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Zirconium Complexes in Aqueous Solution. III. Estimation of Formation Constants[1]

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Data obtained from potentiometric titration of the zirconium–ethylenediaminetetraacetate 1:1 (Zr–EDTA 1:1) chelate at different concentrations were used to estimate the dimerization constant, K_D, and hydrolysis constant, K_a, of the monomeric chelate. Potentiometric data were also used to determine equilibrium constants for the reaction of disodium 1,2-dihydroxybenzene-3,5-disulfonate (Tiron) with the Zr–EDTA 1:1 chelate to form the Zr–EDTA–Tiron 1:1:1 chelate. Spectrophotometric measurements were used to estimate the formation constant of the zirconium–Tiron 1:1 and zirconium–nitrilotriacetate 1:1 chelates and to set limits on the Zr–EDTA 1:1 chelate formation constant. Some data are reported for the corresponding hafnium chelate systems.

Introduction

The elucidation of the behavior of zirconium(IV) salts in aqueous solution requires a knowledge of the species present in solution and the equilibrium constants for the predominant reactions. Unfortunately, zirconium salts undergo extensive hydrolysis in water as well as slow polymerization and aging reactions. The result is that a variety of possible ionic forms must be considered, and the actual species present are not easily ascertained. In the formation of zirconium complexes in which the metal ion is not completely coordinated, which is the subject of this investigation, hydrolysis and polymerization should still be the main reactions. However, in compounds of this type the number of probable hydrolyzed species, as well as the tendency for these species to undergo polymerization, should be substantially reduced.

In previous publications[3,4] a number of simple and mixed zirconium chelate systems, some of which showed stability at high pH, have been reported. In this paper, an estimation is made of equilibrium constants for some of the previously reported reactions.

Experimental

The detailed procedure used in carrying out the potentiometric measurements has been reported previously.[3,4] In brief, titrations were carried out at 24.7 ± 0.05° at 0.01 M ionic strength (potassium chloride) under purified nitrogen.

Spectrophotometric Measurements.—Equilibrium studies of the competition reactions between zirconium(IV) (or hafnium(IV)) and iron(III) for the ligands ethylenediaminetetraacetic acid (EDTA), nitrilotriacetic acid (NTA), and disodium 1,2-dihydroxybenzene-3,5-disulfonate (Tiron) were made with the aid of spectrophotometric measurements.

Spectral measurements in the ultraviolet and visible regions were made with a Cary recording spectrophotometer (Model 14-PM). A 0.10-cm. light path was used for measurements in the ultraviolet region, and a 1.0-cm. path was used for the visible region; in each case the reference cell was filled with 0.10 M potassium chloride solution.

Stock solutions of the ligands and of the zirconium(IV) and hafnium(IV) chlorides were the same as those used for the potentiometric measurements. In addition, a ferric chloride solution (0.2 M in Fe(III) and 1.2 M in H^+) was prepared from reagent grade ferric chloride and hydrochloric acid. The iron(III) content of this stock solution was determined by titration with EDTA in the presence of 5-sulfosalicylic acid as indicator.[5]

Solutions of Fe(III) and of the Fe(III) chelate were first made up at various concentrations to establish the applicability of Beer's law in the concentration range of interest. Measured amounts of ferric chloride stock solution (and of the ligand if the chelate was being prepared), potassium chloride, and distilled water were placed in the titration cell described previously.[3] Base was added slowly to adjust the acidity to $-\log [H^+] = 2.00$ and μ to 0.10. Each mixture was immediately transferred to a brown bottle which was wrapped with opaque paper and stored in the dark until the spectra were run (usually within 2 hr.). After a suitable wave length for each competition study was found (2575 Å. for EDTA systems, 3000 Å. for NTA systems, and 6175 Å. for Tiron), measurements were made at fixed wave length with the recorder chart drive running. Drifts in optical density values could thus be ascertained, and an estimate of the precision of the reading could be made. Except in cases where small drifts were due to photochemical decomposition, optical density values varied by no more than 0.005 optical density unit. Where drifts were observed, the initial optical density was read, and measurements were repeated to check accuracy.

Solutions for the competition experiments were prepared in a similar manner. To determine if equilibrium had been established, three separate experiments were made for the 1:1:1 mole ratio of zirconium(IV) to iron(III) to ligand. In the first experiment, iron and zirconium stock solutions were placed in the cell and the ligand was added thereafter. The final composition of this solution is a function of the relative rates of formation of the corresponding iron(III) and zirconium chelates. In the second and third experiments, the orders of reagent addition were zirconium, ligand, iron and iron, ligand, zirconium. These latter experiments correspond to approaching equilibrium from both directions. The optical densities of these three solutions were the same within experimental error for the competition experiments with zirconium(IV) (or hafnium(IV)) and NTA, and with zirconium and Tiron, showing that equilibrium had been established. On the other hand, the competition of iron and zirconium (or hafnium) for EDTA showed widely divergent optical densities for these experiments, and equilibrium was approached very slowly. In this case, it was therefore only possible to set limits on the equilibrium constant, on the basis of optical density values obtained from approaching equilibrium from both directions. Additional experiments were also carried out at different mole ratios of iron, zirconium, and ligand, to check on the constancy of the equilibrium constants.

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[3] B. J. Intorre and A. E. Martell, *J. Am. Chem. Soc.*, **82**, 358 (1960).

[4] B. J. Intorre and A. E. Martell, *ibid.*, **83**, 3618 (1961).

[5] P. B. Sweetser and C. E. Bricker, *Anal. Chem.*, **26**, 195 (1954).

Mathematical Treatment of Data

Addition of Tiron to the 1:1 Zr–EDTA Chelate.—Data for the 1:1:1 Zr–EDTA–Tiron chelate compound may be tested for fit with various simple mathematical models. Data taken from the buffer region of titrations over the concentration range 1.7×10^{-3} to 5.2×10^{-3} M could be fitted with a model which assumes formation of a dimer in a two-step reaction

$$\mathrm{ML} + \mathrm{H_2A^{2-}} \longrightarrow \mathrm{MLHA^{3-}} + \mathrm{H^+}$$
$$2\mathrm{MLHA^{3-}} \longrightarrow \mathrm{(MLA)_2^{8-}} + 2\mathrm{H^+}$$

where ML is the 1:1 Zr–EDTA chelate and $\mathrm{H_2A^{2-}}$ represents Tiron.

From material balance and electroneutrality considerations

$$T_{\mathrm{ML}} = [\mathrm{ML}] + [\mathrm{MLHA^{3-}}] + 2[(\mathrm{MLA})_2{}^{8-}]$$
$$(m - 2)T_{\mathrm{ML}} + [\mathrm{H^+}] = [\mathrm{MLHA^{3-}}] + 4[(\mathrm{MLA})_2{}^{8-}]$$

Mass action expressions may be written for the two chemical equations above relating to this two-step dimer model

$$K_1 = \frac{[\mathrm{MLHA^{3-}}][\mathrm{H^+}]}{[\mathrm{ML}][\mathrm{H_2A^{2-}}]}$$
$$K_2 = \frac{[\mathrm{H^+}]^2[(\mathrm{MLA})_2{}^{8-}]}{[\mathrm{MLHA^{3-}}]^2}$$

There are only four equations but five unknowns, [ML], $[\mathrm{MLHA^{3-}}]$, $[(\mathrm{MLA})_2{}^{8-}]$, K_1, and K_2. By algebraic substitution, $[\mathrm{MLHA^{3-}}]$ and $[(\mathrm{MLA})_2{}^{8-}]$ may be expressed in terms of [ML], and each species may be expressed conveniently as fractions of T_{ML}. These equations may be solved for K_1 and K_2 at each experimental point by treating [ML] as a parameter and assigning it successive values of 0, $0.1T_{\mathrm{ML}}$, $0.2T_{\mathrm{ML}}$, ...$1.0T_{\mathrm{ML}}$. The series of values of K_1 and K_2 obtained for each experimental point are plotted. If the curves obtained intersect at a unique point, then the values of K_1 and K_2 at that point represent the solution of these simultaneous equations. If the same values of K_1 and K_2 are obtained from titration curves carried out at different concentrations, then one may conclude that this model fits the experimental data.

Dimerization of the Zr–EDTA 1:1 Chelate.—In a recent publication, Bogucki and Martell[6] have shown the existence of a thorium–EDTA dimer. Their mathematical approach, which is based upon a simple model, may be applied without modification to the zirconium–EDTA 1:1 system. The essential points of their method follow, in slightly different notation.

The formation of a monohydroxo chelate species may be represented as

$$\mathrm{ML} \rightleftharpoons \mathrm{MOHL^-} + \mathrm{H^+};\; K_{\mathrm{a}} = \frac{[\mathrm{H^+}][\mathrm{MOHL^-}]}{[\mathrm{ML}]} \quad (1)$$

where ML represents the normal 1:1 chelate. Dimer formation may be represented by

$$2\mathrm{ML} \longrightarrow \mathrm{M_2(OH)_2L_2{}^{2-}} + 2\mathrm{H^+};\; K_{\mathrm{D}} = \frac{[\mathrm{H^+}]^2[\mathrm{M_2(OH)_2L_2{}^{2-}}]}{[\mathrm{ML}]^2} \quad (2)$$

If the aquo chelate, ML, the monohydroxo chelate, $\mathrm{MOHL^-}$, and the dimer, $\mathrm{M_2(OH)_2L_2{}^{2-}}$, are the only significant species, it follows from material balance considerations that

$$T_{\mathrm{M}} = [\mathrm{ML}] + [\mathrm{MOHL^-}] + 2[\mathrm{M_2(OH)_2L_2{}^{2-}}] \quad (3)$$

where T_{M} is the total concentration of metal chelate in all of its forms. Beyond $m = 2$ (m = moles of base added per mole of metal ion), one may deduce from electroneutrality requirements that

$$(m - 2)T_{\mathrm{M}} + [\mathrm{H^+}] = [\mathrm{MOHL^-}] + 2[\mathrm{M_2(OH)_2L_2{}^{2-}}] + [\mathrm{OH^-}] \quad (4)$$

Combination of the above equations gives

$$\frac{(m - 2)T_{\mathrm{M}} + [\mathrm{H^+}]}{[\mathrm{ML}]/[\mathrm{H^+}]} = \frac{[\mathrm{MOHL^-}]}{[\mathrm{ML}]/[\mathrm{H^+}]} + \frac{2K_{\mathrm{D}}[\mathrm{ML}]}{[\mathrm{H^+}]} \quad (5)$$

where the concentration of hydroxyl ion has been neglected since the regions of interest in the titration curve lie in the pH range 5 to 7.

A plot of $[\mathrm{H^+}]((m - 2)T_M + [\mathrm{H^+}])/[\mathrm{ML}]$ *vs.* $[\mathrm{ML}]/[\mathrm{H^+}]$ should give a straight line with a slope equal to $2K_{\mathrm{D}}$ and an intercept at $[\mathrm{ML}]/[\mathrm{H^+}] = 0$ equal to K_{a}, if a dimer is the predominant species. Likewise, it can be shown that a plot of $[\mathrm{H^+}]((m - 2)T_{\mathrm{M}} + [\mathrm{H^+}])/[\mathrm{ML}]$ against $[\mathrm{ML}]^2/[\mathrm{H^+}]^2$ should give a straight line if a trimer is the predominant species.

Spectral Competition Studies.—A convenient method of determining formation constants of metal chelates involves the competition of two metal ions for a ligand, where one of the metal chelates has a strong absorption peak either in the visible or ultraviolet region of the spectrum, with an extinction coefficient much different from that of the free metal ion. A further requirement for accuracy is that the equilibrium constant for the competition reaction must not be very small or very large. These requirements are fulfilled in competition experiments between zirconium(IV) (or hafnium(IV)) and iron(III) for the ligands NTA, EDTA, or Tiron.

The formation constants of zirconium(IV) and iron(III) chelates formed from the metal ion and the ligand L are defined as

$$K_{\mathrm{ZrL}} = \frac{[\mathrm{ZrL^{4-\mathit{n}}}]}{[\mathrm{Zr^{4+}}][\mathrm{L^{\mathit{n}-}}]} \qquad K_{\mathrm{FeL}} = \frac{[\mathrm{FeL^{3-\mathit{n}}}]}{[\mathrm{Fe^{3+}}][\mathrm{L^{\mathit{n}-}}]}$$

The ratio of these constants is

$$\frac{K_{\mathrm{FeL}}}{K_{\mathrm{ZrL}}} = \frac{[\mathrm{FeL^{3-\mathit{n}}}][\mathrm{Zr^{4+}}][\mathrm{L^{\mathit{n}-}}]}{[\mathrm{ZrL^{4-\mathit{n}}}][\mathrm{Fe^{3+}}][\mathrm{L^{\mathit{n}-}}]} = \frac{[\mathrm{FeL^{3-\mathit{n}}}][\mathrm{Zr^{4+}}]}{[\mathrm{ZrL^{4-\mathit{n}}}][\mathrm{Fe^{3+}}]} = K_{\mathrm{eq}}$$

where K_{eq} is the equilibrium constant for the competition reaction

$$\mathrm{Fe^{3+}} + \mathrm{ZrL^{4-\mathit{n}}} \rightleftharpoons \mathrm{Zr^{4+}} + \mathrm{FeL^{3-\mathit{n}}}$$

If K_{FeL} is known and K_{eq} can be determined by spectral measurements or by other means, then K_{ZrL} can be calculated.

a. Corrections for Chloro and Hydroxo Complexing of Iron(III).—Although the above formation constants are defined in terms of the free Fe(III) and Zr(IV) ions, under the experimental conditions employed ($-\log [\mathrm{H^+}] = 2.00$, $\mu = 0.1$ (KCl)), iron(III) is complexed

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

by chloride and hydroxide ions, and zirconium(IV) is polymerized. Accordingly, let us denote the uncorrected concentrations of aquo iron(III), complexed iron(III), uncomplexed zirconium(IV), and complexed zirconium(IV), as deduced from spectral measurements, with the symbol ($'$). The observed optical density in a spectral measurement on a solution containing the iron(III) chelate, the free Fe(III) ion, and complexed iron(III) is equal to

$$\text{O.D.} = \epsilon_{\text{FeL}}(l)[\text{FeL}'^{3-n}] + \epsilon_{\text{Fe}}(l)[\text{Fe}'^{3+}]$$

where l is the cell path length, and the ϵ's represent the corresponding extinction coefficients. From material balance considerations, we have

$$T_{\text{Fe}} = [\text{Fe}'^{3+}] + [\text{FeL}'^{3-n}]$$
$$T_{\text{L}} = [\text{FeL}'^{3-n}] + [\text{ZrL}'^{4-n}]$$
$$T_{\text{Zr}} = [\text{Zr}'^{4+}] + [\text{ZrL}'^{4-n}]$$

where the T's represent the total concentration of the species in the subscript in all its forms.

Since there are four equations and four unknowns, all of the above quantities may be calculated from one optical density measurement made at a suitable wave length. Also, a value for K'_{eq}, the apparent equilibrium constant, may be determined.

$$K'_{\text{eq}} = \frac{[\text{FeL}'^{3-n}][\text{Zr}'^{4+}]}{[\text{ZrL}'^{4-n}][\text{Fe}'^{3+}]}$$

To obtain the true equilibrium constant, K, and the formation constant for the zirconium chelate, K_{ZrL}, the quantities $[\text{Zr}'^{4+}]$ and $[\text{Fe}'^{3+}]$ must be corrected for chloride and hydroxide complexing, yielding values for $[\text{Zr}^{4+}]$ and $[\text{Fe}^{3+}]$, respectively. The method of calculating the corrections follows.

It is assumed that the amount of chloro and hydroxo complexing of the various metal chelate species present is negligible. Then $[\text{ZrL}'^{4-n}] = [\text{ZrL}^{4-n}]$; likewise $[\text{FeL}'^{3-n}] = [\text{FeL}^{3-n}]$ for each system except the iron(III)–Tiron system.

The chloride complexing coefficients for iron(III) have been reported by Rabinowitch and Stockmayer[7] for $\mu \rightarrow 0$ at 25.0°. These are: $\log K_1^{\text{Cl}} = 1.48$, $\log K_2^{\text{Cl}} = 0.65$, and $\log K_3^{\text{Cl}} = -1.0$.

The hydroxo complexing coefficient for iron(III) and dimerization constant for Fe(OH)^{2+} have been reported by Milburn and Vosburgh[8] for $\mu \rightarrow 0$ at 25.0° as $\log K_1^{\text{OH}} = -2.17$ and $\log K_{22} = 1.46$. In order to make corrections for the complexing of iron(III), it is assumed that mixed chloro–hydroxo complexes may be neglected. Thus, the nonchelated iron species assumed are

$$[\text{Fe}'^{3+}] = [\text{Fe}^{3+}] + [\text{FeCl}^{2+}] + [\text{FeCl}_2{}^{+}] + [\text{FeCl}_3] + [\text{FeOH}^{2+}] + 2[\text{Fe}_2(\text{OH})_2{}^{4+}]$$

By substituting for each of the complexed forms its equivalent in terms of the complexing coefficients, one obtains

$$[\text{Fe}'^{3+}] = [\text{Fe}^{3+}](1 + K_1^{\text{Cl}}[\text{Cl}] + K_1^{\text{Cl}}K_2^{\text{Cl}}[\text{Cl}]^2 + K_1^{\text{Cl}}K_2^{\text{Cl}}K_3^{\text{Cl}}[\text{Cl}]^3 + K_1^{\text{OH}}/[\text{H}^+]) + [\text{Fe}^{3+}]^2K_1^{\text{OH}}K_{22}/[\text{H}^+]^2$$

By introducing the known hydrogen ion concentration, chloride ion concentration, and the complexing coefficients, one may determine $[\text{Fe}^{3+}]$ in terms of $[\text{Fe}'^{3+}]$. Since the latter is calculable from the spectral measurements, the $[\text{Fe}^{3+}]$ can be determined.

b. Correction for Chloro and Hydroxo Complexing of Zr(IV).—The correction of $[\text{Zr}'^{4+}]$ for chloro and hydroxo complexing proceeds in a slightly different manner. Although chloro and hydroxo complexing coefficients have been reported[9] for zirconium, the hydroxo constants cannot be applied under our experimental conditions, since they lead to the conclusion that a significant portion of the zirconium should be present as the hydrous oxide precipitate and this is not the case experimentally. The discrepancy lies in the fact that mononuclear hydroxo species are not present in appreciable quantities under the experimental conditions employed in the spectral measurements. Data reported by Kraus[10] and Connick and Zielen[11] indicate that trimers and/or tetramers are the important species in aqueous zirconium solutions with acidities (hydrochloric or perchloric) ranging from 0.5 to 2.0 M. Since our zirconium stock solution is 1.2 M in hydrochloric acid, and since polymerization reactions occur slowly, it is reasonable to assume that zirconium trimer and/or tetramer species are present in our (diluted) experimental solutions. For the purpose of correcting our data for zirconium hydrolysis, it is assumed that the tetramer is the only form of hydrolyzed zirconium present. The equilibrium constant for the formation of this tetramer reported by Zielen is used in the calculation

$$K_{48} = \frac{[\text{Zr}_4(\text{OH})_8{}^{8+}][\text{H}^+]^8}{[\text{Zr}^{4+}]^4} = 1.4 \times 10^9$$

The apparent concentration of zirconium(IV), $[\text{Zr}'^{4+}]$, may be represented as

$$[\text{Zr}'^{4+}] = 4[\text{Zr}_4(\text{OH})_8{}^{8+}] + [\text{Zr}^{4+}] + [\text{ZrCl}^{3+}] + [\text{ZrCl}_2{}^{2+}] + [\text{ZrCl}_3{}^{+}] + [\text{ZrCl}_4]$$

Since all of the species except the tetramer are present in very small concentrations, this equation may be simplified to

$$[\text{Zr}'^{4+}] = 4[\text{Zr}_4(\text{OH})_8{}^{8+}]$$

Introducing the tetramer constant, K_{48}, one may show that

$$[\text{Zr}] = \sqrt{\frac{[\text{H}^+]^8[\text{Zr}'^{4+}]}{5.6 \times 10^9}}$$

Similar calculations were made assuming the presence of the zirconium(IV) trimer species only. The formation constants calculated in this way were 0.5 log unit smaller for each chelate system. It can therefore be seen that the calculated constants are of the same order of magnitude whether trimer or tetramer zirconium species are assumed present in the system.

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(7) E. Rabinowitch and W. H. Stockmayer, *J. Am. Chem. Soc.*, **64**, 335 (1942).

(8) R. M. Milburn and W. C. Vosburgh, *ibid.*, **77**, 1352 (1955).

(9) A. S. Solovkin, *Zh. Neorgan. Khim.*, **2**, 611 (1957).

(10) K. A. Kraus and J. S. Johnson, *J. Am. Chem. Soc.*, **75**, 5769 (1953); J. S. Johnson and K. A. Kraus, *ibid.*, **78**, 3937 (1956).

(11) R. E. Connick and W. H. McVey, *ibid.*, **71**, 3182 (1949); R. E. Connick and W. H. Reas, *ibid.*, **73**, 1171 (1951); R. E. Connick and A. J. Zielen, *ibid.*, **78**, 5785 (1956).

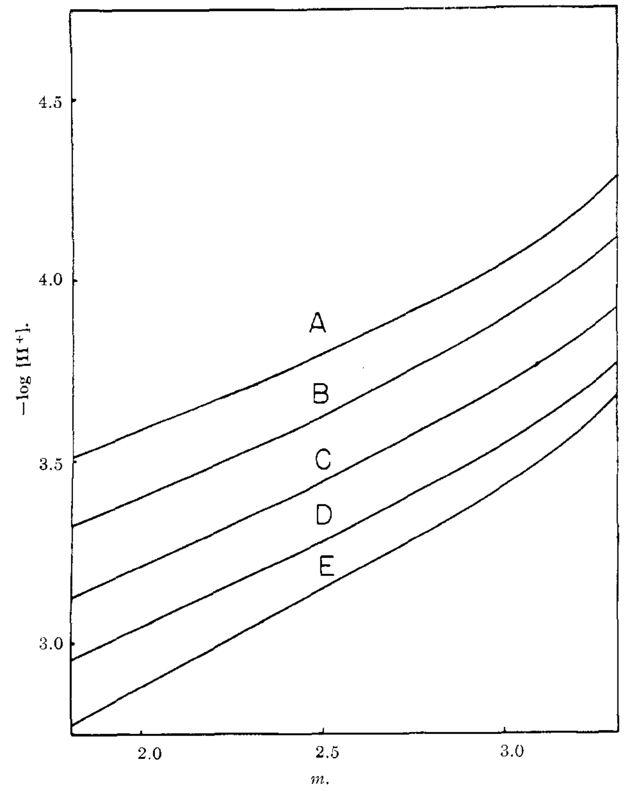

Fig. 1.—Potentiometric titration of the 1:1:1 Zr-EDTA-Tiron system as a function of concentrations at 25° and μ = 0.1 (KCl); m = moles of base per mole of metal ion. A = 4.8×10^{-4} M; B = 9.3×10^{-4} M; C = 1.7×10^{-3} M; D = 3.1×10^{-3} M; E = 5.2×10^{-3} M.

c. Correction for the Protonation of the Iron(III)-Tiron Chelate.—In the calculation of the zirconium(IV)-Tiron 1:1 chelate formation constant, it is necessary to make a correction for the presence of the protonated iron(III)-Tiron chelate. From equilibrium constants reported by Willi and Schwarzenbach,[12] it is readily shown that for the iron(III)-Tiron system

$$\frac{[\mathrm{FeHL}]}{[\mathrm{H}^+][\mathrm{FeL}^-]} = 10^{1.9}$$

At $-\log [\mathrm{H}^+] = 2.00$, $[\mathrm{FeHL}]/[\mathrm{FeL}^-] = 10^{-0.1} = 0.797$.

Since the total amount of chelated iron is distributed between these two forms, we have

$$[\mathrm{FeL}'^-] = [\mathrm{FeL}^-] + [\mathrm{FeHL}] = 1.797[\mathrm{FeL}^-], \text{ or } [\mathrm{FeL}^-] = 0.557[\mathrm{FeL}^{-\prime}]$$

Results

Zr-EDTA-Tiron, 1:1:1.—Data obtained from potentiometric titration of the 1:1:1 Zr-EDTA-Tiron system over the concentration range 1.7×10^{-3} to 5.2×10^{-3} M (see Fig. 1) were used to calculate K_1 and K_2 for the reactions proposed above. The results obtained are shown in Table I.

According to the model proposed, two Tiron molecules act as bridges between two 1:1 zirconium(IV)-EDTA chelate structures. Bridging of metal ions by Tiron has been observed in the thorium-Tiron 1:1.5 system.[13] This model is also consistent with ultracentrifugation measurements on this system.[14]

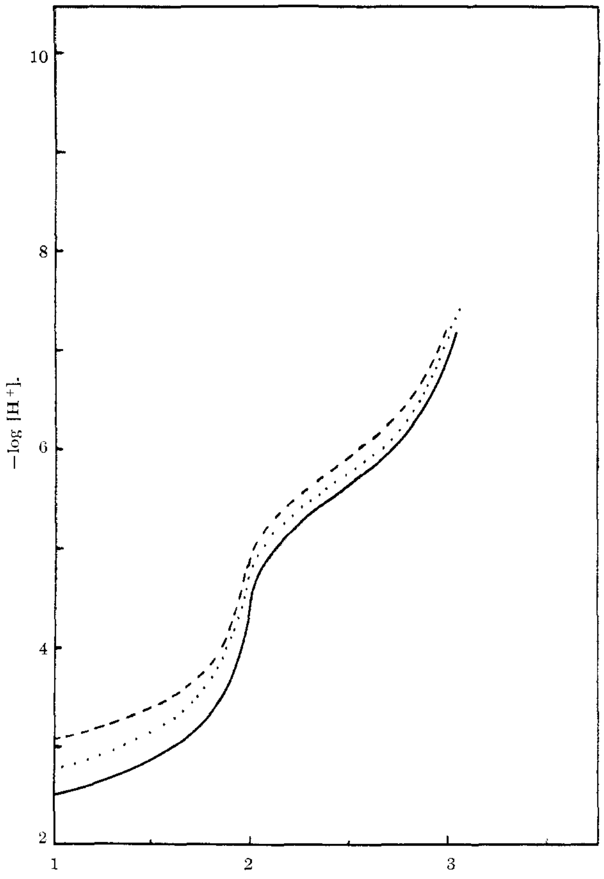

Fig. 2.—Potentiometric titration of the 1:1 Zr-EDTA chelate compound as a function of concentration at 25° and μ = 0.1 (KCl); m = moles of base per mole of metal ion. – – – –, 1×10^{-3} M; · · · ·, 2×10^{-3} M; ———, 4×10^{-3} M.

Table I
Equilibrium Data for the 1:1:1 Zr(IV)-EDTA-Tiron System

Chelate concn.	K_1	K_2
1.7×10^{-3}	0.134	1.8×10^{-4}
2.9×10^{-3}	0.094	4.25×10^{-4}
5.2×10^{-3}	0.121	3.5×10^{-4}

Average values: $K_1 = 0.12 \pm 0.02$; $K_2 = 3.2\ (\pm 0.6) \times 10^{-4}$.

Olation of the Zr(IV)-EDTA Chelate.—Titration of the Zr-EDTA 1:1 chelate was carried out over the concentration range 5×10^{-4} to 4×10^{-3} M, and calculations for dimer formation were carried out in the region from $m = 2.0$ to $m = 2.8$. Beyond this region, reactions were quite slow, and equilibrium measurements could not be obtained. Figure 2 shows the family of Zr-EDTA 1:1 titrations from which calculations were made. Plots of $[\mathrm{H}^+]((m - 2)_{\mathrm{TM}} + [\mathrm{H}^+])/[\mathrm{ML}]$ were made from duplicate titration curves at each concentration and good straight line fits were obtained. Figure 3 shows a typical dimer plot obtained from a single titration curve (open circles). Also shown is a trimer plot for the same data (closed circles), which do not

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(12) A. Willi and G. Schwarzenbach, *Helv. Chim. Acta*, **34**, 528 (1951).

(13) R. F. Bogucki, Y. Murakami, and A. E. Martell, *J. Am. Chem. Soc.*, **82**, 5608 (1960).

(14) R. L. Gustafson and A. E. Martell, unpublished work.

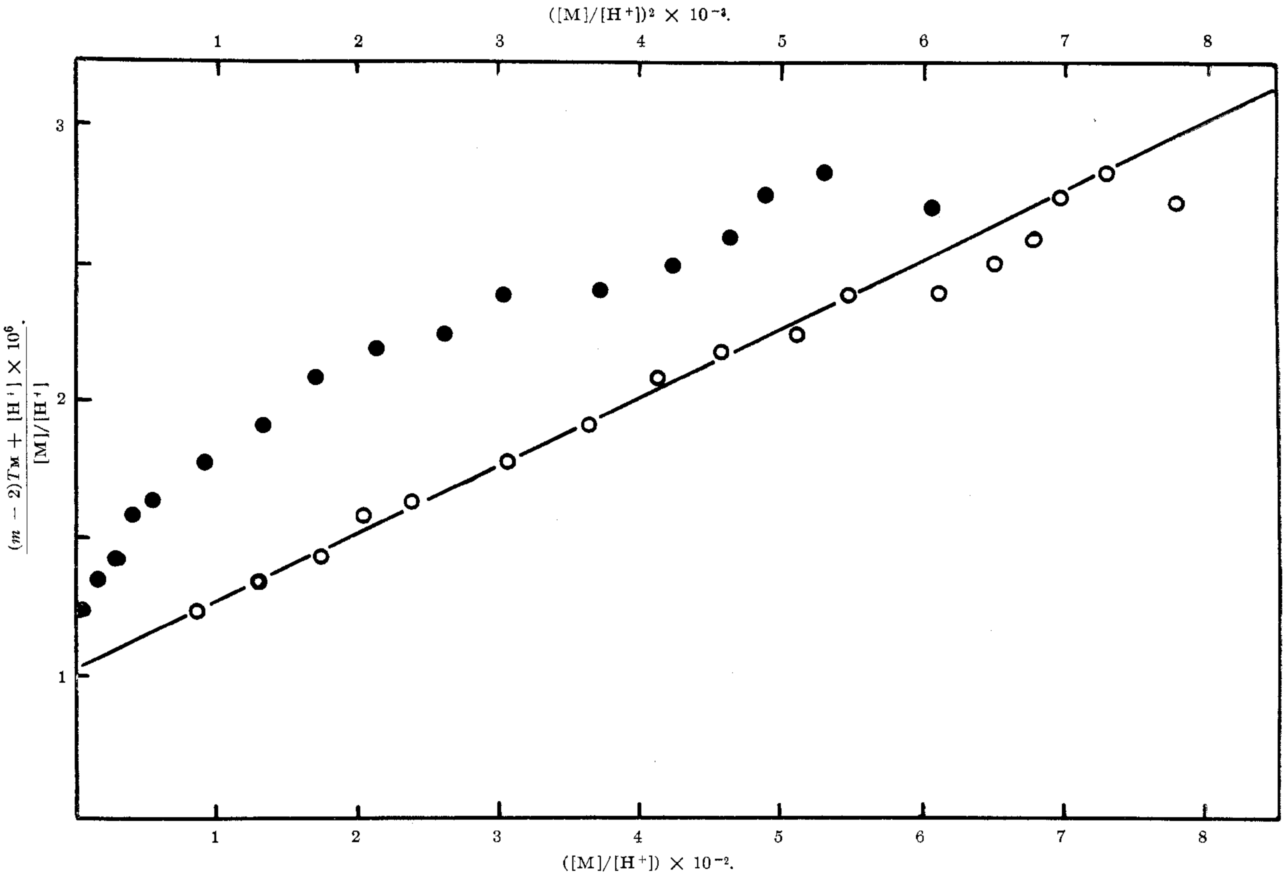

Fig. 3.—Plots of $[H^+]((m-2)T_M + [H^+])/[M]$ against $[M]/[H^+]$ and $[M]^2/[H^+]^2$ for the 1:1 Zr(IV)-EDTA chelate at 25° and μ = 0.1 (KCl). T_M = total concentration of metal in all forms = 4×10^{-3} *M*. For dimer species, use open circles with lower scale as abscissa; for trimer species, closed circles with upper scale as abscissa.

show a linear relationship. From the intercepts and slopes of eight dimer plots, values of K_a and K_D were determined; from these data, values for log K_d were calculated.

As can be seen from the data (see Table II) there is some drift in each set of constants. This suggests that either a side reaction is occurring or that some species which is present to a small extent was neglected in the mathematical treatment of the data.

TABLE II

ZIRCONIUM-EDTA CHELATE DIMER CONSTANTS

Concn., *M*	pK_a	K_D	log K_d
5×10^{-4}	6.60	4.08×10^{-9}	4.27
	6.37	3.46×10^{-9}	4.20
1×10^{-3}	6.20	1.25×10^{-9}	3.50
	6.21	1.33×10^{-9}	3.55
2×10^{-3}	6.11	1.28×10^{-9}	3.32
	6.10	1.21×10^{-9}	3.29
4×10^{-3}	6.07	1.37×10^{-9}	3.28
	5.97	1.20×10^{-9}	3.02

The results at the lowest concentration show the greatest discrepancies. Therefore the six sets of data from the three most concentrated solutions were combined and the least squares method of averaging the data was applied. Figure 4 shows the calculated data for the six most concentrated solutions and the corresponding least squares line. The constants calculated from the least squares line are

$$ML \longrightarrow MOHL^- + H^+ \qquad pK_a = 6.2$$

$$2ML + 2H_2O \longrightarrow M_2(OH)_2L_2^{2-} + 2H^+ \qquad K_D = 1.46 \times 10^{-9}$$

$$2MOHL^- \longrightarrow M_2(OH)_2L_2^{2-} \qquad \log K_d = 3.5$$

In view of the drift in K_d values, it seems that the dimerization reaction is not the only reaction occurring. Although the dimer seems to be the predominant species, perhaps some dihydroxo species, or some trimer species, may be present. Accordingly, the value reported for the dimerization constant, K_d, is an approximate one.

Spectrophotometric Measurements on the EDTA Chelates of Zirconium(IV) and Hafnium(IV).—The optical density of a mixture of zirconium(IV) (or hafnium(IV)), EDTA, and iron(III) in solution depends upon the order in which the materials are mixed. This is due to the fact that the rate of formation of the iron, zirconium, and hafnium chelates is fast, but the rate of exchange of one metal ion for another in the chelate is slow.

When various mole ratios of zirconium(IV) (or hafnium(IV)), iron(III), and EDTA are mixed in this sequence, the apparent equilibrium constant, K'_{eq} (calculated from the spectral measurements neglecting the chloro and hydroxo complexing of the iron and polymerization of the zirconium), remains rather constant. The calculated values for the "apparent" Zr-EDTA 1:1 and Hf-EDTA 1:1 chelates from these data are log K'_{ZrY} = 25.7 ± 0.2 and log K'_{HfY} = 24.9 ± 0.3.

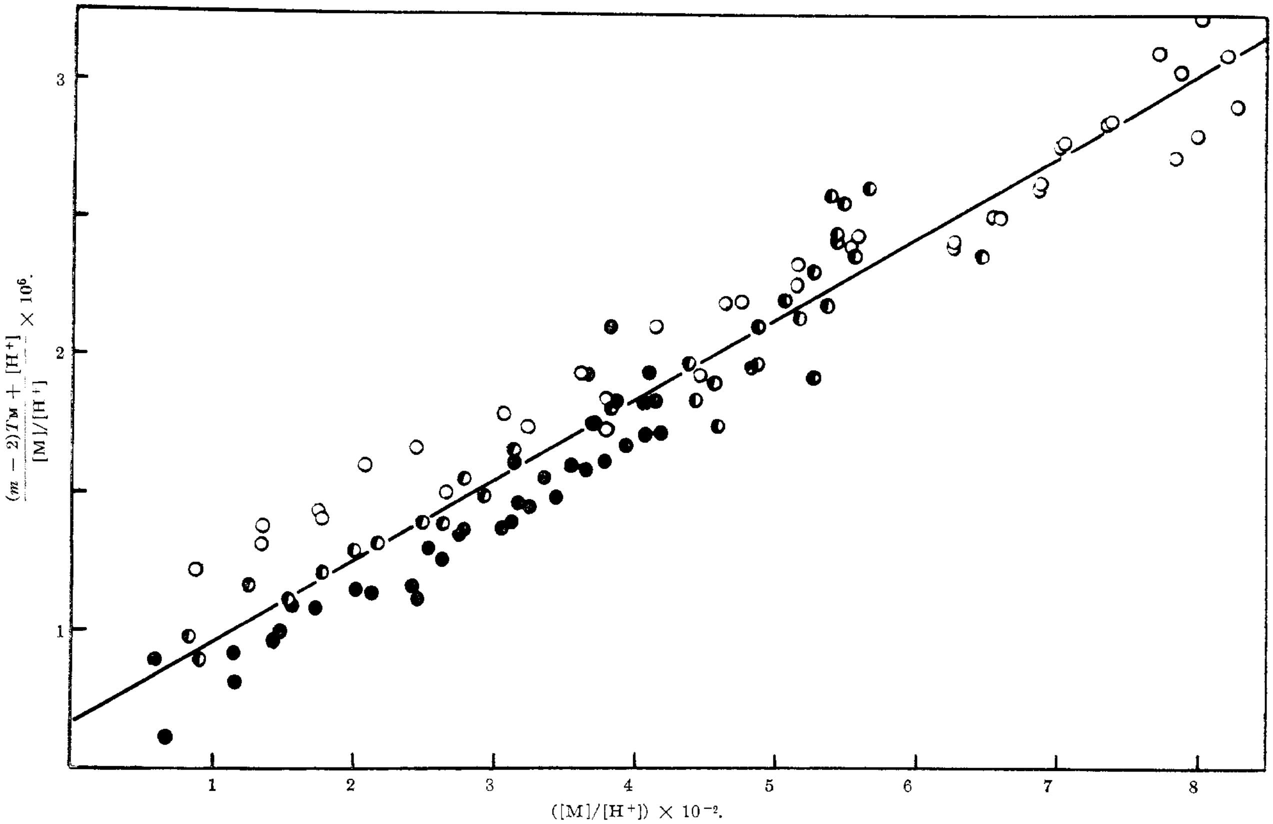

Fig. 4.—Graphical demonstration of formation of a binuclear species for the 1:1 Zr(IV)–EDTA chelate system at 25° and μ = 0.1 (KCl). Data are calculated for the six most concentrated solutions; linear plot obtained from a least squares fit of the data; solid circles, $T_M = 1 \times 10^{-3}$ *M;* half solid circles, $T_M = 2 \times 10^{-3}$ *M;* open circles, $T_M = 4 \times 10^{-3}$ *M.* T_M = total concentration of metal species in all forms.

To determine a true equilibrium constant, however, it is necessary to be able to approach the same equilibrium position from either direction, *i.e.*

$$Zr^{4+} + FeL^- \longrightarrow Fe^{3+} + ZrL$$

$$Fe^{3+} + ZrL \longrightarrow Zr^{4+} + FeL^-$$

When this was attempted with the zirconium–iron–EDTA and hafnium–iron–EDTA systems, the optical densities observed were widely divergent. Moreover, even after standing for a 3-week period, the solutions exhibited only negligible changes in optical density. Thus, the exchange reaction must be a very slow one. Although the position of equilibrium cannot be conveniently determined for the competition of iron(III) and zirconium(IV) (or hafnium(IV)) for EDTA, limits can be set on the formation constants by calculating them from the extreme optical density values obtained from approaching equilibrium from each direction. The true value must certainly lie between the extreme values obtained. The values of K' calculated in this way are given in Table III.

In the case of the zirconium–EDTA chelate, these values for K' can be corrected for chloro and hydroxo complexing of iron(III) and chloro and hydroxo complexing of zirconium(IV). Chloro complexing of zirconium has only a negligible effect, and the hydroxo complexing of zirconium involves a correction for the polymerization of the Zr^{4+} ion. The results of these calculations are given in Table IV. A tabulation of data pertinent to these calculations is given in Table V.

Table III

Reaction mixture	log K'_{ML}
$ZrL + Fe^{3+} \rightarrow$	26.4
$Zr^{4+} + Fe^{3+} + L^{4-} \rightarrow$	25.5
$FeL^- + Zr^{4+} \rightarrow$	23.4
$HfL + Fe^{3+} \rightarrow$	26.1
$Hf^{4+} + Fe^{3+} + L^{4-} \rightarrow$	25.0
$FeL^- + Hf^{4+} \rightarrow$	23.1

Table IV

Reaction mixture	log K_{ZrY}
$ZrL + Fe^{3+} \rightarrow$	29.9
$Zr^{4+} + Fe^{3+} + L^{4-} \rightarrow$	29.4
$FeL^- + Zr^{4+} \rightarrow$	27.7
Average value	29.0 ± 0.9

Table V
Data Used in the Calculation of the Formation Constant of the 1:1 Zr–EDTA Complex

	Molar concentrations for various orders		
Quantity	Fe–Zr–EDTA	Fe–EDTA–Zr	Zr–EDTA–Fe
T_{Fe}	1.91×10^{-3}	Same	Same
T_{Zr}	1.90×10^{-3}	Same	Same
T_L	1.90×10^{-3}	Same	Same
$[Fe'^{3+}]$	1.45×10^{-3}	2.73×10^{-4}	1.51×10^{-3}
$[FeL^-]$	7.60×10^{-4}	1.64×10^{-3}	4.05×10^{-4}
$[ZrL^-]$	1.14×10^{-3}	2.63×10^{-4}	1.50×10^{-3}
$[Zr'^{4+}]$	7.60×10^{-4}	1.64×10^{-3}	4.05×10^{-4}
log K'_{eq}	−0.46	0.57	−1.14
log K'_{ZrL}	25.6	24.5	26.2
$[Fe^{3+}]$	7.44×10^{-4}	1.76×10^{-4}	9.74×10^{-4}
$[Zr^{4+}]$	6.07×10^{-8}	7.39×10^{-8}	5.19×10^{-8}
log K_{eq}	−4.26	−2.58	−4.84
log K_{ZrL}	29.4	27.7	29.9

TABLE VI

Metal	log K_{ML}	Investigators
Fe^{3+}	25.1	Schwarzenbach and Heller[a]
Th^{4+}	23.2	Schwarzenbach, *et al.*[b]
Zr^{4+}	19.4	Morgan and Justus[c]

[a] G. Schwarzenbach and J. Heller, *Helv. Chim. Acta*, **34**, 576 (1951). [b] J. Bjerrum, G. Schwarzenbach, and L. G. Sillén, "Stability Constants," Vol. 1, 1st Ed., The Chemical Society, London, 1957. [c] L. O. Morgan and N. L. Justus, *J. Am. Chem. Soc.*, **78**, 38 (1956).

TABLE VII

System	log K'	log K
Zr(IV)–NTA 1:1	17.0 ± 0.2	20.8 ± 0.1
Hf(IV)–NTA 1:1	16.9 ± 0.1	. . .

TABLE VIII

DATA USED IN THE CALCULATION OF THE FORMATION CONSTANT OF THE 1:1 Zr–NTA COMPLEX

Species present	Molar concn. at various composition ratios of Fe:Zr:NTA 1:1:1	2:1:1	3:1:1
T_{Fe}	1.92×10^{-3}	6.96×10^{-3}	5.43×10^{-3}
T_{Zr}	1.92×10^{-3}	3.47×10^{-3}	1.81×10^{-3}
T_L	1.92×10^{-3}	3.47×10^{-3}	1.81×10^{-3}
$[Fe'^{3+}]$	1.61×10^{-3}	5.79×10^{-3}	4.67×10^{-3}
[FeL]	3.04×10^{-4}	1.16×10^{-3}	7.61×10^{-4}
$[ZrL^+]$	1.61×10^{-3}	2.31×10^{-3}	1.05×10^{-3}
$[Zr'^{4+}]$	3.04×10^{-4}	1.16×10^{-3}	7.61×10^{-4}
log K'_{eq}	−1.45	−1.00	−0.93
log K'_{ZrL}	17.3	16.9	16.8
$[Fe^{3+}]$	9.99×10^{-4}	3.34×10^{-3}	2.80×10^{-3}
$[Zr^{4+}]$	4.83×10^{-8}	6.75×10^{-8}	6.07×10^{-8}
log K_{eq}	−5.04	−4.99	−4.80
log K_{ZrL}	20.9	20.9	20.7

It is of interest to compare the above values obtained in this study with other data for EDTA formation constants reported in the literature (Table VI).

As can be seen from these data, the reported formation constants for the Zr–EDTA chelate, which do not agree with the results reported here, appear unusually low. The difference between the reported value for the Zr–EDTA 1:1 formation constant and that determined in this investigation can be understood on the basis of two considerations. First, these authors apparently used a hydrolyzed zirconium stock solution, since they reported a precipitate in the lower buffer region of the EDTA titration curve. In this investigation, such precipitates were formed only when hydrolyzed zirconium solutions were used. Second, these authors did not make corrections for hydrolysis or polymerization of the Zr^{4+} ion, although they recognized the presence of polymers in their solutions.

The results of these experiments indicate that the formation constant for the zirconium–EDTA 1:1 chelate is higher than that of any other EDTA chelate thus far reported.[13] This is not surprising, considering the small size and high charge of the Zr^{4+} ion.

Chelates of NTA with Zirconium(IV) and Hafnium(IV).—The optical densities of mixtures of zirconium(IV) or hafnium(IV), iron(III), and NTA in solution are independent of the orders of mixing of the reagents. Therefore, equilibrium is attained quickly in these systems. The apparent formation constants for the Zr(IV)–NTA 1:1 and Hf(IV)–NTA 1:1 chelates and the formation constant for the Zr(IV)–NTA 1:1 chelate are given in Table VII.

The data upon which these calculations are based are given in Table VIII. The value of the formation constant of the Zr–NTA 1:1 chelate reported in Table VII is higher than is any other formation constant reported for 1:1 nitrilotriacetate chelates.

The 1:1 Chelate of Tiron and Zirconium(IV).—The optical densities of mixtures of zirconium(IV), iron (III), and Tiron in solution are independent of the orders of mixing of the reagents, indicating a rapid attainment of equilibrium.

TABLE IX

DATA USED FOR CALCULATION OF THE FORMATION CONSTANT OF THE 1:1 Zr-TIRON COMPLEX

Species present	Molar concn. at various composition ratios of Zr:Fe:Tiron 3:1:1	2:1:1	1:1:1	1:2:1	1:3:1
T_{Fe}	1.75×10^{-3}	2.04×10^{-3}	2.51×10^{-3}	4.28×10^{-3}	5.70×10^{-2}
T_{Zr}	5.24×10^{-3}	4.06×10^{-3}	2.51×10^{-3}	2.14×10^{-3}	1.99×10^{-3}
T_L	1.75×10^{-3}	2.03×10^{-3}	2.51×10^{-3}	2.14×10^{-3}	1.99×10^{-3}
$[Fe'^{3+}]$	1.56×10^{-3}	1.49×10^{-3}	1.23×10^{-3}	2.94×10^{-3}	4.45×10^{-3}
$[FeL'^-]$	1.89×10^{-4}	5.46×10^{-4}	1.29×10^{-3}	1.33×10^{-3}	1.25×10^{-3}
[ZrL]	1.56×10^{-3}	1.49×10^{-3}	1.22×10^{-3}	8.01×10^{-4}	6.49×10^{-4}
$[Zr'^{4+}]$	3.68×10^{-3}	2.59×10^{-3}	1.29×10^{-3}	1.33×10^{-3}	1.25×10^{-3}
log K'_{eq}	−0.54	−0.20	+0.04	−0.12	−0.27
log K'_{ZrL}	21.2	20.9	20.7	20.8	21.0
$[Fe^{3+}]$	9.80×10^{-4}	9.38×10^{-4}	7.71×10^{-4}	1.84×10^{-3}	2.77×10^{-3}
$[Zr^{4+}]$	9.01×10^{-8}	8.24×10^{-8}	6.92×10^{-8}	6.99×10^{-8}	6.87×10^{-8}
$[FeL^-]$	1.05×10^{-4}	3.04×10^{-4}	7.16×10^{-4}	7.42×10^{-4}	6.95×10^{-4}
log K_{eq}	−5.21	−4.75	−4.28	−4.45	−4.58
log K_{ZrL}	25.9	25.5	25.0	25.2	25.3

Table IX contains data used to calculate the "apparent" formation constant, K'_{ZrL}, and the true formation constant, K_{ZrL}, for the zirconium–Tiron 1:1 chelate. The values of these constants are $\log K'_{ZrL} = 20.9 \pm 0.1$ and $\log K_{ZrL} = 25.4 \pm 0.3$.

Again the value for the zirconium–Tiron 1:1 formation constant reported above is larger than any other formation constant reported for Tiron chelates thus far.

It can be seen that the zirconium chelate formation constants reported here are exceptionally high. The free Zr^{4+} ion has a marked affinity for the ligands studied in this investigation, because of its small size and large ionic charge.