

[CONTRIBUTION OF THE DEPARTMENT OF CHEMISTRY, CLARK UNIVERSITY]

**Zirconium Complexes in Aqueous Solution. I. Reaction with Multidentate Ligands<sup>1</sup>**

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A study of the interaction of Zr(IV) with a wide variety of chelating agents has resulted in the discovery of a number of chelates with multidentate oxygen donor groups stable over a wide range of *p*H. The most stable chelate compounds were formed with disodium 1,2-dihydroxybenzene-3,5-disulfonate, diethylenetriaminepentaacetic acid, nitrilotriacetic acid, N-hydroxyethylethylenediaminetriacetic acid, N-hydroxyethyliminodiacetic acid and N,N-dihydroxyethylglycine. Ethylenediaminetetraacetic acid was less effective, while trimethylenediaminetetraacetic acid does not lead to the formation of soluble complexes.

The lack of activity in the development of the aqueous coordination chemistry of zirconium(IV) probably is due in large part to the pronounced tendency of zirconium complexes toward hydrolysis and olation reactions even in strongly acid solutions. Associated with these tendencies is the process of aging of zirconium(IV) solutions, in which slow, irreversible reactions are superimposed on the relatively rapid reactions involving complex formation, hydrolysis and olation. Presumably the aging process in its initial stages involves further polymerization of the metal through hydroxo bridges and conversion of hydroxo bridges to oxo linkages. A number of investigators<sup>2-7</sup> have suggested possible structures for the chemical species present in aqueous zirconium(IV) systems on the basis of spectrophotometric and potentiometric measurements, ultracentrifugation and solvent extraction.

A survey of the literature reveals very few ligands with which zirconium(IV) forms water-soluble complexes stable at high *p*H for an extended period of time. Except for some preliminary spectrophotometric measurements of the 1:1 chelates of salicylaldehyde,<sup>8</sup>  $\alpha$ -nitroso- $\beta$ -naphthol, *o,o'*-dihydroxyazobenzene,<sup>9</sup> and of alizarine sulfonate,<sup>10</sup> and a potentiometric study of the 1:1 EDTA-Zr(IV) system,<sup>11</sup> the investigations thus far reported have been carried out in strongly acid solutions. This investigation was therefore initiated with a twofold purpose: the search for zirconium(IV) complexes which are soluble and stable throughout a wide *p*H range, and which are also sufficiently simple that the structure of the water-soluble species formed might be demonstrated readily. The first step in this study was to survey a variety of chelating agents to determine the type of structure that binds the zirconium(IV) ion most strongly and that gives stable coordination compounds at elevated *p*H. Because of the pronounced affinity

of Zr(IV) for oxygen donor atoms, the ligands studied are mainly those which coordinate through carboxyl, hydroxyl and ether groups.

**Experimental**

**Potentiometric Titrations.**—A Beckman Model GS *p*H meter was used to determine hydrogen ion concentrations. Titrations were carried out in a jacketed titration cell of 100-ml. capacity, which was fitted with a magnetic stirrer, nitrogen inlet and outlet tubes, microburet delivery tube and glass and calomel extension electrodes. Measurements were made at a temperature of  $24.7 \pm 0.05^\circ$ . The ionic strength was maintained relatively constant by using a medium of 0.1 *M* potassium chloride and relatively low concentrations of ligand and metal ion. Purified nitrogen was bubbled through the solution in order to exclude carbon dioxide. The molar concentration of metal ion was adjusted to approximately  $2.5 \times 10^{-3}$ .

The electrode system was calibrated with standard acetate buffer according to the method of Michaelis.<sup>12</sup>

A measured quantity of the acid form of the ligand was added directly into the cell and the desired amount of the zirconium(IV) chloride solution then was added slowly from an automatic buret while the mixture was stirred with a magnetic stirrer. The solution then was made up to volume with water and 0.20 *M* KCl solution. When the mixture had reached thermal equilibrium, the excess acid was quickly titrated with base. Increments of base now were added and *p*H meter readings were taken until relatively constant values were obtained. Equilibrium was assumed when successive *p*H readings, separated by adequate time intervals, showed no change in hydrogen ion concentration. Each system was titrated at least twice, once with the reaction mixture made up with a dilute zirconium(IV) stock solution (A) and once with a concentrated zirconium(IV) stock solution (B) (see below). For reaction mixtures prepared with the former solution, equilibrium at *p*H values above 5 was usually reached slowly and several days sometimes were required for the completion of a titration. Except for a few striking exceptions described below, the results with the two stock solutions were essentially the same.

**Reagents.**—Standard zirconium(IV) chloride solutions were made up from the best grade of zirconium tetrachloride obtainable (Titanium Division of the National Lead Corporation). A small amount of the solid was weighed rapidly and was dissolved completely in cold ( $-10^\circ$ ) constant boiling hydrochloric acid. This solution then was diluted carefully with water to give a stock solution (A), which was approximately 0.018 *M* in Zr(IV) and 0.11 *M* in HCl, and a stock solution (B), which was approximately 0.2 *M* in Zr(IV) and 1.2 *M* in HCl. Aliquots of these stock solutions were analyzed gravimetrically for chloride, with and without precipitation of the zirconium as the hydrous oxide. Zirconium was determined gravimetrically by ignition of both the hydrous oxide and the phthalate to ZrO<sub>2</sub>. Zirconium and chloride analyses were self-consistent and agreed within experimental error with the amounts weighed out.

Tiron (disodium 1,2-dihydroxybenzene-3,5-disulfonate) was obtained from the LaMotte Chemical Products Co., Baltimore, Maryland, and was used without further purification after establishment of its purity.

Samples of ethylenediaminetetraacetic acid (EDTA), N-hydroxyethylethylenediaminetriacetic acid (HEDTA),

(1) This work was supported by the U. S. Atomic Energy Commission under Contract AT(30-1)-1823.

(2) R. E. Connick and W. H. McVey, *THIS JOURNAL*, **71**, 3182 (1949); R. E. Connick and W. H. Reas, *ibid.*, **73**, 1171 (1951).

(3) K. A. Kraus, *ibid.*, **75**, 5769 (1953); **78**, 3937 (1956).

(4) A. J. Zielen, UCRL-2268, 1953.

(5) B. A. J. Lister and L. A. McDonald, *J. Chem. Soc.*, 4315 (1952).

(6) E. M. Larsen and A. M. Gammill, *THIS JOURNAL*, **72**, 3615 (1950).

(7) E. M. Larsen and P. Wang, *ibid.*, **76**, 6223 (1954).

(8) M. Bobtelsky and C. Heitner, *Bull. soc. chim. France*, **19**, 938 (1952).

(9) H. B. Jonassen and W. R. DeMonsabert, *THIS JOURNAL*, **76**, 6025 (1954).

(10) E. M. Larsen and S. T. Hirozawa, *J. Inorg. Nuclear Chem.*, **3**, 198 (1956).

(11) L. O. Morgan and N. L. Justus, *THIS JOURNAL*, **78**, 38 (1956).

(12) L. Michaelis, "Physical Methods of Organic Chemistry," Vol. I, 2nd ed., Interscience Publ., Inc., New York, N. Y., 1950, p. 1727.

nitriiotriacetic acid (NTA), N-hydroxyethyl iminodiacetic acid (HIMDA), N,N-dihydroxyethylglycine (HXG) and diethylenetriaminepentaacetic acid (DTPA) were obtained through the courtesy of the Dow Chemical Company, Midland, Michigan. Trimethylenediaminetetraacetic acid (TNTA) was prepared by Mrs. Sonya Westerback of these laboratories. *trans*-N,N'-1,2-Diaminocyclohexanetetraacetic acid (CDTA), and the septadentate and octadentate ligands, [oxybis-(ethylenetriolo)]-tetraacetic acid (OETA), and [ethylenebis-(oxyethylenetriolo)]-tetraacetic acid (EOTA), respectively, were obtained through the courtesy of the Geigy Chemical Corporation. The sample of EOTA was purified by recrystallization from water, but the OETA, which analyzed better than 99% pure, was used without further purification.

All ligands employed were of reagent grade or of the highest available purity and were recrystallized whenever necessary. Stock solutions of the ligands were standardized potentiometrically. Carbonate-free 0.1 molar potassium hydroxide solution was prepared by the method of Schwarzenbach and Biedermann.<sup>13</sup>

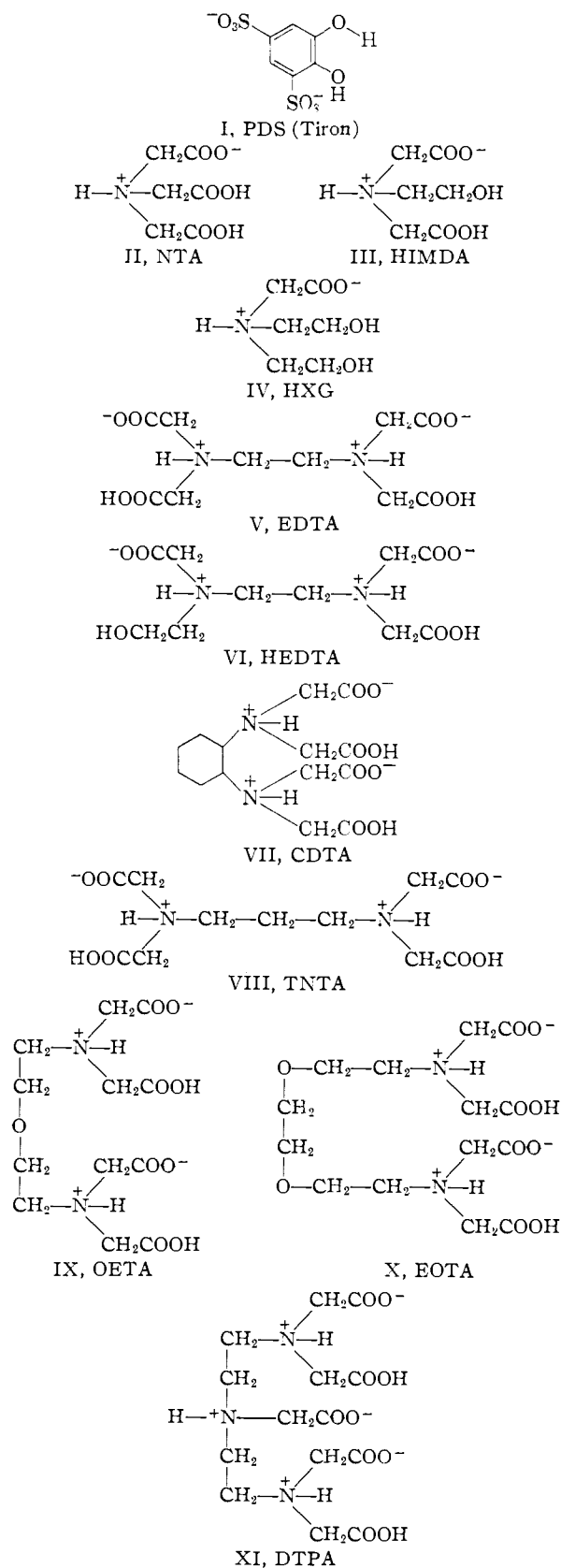
### Results and Discussion

**Bidentate Ligands. Tiron.**—The titration of a solution containing 1 mole of Tiron (structure I) per mole of zirconium(IV) is illustrated in Fig. 1. The resulting titration curve has a steep but definitely sloping inflection between 4 and 5 equivalents of base. Since each mole of Tiron would require only two moles of base, the complexes formed in the low pH buffer region contain from two to three hydroxyl ions attached to each metal ion. The resulting zirconium chelate must be highly polymerized through hydroxo bridges and probably has a structure similar to the one represented by structure XIII.

Potentiometric measurement of the system containing a 2:1 molar ratio of ligand to metal is also shown in Fig. 1. In the initial low pH buffer region hydroxo complexes of the type indicated by formula XIII undoubtedly are formed. At higher pH, however, further uptake of base results in a relatively sharp inflection in the titration curve. This inflection indicates virtual completion of a reaction on the addition of 6 moles of base per mole of metal ion and probably is due to the ultimate formation of a polymerized 2:1 chelate compound having the general form indicated by formula XIV.

Titration of solutions having a 3:1 molar ratio of Tiron to metal ion results in a titration curve (Fig. 1) having an inflection region at 7 equivalents of base, when zirconium stock solution B was used. (Stock solution A yielded a similar curve with an inflection region at 6.75.) This would tend to indicate formation of a structure in which each zirconium is coordinated with 3 ligand molecules and joined together by a relatively small number of hydroxo bridges. However, the possibility of bridging *via* oxygen groups of Tiron cannot be excluded.

The 3:1 curve and the titration curve of the free ligand were found to be additive (in the horizontal direction) throughout the whole pH range to give the titration values obtained experimentally for the 4:1 titration (not shown). Thus the potentiometric data indicate that, at the concentration range employed, no more than three moles of Tiron combine with a gram-ion of zirconium(IV).



(13) G. Schwarzenbach and W. Biedermann, *Helv. Chim. Acta*, **31**, 331 (1948).

Tiron seems to be unusual in giving complete solubility over the entire pH range, even at ratios of ligand to metal as low as 1:1. Most of

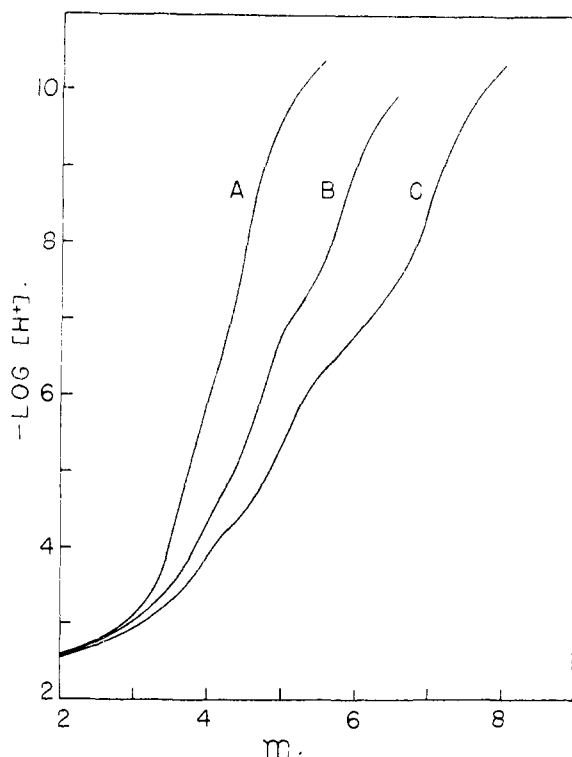


Fig. 1.—Potentiometric titrations of Zr(IV)-Tiron chelates: A, 1:1 Zr(IV)-Tiron; B, 1:2 Zr(IV)-Tiron; C, 1:3 Zr(IV)-Tiron.  $m$  = moles of base added per gram-ion of Zr(IV).

the other bidentate ligands screened (*e.g.*, oxalic acid, 5-sulfosalicylic acid, 8-hydroxyquinoline-5-sulfonic acid, tartaric acid, etc.) yielded precipitates over at least part of the titration curve in the 1:1 mole ratio.

**Quadridentate Ligands. NTA.**—The combination of two moles of nitrilotriacetic acid (structure II) with one of Zr(IV), illustrated in Fig. 2, gives a flat, low  $pH$  buffer region in which six equivalents of base are required, followed by a steep inflection. The extremely steep inflection corresponds to the neutralization of all ligand protons, and suggests the formation of a stable, completely coordinated, 2:1 mononuclear species (XV). In the high  $pH$  buffer region beyond 6 equivalents of base, hydroxyl ions displace the acetate groups, leading to the formation of a precipitate which contains metal and ligand.

The 1:1 NTA-Zr(IV) titration curve in Fig. 3 is rather unusual in that it has a rather steep inflection at 5 equivalents of base with precipitation beginning just below the inflection at  $pH$  about 4. Qualitative analysis, by ashing, and infrared spectra (Nujol mull) showed that the precipitate formed in the  $pH$  region 2 to 8 contains both ligand and metal and therefore was probably a zirconium(IV)-NTA chelate. The precipitate formed at about  $pH$  10 was essentially the hydrous oxide.

The titration of a 2:1 molar ratio of HIMDA (structure III) and Zr(IV), illustrated in Fig. 2 gave a flat, low  $pH$  buffer region up to the point where about 4.5 equivalents of base had been added. Between 4.5 and 5.5 equivalents, a sloping

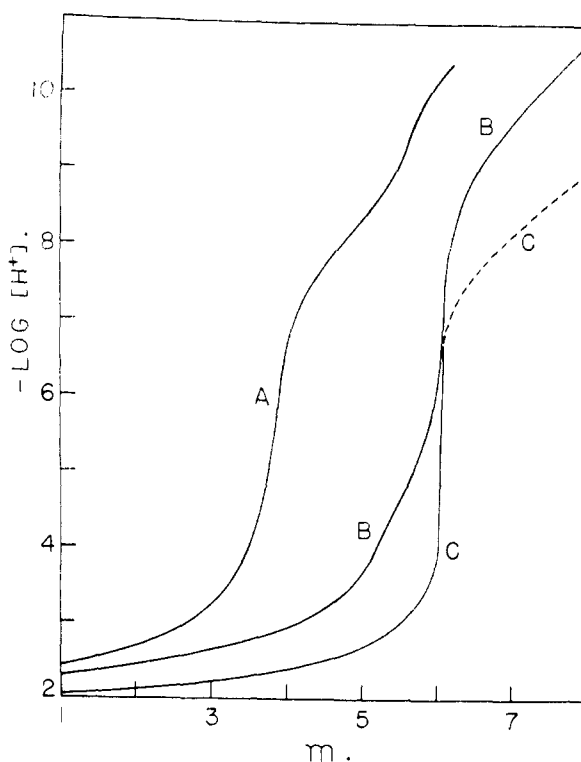


Fig. 2.—Potentiometric titrations of: A, 1:2 Zr(IV)-N-N-dihydroxyethylglycine (HXG); B, 1:2 Zr(IV)-N-hydroxyethyliminodiacetic acid (HIMDA); C, 1:2 Zr(IV)-nitrilotriacetic acid (NTA).  $m$  = moles of base added per gram-ion of Zr(IV). Dashed line indicates presence of solid phase.

region is observed, followed by a steep inflection  $m = 6$ . This system is stable at higher  $pH$  values than is the 2:1 NTA-Zr(IV) chelate, with precipitation occurring at about  $pH$  11 after standing overnight. The shape of the titration curve indicates that stepwise binding of the metal by the donor groups of the ligand must occur, the less basic carboxylate groups (together with the nitrogen atom) coordinating at low  $pH$  (see formula XVI) followed by combination with the alkoxide linkages at higher  $pH$ . Thus the chelate compound is probably completely formed at  $m = 4$ , and the sloping buffer region between  $m = 4$  and  $m = 6$  probably corresponds to association of the metal with the hydroxyl groups with simultaneous displacement of the hydrogen ions to give a quadridentate structure similar to XV. Potentiometric titration of a 1:1 ratio of HIMDA to Zr(IV), illustrated in Fig. 3, gave a precipitate at  $pH$  4.5.

Potentiometric titration of a 2:1 molar ratio of HXG(IV) to Zr(IV), illustrated in Fig. 2, gave a relatively short, low  $pH$  buffer region followed by a sloping, relatively steep, buffer region between 4.0 and 6.0 moles of base. The stabilities of the metal chelate species formed were indicated by the lack of precipitation, even after long standing, after the addition of six equivalents of base, at about  $pH$  10. The sloping region of the curve probably corresponds to dissociation and coordination of the hydroxyethyl groups of the

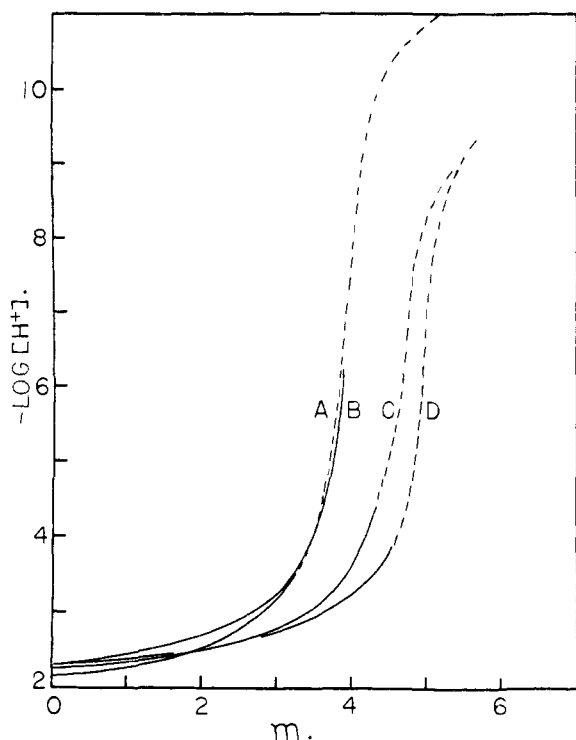


Fig. 3.—Potentiometric titrations of: A, zirconium(IV) chloride; B, 1:1 Zr(IV)-N,N-dihydroxyethylglycine (HXG); C, 1:1 Zr(IV)-N-hydroxyethyliminodiacetic acid (HIMDA); D, 1:1 Zr(IV)-nitrilotriacetic acid (NTA).  $m$  = moles of base added per gram-ion of Zr(IV). Dashed line indicates presence of solid phase.

ligand, as in the case of HIMDA, to give a compound with an arrangement of donor groups similar to that of structure XV. In the case of HXG, however, the larger number of hydroxyethyl groups in the metal chelate greatly accentuates the sloping part of the curve. In view of the absence of a steep inflection even at  $m = 6$ , it seems that reaction with further base may result from the displacement of coordinated ethoxide or carboxylate groups by hydroxyl ions. Thus at  $m = 6$ , several coordinated metal species may be present, the ones requiring more than six equivalents of base being balanced by species requiring less base. The titration of a 1:1 ratio of HXG and Zr(IV), illustrated in Fig. 3, gives a curve which is identical to the 2:1 curve up to  $pH 6$ . Above this  $pH$  precipitation occurs.

Comparison of the NTA, HIMDA and HXG titration curves indicates that: (1) two moles of ligand per gram-ion of Zr(IV) is necessary to form chelates stable at high  $pH$ , (2) the stabilities of these chelates increase in the order  $NTA < HIMDA < HXG$  and (3) alkoxide groups seem to coordinate more effectively with Zr(IV) than do carboxylate groups.

**Sexadentate Ligands. EDTA.**—Potentiometric titration of systems containing a 1:1 molar ratio of EDTA (structure V) to Zr(IV) is illustrated in Fig. 4. Significant differences in behavior were observed between runs made with the zirconium stock solutions A and B, although the shapes of the titration curves were essentially the same.

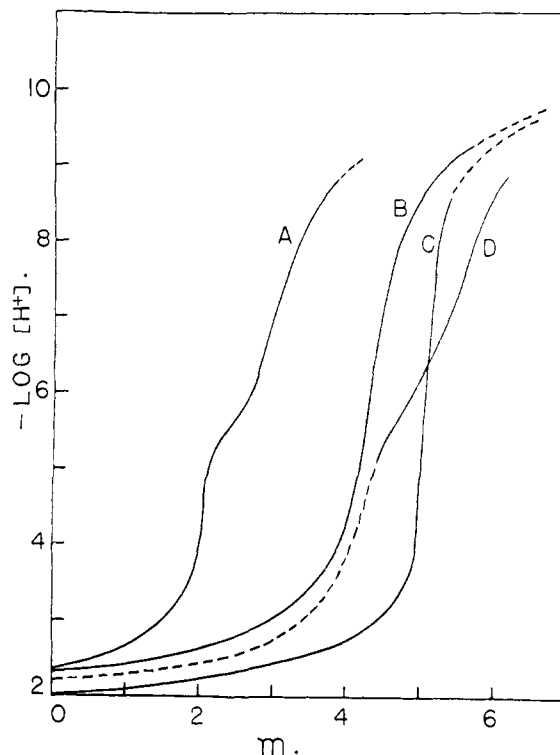
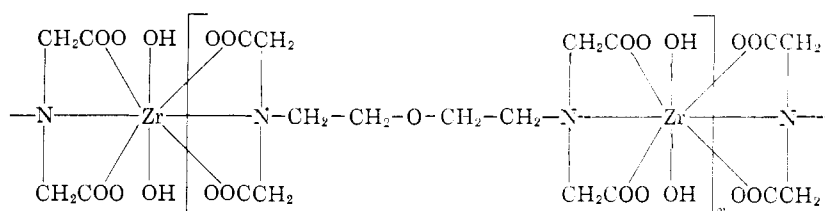


Fig. 4.—Potentiometric titration of: A, 1:1 Zr(IV)-ethylenediaminetetraacetic acid-disodium salt (EDTA); B, 1:1 Zr(IV)-N-hydroxyethylethylenediaminetriacetic acid (HEDTA); C, Zr(IV)-*trans*-cyclohexanediaminetetraacetic acid (CDTA); D, Zr(IV)-diethylenetriaminepentaacetic acid (DTPA).  $m$  = moles of base added per gram-ion of Zr(IV). Dashed line indicates presence of solid phase.

An inflection at two moles of base per mole of ligand (corresponding to the fully dissociated ligand) apparently indicates the formation of a simple chelate of the type represented by XVII. The buffer region at  $pH 6$  between  $m = 2$  and  $m = 3$  indicates the coordination of an additional mole of base with the metal ion and possible simultaneous polymerization to a polynuclear compound. Beyond this region irreversible precipitation of the hydrous oxide takes place. With the concentrated zirconium stock solution B, equilibrium was reached quickly up to  $m = 2.5$ . Beyond this point, a slow reaction took place and  $pH$  meter readings drifted downward. With the dilute zirconium stock solution A,  $pH$  meter readings drifted throughout the titration, indicating that a fast reaction, followed by a slower one, was occurring. With the dilute zirconium stock solution (only) a precipitate formed at the start of the titration, as reported by Morgan and Justus.<sup>11</sup> Contrary to the findings of these workers, however, ashing, nitrogen analysis and infrared spectra demonstrated that the precipitate contained metal and ligand. This precipitate dissolved upon further addition of base, to give a soluble chelate system.

**CDTA.**—Potentiometric titration of a 1:1 ratio of CDTA (structure VII) to Zr(IV), illustrated in Fig. 4, gave a low  $pH$  buffer region similar to that of EDTA, followed by inflections at somewhat above 4 and 5 moles of base, separated by a sloping



XII

buffer region. Although the curve was found to be rather similar to that of EDTA, precipitation was more extensive, occurring in the region between  $pH$  4 and 7 and beyond  $pH$  10. The slope of the first inflection was found to be considerably less than that of the  $Zr(IV)$ -EDTA system. The presence of a precipitate throughout most of the regions of interest precludes a more detailed consideration of this titration curve.

**TNTA.**—The titration of a 1:1 ratio of trimethylenediaminetetraacetic acid, TNTA (structure VIII), to  $Zr(IV)$  resulted in precipitation throughout the entire titration. Comparison with the results for EDTA and CDTA indicates that  $Zr(IV)$  is coordinated more strongly by ligands which form 5-membered rings rather than by those which form 6-membered rings.

**HEDTA.**—The titration of a 1:1 molar ratio of HEDTA (structure VI) to  $Zr(IV)$ , illustrated in Fig. 4, gives the characteristic low  $pH$  buffer region, similar to that of EDTA, which involves the neutralization of four moles of base per mole of ligand and indicates the formation of a simple chelate of the type indicated by XVII. It is notable in this case that the hydroxyethyl group probably is involved in coordination with the metal ion. The sloping region of the curve beyond four equivalents of base indicates further coordination with hydroxyl ions and possible polymerization to polynuclear species. Precipitation occurs beyond  $pH$  9.5.

These data indicate that the replacement of one carboxyl group in EDTA by a hydroxyethyl group greatly stabilizes the aqueous metal chelate formed and helps to give a compound more resistant to hydrolysis. The same effect is observed with the quadridentate ligands, as was noted above.

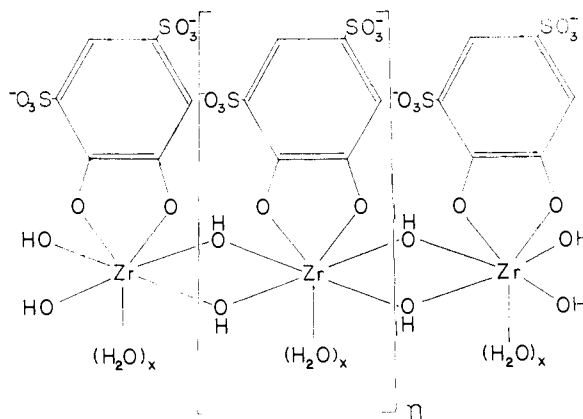
**Septadentate Ligands. OETA.**—The investigation of a 1:1 ratio of OETA (structure IX) to  $Zr(IV)$  gave precipitation over most of the  $pH$  range covered in the titration. In the low  $pH$  buffer region the precipitated species contains metal and ligand and probably has a structure similar to that shown in structure XII. OETA, which contains coordinating groups similar to those in EDTA, would have to coordinate with  $Zr(IV)$  through an ether oxygen in order to be effective. Thus it is seen that the coordination tendency of this ether group toward  $Zr(IV)$  is too weak to balance the steric and electronic effects which result from the interposition of this group between the two iminodiacetate groups of EDTA. No other septadentate ligands are available at the present time.

**Octadentate Ligands. EOTA.**—The potentiometric investigation of EOTA (structure X) gave results similar to those obtained for OETA. The

conclusions made above on the basis of the properties of ligand IX, to the effect that coordination of  $Zr(IV)$  through ether oxygens is quite weak, are thus strengthened by the failure of X, which contains two such ether oxygens, to produce a stable chelate compound. The precipitate formed in this titration was essentially the hydrous oxide of zirconium.

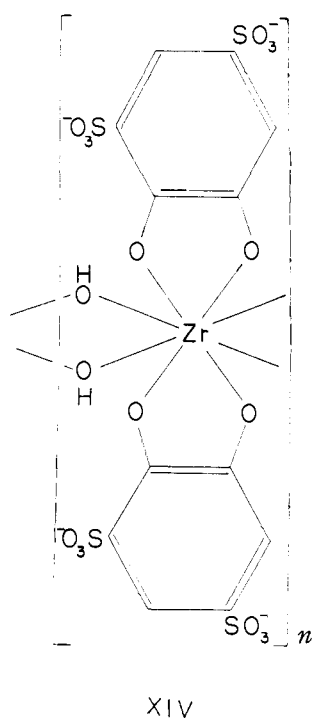
**DTPA.**—The potentiometric titration of a 1:1 molar ratio of DTPA (structure XI) to  $Zr(IV)$  gave remarkably different results, depending upon whether the zirconium stock solution A or B was used. With the concentrated stock solution B, a low buffer region was followed by a steep inflection at  $m = 5$  (see Fig. 4). The titration was marked by the absence of precipitation below about  $pH$  9. This titration curve suggests the formation of a completely coordinated  $Zr(IV)$ -DTPA chelate in which all eight coordination sites of the metal are filled by the eight ligand donor groups.

In sharp contrast, the dilute zirconium stock solution A gave precipitation throughout the entire  $pH$  range, of a partially chelated species. The fact that horizontal addition of the titration curves of zirconium(IV) chloride and of DTPA does not give the observed titration curve further indicates that coordination of the metal with the ligand occurs in this system. Also, the fact that the mid-point of the sloping inflection occurs at 7.5 moles of base per mole of metal indicates that about 2 or 3 hydroxyl groups are coordinated per zirconium(IV) at this point. In the case of the dilute stock solution, therefore, it seems that a coordination polymer is formed. An arrangement is suggested similar to that for the combination of  $Zr(IV)$  with OETA (structure XII).



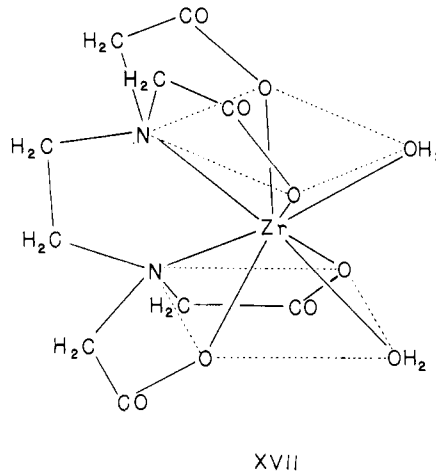
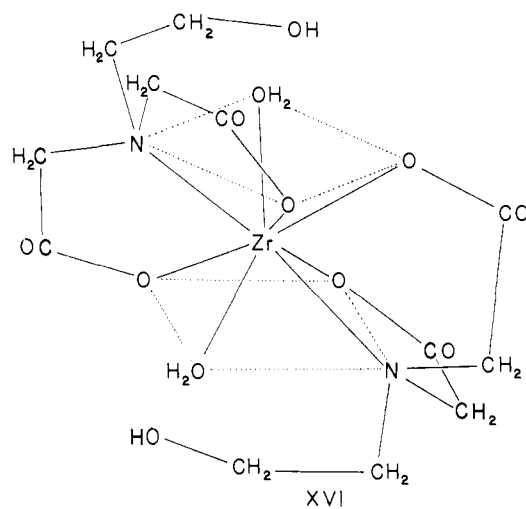
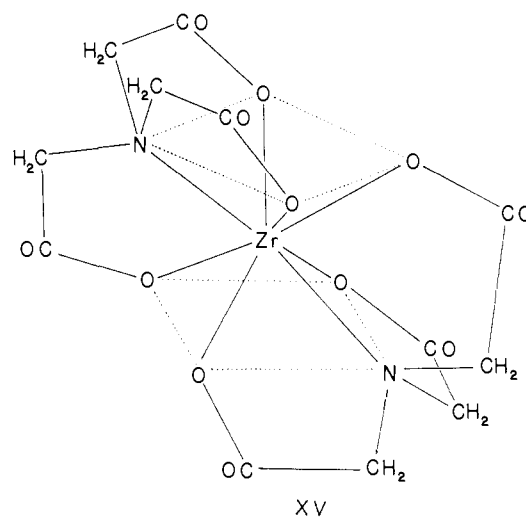
XIII

The results obtained in a semi-quantitative study prior to this investigation indicate that basic



nitrogen is not effective toward Zr(IV) and that a large proportion of negative oxygen donors are required for a ligand to be effective. From the discussion of the tetradentate ligands, as well as the comparison of HEDTA and EDTA, it is apparent that a carboxylate ion coordinates Zr(IV) much less strongly than does the alkoxide ion. This effect, which is not observed in the well known chelates of the divalent transition metals, is due in part to the high coordination number and small radius of the Zr(IV) ion and to the fact that the carboxylate ion is larger than the alkoxide ion, and has a lower charge density. Similar reasoning would lead one to the conclusion that the most effective coordinating group present in these systems, because of its small size and high charge density, is the hydroxyl ion. Thus the increasing order of coordinating tendencies on the basis of the ligands studied thus far is  $R_3\equiv N < R-O-R < RCOO^- < RO^- < OH^- < O^{2-}$ .

A rather surprising result is the similarity in the effectiveness of two equivalents of NTA and one equivalent of DTPA in binding Zr(IV). On the basis of the reactions of these ligands with the transition metal ions, one would expect DTPA to be relatively much more effective as the result of the fact that all coordinating groups are provided by a single ligand anion, rather than by two anions. The Zr:NTA 1:2 chelate is thus more stable than expected, being almost as stable as the Zr:DTPA 1:1 chelate. It should be noted that the main function of employing two ligands rather than a single ligand carrying the same total number of groups would be in relieving steric effects, and to some extent, the mutual repulsions of the negative donor groups. It is seen that the nature of the septadentate and octadentate ligands OETA and EOTA is such as to require the placing of the two binategative iminodiacetate coordinating groups



relatively close together when they are united with a single metal ion. The mutual repulsions of these groups, as well as the strain involved in chelate ring formation involving the ethylene bridges could be relieved by the coordination of two metal ions by each ligand, as is indicated in structure XII.

The data given above also indicate that 5-membered chelate rings are the most stable in the case of Zr(IV). This conclusion is apparent from a

comparison of the coordination tendencies of ligands V and VIII. This conclusion is also supported by other comparisons made in a preliminary phase of this investigation, when it was observed that many bidentate ligands which were known to form 6-membered chelate rings with other metals were not effective with Zr(IV).

All of the results of this investigation are compatible with a maximum coordination number of 8 for aqueous Zr(IV) complexes. Because of the small radius of the Zr(IV) ion, however, complexes and chelates involving a lower coordination number of the metal are also possibly formed.

WORCESTER, MASS.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CLARK UNIVERSITY]

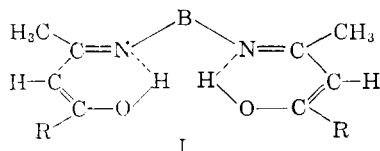
## Dipole Moments of Metal Chelate Compounds. III. Analogs and Polar Substituted Analogs of Bis-acetylacetonethylenediimine<sup>1,2</sup>

BY RICHARD J. HOEY AND ARTHUR E. MARTELL

RECEIVED MARCH 19, 1959

The electric dipole moments of some quadridentate Schiff base chelating agents have been determined and interpreted in terms of the polar groups present and of rotation of the hydrogen-bonded chelate rings about the alkylene bridge. Dipole moment values indicate that polar substituents such as *p*-bromophenyl, *m*-nitro and trifluoromethyl, occupy terminal positions in these molecules. In the benzoylacetonopolymethylenediimine series the dipole moments were found to increase with increasing number of methylene groups.

Earlier papers in this series<sup>3</sup> have reported the results of dipole moment measurements on a series of quadridentate Schiff-base chelating agents and on the corresponding square planar chelates formed with transition metal ions. The present investigation describes similar studies of a number of closely related ligands. Its purpose was to observe the changes in dipole moment resulting from: (1) structural changes in the diimine portion of the Schiff base molecules and (2) the introduction of polar groups into the ligands. The compounds measured are given in Table I and may be represented by formula I in which B is the alkyl (or aryl) radical of the diamine and R represents various polar and non-polar groups.



### Experimental

**Procedure.**—The syntheses and purification of the Schiff base ligands used in this investigation have been given previously.<sup>4,5</sup> The method of measuring the dielectric constants and a description of the cell and heterodyne oscillator were reported in the first paper<sup>3</sup> of this series. In all determinations benzene solutions of the ligands were employed. Because of their low solubilities many of the ligands containing polar groups required heating to obtain complete solution. All solutions employed had concentrations of 1% or less. Specific volumes were determined by means of a Rieschauer pycnometer. The cells used for the measurements were immersed in an oil-bath at 25°; for the determination of an individual dipole moment the temperature remained within  $\pm 0.01^\circ$ .

(1) Abstracted from a dissertation submitted by Richard J. Hovey to the Faculty of Clark University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1958.

(2) This work was supported by the Office of Ordnance Research under Contract No. DA-19-020-ORD-3243.

(3) P. J. McCarthy and A. E. Martell, *THIS JOURNAL*, **78**, 264, 2106 (1956).

(4) P. J. McCarthy, R. J. Hovey, K. Ueno and A. E. Martell, *ibid.*, **77**, 5820 (1955).

(5) R. J. Hovey, J. J. O'Connell and A. E. Martell, *ibid.*, **81**, 3189 (1959).

TABLE I

B	R	Name of ligand
CH(CH <sub>3</sub> )CH <sub>2</sub>	<i>p</i> -C <sub>6</sub> H <sub>4</sub> Br	Bis- <i>p</i> -bromobenzoylacetonopropylenediimine
CH(CH <sub>3</sub> )CH <sub>2</sub>	CF <sub>3</sub>	Bis-trifluoroacetylacetonopropylenediimine
(CH <sub>2</sub> ) <sub>3</sub>	<i>m</i> -C <sub>6</sub> H <sub>4</sub> NO <sub>2</sub>	Bis- <i>m</i> -nitrobenzoylacetonetrimethylenediimine
(CH <sub>2</sub> ) <sub>4</sub>	CH <sub>3</sub>	Bis-acetylacetonetetramethylenediimine
(CH <sub>2</sub> ) <sub>4</sub>	C <sub>6</sub> H <sub>5</sub>	Bis-benzoylacetonetetramethylenediimine
(CH <sub>2</sub> ) <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	Bis-benzoylacetonepentamethylenediimine
CH <sub>2</sub> CH(OH)CH <sub>2</sub>	C <sub>6</sub> H <sub>5</sub>	Bis-benzoylacetonel,3-diimino-2-propanol
<i>m</i> -C <sub>6</sub> H <sub>4</sub>	CH <sub>3</sub>	Bis-acetylacetonem-phenylenediimine

Spectro-grade benzene, obtained from the Eastman Kodak Co., was refluxed over 40-mesh calcium hydride (Metal Hydrides, Inc., Beverly, Mass.) for approximately 48 hours, and then was distilled through a Widmer column, the first and last 15% being rejected. In comparison with the previous method of purifying benzene this new procedure is much simpler and far less time consuming. The dielectric constant of the solvent purified in this manner agreed with the earlier values within the desired limits.

**Calculations.**—The total molar polarization of the solute at infinite dilution ( $P_{2\infty}$ ) was calculated by the method of Halverstadt and Kumler.<sup>6</sup>  $P_{2\infty}$  was obtained by means of the equation

$$P_{2\infty} = \frac{3\alpha v_1 M_2}{(\epsilon_1 + 2)^2} + M_2(v_1 + \beta) \frac{(\epsilon_1 - 1)}{(\epsilon_1 + 2)}$$

where  $\alpha$  and  $\epsilon_1$  are the slope and intercept of the plot of  $\epsilon_2$  (the dielectric constant of a solution) against  $w_2$  (the weight fraction),  $\beta$  and  $v_1$  are the slope and intercept of the plot of  $v_{12}$  (the specific volume of a solution) against  $w_2$ , and  $M_2$  is the molecular weight of the solute. The least-squares method was used in evaluating the various slopes and intercepts.

The dipole moment  $\mu$  is equal to  $0.01281 (P_0 T)^{1/2}$ , where  $T$  is the absolute temperature. The orientation polarization  $P_0$  was obtained by subtracting  $P_E$ , the electronic polarization

(6) I. Halverstadt and W. Kumler, *ibid.*, **64**, 2988 (1942).