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Formation of Mixed Ligand Complexes of Gd(III), Th(IV) and UO_2^{2+} Cations with NTA and Dicarboxylic Acids

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Abstract

The stability constants have been measured in 0.10 M ($NaClO_4$) ionic strength solution at 25 °C for the reaction:

$MX + L = MXL$

where $M = Gd^{3+}$, UO_2^{2+} and Th^{4+}, X = nitrilotriacetate and L = malonate, succinate, gluturate and adipate. These stability constants, for a particular L, follow the order:

$ThXL > UO_2XL > GdXL$

For the different ternary ligands, the stability constants for all three metals decrease from malonate to succinate to glutarate while those for glutorate and adipate are roughly equal for each metal. The results are discussed in terms of formation by the ternary ligand L of monodentate or bidentate complexes.

Introduction

The presence of mixed ligand complexes of the general type $MX_n \cdot Y_m$ in biochemical and in analytical systems has stimulated interest in the factors involved in formation of such species. The trivalent lanthanides and Th(IV) are attractive for such studies due to their high charge and their large and variable coordination numbers as well as the ionic nature of the metal–ligand bonding. Uranyl, UO_2^{2+}, has similar ionic bonding to ligands but restricts coordination to the equitorial plane of the linear dioxo cation. Thus, charge and steric effects as well as statistical probabilities can be studied with these cations and properly chosen ligand systems.

Mixed ligand complexation of the lanthanides has been studied previously [1, 2] but usually with chelating ligands of high dentation – e.g., aminopolycarboxylates such as EDTA (ethylenediaminetetraacetic acid) with $CN = 6$, with smaller aminocarboxylates such as IDA (iminodiacetic acid) with $CN = 3$, and NTA (nitrilotriacetic acid) with $CN = 4$. Some of these same complexes were studied by NMR [3a] and optical spectrometry [3b]. Uranyl and thorium mixed ligand formation has been studied even less (e.g. refs. 4–6). Unfortunately, these earlier studies do not provide a sufficiently common data base for comparison of such effects as coordination number, cationic charge, etc.

In this paper we report the stability constants for formation of MXY complexes of Sm(III), Th(IV) and UO_2^{2+} where X = NTA (nitrilotriacetate) and Y = dicarboxylate. The binary complexation of metal–dicarboxylate ligands has been studied earlier [7–9], allowing comparison with the mixed ligand complexation.

Experimental

Reagents and Solutions

The gadolinium oxide, Gd_2O_3, was dissolved by repeated heating to fuming in perchloric acid. A stock solution of the resulting samarium perchlorates was adjusted to pH 3–4. Working solutions, prepared by dilution from the stock solution were assayed by titration with EDTA using xylenol orange as the indicator and hexamethylenetetramine as a buffer.

The stock solutions of thorium perchlorate were prepared by heating $Th(NO_3)_4$ (Alfa) to fuming in perchloric acid followed by dilution. The concentration of Th(IV) was determined by EDTA titration. The uranyl solutions were prepared similarly from reagent grade uranyl nitrate (Fisher). The concentration of UO_2^{2+} was measured by the Jones reductor method.

Nitrilotriacetic acid and the dicarboxylic acids were dissolved and the concentration determined by titration with standard NaOH solution. All chemicals were reagent grade and deionized distilled water was used for all solutions. $NaClO_4$ was used as the inert electrolyte to adjust all solutions to an ionic strength of 0.10 M. Adjustement of pH was accomplished with NaOH or $HClO_4$.

Procedures

The potentiometric titrations were performed with a PHM 84 Research pH Meter using a combina-

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tion electrode. The pH meter was calibrated with standard buffer solutions of pH 7.000 and 4.000. The solution in the reaction vessel contained metal ions and NTA in 1:1 ratio plus malonic acid. A 0.06 M sodium hydroxide titrant solution was delivered to the reaction vessel from a microburette. The potentiometric titrations were conducted at 298 K and a constant ionic strength of 0.10 M ($NaClO_4$).

The pK_a values for malonic acid from the literature [10] were used in these calculations. These values were: $pK_1 = 2.61$; $pK_2 = 5.27$. The analogous values at $I = 0.10$ M had been determined previously [11] and were used. They were: succinic acid, $pK_1 = 4.00$, $pK_2 = 5.24$; glutaric acid, $pK_1 = 4.13$, $pK_2 = 5.04$; adipic acid, $pK_1 = 4.26$, $pK_2 = 5.03$. The stability constants for the mixed ligand complexation of MNTA (M = Th, UO_2, Sm) with malonate were calculated from mass balance expressions using a non-linear least-squares treatment of data with a computer program developed in this laboratory. Although the pH range for the potentiometric titrations was 3.5–5.5, no correction was necessary for hydrolysis of Th(IV) as the NTA complexation was essentially 100%.

Results and Discussion

Table I is a typical set of potentiometric data. In some titrations, the $\bar{n}$ values exceeded 0.5 and the formation of $M(NTA)L_2$ was included in the data analysis. This yielded more consistent values of K_{MXL} for runs of different maximum $\bar{n}$. However, the values of K_{MXL_2} in these analyses had such large uncertainties that they are not reported. Table II lists the averaged stability constants where

$$K_{MXL} = [MXL]/[MX][L] \tag{1}$$

and X = NTA, L = malonate, succinate, glutarate and adipate. Also included for comparison in Table II are values of K_{ML} where

$$K_{ML} = [ML]/[M][L] \tag{2}$$

The value of log K_{ML} for Gd–malonate was interpolated from those of neighboring lanthanides reported in ref. 10. The other Gd(III) values for log K_{ML} are from ref. 11. For UO_2–glutarate, the value was estimated from values at 0.5 M ionic strength for the glutarate and adipate complexes and 0.1 M for the adipate [15]. No values at 0.1 M ionic strength were available for the thorium complexes, and at 1.0 M only for the malonate and succinate complexes [9]. A modified Born equation (which was calibrated with the uranyl systems at 1.0 M and 0.1 M and the thorium 1.0 M values) was used to calculate the values listed for the thorium complexes. Also given in Table II are the values of Δ defined as:

$$\Delta = \log K_{ML} - \log K_{MXL} \tag{3}$$

Since the NTA ligands occupy 4 coordination sites of the metals, the probability of complexation of a ligand is less than for the simple metal cation. The statistical effect for such partial occupancy of coordination sites has been developed by Bjerrum [12, 13]. If total coordination numbers of 6, 8 and 9 are assigned to UO_2^{2+}, Gd^{3+} and Th^{4+}, respectively, [16], a correction of 0.3 for Gd^{3+} and Th^{4+} and 0.5 for UO_2^{2+} should be applied to the log K_{MXL} values. These corrections are significantly less than the observed differences, Δ, in the log K_{ML} and log K_{MXL} values.

The pattern of stability in ternary complex formation is the same as in binary complexation; *i.e.*, malonate > succinate > glutarate ≈ adipate. This

TABLE I. Potentiometric Data for $UO_2(NTA)^{1-}$ + Adipate Ligand. $T = 298$ K; $I = 0.10$ M ($NaClO_4$)[a]

Titrant volume (ml)	pH	$[L] \times 10^4$ (M)	$\bar{n}$
11.6	3.809	0.551	0.005
12.0	3.886	0.735	0.043
12.4	3.951	0.958	0.078
12.8	4.031	1.242	0.113
13.2	4.097	1.558	0.149
13.6	4.164	1.952	0.177
14.0	4.226	2.382	0.208
14.4	4.289	2.903	0.232
14.8	4.349	3.475	0.259
15.2	4.409	4.133	0.281
15.6	4.467	4.848	0.305

[a] Conditions: $[UO_2(NTA)^-] = 0.002007$ M, volume = 25 ml, $[L^2]_i = 0.008005$ M, titrant = 0.02992 M NaOH, $[H^+]_i = 0.02832$ M.

TABLE II. Stability Constants for Formation of ML and M(NTA)L Complexes. $T = 298$ K; $I = 0.10$ M ($NaClO_4$)

M	L			
	Malonate	Succinate	Glutarate	Adipate
Gd(III) log K_{ML}[a]	4.45	3.42	3.19	3.09
log K_{MXL}[a]	2.74	2.25	2.23	2.34
Δ	1.7	1.2	1.0	0.8
UO_2^{2+} log K_{ML}[b]	5.56	4.48	4.07	4.08
log K_{MXL}[a]	4.29	3.23	2.85	2.98
Δ	1.4	1.3	1.2	1.1
Th log K_{ML}[c]	8.35	7.00	6.60	6.50
log K_{MXL}[a]	4.81	4.68	4.10	4.13
Δ	3.5	2.4	2.5	2.4

[a] Estimated uncertainty ±0.04. [b] Estimated uncertainty ±0.05. [c] Estimated uncertainty ±0.10.

sequence was interpreted [11] in the binary complexes as due to the loss of stability with increasing size of the metal–dicarboxylate ligand chelate ring. Presumably, in the ternary complexes, the sequence of stabilities has the same explanation. Alternately, the lower stability may be related to the ligand functioning in monodentate fashion.

If these dicarboxylate ligands are binding as monodentate species in the ternary complexes, the $\log K_{MXL}$ should be expected to follow the sequence of $pK_{a(1)}$; *i.e.*

$$\text{Mal} \approx \text{Suc} > \text{Glu} \approx \text{Adi}$$

Since $\log K_{MXL}$ for the malonate systems is larger with Gd(III) and UO_2^{2+} than for the succinate value, assignment of bidentation to the malonate systems is reasonable. The mode of binding of the other dicarboxylates in the ternary complexes is not readily assigned from this simple pK_a sequence. Moreover, with Th(IV), even for malonate some question exists since the Δ is so large and $\log K_{MXL}$ is not very different between the malonate and succinate systems.

Another test of the mode of binding is to compare $\log K_{MXL}$ with corresponding values for binary complexation with a monodentate ligand such as acetate. Again, the literature does not provide $\log \beta_{MOAc}$ (OAc = acetate) data in 0.10 M ($NaClO_4$) medium. From the available values, reasonable estimates can be obtained but these must be further adjusted to account for the weaker basicity ($pK_a = 4.6$) of acetate compared to that of the more basic carboxylate ($pK_a = 5.4$–5.7) of the dicarboxylates [16]. The estimated values and the statistically corrected $\log K_{MXL}$ values are shown in Fig. 1. From the relationship of the acetate and the ternary stability constants in this figure, it seems probable that the thorium forms monodentate complexes with all the dicarboxylates. The malonate complexation is probably bidentate in the gadolinium and uranyl systems as is the succinate in the uranyl ternary complex. In the other systems, the correlation in Fig. 1 indicates monodentation of the dicarboxylate ligand.

These conclusions are not readily explainable. Gd(III) and Th(IV) have comparable ionic radii and coordination numbers. The greater ionic charge of Th(IV) would be expected to enhance the attraction to the ternary ligand. While $\log \beta_{ThXL} > \log \beta_{GdXL}$, Δ_{ThXL} is also much larger, reflecting a greater decrease in stability compared to the binary systems. Since there is no obvious steric limitation to ternary bidentate complexation for Th(IV) one possible cause would be the presence of Th(NTA)(OH) at the pH of the experiments. If we assume that $\log \beta_{ThXL} \approx \log \beta_{ThOAc}$ for glutarate and adipate, we can estimate the required value of the hydrolysis constant of the $Th(NTA)^{1+}$ species. Such an estimation gives a value of *ca.* 10^9 which is similar to that of Th^{4+}. Consequently, hydrolysis of $Th(NTA)^{1+}$ does not seem able to account for the surprisingly weak ternary complexation of Th(IV).

Another possibility to account for decreased stability is the presence of steric effects. These would not be anticipated between cations of similar radii and coordination number. Of our three cations, the dioxo uranyl might be expected to be more likely to exhibit steric inhibition to chelation in the ternary complex. However, as shown in Fig. 1, $UO_2(NTA)L^{3-}$ has greater stability relative to the binary acetate complexes than the other metals.

The entropy values for formation of these ternary complexes could be helpful in understanding these stability patterns. Unfortunately, solubilities limit calorimetric measurements of some of these systems but those which have sufficient solubility are being studied presently.

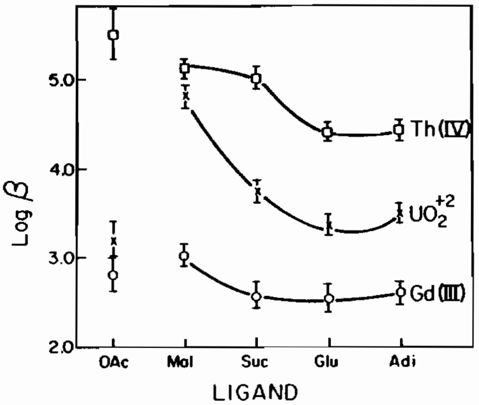

Fig. 1. Correlation of log β for formation of the reaction of M(NTA) + X, where X = acetate (OAc), malonate (Mal), succinate (Suc), glutarate (Glu) and adipate (Adi).

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