The Interaction of Thorium(IV) with Pyrocatechol-3, 5-disulfonate at a 1 : 1.5 Molar Ratio

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In a previous paper[1] potentiometric measurements were reported on the chelating behavior of pyrocatechol-3, 5-disulfonate toward thorium(IV) ion at various molar ratios of ligand to metal ion. For ligand to metal ratios of 1.5 : 1 or higher the formation of a unique chelate of 1.5 : 1 ratio was observed, regardless of the amount of excess ligand present. The nature of this chelate was established by spectrophotometric measurements as well as by extraction[2] and ultracentrifugation[3] studies. The present work consists of a detailed study of the 1 : 1.5 thorium(IV) - pyrocatechol-3, 5-disulfonate system by means of potentiometric measurements to clarify the nature of the dinuclear thorium chelate.

Experimental

Materials.—Disodium pyrocatechol-3, 5-disulfonate (Tiron) was purchased from LaMotte Chemical Products Co., Baltimore, Md., U. S. A. and used without further purification. An aqueous stock solution of this ligand was standardized by potentiometric titration with standard base. Reagent grade thorium nitrate tetrahydrate, $Th(NO_3)\cdot 4H_2O$, purchased from Allied Chemical and Dye Corp., N. Y., was standardized gravimetrically and used to make up a stock solution for use in potentiometric titration.

Potentiometric Measurements. — A Beckman Model GS pH meter equipped with extension glass and calomel electrodes was used to measure hydrogen ion concentration directly. Calibration of the pH meter was performed by the aid of acetic acid buffer as well as standard hydrochloric aicd and sodium hydroxide. Measurements were carried out at 25.0±0.05°C in a jacketed titration cell fitted with a magnetic stirrer, nitrogen inlet and outlet tubes, microburet delivery tube and electrodes. In all titrations the ionic strength was maintained at approximately 0.10 M with potassium nitrate, and a nitrogen atmosphere was maintained.

Results and Discussion

Potentiometric titration curves obtained at three different concentrations for the thorium(IV)-pyrocatechol-3, 5-disulfonate chelate system of a 1.5 : 1 molar ratio of ligand to metal ion are shown in Fig. 1. A sharp inflection region was observed at $m=3.0$ as has been previously observed for chelate systems of higher ligand to metal ratio.[1] On the basis of the rapid equilibria observed in the first buffer region, a simple reaction process is proposed for this range. Since the value of $([H^+]+T_{OH})/T_M$, the number of protons liberated per mole of total thorium species, already exceeds 2.0 at the start of titration, it may be concluded that the 1 : 1 metal chelate is nearly completely formed at this point. Thus, the predominant reaction, which proceeds in the buffer region lying below $m=3.0$, may be represented as:

$$2ThL + H_2L \rightleftarrows Th_2L_3 + 2H^+$$

$$K_D = \frac{[Th_2L_3][H^+]^2}{[ThL]^2[H_2L]} \tag{1}$$

The stoichiometric relations involved in this system[*1] are:

$$T_M = [ThL] + 2[Th_2L_3] \tag{2}$$

$$T_L = [ThL] + 3[Th_2L_3] + [H_2L] \tag{3}$$

$$T_{OH} + [H^+] = 2[ThL] + 6[Th_2L_3] \tag{4}$$

where T_M and T_L represent the total analytical concentration of the metal species and of the ligand species present in a solution, while T_{OH} is the analytical concentration of the hydroxide ions added to a solution during the titrations. Combination and rearrangement of Eqs. 2 through 4 gives expressions for $[Th_2L_3]$, $[ThL]$ and $[H_2L]$ in terms of the measurable or known quantities m, $[H^+]$ and T_M. When these relations are introduced into Eq. 1, the equilibrium constant K_D may be expressed as:

$$K_D = \frac{\{(m-2)T_M+[H^+]\}[H^+]^2}{\{(3-m)T_M-[H^+]\}^3} \tag{5}$$

The logarithm of this equilibrium constant (log K_D) was calculated as 0.89.

In contrast to the first buffer region, the rate of attaining equilibrium was found to be extremely slow in the second buffer region ranging from 3.0 to 4.0. In addition, from the appearance of a second inflection at around $m=4.0$, it is assumed that a simple intramolecular olation reaction takes place

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[1] Y. Murakami and A. E. Martell, *J. Am. Chem. Soc.*, **82**, 5605 (1960).

[2] R. F. Bogucki, Y. Murakami and A. E. Martell, ibid., **82**, 5608 (1960).

[3] R. L. Gustafson and A. E. Martell, ibid., **82**, 5610 (1960).

[*1] Recently, a probable structural formula was presented for the 2 : 3 thorium(IV) - pyrocatechol-3, 5-disulfonate chelate by Martell at the Symposium on Coordination Chemistry, held at Tihany, Hungary, Sept. 14—17, 1964. In his structure the phenoxide groups of Tiron act as bridging components with the retention of high symmetry of a molecule.

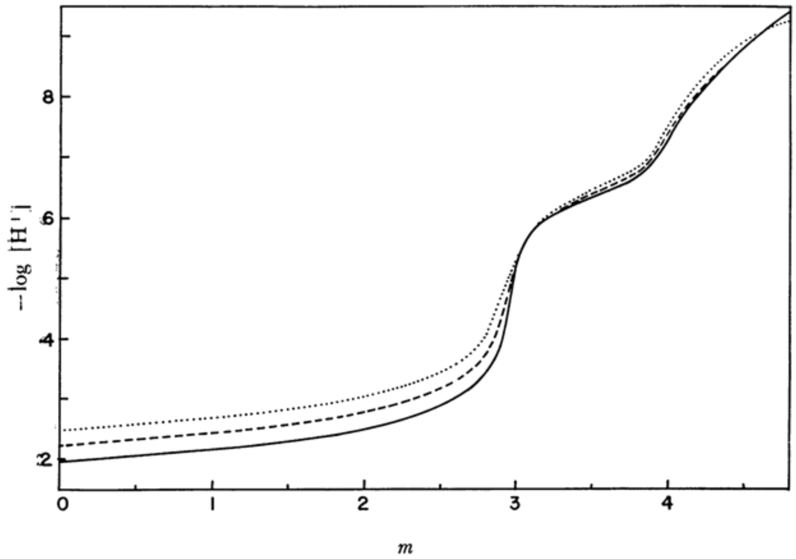
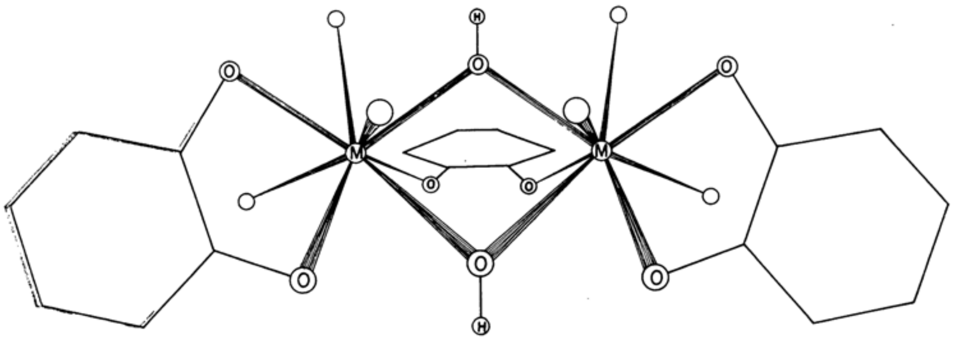


Fig. 1. Potentiometric titration of thorium(IV)-pyrocatechol-3, 5-disulfonate chelate system in 0.10 M KNO_3 at 25°C, with 1.5 : 1 molar ratio of ligand to metal ion at total thorium concentrations of: A, 5.15×10^{-3} M; B, 2.58×10^{-3} M; C, 1.29×10^{-3} M; m=moles of base added per gram-ion of metal. —— A; ---- B; ···· C



I ○, H_2O; Ⓜ, Th

TABLE I. EQUILIBRIUM RELATIONSHIPS FOR Th(IV) CHELATES AT 25°C, μ=0.10 (KNO_3)

Ligand	Type formula	Equilibrium constant	
		Quotient	Log K
EDTA[4]	H_4L	$[ThL]/[ThL(OH)][H^+]$	7.04 ± 0.05
		$[ThL]^2/[Th_2L_2(OH)_2][H^+]^2$	9.82 ± 0.05
		$[Th_2L_2(OH)_2]/[ThL(OH)]^2$	4.3 ± 0.1
CDTA[4]	H_4L	$[ThL]/[ThL(OH)][H^+]$	7.58 ± 0.05
		$[ThL]^2/[Th_2L_2(OH)_2][H^+]^2$	10.84 ± 0.05
		$[Th_2L_2(OH)_2]/[ThL(OH)]^2$	4.3 ± 0.1
Tiron	H_2L	$[Th_2L_3]/[Th_2L_3(OH)_2][H^+]^2$	12.8 ± 0.1
		$[ThL]^2[H_2L]/[Th_2L_3(OH)_2][H^+]^4$	11.9 ± 0.1

EDTA: ethylenediaminetetraacetic acid
CDTA: 1, 2-diaminocyclohexanetetraacetic acid

in the second buffer region.[*2] Thus, the simple dissociation type reaction assumed for this region is:

$$\mathrm{Th_2L_3} \rightleftarrows \mathrm{Th_2L_3(OH)_2} + 2\mathrm{H}^+$$

$$K_{\mathrm{D(OH)_2}} = \frac{[\mathrm{Th_2L_3(OH)_2}][\mathrm{H}^+]^2}{[\mathrm{Th_2L_3}]} \tag{6}$$

Stoichiometric relations consistent with Eq. 6 are:

$$T_{\mathrm{M}} = 2[\mathrm{Th_2L_3(OH)_2}] + 2[\mathrm{Th_2L_3}] \tag{7}$$

$$T_{\mathrm{OH}} + [\mathrm{H}^+] - [\mathrm{OH}^-] = 2[\mathrm{Th_2L_3(OH)_2}] \tag{8}$$

Since $[\mathrm{H}^+]-[\mathrm{OH}^-]$ may be neglected in this pH region, the expression for the equilibrium constant $K_{\mathrm{D(OH)_2}}$ simplifies to:

$$K_{\mathrm{D(OH)_2}} = m'[\mathrm{H}^+]^2/(1 - m') \tag{9}$$

where $m' = m - 3$.

At the half-neutralization point $(m' = 1/2)$, the equilibrium constant becomes equal to the square of the hydrogen ion concentration. Although the present titration data do not provide an equilibrium constant of high accuracy for the above-assumed reaction, an approximate value has been obtained by use of Eq. 9. The estimated constant is given in Table I together with values for the EDTA and the CDTA chelate systems.(4) The dimeric thorium-(IV) - pyrocatechol-3, 5-disulfonate chelate may be considered at least qualitatively to show an olation tendency similar in magnitude to the other thorium chelates listed in Table I. A probable structure for the reaction product (I) is quite similar to that proposed for the ethylenediaminetetraacetate and the 1, 2-diaminocyclohexanetetraacetate chelates of thorium.(4)

In the second inflection region lying beyond $m=4.0$, reaction equilibrium was reached extremely slowly. Therefore, further rearrangement and disproportionation reactions of the chelate formed in the second buffer region presumably take place with the participation of hydroxide ions.

[*2] These experimental data do not eliminate the possibility of olation-polymerization through which the 2 : 3 Th(IV) - pyrocatechol-3, 5-disulfonate chelate further polymerize with hydroxide ions as bridging components. Further detailed studies on the 1 : 1.5 titration curve in much wider concentration range would help to clarify such an interaction.

4) R. F. Bogucki and A. E. Martell, *J. Am. Chem. Soc.*, **80**, 4170 (1958).