

[CONTRIBUTION OF THE DEPARTMENT OF CHEMISTRY, CLARK UNIVERSITY, WORCESTER, MASSACHUSETTS]

Aqueous Zirconium Complexes. II. Mixed Chelates¹BY B. J. INTORRE* AND A. E. MARTELL[‡]

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Zr(IV) chelates in which not all of the coordination sites of the metal are satisfied by a multidentate ligand are found to combine with one or two additional moles of a second multidentate ligand to form more completely coordinated compounds which are more stable than those formed by either ligand alone. Particularly simple and stable are the mixed chelates with one mole of EDTA plus one mole of pyrocatechol-3,5-disulfonate, chromotropic salt, 8-hydroxyquinoline-5-sulfonate, oxalic acid or acetylacetone; one mole of 1,2-diaminocyclohexanetetraacetic acid plus one mole of pyrocatechol-3,5-disulfonate, oxalic acid, 8-hydroxyquinoline-5-sulfonate or acetylacetone; one mole of N-hydroxyethylethylenediaminetriacetic acid plus one mole of pyrocatechol-3,5-disulfonate, or 8-hydroxyquinoline-5-sulfonate; and one mole of nitrilotriacetic acid plus two moles of pyrocatechol-3,5-disulfonate. Other combinations yield soluble Zr(IV) chelate systems which are also quite stable but are somewhat less well-defined.

In the previous paper² on the formation of stable Zr(IV) aqueous chelates with multidentate ligands of various types, it was found that one of the most stable coordination compounds was formed when a 2:1 molar ratio of nitrilotriacetic acid to Zr(IV) was employed. The fact that this chelate, is more stable toward hydrolysis and seems to be more stable toward olation reactions than is the ethylenediaminetetraacetate(EDTA) chelate suggested the possibility of finding additional stable zirconium chelates containing two or more simple ligands, rather than a single ligand of higher multidentate character. The purpose of this paper, therefore, is to describe the properties of aqueous Zr(IV) chelates containing two different ligands in order to determine the types and arrangements of coordinating groups that will give the most stable structures.

Experimental

The experimental techniques employed are the same as those described in a previous publication.² Experimental data are reported for experiments with a concentrated Zr(IV) stock solution (0.2 M in metal ion and 1.2 M in HCl). Titrations carried out with a stock solution 0.02 M in Zr(IV) and 0.1 M in HCl frequently were less satisfactory because of the greater tendency toward hydrolysis and aging of the zirconium stock solution. The sources of the ligands and the methods used for their purification and standardization are also the same as were reported previously. Additional ligands employed in this study which were not previously described are: alizarin-3-sulfonate, 5-sulfosalicylic acid, 5-sulfo-8-hydroxyquinoline and acetylacetone, which were purchased from the Eastman Kodak Co.; 1,8-dihydroxynaphthalene-3,6-disodiumsulfonate (DNS) commonly referred to as "chromotropic salt," which was purchased from Fluka AG., Switzerland; and reagent grade oxalic acid, sodium pyrophosphate, citric acid, lactic acid, tartaric acid and potassium acid phthalate. All chelating agents were of the highest purity obtainable and were further purified when necessary by recrystallization or distillation. Stock solutions of the ligands (except acetylacetone) were standardized by potentiometric titration. The 1,2-diaminocyclohexanetetraacetic acid-(CDTA) stock solution was prepared by forming the disodium salt; 5-sulfo-8-hydroxyquinoline was converted to the sodium salt.

In most of the titrations described below, equilibrium was reached quickly; a few exceptions to this behavior are noted. In the high pH region of many titrations (pH > 10) slow drifts began to occur, which in some cases were followed by the formation of precipitates. Since the glass electrode can be damaged at these high pH values, contact time was kept

as short as possible. Consequently, the upper-most buffer regions of these titration curves do not in general represent equilibrium measurements.

Results

Mixed Chelates of EDTA. Zr-EDTA-Tiron, 1:1:1.—An equimolar mixture of Zr(IV), EDTA and Tiron (pyrocatechol-3,5-disulfonate) gives the remarkable titration curve illustrated by Fig. 1 (A). In this paper, the term EDTA will refer to the disodium salt. At $m = 4$, a very steep inflection occurs. This suggests that all four protons from the ligands are neutralized at this point, and presumably the species in solution have no affinity for H^+ or OH^- (*i.e.*, the system has no buffering capacity). At $m = 4$, it is suggested that a simple zirconium species is predominant, with the composition Zr-EDTA-Tiron, 1:1:1.

While it seems reasonable that Tiron is coordinated through the phenolic oxygens rather than one phenolic oxygen and the neighboring sulfonate group, it was desirable to confirm this idea. Accordingly, the disodium salt of phenol-2,4-disulfonic acid was titrated with Zr(IV) and EDTA in the mole ratio of 1:1:1. The resulting titration curve was superimposable upon the Zr-EDTA 1:1 titration curve showing that the phenol sulfonate has no tendency to bind to the Zr-EDTA complex. This provides strong evidence for the fact that the Tiron residue in the preceding system is bound through its phenol groups.

Zr-EDTA-Chromotropic Salt, 1:1:1.—A very interesting comparison to the Zr-EDTA-Tiron system is afforded by the titration curve of the corresponding chromotropic salt (disodium 1,8-dihydroxynaphthalene-3,6-disulfonate) system (Fig. 1B). A weak inflection is found at $m = 2$, corresponding to the neutralization of two equivalents of acid produced in the binding of EDTA to the Zr(IV) ion. As additional base is added, hydrogen ions dissociated from the chromotropic salt are titrated, and the second ligand combines with the Zr-EDTA chelate. Since at $m = 4$ all of the acid groups of the ligand have been neutralized, it is supposed that a stable mononuclear system is present; *i.e.*, the 1:1:1 chelate is formed and all 8 coordination sites of the metal ion are filled by donor atoms of the ligand. The presence of the first inflection and subsequent buffer region indicates that chromotropic salt has less tendency to bind to the Zr-EDTA chelate than does Tiron. The chromotropic salt-EDTA system provides

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

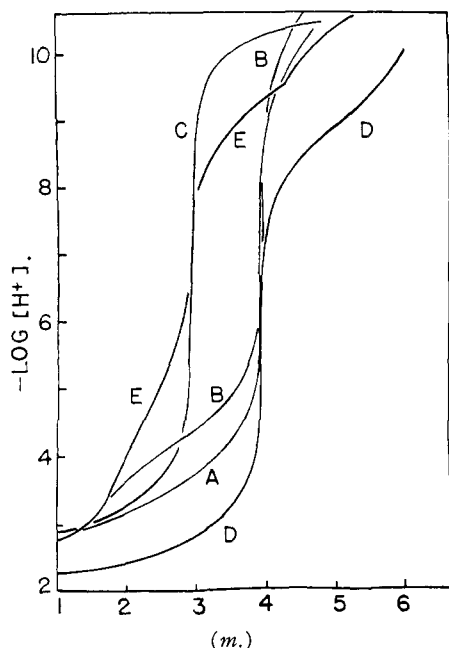


Fig. 1.—Potentiometric titration of Zr(IV) in the presence of equivalent amounts of EDTA and an additional ligand: A, Tiron; B, chromotropic salt; C, 8-hydroxyquinoline sulfonate; D, oxalic acid; E, acetylacetone; $t = 25^\circ$, $\mu = 0.10$ (KCl).

additional evidence that the binding of sulfonated ligands such as Tiron does not proceed through a sulfonate group and the adjacent phenol group but rather through the two phenol groups. Binding through the sulfonate and phenolic groups is sterically impossible in chromotropic acid. In view of the close resemblance of the Tiron and chromotropic acid-EDTA-Zr titrations, it seems that the sulfonate group does not take part in the binding of Zr(IV).

Zr-EDTA-Alizarin Sulfonate, 1:1:1.—The Zr-EDTA-alizarin sulfonate 1:1:1 system offers another interesting comparison to the corresponding Tiron system (Fig. 2B). A sloping inflection occurs between $m = 3.5$ to beyond $m = 4.0$, followed by a steeper inflection, and finally by precipitation near $m = 5$. The sloping region up to $m = 4.5$ is evidence for hydroxyl ions bound to the metal, since only four protons are available from the ligands, and base is being neutralized after these have been titrated. Since eight donors are available, this indicates that either an acetate or a phenolate donor must be displaced from the metal. The reason for this may be steric hindrance from the large alizarin molecule. Presumably, the binding of the alizarin occurs through the phenolic groups.

Zr-EDTA-Potassium Acid Phthalate, 1:1:1.—The titration curve of the mixed EDTA-phthalate chelate illustrated in Fig. 2C has a short sloping inflection and another inflection beyond $m = 4$. The curve corresponds approximately to the curve formed by horizontal addition of the Zr-EDTA and potassium acid phthalate titration curves. A slight precipitate was present throughout the titration making interpretation of the curve un-

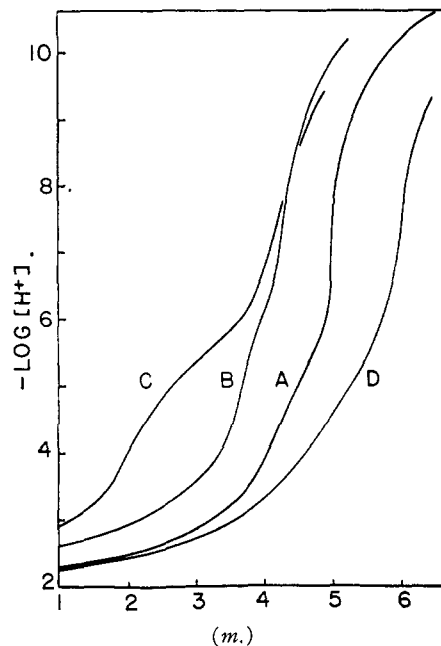


Fig. 2.—Potentiometric titration of Zr(IV) in the presence of equivalent amounts of EDTA and an additional ligand: A, 5-sulfosalicylic acid; B, alizarin sulfonate; C, phthalate; D, pyrophosphoric acid.

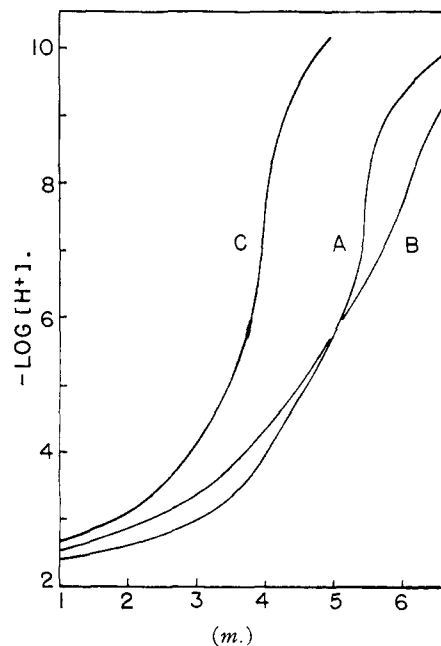


Fig. 3.—Potentiometric titration of Zr(IV) in the presence of equivalent amounts of EDTA and an additional ligand: A, tartaric acid; B, citric acid; and C, lactic acid.

certain, but it appears that the tendency for formation of a mixed Zr-EDTA-phthalate chelate is small.

Zr-EDTA-Tartrate, 1:1:1.—The Zr-EDTA-tartrate system is one of interest since tartaric acid contains a glycol type structure which should give stability at high pH . The titration curve (Fig. 3A) shows a low buffer region from $m = 0$ to $m = 3.5$, a sloping region from $m = 3.5$ to $m = 5.5$, and a

TABLE I

System	Ligand protons available	Inflection at $m =$	Species suggested	Remarks	Titration curve in figure
Zr-EDTA-Tiron 1:1:1	4	4	Completely coordinated 1:1:1 chelate	See text	1A
Zr-EDTA-Chromotropic salt 1:1:1	4	2,4	Same	See text	1B
Zr-EDTA-8-Hydroxyquinoline-5-sulfonate 1:1:1	3	3	Same	1C
Zr-EDTA-Oxalic acid 1:1:1	4	4,6	Same	Beyond $m = 4$ hydroxo groups bind to Zr; pptn. occurs at $m = 6$	1D
Zr-EDTA-Acetylacetone 1:1:1	3	3	Same	Acetylacetone binds before $m = 3$	1E
Zr-EDTA-5-Sulfosalicylic acid 1:1:1	5	5	Same	Pptn. from $m = 0$ to $m = 4.5$; pptn. beyond $m = 6.5$	2A
Zr-EDTA-Alizarin sulfonate 1:1:1	4	4	Same	See text	2B
Zr-EDTA-Potassium acid phthalate 1:1:1	3	2, >4	No mixed chelate forms	See text	2C
Zr-EDTA-Pyrophosphate 1:1:1	6	6	Olated species not a simple system	Pptn. up to $m = 3.7$ pptn. beyond $m = 4.4$	2D
Zr-EDTA-Tartrate 1:1:1	5	5.5	Mixt. or polynuclear syst.	See text	3A
Zr-EDTA-Citrate 1:1:1	6	6	Completely coordinated 1:1:1 chelate	Beyond $m = 6$ hydroxo bridges form no pptn. up to $m = 7.4$	3B
Zr-EDTA-Lactate 1:1:1	4	4	Completely coordinated 1:1:1 chelate	Inflection is similar to Zr-EDTA-sulfosalicylic acid system	3C
Zr-HEDTA-Tiron 1:1:1	6	4 ² / ₃ , 6	Completely coordinated 1:1:1 chelate at $m = 6$	No pptn. at $m = 6.8$ overnight	4A
Zr-HEDTA-Chromotropic acid 1:1:1	6	6	Completely coordinated 1:1:1 chelate	Curve suggests considerable olation	4B
Zr-HEDTA-8-Hydroxyquinoline-5-sulfonate 1:1:1	5	5	Same	More stable than corresponding EDTA system; pptn. near $m = 6$	4C
Zr-HEDTA-Oxalic acid 1:1:1	6	6	Same	4D
Zr-HEDTA-Acetylacetone 1:1:1	5	5	Not a simple system	Stable to $m = 5.5$	4E
Zr-CDTA-Tiron 1:1:1	4	4	Completely coordinated 1:1:1 chelate	No pptn. at $m = 5$ after two weeks	Not shown
Zr-CDTA-Chromotropic salt 1:1:1	4	2,4	Same	Ppt. up to pH 6.0 no ppt. formed thereafter up to $m = 5.3$	Not shown
Zr-CDTA-8-Hydroxyquinoline-5-sulfonate 1:1:1	3	3	Same	Pptn. after several days at $m = 5$	Not shown
Zr-CDTA-Oxalic acid 1:1:1	4	4,6	Same	Pptn. after several days at $m = 7$	Not shown
Zr-CDTA-Acetylacetone 1:1:1	3	3	Completely coordinated 1:1:1 chelate	Not shown
Zr-NTA-Tiron 1:1:1	5	Not a simple system	Slow equil., olated syst.	Not shown
Zr-NTA-Tiron 1:1:2	7	5,7	Completely coordinated 1:1:1 chelate at $m = 7$		5A
Zr-NTA-Oxalic acid 1:1:1	5	Sloping region from $m = 6$ to $m = 8$	Not a simple system	Precipitation throughout titration	Not shown
Zr-NTA-Oxalic acid 1:1:2	7	7	Completely coordinated 1:1:1 chelate forms	1:1:1 chelate, is not very stable	5B
Zr-HIMDA-Tiron 1:1:1	5	Sloping region from $m = 5$ to $m = 6.5$	A mixture, or polymeric, not a simple system	No precipitate formed	Not shown
Zr-HIMDA-Tiron 1:1:2	7	6,7	Mixture	Poorly defined inflections, slow reactions	5C
Zr-Acetylacetone-Tiron 1:2:2	6	No sharp inflection	Not a simple system	Considerable buffering beyond $m = 6$	5D
Zr-NTA-HIMDA 1:1:1	6	About 6	Mixture of chelates		Not shown

steep inflection at $m = 5.5$. This unusual curve suggests: 1, the carboxyl groups probably bind in the low pH region; 2, as the pH increases a rearrangement probably occurs, and the tartaric acid

alkoxy groups begin to donate; and 3, hydroxo bridging probably occurs in the high pH region. The remarkable stability of this chelate system to precipitation at high pH suggests that the alkoxy groups are bound to the metal. The inflection at a half integer value suggests that either a mixture of species or a polynuclear system (perhaps a dimer) is formed.

Other Mixed Chelates of EDTA.—A number of additional mixed chelate systems also were studied potentiometrically in the same manner as those described above. Thus the combination of a molar equivalent of the following ligands with the EDTA chelate of $Zr(IV)$ was observed: 8-hydroxyquinoline-5-sulfonate, oxalate, acetylacetonate, 5-sulfosalicylate, pyrophosphate, citrate and lactate. These systems are described in Figs. 1, 2 and 3, and pertinent data and observations are summarized in Table I.

The mixed chelate of β -thujaplicin with Zr and EDTA at a 1:1:1 mole ratio yielded precipitation throughout the titration range; hence the titration curve could not be interpreted.

Attempts were made to incorporate salicylaldehyde, *o*-nitrophenol, α -nitroso- β -naphthol, sulfate and glycine as bidentate donors to the zirconium-EDTA 1:1 complex. In each case the titration curves obtained could be analyzed by assuming that no binding of the bidentate group takes place, and the addition of the zirconium:EDTA 1:1 and the respective ligand titration curves closely reproduced the experimental curve for the mixture.

Mixed Chelates Containing HEDTA.—As was indicated in a previous publication,² hydroxyethylethylenediaminetriacetic acid (HEDTA) is a somewhat more effective chelating ligand for $Zr(IV)$ than is EDTA at high pH since it contains a hydroxyethyl group in place of one of the acetate groups of EDTA. This group makes available a very basic alkoxide oxygen at high pH and thus helps to stabilize the chelate compound against hydrolytic reactions. It was considered of interest, therefore, to investigate the affinity of the $Zr(IV)$ -HEDTA chelate for additional bidentate donors in the hope of further increasing the stability of the compound toward hydrolysis.

Zr-HEDTA-Tiron, 1:1:1.—Titration of the system containing equivalent amounts of $Zr(IV)$, HEDTA and Tiron (Fig. 4A) gave a short sloping inflection at about $4\frac{2}{3}$ and a much steeper one at $m = 6$. The latter probably corresponds to the completely coordinated metal, thus indicating a simple system. No precipitate was formed overnight at $m = 6.8$ (pH 10.7).

Other ligands which formed 1:1:1 mixed chelates with $Zr(IV)$ and HEDTA are described in Table I and in Fig. 4.

Mixed Chelates Containing CDTA.—In a previous publication² it was shown that CDTA was generally less satisfactory for binding $Zr(IV)$ because of the formation of a precipitate. Since CDTA is more effective than EDTA for divalent metal ions, mixed $Zr(IV)$ chelates of CDTA were studied because of the possibility of forming soluble chelates in the presence of an additional ligand.

Zr-CDTA-Tiron, 1:1:1.—Potentiometric titra-

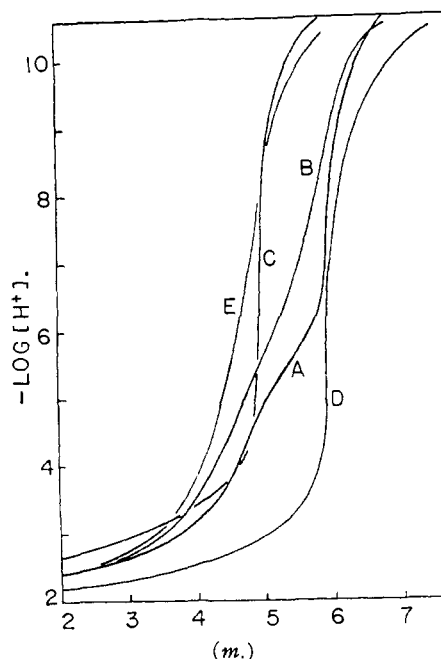


Fig. 4.—Potentiometric titration of $Zr(IV)$ in the presence of equivalent amounts of HEDTA and an additional ligand: A, Tiron; B, chromotropic salt; C, 8-hydroxyquinoline sulfonate; D, oxalic acid; E, acetylacetonate.

tion of the Zr -CDTA-Tiron system shows a steep inflection at $m = 4$ and is almost identical with the corresponding EDTA system. The high stability of this system is indicated by the absence of the precipitation at $m = 5$ even after it was allowed to stand for a period of two weeks.

Similar mixed chelates containing an equivalent of chromotropic salt, 8-hydroxyquinoline-5-sulfonate, oxalate and acetylacetonate, in addition to $Zr(IV)$ and CDTA, were also investigated, and are described in Table I.

Mixed Chelates Containing NTA. Zr-NTA-Tiron, 1:1:1.—The mixture containing equimolar amounts of NTA, Tiron and $Zr(IV)$ gave a titration curve similar in shape to the 1:1:2 curve described below, with the exception that the second buffer region involves less uptake of base. Beyond the second buffer region a slow reaction occurs, and the curve shown is not the equilibrium one. The second buffer region in both systems probably involves neutralization of the Tiron as it coordinates with the metal ion. However, the fact that the 1:1:1 mixture has inflections at fractional neutralization values indicates involvement of hydroxo groups and probable polymerization of the metal chelate(s) present and precludes a simple interpretation.

Zr-NTA-Tiron, 1:1:2.—Potentiometric titration of this system shows a small inflection near $m = 5$ and a steep inflection at $m = 7$ as is indicated in Fig. 5A. The inflection at 7 probably corresponds to the titration of the 7 protons from the ligands, suggesting the formation of a chelate in which the metal is completely coordinated.

Other mixed chelates containing 1:1:1 ratios of Zr , NTA and Tiron, and 1:1:2 molar ratios of Zr , NTA and oxalate ion, are described in Table I.

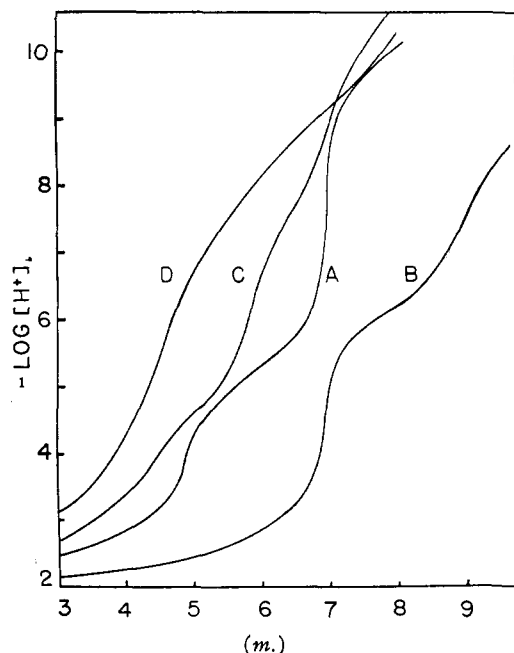


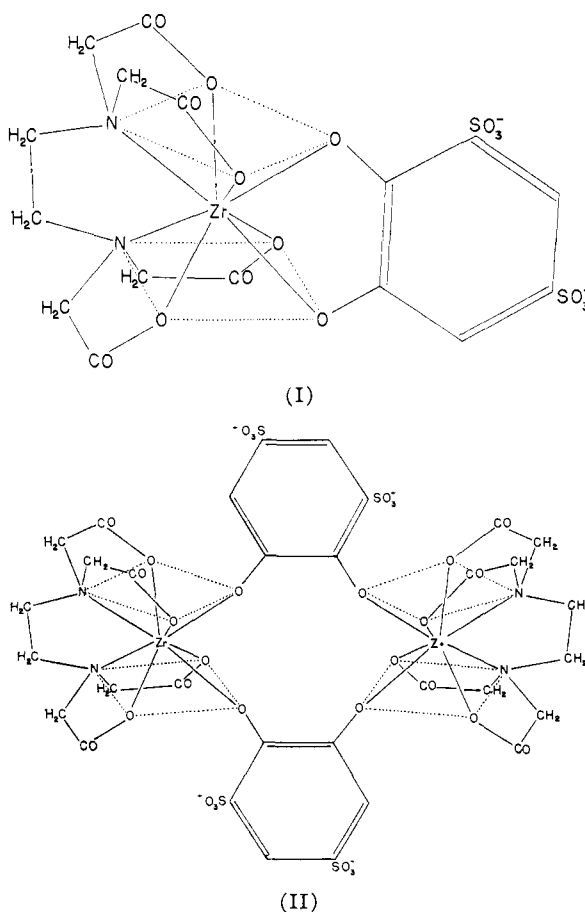
Fig. 5.—Potentiometric titration of Zr(IV) in the presence of the following equivalents of ligands per metal ion: A, 1 NTA and 2 Tiron; B, 1 NTA and 2 oxalic acid; C, 1 HIMDA and 2 Tiron; D, 2 Tiron and 2 acetylacetone.

Other Mixed Chelate Systems. Zr-HIMDA-Tiron.—Mixed chelates containing 1:1:1 and 1:1:2 ratios of Zr(IV), hydroxyethyliminodiacetic acid and Tiron, respectively, also were studied and are described in Table I.

Zr-Acetylacetone-Tiron, 1:2:2.—The titration curve for this system, Fig. 5D, shows a series of overlapping buffer regions (similar to Zr-HIMDA-Tiron, 1:1:2) suggesting that no single simple species is in solution. This idea is further substantiated by the considerable buffering capacity beyond $m = 6$, where all of the ligand protons have been removed.

Up to about $m = 4$, the curve behaves in a manner very similar to that of Zr-Tiron 1:2 mixture, indicating that in this region acetylacetone is not bound. As the pH rises acetylacetone groups coordinate, giving rise to the flattened regions of this curve. The acetylacetone must coordinate the metal ion at higher pH values, since the high pH portions of the titration curve cannot be superimposed upon the Zr-Tiron 1:2 curve even after the acetylacetone dissociation is taken into consideration. It is certain that the hydroxo groups are bound to the metal at high pH , and polymerization probably occurs.

Zr-NTA-HIMDA, 1:1:1.—In view of the interesting properties of the 2:1 NTA and HIMDA chelates described previously,² it was considered of interest to study an equimolar mixture of these two ligands. The resulting titration curve was an average of the 2:1 NTA-Zr and the 2:1 HIMDA-Zr curves. Thus it appears that the mixed chelate does not have special stability or hydrolytic tendencies and that a mixture of the mixed chelate and its disproportionation products probably was present in the experimental solution.



Discussion

The data described above indicate that when Zr(IV) is bound by a chelating agent containing six or fewer donor groups, completion of its coordination requirements with supplementary ligands to satisfy a characteristic coordination number of eight greatly enhances the stability of the chelate, decreases the tendency of the chelate compound to hydrolyze and polymerize, and consequently increases its tendency to form a simple chelate compound.

In general, it is assumed that the simple compound formed will be a mononuclear chelate in which each ligand bound contributes all of its donor groups to the same metal ion. An alternate possibility is that pairs of bidentate ligands may bridge two metal ions to form a completely coordinated simple dimer. Two possible arrangements for typical sexadentate and bidentate ligands are illustrated by I and II.

If the Zr(IV) is already combined with a chelating agent with carboxylate donor groups, the greatest increase in stability is obtained when the secondary ligand contains phenolic or aliphatic hydroxyl groups, which can produce alkoxide anions through displacement of a proton by the metal ion. Thus exceptionally high stability was obtained by the combination of Tiron with the EDTA-Zr(IV), HEDTA-Zr(IV), with the NTA-Zr(IV) chelates.

The stabilizing influence of negative alkoxide ions seems to reach a limit when the complex becomes too negative. Thus it was seen² that only

three moles of Tiron combine simultaneously with a gram-ion of Zr(IV). Also, the stabilizing effect of the additional ligand is not nearly as great when the chelate initially formed already involves combination of alkoxide anions with the metal. The considerable increase of stability observed in these chelates was cut down as the basicity of the auxiliary ligand was reduced.

Although in the case of the quadridentate ligands, NTA, HIMDA and HxG (N,N-dihydroxyethylglycine), it was found that the stabilities of the 2:1 complexes increase with the number of hydroxyalkyl groups, it is possible that in the complex of HxG, the number of such groups was already in excess of what is needed for optimum stability.

On the basis of the titration data given above, the stabilizing influence of bidentate ligands on Zr(IV) chelates of aminopolycarboxylic acids decreases in the order Tiron > chromotropic salt >

acetylacetone > 8-hydroxyquinoline sulfonate > oxalate > 5-sulfosalicylic acid > *o*-phthalic acid. For five-membered rings the order of decreasing basicity of the anions is: Tiron > 8-hydroxyquinoline sulfonate > oxalate. For six-membered chelate rings, the order is chromotropic salt > acetylacetone > 5-sulfosalicylic acid. The position of alizarin-3-sulfonate in this series is not quite obvious from the analysis of the single titration curve available, but the data indicate that it may rank with Tiron and chromotropic salt, in accordance with its basicity.

The titration data given above, and the discussion of relative effectiveness of binding by bidentate ligands, offer evidence that 5-membered chelate rings are the most stable in zirconium complexes and that zirconium(IV) usually attains a characteristic coordination number of eight in its aqueous complexes under favorable conditions.

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An Electron Spin Resonance Study of the Reaction of Pyridine with Potassium: The Formation of Bipyridyl Negative Ion¹

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An electron spin resonance study of the product of the reaction of potassium metal with pyridine in 1,2-dimethoxyethane has been performed. Deuterated species have been synthesized and their negative ions prepared. A comparison of these paramagnetic species with the negative ion of 4,4'-bipyridyl indicates that pyridine has undergone a coupling reaction. Hyperfine coupling constants have been determined for all the magnetic nuclei, and the concept of spin density on the nitrogen atom is discussed.

Introduction

In recent years the study of solutions of aromatic hydrocarbon negative ions, positive ions and neutral free radicals, by electron spin resonance techniques, has yielded much information about the unpaired spin distribution in these molecules. Theoretical studies of these spin distributions have indicated that a σ - π exchange mechanism is responsible for the observed isotropic proton hyperfine interactions²⁻⁵ and that an estimation of the spin density on a carbon atom is possible once the contiguous proton hyperfine interaction is known. The carbon spin density is estimated by the equation $A_H = Q\rho$, where Q is a constant of magnitude -22.4 gauss.⁶⁻⁷

The hyperfine interaction of a nucleus in the ring of a free radical has been observed in only a few cases, by means of a complex isotopic synthesis^{8,9} or by observing natural abundant isotopic splitting.¹⁰ The study of heterocyclics, of which little

has been reported, will yield information about the hyperfine interaction of magnetic aromatic ring nuclei.

We attempted to undertake a study of pyridine negative ion with the hope that a knowledge of its spin distribution would greatly help the work on more complex heterocyclics, as benzene negative ion did for aromatic hydrocarbons. Unfortunately, the paramagnetic product obtained when pyridine had reacted with potassium turned out to be not pyridine negative ion, but 4,4'-bipyridyl negative ion. Accordingly we have made a study of this paramagnetic species, determined coupling constants for all the magnetic nuclei and discussed the spin density at the nitrogen atom.

Results

In an attempt to prepare pyridine negative ion, an investigation of the reaction of potassium metal with pyridine in 1,2-dimethoxyethane was undertaken. Hydrocarbons, such as naphthalene or anthracene, react almost immediately with an alkali metal to yield a highly colored paramagnetic solution. The reaction with pyridine, however, is quite slow in comparison and must be performed at about -50 to -70° . It was observed that if a solution of pyridine in 1,2-dimethoxyethane was allowed to remain in contact with the alkali metal for only short periods of time, an intensely purple solution was obtained, which exhibited a copious hyperfine structure. If however the solution re-

(1) This work was performed under the auspices of the U. S. Atomic Energy Commission.

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