Complex Formation Between Uranium(VI) and Thorium(IV) Ions with some α-Amino-acids

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Proton, uranyl, and thorium complex formation of the α-amino-acids (H_2L) serine, cysteine, methionine, threonine, alanine and other substituted glycines with UO_2^{2+} and Th^{4+} have been measured potentiometrically at 25 °C and constant ionic strength [I = 0.10 mol dm^{-3} (KNO_3)]. It was assumed that the complex species [ML] and [ML_2] only were formed. Comparison of the results for alanine and those for serine, cysteine, and methionine suggest only limited bonding between the metal ions and the sulphur atom in cysteine and methionine but somewhat stronger bonding with the oxygen atom in serine.

In recent years a considerable amount of work has been carried out on some aminopolycarboxylic acid complexes with uranyl or thorium ions using different techniques,[1-4] but little work has been reported on α-amino-acid complexes of uranium and thorium. Typical formation constants for uranyl complexes of nitrilotriacetic acid and glycine have been reported as log k = 9.56 ± 0.03 and 7.53 respectively.[5,6] However in some cases high values have been obtained for these acids.

The only example of a related investigation so far was by Cefola *et al.*[5] who studied complexes of glycine and alanine with UO_2^{2+} ions. Studies of mixed-ligand complexes of uranyl and thorium ions with amino-acids and carboxylic acids have been published recently [7,8] each suggesting relatively strong bond formation between the ions and the oxygen donors. We wish to report the results of a study of the proton, UO_2^{2+}, and Th^{4+} ion complexes of a series of α-amino-acids containing sulphur and oxygen atoms having a certain affinity to chelate with metal ions in co-operation with the oxygen and nitrogen of the amino-acid. The amino-acids studied were a series of carbon-substituted glycines of general formula $RCH(NH_2)COOH$, where R = CH_2OH, CH_2S, CH_3, $CH_3CH(OH)$, $(CH_3)_2CH$, $CH_3SCH_2CH_2$, $(CH_3)_2CHCH_2$, $C_6H_5CH_2$, or $C_2H_5CH(CH_3)$ all of which are able to form five-membered chelate rings. For comparison, complexes of serine and cysteine were investigated. Complexes of serine showed greater stability than those of cysteine or alanine due to the presence of an OH group which showed an affinity to form an extra bond with the metal ions studied in this work. In contrast to valine, leucine, or isoleucine, the amino-acids methionine or cysteine must form more stable complexes since they contain a sulphur atom. However, the results obtained showed different results and gave a weak indication of sulphur–metal bonding.

Experimental

Procedure.—The pH titrations were carried out in solutions of low ionic strength in a manner similar to that described previously for the Cu^{2+}–iminodiacetic acid system.[9] Titrations were performed with a Mettler DK31 digital pH meter employing a combined electrode calibrated in terms of hydrogen ion concentration, [H^+], at 25 °C. Buffer solutions used in the present study were prepared from a solution of potassium hydrogenphthalate (pH 4.005) and a KH_2PO_4–Na_2HPO_4 mixture (pH 6.855). The electrode was calibrated by both buffers before and after each titration and agreement was always better than 0.005 pH units. All solutions were made up in a background of KNO_3 (total I = 0.1 mol dm^{-3}). The amino-acids under study were converted to the fully protonated form by adding the calculated amount of standard HNO_3 and were then titrated with carbonate-free alkali using a Mettler DV 210 automatic burette dispensing 0.02 ± 0.001 cm^3 of alkali at each reading. Solutions of 1 : 2 or 1 : 5 metal to ligand concentrations were titrated with alkali and at the beginning of each titration the total volume of solution in the cell was always kept at 30 cm^3. Throughout this study uranyl and thorium nitrate (AnalaR) were used for the preparation of metal-ion solutions. The amino-acids were obtained from Merck (Germany) and were recrystallised using water–ethanol.

Calculations.—For the hydrogen and metal ions, formation constants were calculated from potentiometric titration curves by methods described elsewhere.[10,11] Excellent agreement was found for values of log β_1 and log β_2 when ligand–metal ratios of 5 : 1 were used. However the errors in values for log β_2 were somehow larger since the percentage of the bis complexes was always small. At higher pH, when ligands were titrated in the presence of a metal ion, precipitation occurred. In such instances therefore, only the data obtained before precipitation were considered and used to calculate the log β_1 and log β_2 values. The proton and metal complex formation constants were calculated using the Cyber 170 (CDC) electronic computer at the Nuclear Research Centre, Tehran.

Results and Discussion

Values calculated for the proton, uranyl, and thorium complex formation constants are given in Table 1. Literature data determined under similar experimental conditions of temperature and ionic strength are also given for comparison.

The results of the ligand proton complex formation measurements are typical of those which have been found for simple α-amino-acids with the trends expected from inductive effects of the substituents explained earlier.[12] The values of log β_{HL} decrease as the donor group changes from $-NH_2$ to $-OH$ to $-SH$. This decrease parallels the order of decreasing basicity of the ligand in any given series. However the possibility of a steric effect has been demonstrated by Lenz and Martell [13] for L-cysteine with log β_{HL} = 8.13 and DL-penicillamine with log β_{HL} = 7.88 in 0.1 mol dm^{-3} potassium nitrate. For cysteine, the values are lower than those for methionine due to the presence of an ionizable sulphydryl group compared to a $-SMe$ group in methionine. The protonation of serine or cysteine is lower than that of DL-alanine because of the electron-withdrawing properties of the OH or SH in the β position, the electron density associated with the nitrogen atom of serine and cysteine being decreased relative to that of alanine; hence the weakening of the N–H bond.

Table 1. Proton, uranyl, and thorium complex formation constants for the amino-acids at 25 °C and I = 0.1 mol dm^{-3}. Standard deviations are given in parentheses

	H_2L		UO_2^{2+}		Th^{4+}	
	log β_{HL}	log β_{H_2L}	log β_1	log β_2	log β_1	log β_2
DL-Alanine	9.592(3)	12.067(8)	7.33(2)	14.97(4)	7.18(8)	14.51(3)
	9.70 [a]					
DL-Phenylalanine	9.168(4)	11.610(8)	6.77(1)	13.91(1)	7.84(1)	14.51(3)
D-Serine	9.16(4)	11.509(9)	8.66(3)	14.66(3)	8.25(3)	16.75(6)
D-Threonine	9.035(3)	11.515(6)	6.65(3)	12.08(4)	7.21(2)	14.01(6)
	9.03 [a]					
D-Methionine	8.921(3)	11.271(6)	6.41(1)	13.38(2)	6.82(4)	13.48(6)
	9.052 [b]	11.203 [b]				
D-Cysteine	8.244(4)	10.552(8)	5.84(2)	11.85(5)	7.51(8)	14.80(4)
	8.33 [c]	10.50 [c]				
DL-Valine	9.603(2)	12.242(9)	7.10(1)	14.72(2)	8.30(1)	14.23(4)
	9.50 [a]					
L-Leucine	9.621(2)	12.266(6)	7.13(3)	14.36(7)	8.25(5)	14.14(9)
L-Isoleucine	9.652(4)	12.350(9)	7.02(3)	14.66(8)	8.26(1)	14.22(2)

[a] Ting Po and G. H. Nancollas, *Inorg. Chem.*, 1972, **11**, 2414. [b] M. Israeli and L. D. Pettit, *J. Inorg. Nucl. Chem.*, 1975, **37**, 999. [c] D. D. Perrin and I. J. Sayce, *J. Chem. Soc. A*, 1968, 53.

For phenylalanine and alanine the basicity order can also be explained in terms of different inductive effects. For the remaining simple amino-acids the order of increasing stability alanine > valine > leucine > isoleucine explains the increasing inductive effects in the series.

In all titrations with uranyl a light yellow coloured solution was produced. In spite of the almost constant concentration used and under identical experimental conditions, at a given pH all the complexes of uranium were more soluble than those of thorium and the solubility decreased as the alkyl chain increased in length thus providing a type of steric hindrance in the co-ordination. The solubility trend for uranyl α-amino-acids is in good agreement with the Cu^{II} amino-acids found by Graddon and Munday.[14] Their solubilities could be explained in terms of the interference between the alkyl chain in the molecules and the water molecules co-ordinated to the metal ion, both groups being normal to the plane of the chelate ring, causing dehydration of the ion and therefore a decrease in hydrophilic character and hence in solubility. From $\bar{n}$ values at the point at which precipitation commenced the order of solubility in the series of complexes studied was found to be: serine > threonine > alanine > cysteine > methionine > valine > isoleucine > leucine > phenylalanine.

Figure 1 shows the typical formation curves for mixtures of the amino-acids with uranyl and thorium ions. The irregularities in the formation curves of uranyl and thorium with D-methione are probably due to other equilibria. In the case of thorium there might be an intermediate complex with a ratio of three ligands to one thorium ion, or perhaps all the molecules of the amino-acids do not co-ordinate initially through all points of attachment. The slope of the formation curves of thorium with valine and isoleucine differ from the expected theoretical slope. However, the deviations are slight and the formation constants presented in Table 1 are probably no less reliable than the other constants given. The slope of the formation curves of uranyl with serine and threonine show no appreciable deviation from the theoretical slope for a 2 : 1 complex. However, the curves are somewhat unusual in that an $\bar{n}$ value of 2 is exceeded. The slight irregularities are probably due to the simple addition reaction to form a 2 : 1 complex. The formation curve for complexes of Th^{4+} with leucine seemed unusual probably because species other than [ML] and [ML_2] (H_2L = amino-acid) are formed in solution. Similarly the formation curves with methione as is shown in Figure 1(*d*) are not symmetrical when $\bar{n} \simeq 1$ due to the formation of precipitates. However, the constants were calculated by a least-squares treatment [11] and the experimental data always produced a good straight line with a high correlation coefficient.

Table 2. A quantitative comparison of log β_{HL} − log β_1

Ligand	log β_{HL} − log β_1	
	UO_2^{2+}	Th^{4+}
DL-Alanine	2.26	2.41
DL-Phenylalanine	2.39	1.32
D-Serine	0.5	0.91
DL-Threonine	2.38	1.82
D-Methionine	2.51	2.1
D-Cysteine	2.4	0.73
DL-Valine	2.5	1.3
L-Leucine	2.49	1.37
L-Isoleucine	2.63	1.39

The potentiometric titration curves for mixtures of the amino-acids with uranyl and thorium are shown in Figure 2. Stability constants derived from such titrations are summarised in Table 1. For thorium the stabilities with all ligands are shown to be higher than for uranyl. This could be attributed to two oxygen atoms already present on the uranyl ion and hence UO_2^{2+} has only four positions (in contrast to Th^{4+} with six) available for co-ordination with two ligand molecules. Rajan and Martell [15] have reported the formation of 1 : 1 complexes of UO_2^{2+} with iminodiacetic acid and no evidence for the presence of 2 : 1 complexes is given. In a later publication, Bogucki and Martell [16] demonstrated that 1 : 2 complexes of Th^{4+} with methyliminodiacetic acid or nitrilotriacetic acid are formed and a possible co-ordination of eight has been suggested for Th^{4+}.

A quantitative comparison of the values for log β_{HL} − log β_1 given in Table 2 correlates the affinity of the ligands for the metal ions relative to that of protons. A comparison of the results for serine and α-alanine shows the expected increase in stabilities of uranyl and thorium with serine, presumably caused by the additional chelate ring provided by a hydroxy-group. The contribution of the oxygen donor atom of the hydroxy-group in serine is very pronounced in the case of the uranyl chelate but is only very small in the thorium chelate. Thermodynamic studies for complexes of the transition-metal ions with both serine and threonine as well as α-alanine and

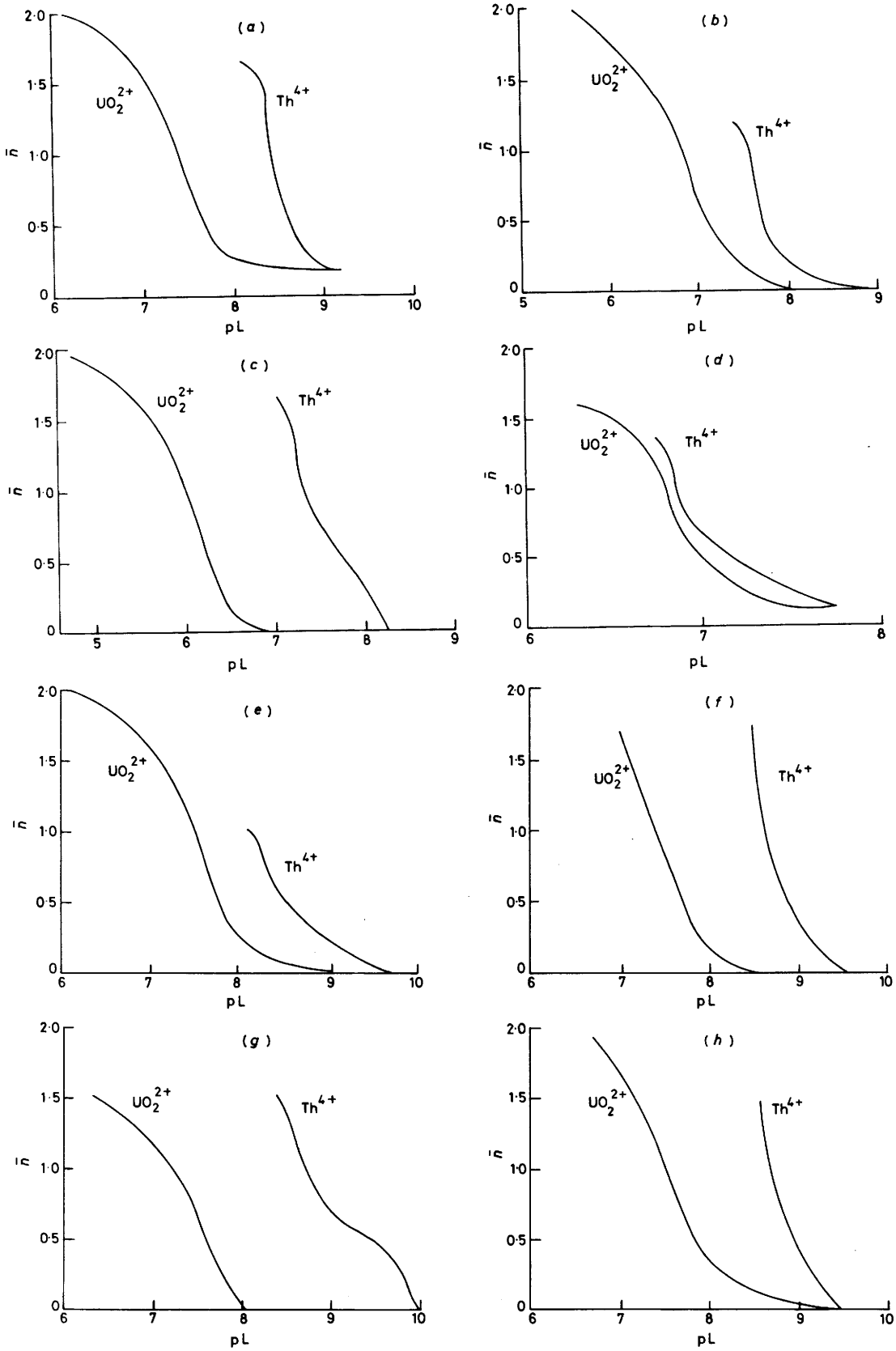

Figure 1. Formation curves for complexes (25 °C) of (*a*) D-serine, (*b*) DL-threonine, (*c*) D-cysteine, (*d*) D-methionine, (*e*) DL-alanine, (*f*) DL-valine, (*g*) L-leucine, and (*h*) L-isoleucine where $\bar{n}$ = degree of formation, defined as the average number of ligand molecules bound per mole of metal and pL = − log [L], where [L] is the free ligand concentration

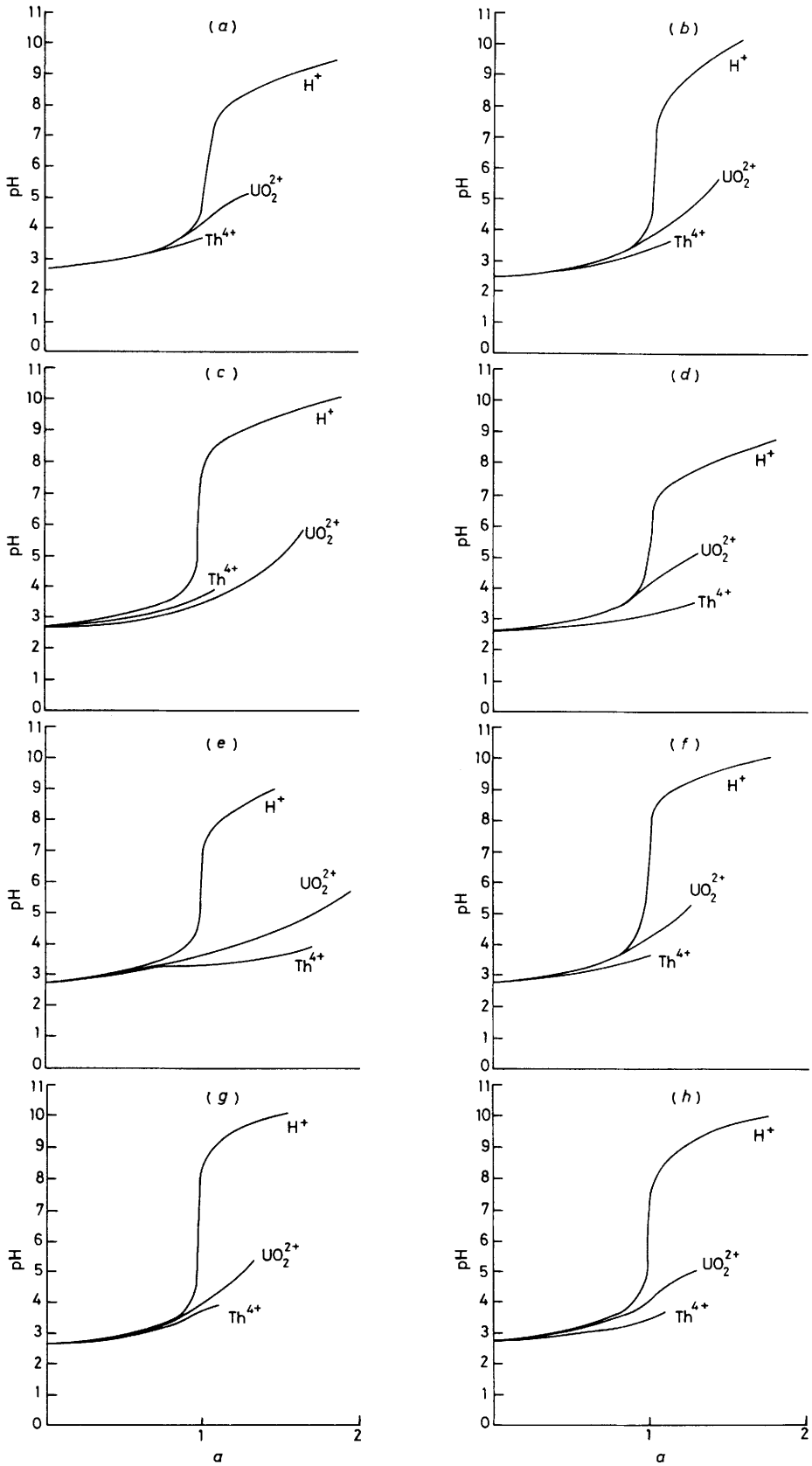

Figure 2. Titration curves in the absence and presence of UO_2^{2+} and Th^{4+} at 25 °C for (*a*) D-serine, (*b*) DL-threonine, (*c*) DL-valine, (*d*) D-cysteine, (*e*) D-methionine, (*f*) L-isoleucine, (*g*) DL-alanine, and (*h*) L-leucine, where *a* is the number of moles of OH^- added per mole of acid (ligand)

α-aminobutyric acid reported by Sharma and Mathur [17] showed lower enthalpy changes and higher entropy changes for the former system than for the latter, *i.e.* stronger bonding with serine and threonine. Nevertheless, confirmation of the non-involvement of the hydroxy-group in co-ordination with metal ions is available from the proton magnetic resonance studies of Cd^{2+} complexes of serine.[18] On the basis of potentiometric data alone, it is not possible to determine if extra bonding occurs between the hydroxy-group of the ligand. However, as a result uranyl and thorium ions are generally classified as ' hard ' in character and should show a marked preference to bond with ^{-}OH (classified as hard donor group). As could be expected the ' soft ' Cd^{2+} or some transition-metal ions may be borderline and should behave differently to the two metal ions studied here.

Compared with alanine, the phenyl derivative forms weaker chelates with metal ions due to the decrease in basicity of the ligand and steric hindrance caused by the phenyl group. From Table 2 values for cysteine particularly in the case of Th^{4+} are lower than those of methionine. It is clear that a mercapto-sulphur (as found in the sulphydryl group) co-ordinates far more strongly to the metals than the sulphide sulphur found in methione.

As a general conclusion, the stabilities of all ligands studied in this work follow the order found for protonation. Evidence suggests limited chelation through sulphur but much stronger chelation through an oxygen atom.

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