

It is also interesting to note that the over-all stability constants ($\log K_{MA} + \log K_{MA_2}$) of AAPDA and GTDA for cadmium are higher than those for zinc, although the stabilities of their 1:1 cadmium chelates are nearly the same as those of their zinc chelates. Such strong affinity for cadmium has been reported for a very limited number of ligands such as catechol-*O'*,*O'*-diacetic acid¹¹ or bis(2-aminoethyl ether)-*N,N,N',N'*-tetraacetic acid.¹² Since all of these ligands have

the coordinating oxygen, it is quite probable that their unusual affinity for cadmium ion is related to the coordination of oxygen to the metal ion.

Acknowledgment.—The authors are grateful to the Ministry of Education, Japanese Government, for a grant in support of this work.

(11) T. Hatsutori, K. Suzuki, and K. Yamasaki, Abstracts of Papers, 12th Symposium on Coordination Chemistry sponsored by the Chemical Society of Japan, Tokyo, 1962, p. 115.

(12) J. H. Holloway and C. N. Reilly, *Anal. Chem.*, **32**, 249 (1960).

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Metal Chelates of Mercaptosuccinic and α,α' -Dimercaptosuccinic Acids¹

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The interaction of metal ions with α -mercaptosuccinic acid and with α,α' -dimercaptosuccinic acid has been determined by potentiometric measurement of hydrogen ion concentration. With mercaptosuccinic acid, evidence is presented for the formation of complexes having 1:1 and 2:1 molar ratios of ligand to metal, as well as for zinc and nickel hydroxo complexes. For α,α' -dimercaptosuccinic acid, the existence of 1:1 and 2:1 complexes is established together with various protonated and hydroxo complexes. Equilibrium constants are reported for soluble metal chelate systems, and the equilibrium data are interpreted in terms of the probable structure of the complexes formed.

Introduction

The ligand α,α' -dimercaptosuccinic acid, DTTA, is of special interest as a sequestering agent for metal ions, since it has two mercapto groups available for chelate ring formation. In order to study this reagent the potentiometric studies of Agren and Schwarzenbach² were extended to additional metal ions. For comparison and as a possible means of providing a better understanding of the properties of α,α' -dimercaptosuccinic acid, the analogous α -mercaptosuccinic acid, TMA, was studied with a variety of metal ions, considerably extending the previous work of Cheney, *et al.*³

Experimental

Reagents.—A sample of α -mercaptosuccinic acid (TMA), purchased from Evans Chemetics, Inc., New York, N. Y., was certified to be 99.67% pure and was used without further purification. The pure *meso*- α,α' -dimercaptosuccinic acid was purchased from Dojindo and Co., Kumamotoshi, Japan, and had been synthesized by the method of Gerecke, *et al.*⁴ The mercaptosuccinic acid melted at 152–153°, lit. 148°,⁵ 149–150°,⁶ 153–154°,⁷ and the α,α' -dimercaptosuccinic acid softened at 194°, lit. 190–191°,⁷ 210–211°,⁴ and decomposed at 207–211°.

A sulfur analysis of α,α' -dimercaptosuccinic acid by Micro-Tech Laboratories, Skokie, Ill., gave 35.10% calculated, 35.87, 35.72% found. Both ligands were standardized by potentiometric titration, using standard carbonate-free sodium hydroxide. The quality of the titration curves affirmed the high purity of the

ligands indicated above. Metal ion solutions were prepared from Fisher reagent grade metal nitrates except for Mn(II) and Hg(II), which were obtained as the sulfate and chloride, respectively. The metal salt solutions were standardized by titration with ethylenediaminetetraacetic acid by standard methods.

Potentiometric Measurements.—Measurements of hydrogen ion concentration were carried out in a 100-ml. jacketed titration cell, which was fitted with a magnetic stirrer and a tightly-fitting rubber stopper through which were inserted nitrogen inlet and outlet tubes, a microburet delivery tube, and glass and calomel extension electrodes. A Beckman Model GS pH meter was used to determine hydrogen ion concentrations. The electrodes were calibrated by comparing the meter reading during the titration of standard acetic acid under the same experimental conditions with hydrogen ion concentrations calculated from the data tabulated by Harned and Owen.⁸ In the pH regions below 3.5 and above 10.5, the pH meter was calibrated by adding known amounts of hydrochloric acid and sodium hydroxide, respectively. All potentiometric titrations and calibrations were made at 25.05 \pm 0.05° and at an ionic strength adjusted to 0.10 *M* (or in some cases 1.0 *M*) with potassium nitrate.

Calculations

All calculations were made with the aid of an IBM 1620 computer at the Computation Center of Illinois Institute of Technology, using programs written by G. R. L. To ensure accuracy, individual spot calculations were made for each equation.

Acid Dissociation Constants.—The acid dissociation constants of TMA and DTTA were calculated by a combined algebraic-geometric method. The equilibria and dissociation constants involved are

$$K^H_j = \frac{[H^+][H_{n-j}L]}{[H_{n-j+1}L]}$$

(8) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 2nd Ed., Reinhold Publishing Corp., New York, N. Y., 1950, p. 523.

(1) This work was supported by the U. S. Atomic Energy Commission under Grant No. AT(11-1)-1020.

(2) A. Agren and G. Schwarzenbach, *Helv. Chim. Acta*, **38**, 1920 (1955).

(3) G. E. Cheney, Q. Fernando, and H. Freiser, *J. Phys. Chem.*, **63**, 2055 (1959).

(4) M. Gerecke, E. A. H. Friedheim, and A. Bossi, *Helv. Chim. Acta*, **49**, 955 (1961).

(5) E. Bilman, *Ann.*, **339**, 351 (1905).

(6) B. Holmberg, *Arkiv Kemi, Mineral. Geol.*, **6**, 1 (1916).

(7) I. R. Klotz, G. H. Czerlinski, and H. A. Fiess, *J. Am. Chem. Soc.*, **80**, 2920 (1958).

where n is the total number of titrable protons per ligand and j is the j th proton ionized. In the case of TMA, n is equal to 3; for DTTA, n is equal to 4.

For each of the acids, there are two separate buffer regions. For TMA, there is a lower buffer region covering two equivalents of base and a higher buffer region with one equivalent of base. For DTTA, both the upper and lower buffer regions each cover an area of two equivalents of base.

For the single equivalent buffer region of TMA, the evaluation of the ionization constant was carried out with the usual algebraic relationships.

For a two-equivalent buffer region, if T_a represents the total concentration of ligand species and a represents the number of equivalents of base per mole of ligand from the previous well-defined equivalence point

$$K_1 = \frac{[H^+][HL^-]}{[H_2L]} \quad (1)$$

$$K_2 = \frac{[H^+][L^{2-}]}{[HL^-]} \quad (2)$$

with the aid of the usual mass balance and stoichiometric relationships, one obtains K_1 and K_2 in a slope-intercept equation

$$\frac{1}{K_1} = K_2 \frac{A}{B} - B \quad (3)$$

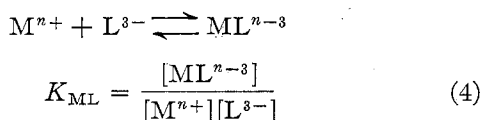
where

$$A = \frac{(a-1)T_a + [H^+] - [OH^-]}{(2-a)T_a - 1} \frac{[H^+]}{[H^+]}$$

$$B = \frac{(a-1)T_a + [H^+] - [OH^-]}{[H^+](aT_a + [H^+] - [OH^-])}$$

which may be fitted by least squares to evaluate K_1 and K_2 . Equation 3 may be evaluated at any buffer region of interest if a is calculated from the beginning of that particular buffer region. In this way K_3 and K_4 of DTTA were calculated.

Chelate Stability Constants.—For the evaluation of the equilibrium constant for an equimolar interaction of TMA with metal ions



If T_m is the total concentration of the metal present in solution, then

$$K_{ML} = \frac{T_m - X[L^{3-}]}{X[L^{3-}]^2} \quad (5)$$

where

$$X = 1 + \frac{[H^+]}{K_1} + \frac{[H^+]^2}{K_1 K_2} + \frac{[H^+]^3}{K_1 K_2 K_3}$$

$$Y = 3 + \frac{2[H^+]}{K_1} + \frac{[H^+]^2}{K_1 K_2}$$

$$[L^{3-}] = \frac{3T_m + [OH^-] - [H^+] - aT_m}{3X - Y}$$

For the evaluation of K_{ML} and K_{ML_2} , the equation developed by Richard, Gustafson, and Martell⁹ was placed in the slope-intercept form

$$\frac{T_m - [L^{3-}]X}{X[L^{3-}]^2} = -\frac{T_a - [L^{3-}]X}{K_{ML}[L^{3-}]^3 X} + K_{ML_2} \quad (6)$$

where

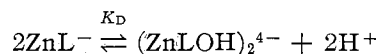
$$K_{ML_2} = \frac{[ML_2^{n-6}]}{[ML^{n-3}][L^{3-}]}$$

$$[L^{3-}] = \frac{(3-a)T_a + [OH^-] - [H^+]}{Z}$$

$$Z = \frac{3[H^+]^3}{K_1^3 K_2^3 K_3^3} + \frac{2[H^+]^2}{K_1^2 K_2^3} + \frac{[H^+]}{K_1^3}$$

Evaluation of (6) at different points in the buffer region with adjustment to a least-squares fit gives K_{ML} as the negative inverse of the slope and K_{ML_2} as the intercept.

The formation constant of the Zn(II)-TMA hydroxo complex may be evaluated as a simple acid dissociation constant. If the initially formed TMA hydroxo complex undergoes further reaction to form the dimer, the following equations describe the equilibria



$$K_H = \frac{[ZnLOH^{2-}][H^+]}{[ZnL^-]} \quad (7)$$

$$K_D = \frac{[(ZnLOH)_2^{4-}][H^+]^2}{[ZnL^-]^2} \quad (8)$$

If a represents the equivalents of base per mole of metal chelate in the buffer region involving the hydrolysis reaction and T_M is the total metal ion concentration in all its species, then

$$K_H + 2K_D \frac{[ZnL^-]}{[H^+]} = \frac{(T_M - [ZnL^-])[H^+]}{[ZnL^-]} \quad (9)$$

α,α -Dimercaptosuccinic Acid.—Since the equilibria involved in DTTA complexes are much more complicated than those of TMA, the equations developed for TMA could not be utilized. Instead, the equations presented by Agren and Schwarzenbach² were employed.

For the one-to-one metal-ligand systems, the species present at various pH values are MH_2L^{n-2} , MHL^{n-3} , ML^{n-4} , $M(OH)L^{n-5}$, together with the various ionized forms of DTTA.

The ionization constants of MHL^{n-3} and ML^{n-4} may be calculated as simple acid dissociation constants for buffer regions that occur between the a values 3 to 4 and 4 to 5, respectively. The acid dissociation con-

(9) C. F. Richard, R. L. Gustafson, and A. E. Martell, *J. Am. Chem. Soc.*, **81**, 1033 (1959).

stant of MH_2L^{2-} was calculated with the equation developed by Schwarzenbach, *et al.*¹⁰

$$\alpha[\text{L}^{4-}] = [\text{H}_4\text{L}] + [\text{H}_3\text{L}^-] + [\text{H}_2\text{L}^{2-}] + [\text{HL}^{3-}] + [\text{L}^{4-}]$$

$$\beta[\text{L}^{4-}] = 4[\text{H}_4\text{L}] + 3[\text{H}_3\text{L}^-] + 2[\text{H}_2\text{L}^{2-}] + [\text{HL}^{3-}]$$

$$\gamma[\text{ML}^{2-}] = [\text{MH}_2\text{L}] + [\text{MHL}^-] + [\text{ML}^{2-}]$$

$$\delta[\text{ML}^{2-}] = 2[\text{MH}_2\text{L}] + [\text{MHL}^-]$$

Then

$$T_m = [\text{M}^{2+}] + \gamma[\text{ML}^{2-}] \quad (10)$$

$$T_a = \alpha[\text{L}^{4-}] + \gamma[\text{ML}^{2-}] \quad (11)$$

$$(4 - a)T_a + [\text{H}^+] - [\text{OH}^-] = \beta[\text{L}^{4-}] + \delta[\text{L}^{4-}] \quad (12)$$

Using the ionization constants for DTTA and the known ionization constants of the DTTA protonated complexes, the coefficients in eq. 10-12 are found to be

$$\alpha = \frac{[\text{H}^+]^4}{K^{\text{H}}_1 K^{\text{H}}_2 K^{\text{H}}_3 K^{\text{H}}_4} + \frac{[\text{H}^+]^3}{K^{\text{H}}_2 K^{\text{H}}_3 K^{\text{H}}_4} + \frac{[\text{H}^+]^2}{K^{\text{H}}_3 K^{\text{H}}_4} + \frac{[\text{H}^+]}{K^{\text{H}}_4} + 1 \quad (13)$$

$$\beta = \frac{4[\text{H}^+]^4}{K^{\text{H}}_1 K^{\text{H}}_2 K^{\text{H}}_3 K^{\text{H}}_4} + \frac{3[\text{H}^+]^3}{K^{\text{H}}_2 K^{\text{H}}_3 K^{\text{H}}_4} + \frac{2[\text{H}^+]^2}{K^{\text{H}}_3 K^{\text{H}}_4} + \frac{[\text{H}^+]}{K^{\text{H}}_4} \quad (14)$$

$$\gamma = \frac{[\text{H}^+]^2}{K_{\text{MH}_2\text{L}} K_{\text{MHL}}} + \frac{[\text{H}^+]}{K_{\text{MHL}}} + 1 \quad (15)$$

$$\delta = \frac{2[\text{H}^+]^2}{K_{\text{MH}_2\text{L}} K_{\text{MHL}}} + \frac{[\text{H}^+]}{K_{\text{MHL}}} \quad (16)$$

Upon solving eq. 10-16, one is led to complicated expressions for $[\text{ML}^{2-}]$, $[\text{L}^{4-}]$, and $[\text{M}^{2+}]$ which may be inserted in eq. 4, using the points of the buffer region of the titration curve between $a = 2$ and 4.

For the determination of K_{ML_2} , the two-to-one molar DTTA-metal curve is used. The equations used for calculation purposes are similar to those of the preceding section.

$$T_m = [\text{ML}^{2-}] + [\text{MLOH}^{3-}] + [\text{ML}_2^{6-}] + [\text{ML}_2\text{OH}^{7-}] \quad (17)$$

$$T_a = [\text{H}_2\text{L}^{2-}] + [\text{HL}^{3-}] + [\text{L}^{4-}] + T_m + [\text{ML}_2^{6-}] + [\text{ML}_2\text{OH}^{7-}] \quad (18)$$

$$(4 - a)T_a + [\text{H}^+] - [\text{OH}^-] = 2[\text{H}_2\text{L}^{2-}] + [\text{HL}^{3-}] - [\text{MLOH}^{3-}] - [\text{ML}_2\text{OH}^{7-}] \quad (19)$$

The various concentration expressions in eq. 17-19 are equivalent to

$$\alpha[\text{L}^{4-}] = [\text{H}_2\text{L}^{2-}] + [\text{HL}^{3-}] + [\text{L}^{4-}]$$

$$\beta[\text{L}^{4-}] = 2[\text{H}_2\text{L}^{2-}] + [\text{HL}^{3-}]$$

$$[\text{ML}^{2-}] + [\text{MLOH}^{3-}] = \left[1 + \frac{1}{[\text{H}^+]K_{\text{MLOH}}} \right] [\text{ML}^{2-}]$$

$$[\text{MLOH}^{3-}] = \frac{[\text{ML}]}{[\text{H}^+]K_{\text{MLOH}}}$$

$$[\text{ML}_2^{6-}] + [\text{ML}_2\text{OH}^{7-}] = \left[1 + \frac{1}{[\text{H}^+]K_{\text{ML}_2\text{OH}}} \right] [\text{ML}_2^{6-}]$$

$$[\text{ML}_2\text{OH}^{7-}] = \frac{[\text{ML}_2^{6-}]}{[\text{H}^+]K_{\text{ML}_2\text{OH}}}$$

The terms α and β are equal to the last three and the last two expressions of eq. 13 and 14, respectively. $K_{\text{ZnL}_2\text{OH}}$ was evaluated by solving eq. 17-19 and inserting various plausible values of the constant. Once the value of $K_{\text{ML}_2\text{OH}}$ is obtained, K_{ML_2} may be evaluated in a manner analogous to K_{ML} .

For the calculation of the formation constant, $K_{\text{Zn}_2\text{L}}$, of the binuclear zinc complex, the titration curve of the ligand in the presence of about a tenfold excess of zinc is used. The curve is equivalent to the dissociation of a tetrabasic acid. The ionization constants may be calculated from eq. 6. The equations for the last two protons involved are

$$\frac{1}{K^{\text{H}}_4} = \frac{[\text{HL}^{3-}] + [\text{ZnHL}^-]}{[\text{H}^+]([\text{L}^{4-}] + [\text{ZnL}^{2-}] + [\text{Zn}_2\text{L}])}$$

$$= \frac{1}{K^{\text{H}}_4} \frac{1 + [\text{Zn}^{2+}]K_{\text{ZnHL}}}{1 + [\text{Zn}^{2+}]K_{\text{ZnL}} + [\text{Zn}^{2+}]^2 K_{\text{ZnL}} K_{\text{Zn}_2\text{L}}} \quad (20)$$

$$\frac{1}{K^{\text{H}}_3} = \frac{[\text{H}_2\text{L}^{2-}] + [\text{ZnH}_2\text{L}]}{[\text{H}^+]([\text{HL}^{3-}] + [\text{ZnHL}^-])}$$

$$= \frac{1}{K^{\text{H}}_3} \frac{1 + [\text{Zn}^{2+}]K_{\text{ZnH}_2\text{L}}}{1 + [\text{Zn}^{2+}]K_{\text{ZnHL}}} \quad (21)$$

From eq. 20, the constant $K_{\text{Zn}_2\text{L}}$ may be calculated, and from eq. 21 the value of $K_{\text{ZnH}_2\text{L}}$ may be calculated.

The formation constants of the metals with the protonated ligands may be calculated from the ionization constants of the protonated complexes by

$$K_{\text{MHL}}^{\text{M}} = \frac{K_{\text{ML}} K^{\text{H}}_4}{K_{\text{MHL}}} \quad K_{\text{MH}_2\text{L}} = \frac{K_{\text{MHL}}^{\text{M}} K^{\text{H}}_3}{K_{\text{MH}_2\text{L}}^{\text{M}}}$$

The potentiometric curve of mercaptosuccinic acid (Figures 1 and 2) shows two distinct buffer regions, one in the pH range 3 to 5, and the second at pH 9 and 11. The first of these buffer regions corresponds to two equivalents of base, indicating that the two carboxyl groups of the ligand have overlapping dissociation constants. The second buffer region obviously corresponds to the dissociation of the weakly acid mercapto group. The equilibrium constants calculated for these dissociation reactions are given in Table I.

The values reported for TMA are the average of six titrations and all values have a standard deviation of ± 0.02 . An average of eight points was used for calculation purposes in each buffer region.

(10) G. Schwarzenbach, A. Willi, and R. O. Bach, *Helv. Chim. Acta*, **30**, 1303 (1947).

TABLE I

Acid	pK^H_1	pK^H_2	pK^H_3	pK^H_4	Method ^a	$\mu, ^b M$	$t, ^\circ C.$	Ref.
TMA ^c	2.53	4.44	9.73		Gl.	1.0 (KNO ₃)	25	...
	3.64	4.64	10.37		Gl.	0.1 (KNO ₃)	25	...
	3.30	4.94	10.64		Gl.	...	25	4
	3.29				Cond.	~0	25	e
DTTA ^d	2.71	3.48	8.89	10.79	Gl.	0.1 (KNO ₃)	25	...
	2.40	3.46	9.44	11.82	Gl.	0.1 (KCl)	20	3

^a Gl. = potentiometric measurements of hydrogen ion concentrations with glass electrodes; cond. = conductometric determination of hydrogen ion concentration. ^b Approximate total ionic strength given, adjusted with supporting electrolyte indicated. ^c TMA = α -mercaptosuccinic acid (thiomalic acid). ^d DTTA = *meso*- α, α' -dimercaptosuccinic acid (*meso*-dithiotartaric acid). ^e A. Rosenheim and W. Stadler, *Ber.*, **38**, 2687 (1905).

The potentiometric curves of DTTA (Figure 3) show two buffer regions, one between pH 3 and 5 and the second between pH 8 and 10. Each of these buffer regions is the equivalent of two equivalents of base. This indicates that the two mercapto groups as well as the two carboxyl groups have overlapping ionization reactions. The ionization constants of DTTA, collected

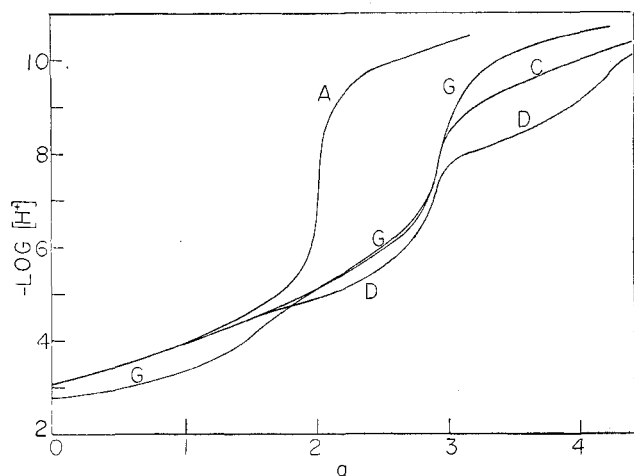


Figure 1.—Potentiometric titration of A, $1.38 \times 10^{-3} M$ α -mercaptosuccinic acid (TMA) solution; and TMA in the presence of equimolar amounts of Ni(II), C; Zn(II), D; and Ag(I), G; a = moles of sodium hydroxide added per mole of TMA; $t = 25^\circ$; $\mu = 0.1 M$ KNO₃.

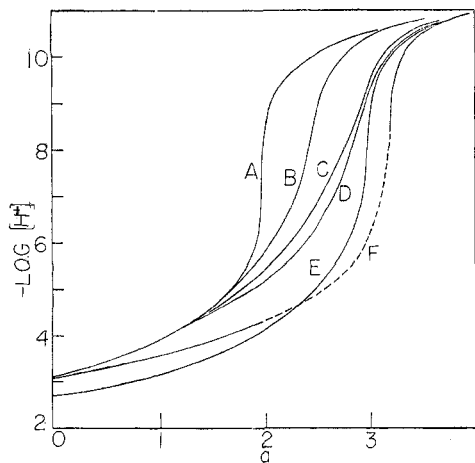


Figure 2.—Potentiometric titration of A, $1.917 \times 10^{-3} M$ α -mercaptosuccinic acid (TMA) solution; and TMA in the presence of $9.585 \times 10^{-4} M$ Co(II), B; Ni(II), C; Zn(II), D; Hg(II), E; and Cd(II), F; a = moles of sodium hydroxide added per mole of TMA; $t = 25^\circ$; $\mu = 0.1 M$ KNO₃.

in Table I, are the average of eight runs and have standard deviations of ± 0.02 , except for pK_4 , for which the deviation is ± 0.05 . An average of twenty points per buffer region was used for calculation purposes in each of the determinations.

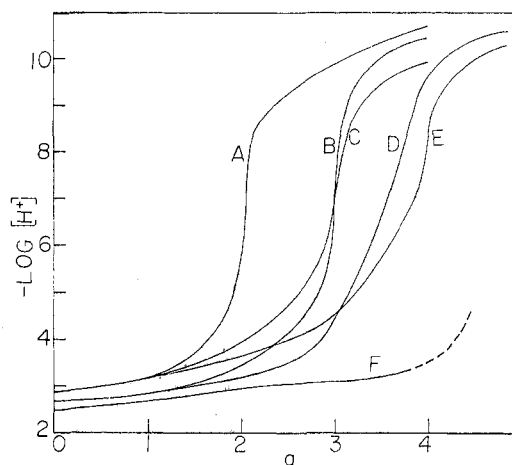


Figure 3.—Potentiometric titration of A, $1.511 \times 10^{-3} M$ α, α' -dimercaptosuccinic acid (DTTA) solution; $1.165 \times 10^{-3} M$ DTTA in the presence of $5.826 \times 10^{-4} M$ Ni(II), B; and Zn(II), C; $1.511 \times 10^{-3} M$ DTTA in the presence of $1.511 \times 10^{-3} M$ Ni(II), D; and Zn(II), E; $1.165 \times 10^{-3} M$ DTTA in the presence of $1.292 \times 10^{-2} M$ Zn(II), F; a = moles of sodium hydroxide added per mole of ligand; $t = 25^\circ$; $\mu = 0.1 M$ KNO₃.

Thiomalic Acid.—The titration curves of TMA in the presence of an equivalent amount of metal ion show the displacement of three protons per molecule of TMA. This indicates that the metal is coordinated through the sulfur of a mercapto group, as well as through the carbonyl groups. In the case of silver(I) and nickel(II), the only complex which can be deduced from the titration curve is the 1:1 complex. In the case of silver(I), which has two strong linear coordination tendencies for nitrogen and sulfur donors in aqueous solution, there is no further reaction with base. However, with nickel, there does appear to be a reaction with base. Since there are water molecules in the coordination sphere which might dissociate, the formation of a hydroxo metal chelate is a strong possibility. When the zinc(II) curve is examined it is to be noted that a separate buffer region exists at much lower pH than that observed for nickel(II). In the absence of the appearance of a solid phase, this can only mean the formation of a monohydroxo complex. Thus it

seems that TMA acts as a terdentate ligand, as already has been assumed.³

For the 2:1 ligand-metal curves, six equivalents of hydrogen ion are displaced per mole of metal ion present for the metal ions Ni(II), Zn(II), Hg(II), and Cd(II). This observation again shows that the metal ions are chelated through the mercapto sulfur atom. During the titration of cadmium(II), a white precipitate formed upon the addition of two equivalents of base per mole of ligand but dissolved at $a = 3$. A white precipitate was also formed with the lead(II) ion.

With manganese(II) a complex is formed but no reproducible nor meaningful stoichiometry was observed in any titration. This result is in agreement with the observations of Cheney, *et al.*,³ and, consequently, the reaction was not further studied.

Upon the addition of copper(II) to a solution of TMA, the solution turned deep purple and, upon standing in the presence of air, deposited a black precipitate after the passage of approximately 1 week. Immediate titration of the solution under nitrogen did not yield meaningful or reproducible stoichiometry. Since it seemed that an oxidation-reduction reaction involving Cu(I) as suggested by Klotz was probably taking place, the reaction of Cu(II) with TMA and DTTA was not further investigated.

If an equimolar amount of TMA and cobalt(II) is titrated, no reproducible end point is obtained, although the end point always falls between two and three equivalents of base. If, however, a two-to-one molar ratio of ligand to cobalt(II) is titrated, an inflection is obtained at 2.5 equivalents of base per mole of ligand. This was interpreted as the formation of a one-to-one complex in the presence of two moles of ligand.

There was no evidence for complex formation between TMA and calcium(II), magnesium(II), and strontium(II) ions.

The stability constants for the various metals and TMA are compiled in Table II.

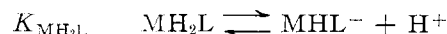
TABLE II
STABILITY CONSTANTS OF METAL CHELATES OF
THIOMALIC ACID AT 25°

Metal	log K_{ML}	log K_{ML_2}	Color	μ, M	Ref.
Ag(I)	7.85	...	Colorless	0.1 (KNO ₃)	
Co(II)	6.88		Yellow-brown	0.1 (KNO ₃)	
	6.31		4
Hg(II)	9.94	8.13	Colorless	0.1 (KNO ₃)	
Ni(II)	7.6	6.21	Pink; $a > 3$	0.1 (KNO ₃)	
$K(NiLOH^{2-} + H^+ \rightleftharpoons NiL^-)$		9.37	Colorless	0.1 (KNO ₃)	
	7.97	4.90	4
Zn(II)	8.24	6.32	Colorless	0.1 (KNO ₃)	
	7.52	...	Colorless	1.0 (KNO ₃)	
$K(ZnLOH^{2-} + H^+ \rightleftharpoons ZnL^-)$		8.36	Colorless	0.1 (KNO ₃)	
$K(ZnLOH^{2-} + H^+ \rightleftharpoons ZnL^-)$		8.01	Colorless	1.0 (KNO ₃)	

^a No evidence of complex formation. ^b No supporting electrolyte.

α, α -Dimercaptosuccinic Acid.—The potentiometric equilibrium curve of equimolar amounts of DTTA and

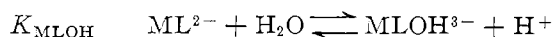
metal ions shows that di- and monoprotonated complexes are formed on the addition of up to 3 equivalents of base, in accordance with the reactions



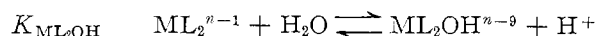
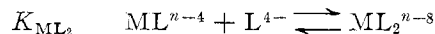
The monoprotonated complexes dissociate further to the "normal" complexes in separate buffer regions between the a values of 3 and 4.



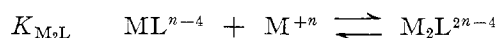
At greater than four equivalents of base, the potentiometric equilibrium curves do not exhibit the pH expected from the amount of excess base added, indicating that the chelate ML^{2-} still has faintly acidic properties and forms a monohydroxo complex



The potentiometric curves for a 2:1 molar ratio of DTTA to metal ion served for the determination of the second association constant of the metal ion with DTTA. The inflection at an a value of 3 corresponds to the formation of the 1:1 complex, but the region between $a = 3$ and 4 is lower than would be expected, even allowing for $[ML(OH)]^{3-}$. This means that the chelate ML_2 forms, together with, as Schwarzenbach² has shown in the case of Zn(II), a monohydroxo complex



The metal excess curve may be regarded as the ionization of DTTA in a new medium, in which the free metal ion concentration remains relatively constant. In this system, the curve between $a = 3$ and 4 is lowered considerably when compared to the equivalent curve. This indicated that another metal ion combines with the 1:1 complex



The various chelate formation constants calculated for DTTA are compiled in Table III.

The formation constants of the metals with the protonated species are calculated from the association constants of hydrogen ion with the unprotonated complex. (The association constant is simply the reciprocal of the dissociation constant of the acidic complex.) These constants, as well as the apparent ionization constants (K'_n) of DTTA in the presence of excess metal (Zn(II)), are collected in Table IV.

The above general remarks for the DTTA potentiometric curves hold for nickel(II) and zinc(II), with the exception that DTTA does not combine with a second mole of nickel. A yellow precipitate is formed when 1:1 as well as 2:1 molar ratios of Ag(I) to DTTA are brought together in solution. For the 1:1 ratio, the precipitate goes into solution at $a = 3$, indicating that a soluble 1:1 complex is formed. For the 2:1 ratio, the precipitate goes into solution at $a = 4$, indicating

TABLE III
 STABILITY CONSTANTS OF METAL CHELATES OF DTTA AT 25° AND $\mu = 0.1 M KNO_3$

Metal	$K_{MH_2L}^M$	K_{MHL}^M	K_{ML}	pK_{MLOH}	K_{ML_2}	pK_{ML_2OH}	K_{M_2L}	Color
Ni(II)	3.9	9.5	11.69	11.14	2.64	10.4	<i>b</i>	Yellow-green
Zn(II)	3.8	9.3	14.42	10.11	3.32	9.4	4.07	Colorless
	2.8 ^a	9.6 ^a	15.82 ^a	12.28 ^a	3.57 ^a	9.7 ^a	3.85 ^a	

^a Ref. 2; $\mu = 0.1 M$, 20°. ^b None formed.

the formation of a binuclear complex. Back titration of these solutions leads to immediate reprecipitation at $a = 3$ and $a = 4$, respectively. Cobalt(II) formed soluble yellow complex(es), but reproducible potentiometric titrations could not be obtained. In the presence of two equivalents of DTTA, lead(II) forms a white precipitate, which goes into solution at $a = 3$, indicating that a 2:1 DTTA-Pb complex is formed. Cadmium(II) forms a white precipitate which does not dissolve in base. There was no evidence for complex formation between DTTA and alkaline earth ions.

 TABLE IV
 IONIZATION CONSTANTS OF PROTONATED METAL CHELATES OF DTTA

Metal	pK_{MHL}	pK_{MH_2L}	$pK^{H'1}$	$pK^{H'2}$	$pK^{H'3}$	$pK^{H'4}$
Ni(II)	8.7	3.3				
Zn(II)	5.7	3.4	~1.5	~2.5	2.7	3.5
	5.6 ^a	2.7 ^a	~2.4 ^a	~2.9 ^a	2.7 ^a	3.5 ^a

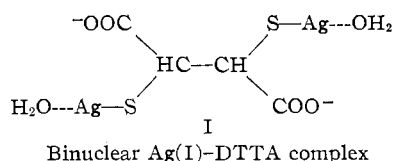
^a Ref. 2; 20°.

Copper(II), as in the case of TMA, undergoes reduction to copper(I). These findings are in accord with those of Klotz, *et al.*⁷

Discussion

TMA.—With silver(I), which has a coordination number of two, arranged in a linear fashion, TMA must function as a mono- or bidentate ligand. Since three equivalents are displaced when the molar ratio of ligand to metal ion is 1:1, the Ag(I) is probably coordinated through the sulfur atom.

It is interesting to note that Ag(I) does not form a complex having a 2:1 ratio of TMA to metal ion. Thus when one mercaptide group is coordinated to Ag(I), there seems to be little or no tendency to displace a coordinated water molecule (or possibly the carboxylate group of the ligand) to give a complex in which two negative mercaptide groups are bound to the same Ag(I) ion. The same phenomenon was observed with DTTA, where potentiometric data indicate coordination with only one sulfur atom. This is in accord with the formation of a binuclear complex, I, when the ratio of metal ion to ligand is 2:1.



With nickel(II) and zinc(II), TMA acts as a terdentate ligand. As only three of the four coordination positions are occupied by the TMA in the zinc com-

plex, a hydroxo complex is formed, which probably has a tetrahedral arrangement of donor groups about the metal ion. Variation of the potentiometric titration curves as a function of metal ion concentration in the 1:1 Zn(II)-TMA systems indicated the possibility of polynuclear complex formation. When dimerization was tested with eq. 9, a series of curves was obtained rather than the linear plot predicted. A careful potentiometric reinvestigation of the buffer region involving hydrolysis of the metal chelate was carried out by prior adjustment of supporting electrolyte to give the same ionic strength at 3.5 equivalents. When this was done, the various titration curves intersected at 3.5 equivalents of base, indicating that only a mononuclear hydroxo metal chelate is formed.

With nickel(II), a high pH buffer region between $a = 3$ and 4 indicates that a hydroxo metal chelate is also formed, with a pK of 9.37. When the molar ratio of ligand to metal ion is 2:1, the structure of the Ni(II) is square-planar, while those of zinc and mercury are tetrahedral. The square-planar configuration of the Ni(II) complex is assigned on the basis of the appearance of a pink color during the titration. The color of the complex may be used to distinguish between square-planar, tetrahedral, and octahedral.¹¹

Cobalt(II) is interesting in this connection as it forms only a one-to-one chelate, and does so only in a two-to-one molar ratio, the reaction being nonstoichiometric in the one-to-one titrations. There appears to be no reasonable explanation for this phenomenon on the basis of evidence presently available. No conclusion on this question may be drawn. Precipitation of the white Cd(II) complex between $a = 2$ and 3 precluded calculation of a formation constant.

The stability constants collected in Table II show the relative stabilities of the chelates to be $Hg > Zn > Ag > Ni > Co$. The order of stability is that which would be expected upon examination of other mercapto acid-metal constants^{8,11,12} with the exception of Ag(I), for which, as yet, no other formation constants have been reported.

The stability constants of TMA complexes are, on the whole, considerably higher than those of its nitrogen and oxygen analogs,¹³ aspartic and malic acids, respectively. This would indicate that sulfur has better donating properties for the metal ions investigated than either oxygen or nitrogen. This is especially reasonable when the DTTA stability constants are examined,

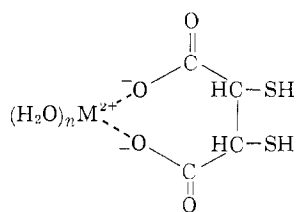
(11) W. Manch and W. C. Fernelius, *J. Chem. Educ.*, **38**, 192 (1961).

(12) W. Stricks, I. M. Kolthoff, and A. Heyndrick, *J. Am. Chem. Soc.*, **76**, 1515 (1954).

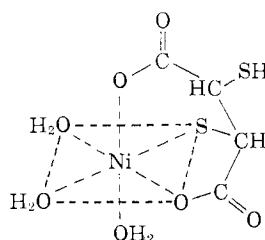
(13) J. Bjerrum, G. Schwarzenbach, and L. G. Sillén, "Stability Constants. Part I. Organic Ligands," Special Publication No. 6, The Chemical Society, London, 1957.

whereby the first formation constant for Zn-DTTA is 10^{15} , while for Zn-tartaric acid it is 10^8 .

DTTA.—The magnitudes of the formation constants of the diprotonated Ni(II) and Zn(II) chelates (Table IV) indicate that coordination takes place through the two carboxyl groups, especially since the nickel constant is greater than that of zinc. It already has been mentioned above that when coordination takes place through oxygen and sulfur, the zinc chelate is the more stable. The fact that the ligand is only bidentate and the large size of the chelate ring formed, are in accord with the fairly low value of the stability constant. The probable structure of these chelates is indicated by II.

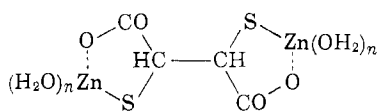


II
Diprotonated complexes
of Ni(II) and Zn(II)



III
Terdentate monoprotonated
Ni(II)-DTTA chelate

At higher pH there is a separate buffer region corresponding to the formation of a monoprotonated complex. Displacement of the proton from the sulfur atom and the high value for the formation of the monoprotonated complexes of zinc(II) and nickel(II) ($\sim 10^9$) show that coordination is through one of the sulfur atoms as illustrated for Ni(II) by III. Further neu-



IV
Binuclear Zn(II)-DTTA chelate

tralization of the monoprotonated chelate results in the formation of a chelate in which the ligand is probably bidentate and is coordinated strongly to the metal ions

through the mercaptide groups. Only weak interactions between the carboxylate ions and the metal ion are allowed in this chelate compound, because of steric restrictions on the ability of the carboxylate groups to approach the metal ion closely. The very high formation constant for the 1:1 complex (zinc 10^{14} , nickel 10^{12}), as well as the higher stability of the Zn(II) complex, is what would be expected for coordination through the two sulfur atoms. The nature of the coordination of this ligand to Ni(II) and Zn(II) results in an interesting reversal in the relative stabilities of the chelate formed as a function of pH. At low pH coordination through oxygen renders the Ni(II) chelate more stable, while at higher pH coordination through one or two sulfur atoms makes the Zn(II) chelate more stable. These results may be observed qualitatively from the relative positions of the titration curves (D and E, Figure 3).

The formation of the 1:1 complex in neutral and alkaline media is followed at higher pH by the dissociation of a proton from one of the remaining water molecules in the coordination sphere of the metal ion to form a hydroxo complex.

When the molar ratio of ligand to metal ion is 2:1, it is necessary to assume that the species ML_2OH is present, in addition to ML , ML_2 , and $MLOH$, in order to obtain a constant value for the stability constant. If this hydroxo complex is present for zinc, then this means that the coordination of zinc is probably octahedral.

The low formation constant for the addition of a second mole of DTTA to the 1:1 complex is reasonable when it is looked upon as the addition of a highly charged negative ion to a dinegative complex, plus a large saturation effect resulting from the high polarizability of the mercapto group.

Examination of the excess curve shows that there is a continuous buffer region between $a = 3$ and 4, corresponding to the addition of a second mole of zinc to the 1:1 chelate. The structure IV is suggested for the binuclear chelate, since five-membered chelate rings are more stable than seven-membered rings,¹⁴ which would be present in the alternative binuclear structure.

(14) A. E. Martell and M. Calvin, "The Chemistry of the Metal Chelate Compounds," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1959, p. 134f.