	7.65	7.72	7.97
	$\log K_{\text{MAL}}^{\text{MA}}$ (IMDA)	8.29	8.36	8.43	8.68
	$-\Delta \log K$ (IMDA)	0.12	0.12	0.12	0.12
	$\log K_{\text{MAL}}^{\text{MA}}$ (NTA)	8.24	8.26	8.38	8.48
	$-\Delta \log K$ (NTA)	0.17	0.22	0.17	0.32
	$\log K_{\text{MAL}}^{\text{MA}}$ (HEDTA)	7.85	7.88	7.92	8.13
	$-\Delta \log K$ (HEDTA)	0.56	0.60	0.63	0.67
	$\log K_{\text{MAL}}^{\text{MA}}$ (EDTA)	7.61	7.68	7.83	7.93
	$-\Delta \log K$ (EDTA)	0.80	0.80	0.72	0.87
	$\log K_{\text{MAL}}^{\text{MA}}$ (CDTA)	7.52	7.60	7.68	7.91
	$-\Delta \log K$ (CDTA)	0.89	0.88	0.87	0.89
	$\log K_{\text{MAL}}^{\text{MA}}$ (DTPA)	6.40	6.47	6.63	6.66
	$-\Delta \log K$ (DTPA)	2.01	2.01	1.92	2.14
Th^{4+}	$\log K_{\text{ML}}^{\text{M}}$	9.71	9.73	9.80	10.05
	$\log K_{\text{ML}_2}^{\text{ML}}$	9.52	9.59	9.66	9.91
	$\log K_{\text{MAL}}^{\text{MA}}$ (IMDA)	9.66	9.70	9.76	10.00
	$-\Delta \log K$ (IMDA)	0.05	0.03	0.04	0.05
	$\log K_{\text{MAL}}^{\text{MA}}$ (NTA)	9.63	9.68	9.71	9.92
	$-\Delta \log K$ (NTA)	0.08	0.05	0.09	0.13
	$\log K_{\text{MAL}}^{\text{MA}}$ (HEDTA)	9.54	9.61	9.69	9.92
	$-\Delta \log K$ (HEDTA)	0.17	0.12	0.11	0.15
	$\log K_{\text{MAL}}^{\text{MA}}$ (EDTA)	8.17	8.23	8.25	8.70
	$-\Delta \log K$ (EDTA)	1.54	1.50	1.55	1.35
	$\log K_{\text{MAL}}^{\text{MA}}$ (CDTA)	7.80	7.87	8.00	8.26
	$-\Delta \log K$ (CDTA)	1.91	1.86	1.80	1.79
	$\log K_{\text{MAL}}^{\text{MA}}$ (DTPA)	7.12	7.18	7.28	7.51
	$-\Delta \log K$ (DTPA)	2.59	2.55	2.52	2.54

Standard deviation: ± 0.01 to ± 0.05

carbonate-free 0.2 mol dm⁻³ NaOH was used as titrant. A digital pH-meter (Elico, LI – 120) with an accuracy of ± 0.01 pH unit was used for pH titrations. The formation constant values ($\log K_{ML}^M$, $\log K_{ML_2}^{ML}$ and $\log K_{MAL}^{MA}$) were refined by the linear plot method (Rossotti and Rossotti 1955) and statistically by the 'Q-test' (Pecsok *et al* 1976). The refined values of formation constants and those of $\Delta \log K (= \log K_{ML}^M - \log K_{MAL}^{MA})$ are presented in table 1.

3. Results and discussion

The pH titration curves (not shown) clearly indicate the formation of mixed ligand MAL complexes in two steps as $M + A \rightleftharpoons MA$, $MA + L \rightleftharpoons MAL$. Th^{4+} shows greater reactivity than UO_2^{2+} as in the former the binary and ternary complex curves are separated from the ligand curve at relatively lower pH values. Absence of precipitation in the ternary systems indicates saturation of the coordination sphere of the metal ions leaving no scope for the formation of hydroxo species.

The observed sequence in $\log K_{MAL}^{MA}$ values (cf. table 1) is $IMDA > NTA > HEDTA > EDTA > CDTA > DTPA$ with respect to the primary ligands. This order is largely a consequence of the Coulombic effect involved in the combination of MA species with L as explained below. The MA chelates formed with Th^{4+} are $[Th \cdot IMDA]^{2+}$, $[Th \cdot NTA]^+$, $[Th \cdot HEDTA]^+$, $[Th \cdot EDTA]^0$, $[Th \cdot CDTA]^0$ and $[Th \cdot DTPA]^-$; and those with UO_2^{2+} are $[UO_2 \cdot IMDA]^0$, $[UO_2 \cdot NTA]^-$, $[UO_2 \cdot HEDTA]^-$, $[UO_2 \cdot EDTA]^{2-}$, $[UO_2 \cdot CDTA]^{2-}$ and $[UO_2 \cdot DTPA]^{3-}$. Complexation with resorcinol or its derivative, L^- (only one proton dissociates significantly in the pH region of ternary complexation) involves either a smaller Coulombic attraction or a charge repulsion; the latter increases on going across the series of complexones from IMDA to DTPA. Statistical considerations also favour the observed trend; with gradual increase in the denticity of primary ligand (denticity of A:IMDA = 3, NTA = 4, HEDTA = 5, EDTA = 6, CDTA = 6, DTPA = 8) fewer coordination positions are available for occupation by the secondary ligand. Actinides, including UO_2^{2+} are known to exhibit higher coordination numbers (Bagnall 1975). The formation of present mixed ligand complexes indicates the expansion of the coordination sphere of Th^{4+} (with DTPA as primary ligand) and of UO_2^{2+} with EDTA, CDTA and DTPA (Carey and Martell 1967).

The observed stability sequence in $\log K_{MAL}^{MA}$ (and also in $\log K_{ML}^M$ and $\log K_{ML_2}^{ML}$) values with respect to the secondary ligands is 4-Cl-res > 5-Me-res > 2-Me-res > res, which is the order of ligand basicity. Between Th^{4+} and UO_2^{2+} the former metal ion forms more stable binary and ternary complexes than the latter. The charge-size ratio, the entropy factor (ΔS), the steric and Coulombic effects evidently work in favour of Th^{4+} making its complexes more stable.

The $\Delta \log K$ values (cf. table 1) are all negative in agreement with earlier similar observations (Bhattacharya 1981; Verma and Saxena 1987, 1988) that complexation with charged primary and secondary ligands invariably leads to negative values of $\Delta \log K$ irrespective of the nature of metal–ligand bonding. In the absence of $M \rightarrow L$ π -bonding the overall charge density around the metal ion is either diminished (with neutral/charged A) or becomes negative (with charged A, i.e. A^{n-}) and hence the affinity of MA towards L becomes lesser than that of M_{aq}^{m+} resulting in the sequence $\log K_{ML}^M > \log K_{MAL}^{MA}$, which yields negative values of $\Delta \log K$. Larger negative values of $\Delta \log K$ are observed with greater negative charge on A^{n-} .

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