

[CONTRIBUTION OF THE DEPARTMENT OF CHEMISTRY, CLARK UNIVERSITY]

Hydrolytic Tendencies of Metal Chelate Compounds. II. Effect of Metal Ion¹

BY R. C. COURTNEY, R. L. GUSTAFSON, S. CHABEREK, JR., AND A. E. MARTELL

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The hydrolysis of 1:1 metal chelates of Zn(II), Mn(II), Fe(II), Hg(II), La(III), Fe(III), Cr(III), Th(IV), Ti(IV) and Sn(IV) were studied potentiometrically in order to ascertain the effect of variation of the metal ion on acid dissociation of coordinated water molecules. A total of 14 ligands were investigated in order to obtain stable water-soluble systems containing these partially chelated metal ions. A study of the titration curves for these systems showed that hydrolytic tendencies of metal chelates vary with the metal in the following approximate order: Mn(II) < Zn(II) < La(III) < Cu(II) < Fe(III), Cr(III) < Th(IV) < Ti(IV), Sn(IV). For the metals investigated the charge of the ion was found to be somewhat more important than the electronegativity of the metal in determining hydrolytic tendencies. In the case of La(III), a reversal was noted in that it was found to fall within the group of bivalent metal ions.

In connection with work being conducted in these laboratories on the catalytic properties of metal ions, it was considered desirable to investigate the effect of changing the metal ion on the tendency to form hydroxo complexes. These compounds are of interest in view of observations by Wagner-Jauregg, *et al.*,² and by Courtney, *et al.*,³ of a wide variation in the catalytic properties of metal chelates with a change in the metal ion. Since hydrolytic tendencies of metal ion seem to show some correlation with the catalytic activity of these ions in the hydrolysis of diisopropylphosphorofluoridate (DFP) and similar substances, a study of the variation of hydrolytic tendencies with various physical and chemical properties of the metal ion would be of interest.

The first quantitative measurement of the formation of hydroxo metal chelates was reported by Schwarzenbach and Heller^{4,5} for the ethylenediaminetetraacetato⁴ and nitrilotriacetato⁵ Fe(II) and Fe(III) chelates. Later, Schwarzenbach and Sandera⁶ described the hydroxo forms of the ethylenediaminetetraacetato chelates of the V(IV) and V(III) ions. Chaberek and Martell have described the hydroxo iron(III) complexes of 3-hydroxypropyliminodiacetic acid,⁷ 2-hydroxyethyliminodipropionic acid⁷ and dihydroxyethylglycine⁸; the corresponding *pK* values were not reported. Although Chaberek and Martell⁹ suggested that the metal chelate of Fe(III) with hydroxyethyl-ethylenediaminetriacetic acid was bound through a dissociated ethoxide group, it is also possible to interpret the results on the basis of a metal-bound hydroxyl group. Prue and Schwarzenbach¹⁰ have also reported the formation of a hydroxo complex of diethylenetriamine-Hg(II). Recently the monohydroxodipyridyl-Cu(II) has been reported by Wagner-Jauregg, *et al.*,² while the equilibria in-

volving this compound, as well as the hydroxides of *o*-phenanthroline-Cu(II) and of ethylenediamine-Cu(II), have been measured quantitatively by Ryland, *et al.*¹¹ The hydrolytic tendencies of various Cu(II) chelates have been reported recently by Martell, *et al.*¹²

Experimental

The experimental method consisted of potentiometric titration of the chelating agent in the absence of and in the presence of the metal ions being investigated. The specific details used in this investigation have been described in a preceding publication.¹²

Reagent grade nitrates of all metals were used except for Sn(IV) which was obtained as a chloride. Standardization of the metal solutions consisted for the most part of evaporation and subsequent ignition to the corresponding oxides. Zinc(II) was standardized by the titration with standard disodium dihydrogen ethylenediaminetetraacetic (Na₂EDTA) reagent with Eriochromschwarz-T as an indicator in ammoniacal solution.¹³ Thorium(IV) was standardized by titration with Na₂EDTA with alizarin red indicator,¹⁴ while manganese(II) was determined by titration with the salt of nitrilotriacetic acid, brom thymol blue being used as an indicator.

Samples of ethylenediaminetetraacetic acid (EDTA), N-hydroxyethylethylenediaminetriacetic acid (HEDTA), N,N'-dihydroxyethylethylenediaminediacetic acid (HEDDA), N-hydroxyethyliminodiacetic acid (HIMDA), N,N'-dihydroxyethylglycine (2-HxG), and nitrilotriacetic acid (NTA), were obtained through the courtesy of Versenes, Inc., Framingham, Massachusetts. Samples of N-hydroxyethylethylenediamine and N,N'-dihydroxyethylethylenediamine were obtained from Carbide and Carbon Chemical Co., purified by fractional distillation and converted to the corresponding hydrochlorides. The ligands 5-sulfosalicylic acid (5-SSA) and 1,8-dihydroxynaphthalene-3,6-disodium sulfonate (DNS) were purchased from Eastman Kodak Co. Pyrocatechol-3,5-disodium sulfonate (PDS) was purchased from LaMotte Chemical Products Corp., Baltimore, Maryland. The 1,3-diaminopropane was obtained from the Sharples Chemical Company. A sample of pyridoxamine dihydrochloride (PYR) was obtained from Nutritional Biochemicals Corporation, Cleveland, Ohio, and was used without further purification. Standardization of the aqueous solutions of the chelating agents was effected by means of potentiometric titration with either standard carbonate-free potassium hydroxide or hydrochloric acid. Each of the 50 titration curves shown involved the determination of 40-50 individual determinations of hydrogen ion concentration.

Results

The potentiometric data obtained on the metal chelates outlined above are summarized in Table

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(13) G. Schwarzenbach, "Die Komplexometrische Titration," Ferdinand Enke Verlag, Stuttgart, 1955, p. 68.

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(1) This paper reports work done under contract with the Chemical Corps, U. S. Army, Washington 25, D. C.

(2) T. Wagner-Jauregg, B. E. Hackley, Jr., T. A. Lies, O. O. Owens and R. Proper, THIS JOURNAL, **77**, 922 (1955).

(3) R. C. Courtney, R. L. Gustafson, S. J. Westerback, H. Hyytiäinen, S. C. Chaberek, Jr., and A. E. Martell, *ibid.*, **79**, 3030 (1957).

(4) G. Schwarzenbach and J. Heller, *Helv. Chim. Acta*, **34**, 576 (1951).

(5) G. Schwarzenbach and J. Heller, *ibid.*, **34**, 1889 (1951).

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(7) S. Chaberek, Jr., and A. E. Martell, THIS JOURNAL, **76**, 215 (1954).

(8) S. Chaberek, Jr., R. C. Courtney and A. E. Martell, *ibid.*, **75**, 2185 (1953).

(9) S. Chaberek, Jr., and A. E. Martell, *ibid.*, **77**, 1477 (1955).

(10) J. E. Prue and G. Schwarzenbach, *Helv. Chim. Acta*, **33**, 985 (1950).

TABLE I
 STABILITIES AND DISSOCIATION CONSTANTS OF METAL CHELATES

Metal ion	Ligand	Type formula of ligand	Equilibrium quotient	log K	Remarks
Zn(II)	EDTA	H ₄ A	[ZnA]/[Zn][A]	16.5, ^a 20°
Zn(II)	HEDTA	H ₃ AOH	[ZnAOH]/[Zn][AOH]	14.5, ^b 20°
Zn(II)	HEDDA	H ₂ A(OH) ₂	[ZnA(OH) ₂]/[Zn][A(OH) ₂]		
Zn(II)	NTA	H ₃ A	[ZnA]/[Zn][A]	10.4, ^c 20°	Some ppt. at pH 8
Zn(II)	HIMDA	H ₂ AH	[ZnAOH]/[Zn][AOH]	8.6, ^d 30°	
Zn(II)	2-HxG	HA(OH) ₂	[ZnA(OH) ₂]/[Zn][A(OH) ₂]	5.4, ^e 30°	
Zn(II)	PDS	A(OH) ₂	[ZnAO ₂]/[Zn][AO ₂]	11.07	
		A(OH) ₂	[ZnAO ₂]/[Zn][OH]A(OH) ₂ [H ⁺]	8.0	Ppt. above pH 10
Zn(II)	5-SSA	H ₂ AOH	Little or no chelation		Ppt. above pH 7
Zn(II)	DNS	A(OH) ₂	Little or no chelation		Ppt. above pH 7
Zn(II)	DAP	A	Weak, easily disproportionated chelates formed		Ppt. above pH 7
Zn(II)	HEN	AOH	Weak, easily disproportionated chelates formed		Ppt. above pH 7
Zn(II)	2-HEN	A(OH) ₂	Weak, easily disproportionated chelates formed		Ppt. above pH 7
Mn(II)	EDTA	H ₄ A	[MnA]/[Mn][A]	14.0 ^a
Mn(II)	HEDTA	H ₃ AOH	[MnAOH]/[Mn][AOH]	10.7, ^b 30°
Mn(II)	HEDDA	H ₂ A(OH) ₂	[MnA(OH) ₂]/[Mn][A(OH) ₂]		
Mn(II)	NTA	H ₃ A	[MnA]/[Mn][A]	7.4, ^c 20°	
Mn(II)	HIMDA	H ₂ AOH	[MnAOH]/[Mn][AOH]	5.6, ^d 30°	Ppt. above pH 10
Mn(II)	2-HxG	HA(OH) ₂	[MnA(OH) ₂]/[Mn][A(OH) ₂]	3.1, ^e 30°	Ppt. above pH 9.5
Mn(II)	PDS	A(OH) ₂ ⁻²	[MnAO ₂]/[Mn][AO ₂]	8.6
Mn(II)	DNS	(A(OH) ₂) ⁻²	Little if any chelate formation		Ppt. above pH 9
Mn(II)	5-SSA	(H ₂ AOH)	Little if any chelate formation		Ppt. above pH 8
Mn(II)	2-HEN	(A(OH) ₂)	Little if any chelate formation		Ppt. above pH 6
Hg(II)	DIEN	A	[HgA]/[Hg][A]	21.8, ^h 20°	
			[HgA]/[Hg][OH]A[H ⁺]	7.7, ^h 20°	
La(III)	EDTA	H ₄ A	[LaA]/[La][A]	15.50, ^a 20°	
			[LaA]/[La][OH]A[H ⁺]	..	
La(III)	HEDTA	H ₃ AOH	[LaAOH]/[La][AOH]	12.8	
La(III)	HEDDA	H ₂ A(OH) ₂	[LaA(OH) ₂]/[La][A(OH) ₂]	9.3	
			[LaA(OH) ₂]/[La][OH]A(OH) ₂ [H ⁺] or [LaA(OH) ₂]/[LaAO(OH)] [H ⁺]	8.4	
La(III)	HIMDA	H ₂ AOH	[LaAOH]/[La][OH]AOH[H ⁺] or [LaAOH]/[LaAO][H ⁺]	8.5	
La(III)	2-HxG	HA(OH) ₂	[LaA(OH) ₂]/[La][A(OH) ₂]	5.0	Ppt. above pH 9
La(III)	5-SSA	H ₂ AOH	[LaAO]/[La][AO]	9.11	Ppt. above pH 8
			[LaAO]/[La][OH]AO[H ⁺]	..	
La(III)	PDS	A(OH) ₂	[LaAO ₂]/[La][AO ₂]	12.9	
			[LaAO ₂]/[La][OH]AO ₂ [H ⁺]	8.3	
Fe(III)	HEDTA	H ₃ AOH	[FeAOH]/[Fe][AOH]	19.6 ^j	
			[FeAOH]/[FeAO][H ⁺]	3.88 ^j	
			[FeAO]/[Fe][OH]AO[H ⁺]	9.05 ^j	
			[Fe[OH]AO]/[Fe[OH] ₂ AO][H ⁺]	10.22 ^j	
Fe(III)	HEDDA	H ₂ A(OH) ₂	[FeA(OH) ₂]/[Fe][A(OH) ₂]	15 ^k	
			[FeA(OH) ₂]/[FeAO(OH)] ² [H ⁺]	2.2 ^k	
			[FeAO(OH)]/[FeAO ₂][H ⁺]	5.5 ^k	
Fe(III)	HIMDA	H ₂ AOH			Ppt. above pH 5.5
Fe(III)	2-HxG	HA(OH) ₂			Ppt. above pH 8
Fe(III)	PDS	A(OH) ₂	[Fe[OH]AO ₂]/[Fe][AO ₂][OH]	20.7, ^l 20°	
Fe(III)	DNS	A(OH) ₂			
Fe(III)	PYR	AOH	[Fe[OH]AO]/[Fe][AO][OH]	5 ⁿ	Ppt. above pH 5
Fe(III)	NTA	H ₃ A	[FeA]/[Fe][A]	8.2, 20°	
			[FeA]/[Fe][OH]A[H ⁺]	4.08, ^f 20°	
			[Fe[OH]A]/[Fe[OH] ₂][H ⁺]	7.77, ^f 20°	
Fe(III)	EDTA	H ₄ A	[FeA]/[Fe][A]	25.1, ^o 20°	
			[FeA]/[Fe[OH]A][H ⁺]	7.52, ^o 20°	
			[Fe[OH]A]/[Fe[OH] ₂ A][H ⁺]	9.44, ^o 20°	
Cr(III)	EDTA	H ₄ A	[CrA]/[Cr][A]	7.39, ^o 20°	
Cr(III)	2-HxG	HA(OH) ₂	[CrAO ₂]/[Cr[OH]AO ₂][H ⁺]	8.1	
Th(IV)	EDTA	H ₄ A	[ThA]/[Th][A]	23.2 ^r	
			[Th[OH]A]/[ThA][H ⁺]	6.5	
Th(IV)	HEDTA	H ₃ AOH	[ThAOH]/[Th][AOH]	15.4	
			[ThAOH]/[Th[OH]AO][H ⁺] ² or [ThAOH]/[Th[OH] ₂ AOH][H ⁺] ²	8.2	

Th(IV)	NTA	H ₃ A	[ThA]/[Th][A]	12.4	
			[ThA]/[Th[OH] ₂ A][H ⁺] ^a	8.2	
Th(IV)	HIMDA	H ₂ AOH	[ThAOH]/[Th][AOH]	10.7	
			[ThAOH]/[Th[OH]AO][H ⁺] ^b		
			or [ThAOH]/[Th[OH] ₂ AOH][H ⁺] ^c	7.8	
Th(IV)	2-HxG	HA(OH) ₂	Only partial chelate formation		Ppt. of Th(OH) ₄ at pH 6
Th(IV)	2-HEN	A(OH) ₂	Little if any chelation		Ppt. of Th(OH) ₄ at pH 4.2
Th(IV)	5-SSA	H ₂ AOH	No chelate formation		Ppt. of Th(OH) ₄ at pH 3.0-3.2
Th(IV)	HEDDA	H ₂ A(OH) ₂	[ThA(OH) ₂]/[Th][A(OH) ₂]	12.8	
			[ThA(OH) ₂]/[ThAO ₂][H ⁺] ^d or	7.8	
			[ThA(OH) ₂]/[Th[OH] ₂ A(OH) ₂][H ⁺] ^e		
Sn(IV)	PDS	A(OH) ₂	[Sn(OH) ₂ (AO ₂) ₂]/[Sn][OH] ² [AO ₂] ^f		
Sn(IV)	5-SSA	H ₂ AOH	[Sn(OH) ₂ AO]/[Sn][OH] ² [AO]		

^a Ref. 15. ^b Ref. 16. ^c Ref. 17. ^d Ref. 18. ^e Ref. 8. ^f Ref. 5. ^g Ref. 4. ^h Ref. 10. ⁱ Ref. 6. ^j Ref. 19. ^k Ref. 20. ^l Ref. 21. ^m Ref. 22. ⁿ Ref. 23.

I. The symbols used to describe the formulas of the metal chelates in Table I involve the notation H_mA(OH)_i, for the ligand and the formula (M-[OH]_kAO_j(OH)_{i-j})^{n-m-j-k} for the chelates formed by combination of one mole of ligand with one gram ion of the metal ion M⁺ⁿ. References to the literature for the equilibrium constants in Table I are indicated by footnotes. Quantitative data listed without literature references were obtained from potentiometric titrations illustrated in Figs. 1-7.

Discussion

The metals listed in Table I will be taken up in the approximate order of their increasing tendency toward hydrolysis: Mn(II), Zn(II), La(III), Fe(III), Cr(III), Th(IV), Sn(IV) and Ti(IV). The results obtained with Cu(II) were described previously,¹¹ and are referred to in the following discussion only for purposes of comparison with the additional metals reported in this paper.

Mn(II) Chelates.—The Mn(II) chelates listed in Table I are notable in the lack of any tendency toward hydrolysis. For the wide variety of ligands investigated, it seems that if the metal chelate formed has sufficient stability to show a pH effect (pH lowering of ligand curve), the electron density about the metal is then sufficient to prevent subsequent hydrolysis, even when free aquo positions are present in the coordination sphere of the metal. In cases where the stability of the metal chelate compound is relatively weak, dissociation occurs around pH 9 and the normal hydroxide precipitates. Examples of this type of behavior are illustrated in Figs. 2 and 3.

Zn(II) Chelates.—The Zn(II) chelates investigated were remarkable in the lack of well-developed tendencies to form hydroxo complexes. The more stable Zn(II) chelate compounds such

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(16) S. Chaberek, Jr., and A. E. Martell, *THIS JOURNAL*, **77**, 1477 (1955).

(17) G. Schwarzenbach and E. Freitag, *Helv. Chim. Acta*, **34**, 1492 (1951).

(18) S. Chaberek, Jr., R. C. Courtney and A. E. Martell, *THIS JOURNAL*, **74**, 5057 (1952).

(19) R. Skochdopole and S. Chaberek, unpublished.

(20) S. Chaberek, Jr., and F. C. Bersworth, *Science*, **118**, 280 (1953).

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

(22) J. Heller and G. Schwarzenbach, *ibid.*, **34**, 1876 (1951).

(23) R. L. Gustafson and A. E. Martell, *Arch. Biochem. Biophys.*, **68**, 485 (1957).

as those of EDTA, HEDTA, NTA and 2-HEDDA have no tendencies toward reaction with base beyond the neutralization of hydrogen ions displaced by the metal from amino and carboxyl groups. In the case of HIMDA and 2-HxG, which have only one amino donor group, the titration curves in Figs. 2 and 3 indicate the possibility

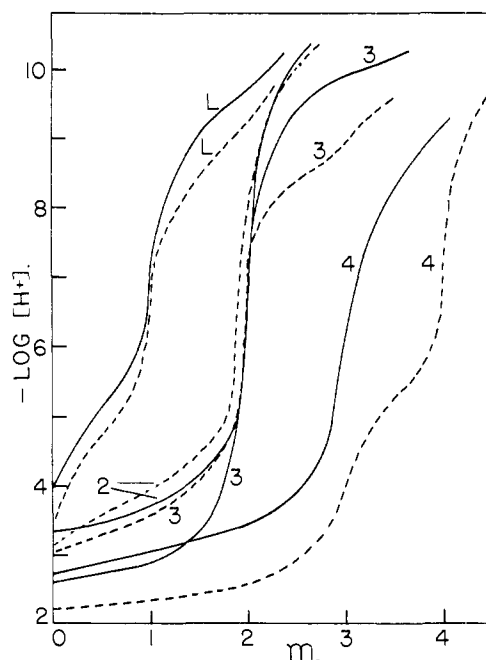


Fig. 1.—Potentiometric titration of N-hydroxyethyl-ethylenediaminetriacetic acid (HEDTA), —, and N,N'-dihydroxyethyl-ethylenediaminediacetic acid (HEDDA), - - - -, in the presence of an equivalent concentration of various metal ions at 25°: L, ligand; 2, Mn(II); 3, La(III); 4, Fe(III); $\mu = 0.1$; m = moles of base added per gram-ion of metal present.

of the formation of either hydroxo complexes or alkoxo complexes in which the ethoxyl hydrogen is displaced by the metal. The pK values seem to be approximately 8.1 and 8.3 for 2-HxG and HIMDA, respectively. The higher pK of the HIMDA chelate is probably due the greater concentration of negative charge about the Zn(II) ion.

The most stable hydroxo complex of the Zn(II) ion is formed by Tiron (Fig. 5). The normal che-

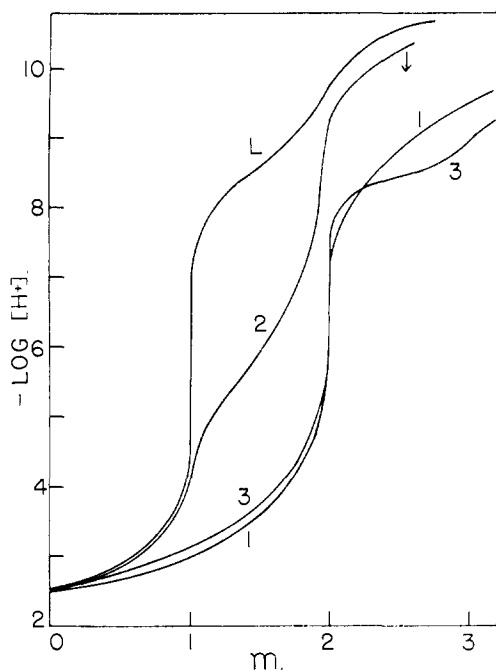


Fig. 2.—Potentiometric titration of N-hydroxyethyliminodiacetic acid (HIMDA) at 25° in the presence of an equivalent concentration of various metal ions: L, ligand; 1, Zn(II); 2, Mn(II); 3, La(III); $\mu = 0.1$.

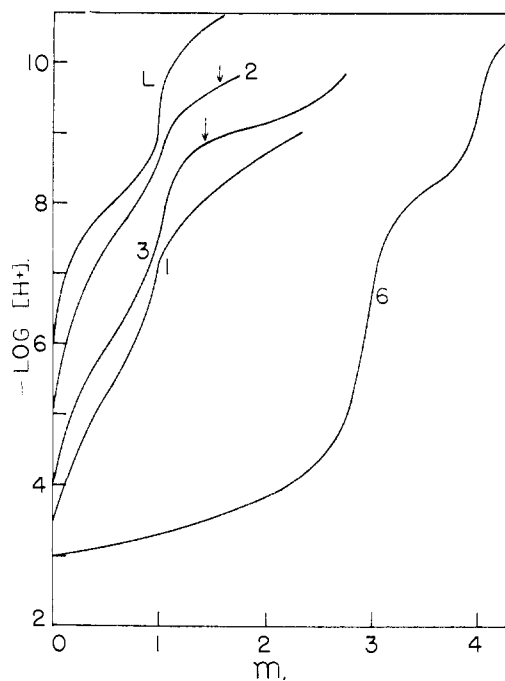
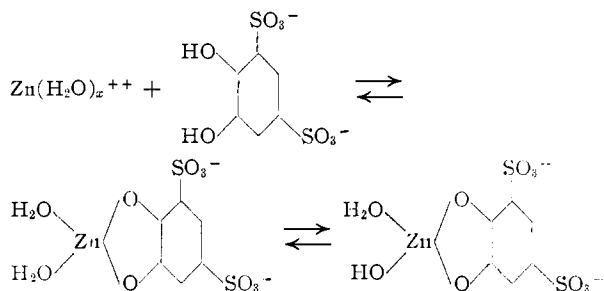


Fig. 3.—Potentiometric titration of N,N-dihydroxyethylglycine (2-HxG) in the presence of an equivalent concentration of various metal ions at 25°: L, ligand; 1, Zn(II); 2, Mn(II); 3, La(III); 6, Cr(III); $\mu = 0.1$.

late is formed with the displacement of two protons from the ligand, to give the structure shown.



A second step in the titration curve indicates the formation of a monohydroxo chelate, indicated above, in which one mole of hydroxide ion is bound per gram ion of metal. The stability of this compound is shown by the subsequent rise in the titration curve indicating that the metal chelate does not dissociate to form the zincate ion. In contrast to the behavior of Tiron, chromotropic salt and 5-sulfosalicylic acid, which have similar structures, do not form stable chelate compounds with the Zn(II) ion.

The above evidence indicates that the formation of hydroxo chelates of Zn(II) requires the formation of a fairly stable chelate with a ligand containing relatively few (2) donor groups. Thus far, Tiron (PDS) is the only ligand investigated which clearly fits these requirements.

Fe(III) Chelates.—The iron chelate compounds which were investigated are characterized by the wide variety of hydrolytic reactions illustrated in Figs. 1 and 6. In addition to a strong tendency of the Fe(III) ion to undergo hydrolysis, there is a tendency for this ion to induce dissociation of pro-

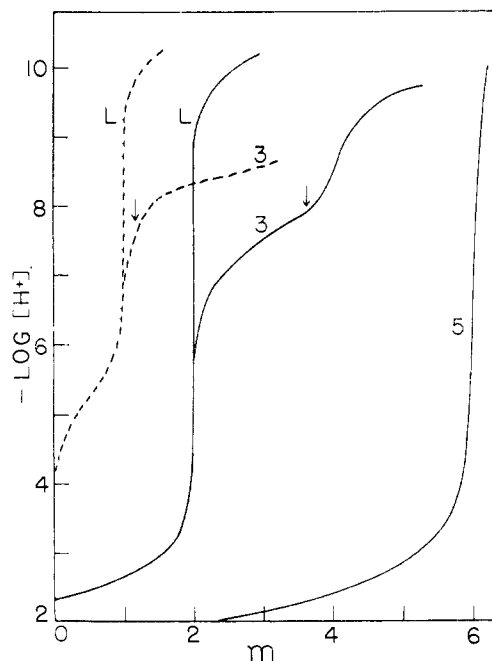


Fig. 4.—Potentiometric titration of 5-sulfosalicylic acid (5-SSA), —, and of chromotropic salt (DNS), - - - -, in the presence of equivalent amounts of various metal ions at 25°: L, ligand; 3, La(III); 5, Sn(IV).

tons from hydroxyalkyl groups when these groups are in a position to form chelate rings with the metal. In many cases, the resulting compounds are tautomeric with structures containing an OH group attached directly to the metal.

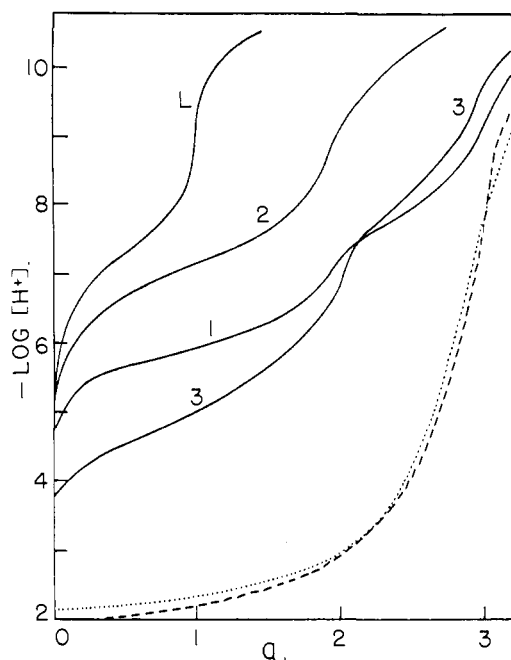
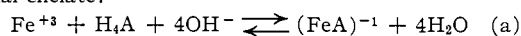


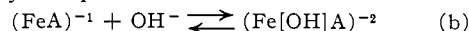
Fig. 5.—Potentiometric titration of Tiron (PDS), in the presence of equivalent amounts of various metal ions at 25°: L, ligand; 1, Zn(II); 2, Mn(II); 3, La(III); ----- 2:1 curve for Ti(IV); 2:1 curve for Sn(IV); $\mu = 0.1$; a = moles of base added per mole of ligand present.

The hydrolysis of the Fe(III)-EDTA chelate involves two steps with pK values at 7.5 and 9.4. The reactions which take place may be represented by the equations

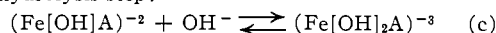
normal chelate:



first hydrolysis step:



second hydrolysis step:



The formation of the mono- and dihydroxo iron EDTA chelates must involve an opening of a chelate ring in each case. Thus the two hydrolysis reactions indicated by equations b and c may be visualized as the displacement of a bound acetate group by a hydroxide ion. It is interesting to note that the corresponding iron chelate of nitrilotriacetic acid also undergoes two successive hydrolysis steps with pK values at 4.1 and 7.8. These reactions may be considered analogous to those of the corresponding EDTA chelate. It is noted, however, that the pK values of the nitrilotriacetic chelate are much lower than those of the EDTA chelate. This difference is primarily due to the difference in charge of the complexes involved, the more negatively charged EDTA derivative reacting less readily with negative hydroxide ion. It is also probable that the less complete coordination of Fe(III) by nitrilotriacetate allows the hydrolysis to take place much more readily by simple removal of protons from the coordinated water molecules in this complex.

The type of hydrolysis undergone by iron chelates of ligands containing hydroxethyl groups seems

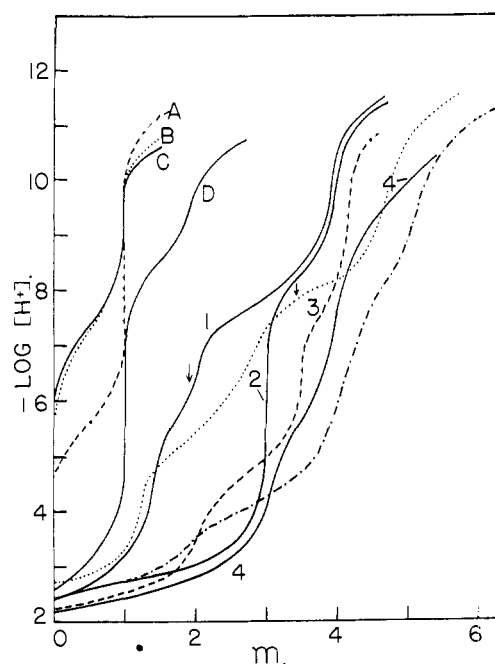


Fig. 6.—Potentiometric titration of various ligands at 25° in the presence of equivalent amounts of Fe(III): A or 1, chromotropic salt (DNS); B or 2, N,N-dihydroxyethylglycine (2-HxG); C or 3, Tiron (PDS); D or 4, N-hydroxyethyliminodiacetic acid; ----- 2:1 Tiron/Fe(III); 2:1 DNS/Fe(III); $\mu = 0.1$; m = moles of base added per gram-ion of metal present.

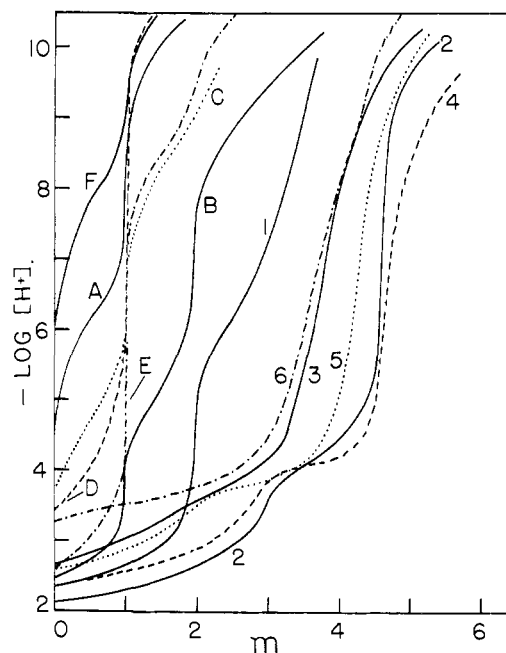
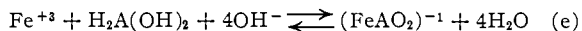
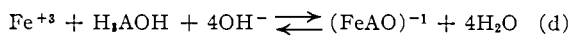


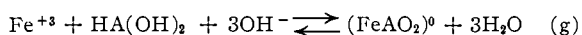
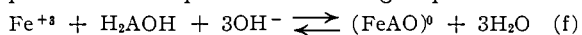
Fig. 7.—Potentiometric titration of various ligands at 25° in the presence of equivalent amounts of Th(IV): A or 1, Na₂EDTA; B or 2, HEDTA; C or 3, HEDDA; D or 4, NTA; E or 5, HIMDA; F or 6, HxG; letters refer to ligands, numbers to ligand + metal ion; $\mu = 0.1$; m = moles of base added per gram-ion of metal.

to differ considerably from the hydrolytic reactions of the iron(III) EDTA and NTA chelates. In the

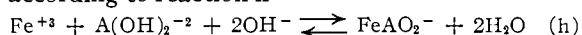
case of N-hydroxyethylethylenediaminetriacetic acid (HEDTA) and of N,N'-dihydroxyethylethylenediaminediacetic acid (HEDDA), illustrated in Fig. 1, the initial combination of the metal ion with the ligand involves a displacement of a proton from each hydroxyethyl group present as is indicated by the reactions



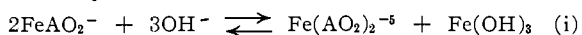
An alternative explanation of reactions d and e could involve simple coordination of the metal with the amino and carboxylate groups of the ligand plus coordination with one or two free hydroxyl groups, thus leaving the hydroxyethyl groups uncoordinated with the metal ion. Such an interpretation, however, would ignore the considerable enhancement of the iron chelate stability resulting from the attachment of the hydroxyethyl groups to the ligand. Evidence is given in Fig. 6 for similar reactions of N-hydroxyethyliminodiacetic acid (HIMDA) and of N,N'-dihydroxyethylglycine (2-HxG), illustrated by equations f and g, which are also believed to involve direct coordination with the hydroxyalkyl group with simultaneous displacement of a proton from this group.



The potentiometric titration curves of Tiron and iron(III) having ligand to metal ratios of 1:1 and 2:1 are plotted in Fig. 6. The first inflection for both curves occurs at two moles of base per gram ion of metal. The initial reaction step, therefore, is the formation of a 1:1 metal chelate, FeAO_2^- , according to reaction h



The nature of the subsequent interaction with metal is not clear. No precipitation was observed during either of the metal-Tiron titrations. This is somewhat surprising in view of the fact that Schwarzenbach and Willi²¹ found that Fe(III)-Tiron chelates having ligand to metal ratios of 1:1 (blue), 2:1 (violet), and 3:1 (red) are formed. Further interaction of the 1:1 chelate to give higher chelated forms in solutions containing equimolar amounts of ligand and Fe(III) ions would result in the disproportionation of this complex to a higher form and ferric hydroxide.

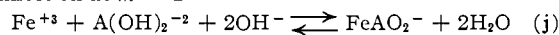


Schwarzenbach found that precipitation under these conditions did occur at a pH below 5.

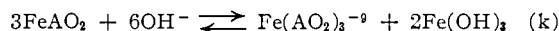
The pH readings in the "m" interval of 3-4 of the 1:1 curve exhibited a drift, and consequently the presence of an inflection at $m = 3.5$ may be fortuitous. Inflections at m values of 2 and 4 of the 1:1 curve and at 4 and 5 of the 2:1 curve, as well as observed color changes, substantiate the formation of the higher chelates, or of more basic (hydroxo) forms of the 1:1 chelate. In view of the absence of precipitation of ferric hydroxide at higher pH, the possibility of forming metal chelates with a higher ratio of ligand to metal must be considered doubtful until additional experimental evidence becomes available.

1:1 Curve

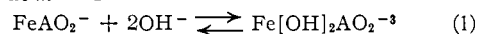
Inflection at $m = 2$



Inflection at $m = 4$

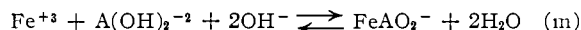


Inflection at $m = 4$

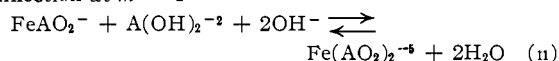


2:1 Curve

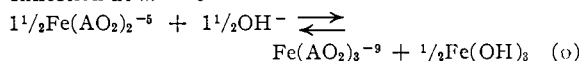
Inflection at $m = 2$



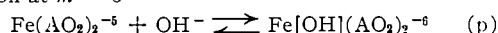
Inflection at $m = 4$



Inflection at $m = 5$

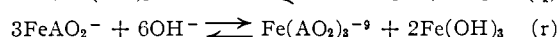
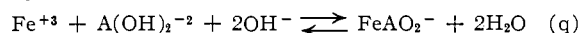


Inflection at $m = 5$

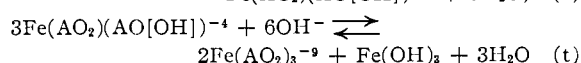
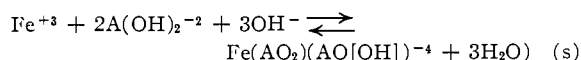


Further study of these systems is necessary before further conclusions can be made concerning the formulas of the metal chelates in solution.

The potentiometric titrations of chromotropic salt and ferric nitrate with ligand to metal ratios of 1:1 and 2:1 are illustrated in Fig. 6. The metal chelate compounds formed are considerably less stable than those of Tiron, with precipitation occurring at pH 6.5 and 7.7 for the 1:1 and 2:1 compounds, respectively. In the case of the 1:1 chelate, two moles of base are utilized per mole of chelate compound before disproportionation with the formation of ferric hydroxide occurs. The strong inflection at approximately four moles of base per mole of ligand corresponds to the possible formation of the normal 3:1 chelate (reaction q), followed by precipitation of the remainder of the iron as ferric hydroxide, in accordance with reaction r



For the 2:1 chelate, the inflection at three moles of base per mole of metal ion corresponds to the displacement and neutralization of all but one of the phenolic hydrogens. The final steep inflection corresponds to the utilization of two additional moles of base per mole of metal ion, and probably represents disproportionation to ferric hydroxide and the normal 3:1 chelate, as before. These two successive steps may be represented by equations s and t



Since disproportionation takes place to form ferric hydroxide and a metal chelate, it is to be expected that at high pH the same chelate will be produced regardless of the initial ratio of ligand to metal ion. This conclusion seems to be strengthened somewhat by the similarity of the 1:1 and 2:1 curves above pH 8,

Fe(II) Complexes.—It is interesting to note that the hydrolysis of the Fe(II) chelates of EDTA and NTA, reported by Schwarzenbach, *et al.*, show a much weaker tendency to hydrolyze than do the corresponding Fe(III) chelates. The Fe(II)-EDTA chelate undergoes two overlapping hydrolysis steps with high pK values of 9.1 and 9.9 while the corresponding NTA chelate has been reported to have the very high pK value of 10.6. The weak hydrolytic tendencies of these Fe(II) chelates are to be expected from the position of the ferrous ion in the first transition series (*i.e.*, between Mn(II) and Co(II)).

Metal Chelates of Cr(III).—The hydrolytic tendency of the Cr(III) ion is undoubtedly very interesting and is probably as well developed as that of Fe(III). However, because of the slowness with which equilibrium is attained in solutions containing Cr(III) salts, and the long period of time required to make sufficient measurements to obtain a titration curve, only one Cr(III) system, that of 2-HxG, was studied. In this case, the titration was carried on very slowly, over a period of months, in order to make certain that the data represent the true equilibria taking place. The titration curve, illustrated in Fig. 3, shows a well-developed inflection when three moles of base was added per mole of Cr(III) salt present. This indicated that the initial reaction is very similar to that of the ferric ion in which the 2-HxG behaved as a tetradentate ligand involving simultaneous dissociation of the two protons attached to the hydroxyethyl groups. Unlike the ferric chelate, however, the chromium compound showed an additional well developed hydrolysis step with a pK value of 8.1. This reaction must involve the removal of a proton from one of the remaining coordinated water molecules still attached to the metal ion at the end of the first chelation step. Using this chelating agent as an example, it would seem that chromium chelates hydrolyze still more readily than those of Fe(III).

This is also apparent from the pK values of the first hydrolysis step of the Fe(III) and Cr(III)-EDTA chelates, reported by Schwarzenbach. The pK value given for the chromium(III) chelate (7.39) is somewhat lower than that of Fe(III) (7.52), indicating a greater tendency of Cr(III) to interact further with hydroxide ions.

Chelates of Lanthanum(III).—The general characteristics of lanthanum chelates indicates much lower hydrolytic tendencies than do chelates of the other trivalent metals investigated, such as those of Fe(III) and Cr(III). La(III) forms a normal chelate with EDTA which undergoes no further hydrolysis. Figure 1 indicates that a similar result is obtained with HEDTA. On the other hand, with the ligands HEDDA (Fig. 1), and HIMDA (Fig. 2), there are hydrolytic steps with pK values of 8.4 and 8.5, respectively, showing that an additional hydroxyl group may become bound to the metal ion. The generalization which may be drawn here is that a separate hydrolysis step can take place in La(III) chelates when the charge on the chelate compound is not less than +1. The fact that a hydrolytic step is not observed in the

case of 2-HxG (Fig. 3) is, no doubt, due to insufficient stability of the complex itself, which is evidenced by precipitation of lanthanum hydroxide above pH 9. It is further interesting to note that in all cases where the hydrolysis step occurs, the charge on the metal ion and the groups directly attached to it change from +1 to 0. The reason for not observing hydrolysis involving changes in charge from +2 to smaller values, is probably due to the fact that chelates of lanthanum with a +2 charge are not sufficiently stable to prevent the precipitation of La(III) hydroxide in the region where combination with hydroxo groups would normally occur.

The ideas described above are borne out by an examination of the behavior of La(III) chelates of 5-sulfosalicylic acid (5-SSA) and of pyrocatechol-3,5-disodium sulfonate (PDS) illustrated in Figs. 4 and 5, respectively. The La(III)-5-SSA chelate reacts immediately with two moles of base to form a chelate in which the carboxylate ion and the hydroxide group are attached to the metal. The weakness of this complex is apparent from the fact that the proton is not displaced from the phenolic group on coordination with the metal, and that the chelate compound decomposes above pH 8 with a precipitation of La(III) hydroxide. The La(III) chelate of PDS, however, is formed by the direct displacement of the two phenolic hydrogens by the metal ion. The resulting chelate compound then undergoes a separate hydrolysis step at a higher pH to give a monohydroxo chelate. The fact that the net charge of the metal ion and the groups attached to it is equal to 0 is in conformity with the principles outlined above. It is further interesting to note that the pK values of the three hydroxo chelates of La(III) listed in Table I are very nearly the same (8.4 ± 0.1). This is probably the reflection of the critical nature of conditions required to produce hydroxo complexes of lanthanum chelates.

Metal Chelates of Th(IV).—In general, the Th(IV) chelates may be considered to resemble somewhat the chelates of Fe(III), with the modification that stable chelates of Th(IV) are formed only with the more negative ligands which form stable complexes of Fe(III). Thus the titration curves in Fig. 7 indicate the formation of stable thorium chelates of EDTA, HEDTA, HEDDA, NTA and HIMDA while 2-HxG, 2-HEN and 5-SSA do not form stable coordination compounds with thorium(IV) salts. The thorium-EDTA chelate, which is neutral, readily hydrolyzes to form a hydroxo chelate with an apparent pK value of 6.8. This is probably a result of the incomplete coordination of Th(IV) by EDTA, and the displacement of hydrogen ions from the water molecules remaining in the coordination sphere of Th(IV) after complete chelation with the hexadentate EDTA ligand. The interaction of Th(IV) with HEDTA on the other hand seems to result in the formation of a normal chelate, involving the reaction of three moles of base per mole of metal. At low pH , however, $1\frac{2}{3}$ additional moles of base react per mole of metal ion in two overlapping steps. Similar double hydrolysis steps also take place with NTA and HIMDA. It is interesting to note

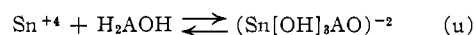
the similarity of the reactions with HEDTA and NTA. In both cases, the initial thorium chelate formed has a +1 charge. The hydrolysis steps involving the addition of two moles of base to the metal chelate take place at the same *p*H values. The mid-point of the buffer regions are found to occur at *p*H 4.1, indicating similar hydrolytic tendencies. It is of further interest that two additional ligands HEDDA and HIMDA give two-step hydrolysis reactions with mid-point values of 3.9. The greater tendency of the latter compounds toward hydrolysis is in agreement with their greater positive charge.

The unexpected, and in some cases, uncertain, stoichiometry of the hydrolytic reactions of these Th(IV) chelates is an indication that they probably cannot be explained on the basis of the formation of simple monohydroxo mononucleate chelates.²⁴ In the EDTA-Th(IV) curve, for example, the usual sharp inflection at *m* = 3 is not found, indicating that the hydrolysis reaction proceeds beyond the monohydroxo chelate. Detailed analysis of this buffer region, which is now being prepared for publication, seems to indicate the presence of a binuclear chelate. Reaction of the "normal" HEDTA chelate with an additional 1²/₃ moles of base, followed by a steep inflection, indicates the possibility of polynuclear chelates. Similar possibilities exist for the remaining Th(IV) chelates illustrated in Fig. 7. The formation of hydroxo bridges in the chelate compounds of the actinide elements is now being studied in these laboratories, and will be reported at a later date when the reactions involved have become sufficiently elucidated.

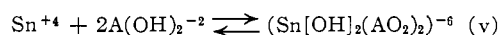
Metal Chelates of Sn(IV).—The chemical properties of Sn(IV) salts in aqueous solution are dominated by the tendency to undergo hydrolysis. The titration of stannic chloride proceeds with complete hydrolysis to the dioxide on the addition of 4 moles of base per mole of stannic ion. As is indicated in Fig. 4, the presence of an equimolar amount of 5-SSA requires exactly the quantity of base (6 moles) that would be required by the titration if the metal ion and the ligand were taken separately. The fact that a very stable complex is formed is indicated, however, by the absence of a precipitate during the

(24) It is interesting to note that Feldman, *et al.*, (J. Feldman, J. R. Havill and W. F. Neuman, *THIS JOURNAL*, **76**, 4726 (1954)) interpreted a 2²/₃ factor in titrations of UO₂(VI) chelates in terms of a transition from a dinuclear to a trinuclear form.

entire titration and by the fact that the initial portion of the titration curve lies at considerably lower *p*H values than those of the metal and ligand taken separately. The reaction which occurs may be represented by the equation

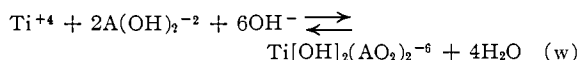


where H₂AOH represents the ligand. The product is represented as having 3 hydroxo groups attached to the metal ion. This compound, however, is probably polymeric as the result of the intramolecular condensation of some of the hydroxyl groups. With PDS, the Sn⁺⁴ ion produces a stable chelate compound containing two ligands per metal ion. The product is formed initially upon the addition of 6 moles of base per mole of chelate formed (Fig. 5). Further addition of base results in additional hydrolysis until at *p*H 10, 7 moles of base per gram-ion of metal are required. The chelate compound initially formed may be represented by the equation



It is understood that the product indicated may contain additional OH groups attached to the metal as the *p*H of the solution is increased. This product as well as the one discussed above probably is polymeric. In both cases the probability of condensation through the metal-bound hydroxide groups is indicated by the slowness with which equilibrium was attained during the titration.

Hydrolysis of Ti(IV) Chelates.—The tetrapositive titanium ion was probably the most readily hydrolyzed of all the metal ions investigated. For the variety of ligands tested, only PDS gave a stable system which could not be titrated to high *p*H without precipitation. The titration curve shown in Fig. 5 indicates that 6 moles of base is required per mole of metal ion. The reaction which takes place is represented schematically by equation (w)



If Ti(IV) is assigned a coordination number of 6, at least two hydroxyl groups must be coordinated with the metal. The 2:1 metal chelate indicated above is also probably polymeric as was true of Sn(IV) compounds.

WORCESTER, MASS.