Complex Formation with
Triethylenetetraminehexaacetic Acid
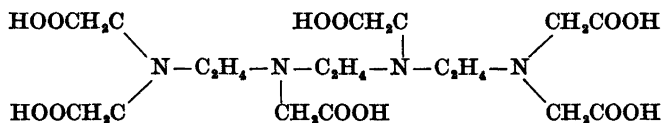
II. Mercury Chelates*

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The complex formation of triethylenetetraminehexaacetic acid (TTHA or H_6X) with bivalent mercury ions is reported, and the stability constants are calculated from potentiometric measurements. In aqueous 0.1 M $NaClO_4$ solution three mononuclear complex species seem to exist: $Hg(II)H_2X^{2-}$, $Hg(II)HX^{3-}$ and $Hg(II)X^{4-}$. The binuclear compounds $Hg_2(II)X^{2-}$, $Hg_2(II)(OH)X^{3-}$ and $Hg_2(II)(OH)_2X^{4-}$ are formed. The existence of trinuclear complexes $Hg_3(II)X$ as well as different hydrolysis compounds seems possible from the titration data.

Although the reagent triethylenetetraminehexaacetic acid (TTHA or H_6X) was synthetized about ten years ago,[1] very little information concerning its chelating properties has been reported.[2-6] Since the reagent has become of increasing importance in analytical chemistry, studies on the complex formation are of interest. In particular, knowledge of the mercury complexes is valuable as the reagent is of importance in polarographic studies, and for analytical purposes, using mercury indicator electrodes.

TTHA with the formula

$$\begin{array}{ccccc}
\text{HOOCH}_2\text{C} & & \text{HOOCH}_2\text{C} & & \text{CH}_2\text{COOH} \\
& \diagdown & | & & \diagup \\
& \text{N}-\text{C}_2\text{H}_4-\text{N}-\text{C}_2\text{H}_4-\text{N}-\text{C}_2\text{H}_4-\text{N} & & \\
& \diagup & | & & \diagdown \\
\text{HOOCH}_2\text{C} & & \text{CH}_2\text{COOH} & & \text{CH}_2\text{COOH}
\end{array}$$

has a maximum of ten coordinating centers, and the coordination number of bivalent mercury is usually low (2 or 4). Thus polynuclear compounds as well as mixed complexes with hydrogen ions are highly probable.

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* Part I. *Acta Chem. Scand.* **19** (1965) 1797.

EXPERIMENTAL

Materials. Triethylenetetraminehexaacetic acid was supplied by Geigy Chemical Company, Basel, Switzerland. The compound was purified by recrystallization from water.

A standard solution of bivalent mercury was prepared by dissolving a known quantity of reagent grade mercury metal in concentrated nitric acid. The solution was evaporated to a small volume in order to reduce the quantity of excess acid and nitrogen oxides. The determination of the excess free acid in this Hg^{2+} solution could not be performed by direct titrations, as successive hydrolysis products are formed during the titration and no definite end-point could be obtained. A 1:1 Hg^{2+}-EDTA solution was therefore prepared, and was titrated with standard NaOH. In this case no hydrolysis is possible in the pH-range measured. The excess acid could therefore be determined from the experimentally obtained inflection on the titration curve.

Triethylenetetraminedisulphate was obtained from J. T. Baker Chemical Company, Philipsburg, N. J. All the remaining chemicals were of reagent grade.

Methods. All the data were obtained at 25°C ± 0.1° and the ionic strength was kept at 0.1 by addition of sodium perchlorate.

The potentials were measured at zero current (with a Multiflex galvanometer) *vs.* a saturated calomel electrode connected to the solution with a KCl-agar bridge. The indicator electrode was a J-tube mercury electrode as described by Holloway and Reilley.[8]

The pH values were determined with a Beckman Zeromatic pH-meter or a Radiometer automatic titrator.

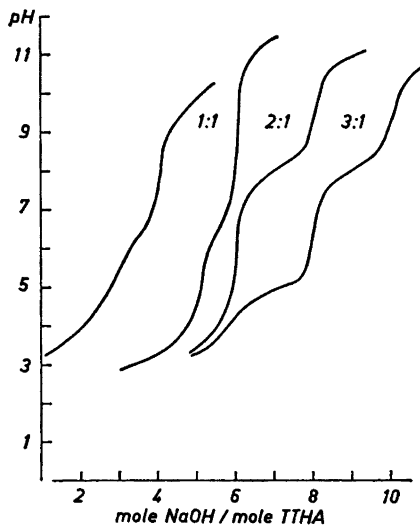The Radiometer Polarograph PO4 was used for the polarographic measurements.

Fig. 1. Titration curves of 1.00 × 10⁻³ M TTHA alone and in the presence of one, two, and three equivalents of bivalent mercury (0.1 M NaClO₄, 25°C).
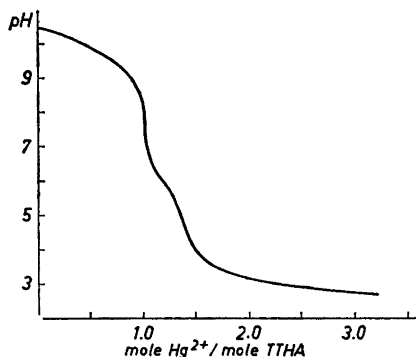
Fig. 2. Titration, in the presence of 5.50 equivalents of NaOH, of 5.00 × 10⁻⁴ M TTHA with Hg^{2+}. The simultaneously added free acid in the standard Hg^{2+} solution is neutralized with a calculated quantity of standard NaOH solution prior to the registration of the pH.

RESULTS

Titration data of TTHA, without and in the presence of 1, 2, and 3 equivalents of Hg^{2+} are indicated in Fig. 1. Measurements with a great excess of metal ions were not carried out because hydrated mercury oxide precipitates even at low pH values.

The system Hg(II)-TTHA in ratio 1:1. When mercury ions combine with triethylenetetraminehexaacetic acid, an exchange of metal ions with protons in the acid takes place. This results in a marked lowering of the pH of the solution, as is apparent from the titration curves presented in Fig. 1. Fig. 2 gives the pH of a TTHA-solution with 5.50 equivalents of base as a function of successive addition of Hg^{2+}. (The excess acid in the mercury solution was neutralized with calculated quantities of base prior to the registration of the pH-value).

The titration curve of 1:1 Hg(II) and TTHA is an illustrative example of a clear-cut stepwise formation of a monohydrogen and a normal 1:1 mercury complex. With 6 equivalents of base the reaction is

$$Hg^{2+} + H_6X + 6OH^- = HgX^{4-} + 6H_2O \qquad (1)$$
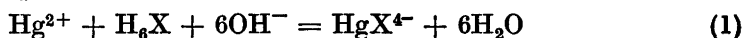
The inflection at 5 equivalents of base may be represented by the reaction

$$HgX^{4-} + H^+ = HgHX^{3-} \qquad (2)$$
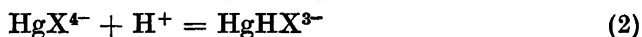
No sharp inflection is observed on the curve when less than 5 equivalents are added, but as discussed later, a closer examination of the curve between 3 and 4 equivalents of added base indicates the formation of a dihydrogen chelate according to the reaction

$$HgHX^{3-} + H^+ = HgH_2X^{2-} \qquad (3)$$
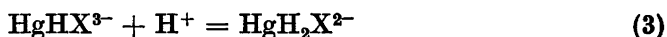
No hydroxyl complexes or complexes with more than two associated protons were found.

2:1 Compounds. With solutions of two equivalents of metal ions per equivalent of TTHA, very different titration curves are obtained. A steep inflection is observed when 6 equivalents of base are added. No inflection is observed when 5 equivalents are added, and compared to the titration curve for the 1:1 ratio of mercury to TTHA, a marked lowering of the pH of the solution is observed after addition of the second equivalent of mercury ions. This indicates the formation of binuclear compounds and may be due to the reaction

$$2Hg^{2+} + H_6X^- + 6OH^- = Hg_2X^{2-} + 6H_2O \qquad (4)$$

The considerable lowering of the pH relative to the solution with 1:1 mole ratio is explained by assuming that binuclear complexes will not retain any of the six acid protons of TTHA. Thus the mononuclear compounds exchange protons with mercury ions, *e.g.* according to

$$HgHX^{3-} + Hg^{2+} = Hg_2X^{2-} + H^+ \qquad (5)$$
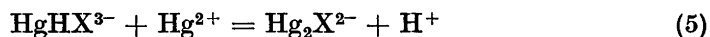
Further addition of base beyond 6 equivalents gives no inflection until 8 equivalent are added. This observation is in accordance with the reaction

$$Hg_2X^{2-} + 2OH^- = Hg_2X(OH)_2^{4-} \qquad (6)$$
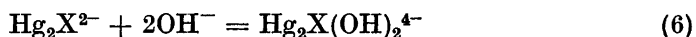
though overlapping reactions resulting in the formation of $Hg_2X(OH)^{3-}$ are possible. No binuclear compounds with the number of hydroxyl groups exceeding two, are found to exist.

Polymer complex compounds. Polymerization through the formation of diol compounds has often been reported to be intermediate steps in the hydrolysis and precipitation of hydroxides. The formation of such polymer compounds has recently also been noted with chelates.[9] The hydrolysis of the Hg^{2+} ion has been reported by Hietanen *et al.*[10] No polynuclear (or polymer) products were found to exist in the concentration range investigated. Formation of polymer compounds from 1:1 or 2:1 TTHA complexes was therefore not expected. This assumption was verified experimentally by utilizing the fact that upon addition of base to equivalent amounts of mercury ions and TTHA, the $\bar{n}$ (formation function [15]) will depend only on equivalents of base added per equivalent of TTHA if solely monomer products are formed, but will neccessarily depend on the concentration of the complex if polymer compounds are formed. Similar considerations are valid for polymerization of binuclear chelates. With 6.5 equivalents of base added, the reaction

$$2HgX^{4-} + 2OH^- = Hg_2(OH)_2X_2^{10-} \tag{7}$$
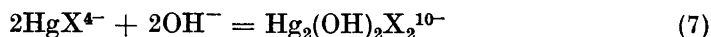
will result in a decrease in the $\bar{n}$ value of the solution since the compound $Hg(OH)X^{5-}$ does not exist in any quantity. The diol reaction

$$2Hg_2X^{2-} + 2OH^- = Hg_4(OH)_2X_2^{6-} \tag{8}$$

also results in a decrease in the pH value at 6.5 equivalents of base in the solution.

Reactions 7 and 8 will be displaced towards right with increasing concentrations and will cause shifts of the $\bar{n}$ values with dilution, if dimeric compounds exist.

Two saturated solutions were prepared, one with equimolar ratio of Hg^{2+} and TTHA, and the other with mole-ratio 2:1 of Hg^{2+} and TTHA. To the mixtures was added a 0.1 M $NaClO_4$ solution until all the solid phase dissolved. When the equilibria were established, the pH values were measured. The solutions were then diluted ten times by "titration" with a 0.1 M $NaClO_4$ solution. The $\bar{n}$ values were calculated from the pH measurements. For the 1:1 and also for the 2:1 solution the $\bar{n}$ was observed to be independent of dilution. This is taken as a proof that within the experimental errors, no diol-polymerization occurs.
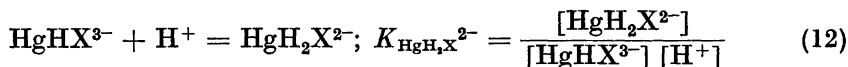
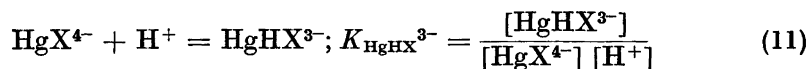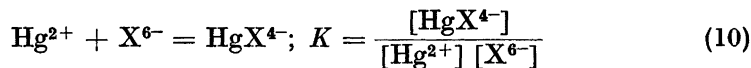## DETERMINATION AND CALCULATION OF STABILITY CONSTANTS

1:1 Chelates. The acid dissociation constants of TTHA have been reported by Grimes *et al.*[11] With

$$H_6X = H_5X^- + H^+; \quad k_1 = \frac{[H^+][H_5X^-]}{[H_6X]} \tag{9}$$
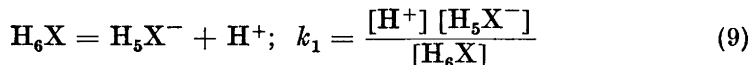
and k_2 to k_6 are defined, analogously, the reported pk_1 to pk_6 values are 2.46, 2.52, 4.00, 5.98, 9.55, 10.33, respectively.

In order to describe the equilibrium species, the following reactions and constants are defined:

$$Hg^{2+} + X^{6-} = HgX^{4-}; \quad K = \frac{[HgX^{4-}]}{[Hg^{2+}] [X^{6-}]} \tag{10}$$

$$HgX^{4-} + H^+ = HgHX^{3-}; \quad K_{HgHX}{}^{3-} = \frac{[HgHX^{3-}]}{[HgX^{4-}] [H^+]} \tag{11}$$

$$HgHX^{3-} + H^+ = HgH_2X^{2-}; \quad K_{HgH_2X}{}^{2-} = \frac{[HgH_2X^{2-}]}{[HgHX^{3-}] [H^+]} \tag{12}$$

A direct calculation of the stability constant K from the titration data is impossible because the value of the constant is too high. The complex does not dissociate in measurable amounts even in the most acid solutions. The stability constants of the mercury-DTPA complex and of the EDTA complex are $10^{26.7}$ [12] and $10^{21.8}$, [13] respectively; for the TTHA complex a constant of the same order of magnitude is expected.

A method that is often used in the case of stable complexes is to introduce a second chelating agent, $e.g.$ triaminotriethylamine (tren), and a second metal ion which is chelated only by the ligand to be investigated, for example Ca^{2+} ions. The synthesis of tren was difficult and gave a very low yield, and as the compound was not available commercially, triethylenetetramine (trien) was used. The properties of this reagent are very similar to those of tren, but its tetra-protonated cation acid has to be considered. The acid dissociation constants of trien as well as the stability constant of the mercury-trien chelate have been determined by Schwarzenbach.[14] The stability constant of the Ca^{2+}-TTHA (1:1) complex has been determined by Grimes $et\ al.$[11] (log K = 10.06). Calcium ions are only chelated by TTHA and not by trien. The resulting equilibrium is defined by the total equation:

$$HgX^{4-} + Ca^{2+} + H_4trien^{4+} = Hgtrien^{2+} + CaX^{4-} + 4H^+ \tag{13}$$
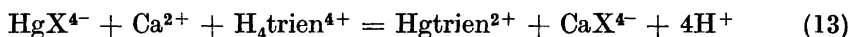
which shows that the degree of exchange may be determined by pH measurements. Knowledge of the degree of exchange enables one to calculate the stability constant of the mercury-TTHA 1:1 complex when the other equilibrium constants are known.

Eqn. 13 represents a simplification of the actual conditions since protonated chelates should be taken into account. Grimes $et\ al.$[11] have reported the existence of the two-protonated Ca-TTHA chelates, CaH_2X^{2-} and $CaHX^{3-}$, with the acid step stability constants $10^{2.4}$ and $10^{8.07}$, respectively. A protonated mercury-trien complex $HgHX^{3-}$ with the acid step stability constant $10^{5.6}$ has been reported by Schwarzenbach.[14] The acid step stability constants of the 1:1 mercury-TTHA chelates are reported later in this paper and used in the calculations below.

Equimolar quantities (10^{-3} M) of triendisulphate, TTHA, Ca^{2+} and Hg^{2+} were titrated with a standard NaOH solution. From the observed pH of the solution, the number of equivalents of base added enables one to determine the stability constant of the Hg-TTHA complex. From every observed point

on the titration curve a value of the stability constant is obtained. A calculation of standard deviation of the constants is therefore easily done from these data.

As the calculations are rather complex, they were carried out on a digital computer (the Danish Gier computer). The system is described by the following equations: The proton equation (1 equation); mass balance of Ca^{2+} (1 equation); mass balance of Hg^{2+} (1 equation); mass balance of trien (1 equation); mass balance of TTHA (1 equation); dissociation of TTHA (6 equations); dissociation of trien (4 equations); protolysis of the hydrogenated Hg-TTHA complexes (2 equations); protolysis of the hydrogenated Ca-TTHA complexes (2 equations); protolysis of the hydrogenated Hg-trien complex (2 equations); dissociation of the Hg-trien complex (1 equation); dissociation of the Ca-TTHA complex (1 equation); and finally eqn. 10 which defines the equation for the constant to be calculated.

To evaluate the stability constant, 22 unknown parameters have to be eliminated from the 23 equations above. Due to the complexity of the calculation, the only approximation which undoubtly always would be correct is to consider the concentration of free mercury ions to be zero in sums. The first 20 equations are linear and 19 of them contain the same 20 unknowns. One of the 20 parameters is preliminarily considered as a constant; the $[X^{6-}]$ was chosen, as this will result in the simplest calculations. The solution of this linear equation system was performed by means of the determinant method commonly known as Cramer's rule. Each parameter is then obtained as the ratio of two determinants. The denominators are true constants, and the enumerator determinant is set equal to a sum of two determinants, one with only constants and the other a product of $[X^{-6}]$ and another determinant with constants only. It is thus possible to express all the 19 parameters as

$$\alpha_i[X^{6-}] + \beta_i \qquad (1 \leqslant i \leqslant 19) \qquad (14)$$

The constants α and β are both obtained as the ratio of two (19 $\times$ 19) determinants which are calculated in a few seconds with the computer. The parameters in the last (20th) linear equation are then substituted by eqn. 14. This enables one to determine $[X^{6-}]$. Inserting the obtained value for $[X^{6-}]$ in eqn. 14, the parameters are found. By combining the obtained values with the two non-linear equations, all the concentrations may be calculated and the desired stability constant is determined. From the average of 39 calculated values, the logarithm of the stability constant K, as defined by eqn. 10 is

$$\log K = 25.27 \text{ with standard deviation } 0.08.$$

The determination of the stability constants of the mercury complexes and the calculations from the experimentally obtained data were originally expected to be greatly facilitated by use of a mercury electrode inserted into a solution of a mercury complex having an excess of complexing agent, the potential being measured vs. a reference (calomel) electrode. For preliminary investigations, a mercury electrode was used with a solution of 10^{-3} M Hg^{2+}, 2×10^{-3} M TTHA and 0.1 M $NaClO_4$. The pH of this solution was varied by addition of NaOH or $HClO_4$ and the potential vs. S.C.E. determined at different pH values. No reproducible and reliable results were obtained, however, and the method could therefore not be used to determine the stability constant.

The stability constant could not be determined by polarographic methods as the results were found to be non-reproducible.

The bad reproducibility of these two methods seems to be connected with the formation of sparely soluble compounds which surround the mercury electrodes. These, probably polynuclear, compounds are described later in this paper.

The step stability constants of hydrolyzed 1:1 complexes of mercury were determined from the titration data by Bjerrum's method.[15] Hydrogen or hydroxyl ions are considered as ligands which react with the mercury-TTHA complex. It is then assumed that the dissociation of the complex to metal ions and free ligand is negligible. From the formation function it could be concluded that the complex $HgX(OH)^{5-}$ does not exist within the experimental errors. No defined inflection below 5 equivalent of base added was observed on the titration curve, but formation function calculations indicated the existence of the biprotonated chelate HgH_2X^{2-}. The compound HgH_3X^- was not observed.

The stability constants found from half $\bar{n}$ values were corrected as outlined in a previous paper.[16] The results are presented in Table 1.
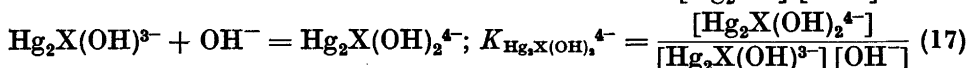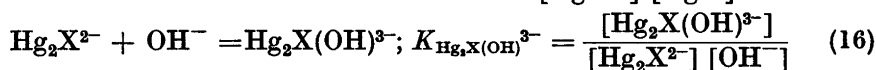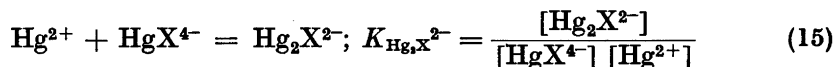
Table 1. Stability constants of mercury(II) chelates of TTHA and related compounds. The constants for the TTHA complexes are valid at 25°C, in 0.1 M NaClO$_4$.

Complex formed	Constant	X = NTA	X = EDTA	X = DTPA	X = TTHA
HgX^{4-}	$\log K$	12.7^a	21.8^b	26.7^c	25.27
$HgHX^{3-}$	$\log K_{HgHX}{}^{3-}$		3.1^b	4.2^c	6.55
HhH_2X^{2-}	$\log K_{HgH_2X}{}^{2-}$				3.30
$Hg(OH)X^{5-}$	$\log k$	8.6^a	4.9^b		
Hg_2X^{2-}	$\log K_{Hg_2X}{}^{2-}$				8.4
$Hg_2X(OH)^{3-}$	$\log K_{Hg_2X(OH)}{}^{3-}$				6.1
$Hg_2X(OH)_2^{4-}$	$\log K_{Hg_2X(OH)_2}{}^{4-}$				5.9

^{a} Ref. 19. ^{b} Ref. 13. ^{c} Ref. 12.

Binuclear chelates. Due to the low coordination number of bivalent mercury and the high number of possible bonding groups in TTHA, binuclear compounds appear, as quantitatively discussed previously in this paper. From the decrease of the pH of the 2:1 compared with the 1:1 solutions, calculations of the stability constants are possible, using the stability constants of the 1:1 chelates given above.
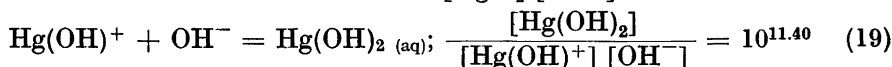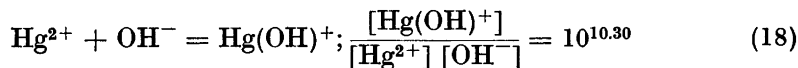
The equilibrium constants of the binuclear chelates are defined as follows:

$$Hg^{2+} + HgX^{4-} = Hg_2X^{2-}; \quad K_{Hg_2X}{}^{2-} = \frac{[Hg_2X^{2-}]}{[HgX^{4-}][Hg^{2+}]} \quad (15)$$

$$Hg_2X^{2-} + OH^- = Hg_2X(OH)^{3-}; \quad K_{Hg_2X(OH)}{}^{3-} = \frac{[Hg_2X(OH)^{3-}]}{[Hg_2X^{2-}][OH^-]} \quad (16)$$

$$Hg_2X(OH)^{3-} + OH^- = Hg_2X(OH)_2^{4-}; \quad K_{Hg_2X(OH)_2}{}^{4-} = \frac{[Hg_2X(OH)_2^{4-}]}{[Hg_2X(OH)^{3-}][OH^-]} \quad (17)$$

The equilibrium constant $K_{Hg_2X}{}^{2-}$ is calculated directly from the 2:1 titration data. It has to be assumed that negligible quantities of three-nuclear or higher complexes are formed under these experimental conditions. Due to the very high stability constant of the mononuclear chelate ($\log K = 25.27$) it is reason-

able to assume that the dissociation of the complexes to metal and free ligand is negligible. Further no hydrogen-containing ions of the binuclear chelate (*e.g.* Hg_2HX^-) are assumed to exist under the same experimental conditions. This assumption is plausible because the tendency to form hydrogen complexes decreases with the number of metal ions bound to the ligand.

The hydrolytic properties of the Hg^{2+} ion have been studied by Hietanen and Sillén.[10] The following constants for the hydrolysis were reported:

$$Hg^{2+} + OH^- = Hg(OH)^+; \frac{[Hg(OH)^+]}{[Hg^{2+}][OH^-]} = 10^{10.30} \qquad (18)$$

$$Hg(OH)^+ + OH^- = Hg(OH)_{2\ (aq)}; \frac{[Hg(OH)_2]}{[Hg(OH)^+][OH^-]} = 10^{11.40} \qquad (19)$$

The following equations then completely define the system:

$$C_{Hg} = [Hg^{2+}] + [Hg(OH)^+] + [Hg(OH)_2] + [HgX^{4-}] + [HgHX^{3-}] + \\ + [HgH_2X^{2-}] + 2[Hg_2X^{2-}] \qquad (20)$$

$$C_X = [HgX^{4-}] + [HgHX^{3-}] + [HgH_2X^{2-}] + [Hg_2X] \qquad (21)$$

$$(6-a)C_X - [H^+] + [OH^-] = [HgHX^{3-}] + 2[HgH_2X^{2-}] - [Hg(OH)^+] - \\ 2[Hg(OH)_2] \qquad (22)$$

Since the equilibrium constants above are known, $K_{Hg_2X}^{2-}$ may be calculated. A computer programme was worked out and

$$\log K_{Hg_2X}^{2-} \text{ was found to be } 8.4$$

From the 2:1 titration curves, the products of hydrolysis of the 2:1 chelate were studied. The Bjerrum method can not be applied directly as the ligand considered (Hg_2X^{2-}) is partially dissociated to the mononuclear chelate and mercury hydroxides. However, the method may be used by defining the "composite acid" (pH dependent) dissociation constants:

$$k_1 = \frac{[Hg_2(OH)X^{3-}] + [Hg(OH)^+]}{[OH^-][(HgX^{4-})] + [Hg^{2+}] + [Hg_2X])} \quad \text{and} \qquad (23)$$

$$k_2 = \frac{Hg_2(OH)_2X^{4-}] + [Hg(OH)_2)}{[OH^-]([Hg_2(OH)X^{3-}] + [Hg(OH)^+])} \qquad (24)$$

The non-hydroxylated forms ($HgX^{4-} + Hg^{2+} + Hg_2X^{2-}$) were considered to be the "central ion" and hydroxyl ions were taken to be ligands. The application of a modified Bjerrum's method is thus possible. The obtained step stability constants k_1 and k_2 (from $\bar{n}$ plots) were corrected as outlined previously.[16] The obtained values were $\log k_1 = 6.10$ and $\log k_2 = 5.95$.

The stability constants, which are to be found, are defined by eqns. 16 and 17. From the magnitude of the stability constants, the concentrations of the binuclear compounds in eqns. 23 and 24 have to be considerably higher than those of the other compounds. The stability constants were found to be:

$$\log K_{Hg_2X(OH)}^{3-} = 6.1 \text{ and } \log K_{Hg_2X(OH)_2}^{4-} = 5.9$$

Polynuclear compounds with three or more central atoms. From the titration curve with three equivalents of Hg^{2+} per equivalent of ligand, the existence

of polynuclear complexes might be inferred. The curve has two inflections, occurring at the addition of 8 and 10 equivalents of base. A solution of TTHA containing 5.5 equivalents of base, titrated with standard Hg^{2+} solution (Fig. 2), also resulted in a pH curve which seems to indicate polynuclear compounds. But because of the complexity of the measurements and calculations, and due to the occurrence of precipitates of partially unknown composition, this was not further studied.

Slightly soluble complexes. The TTHA acid is slightly soluble, but as the solubility increases with increasing pH of the solution, no precipitate occurred in the present studies. Nor did any solid phases form during the 1:1 titrations, even in the most acid solutions. This is in contrast to the 2:1 system, where preparation of 2:1 solutions always resulted in the formation of a white precipitate prior to the addition of base. The precipitate slowly dissolved when the base was added. The titration was therefore performed by adding a known quantity of base, and the solution was back-titrated with standard perchloric acid. In that case no precipitate was formed, except in a very acid solution. Recently, Strafelda *et al.*[17] have reported a slightly soluble silver salt of EDTA, with the formula $Ag_2H_2(C_{10}H_{12}N_2O_8)$ of a diprotonated disilver EDTA. A similar compound of Hg-TTHA is the Hg_2H_2X chelate. From combustion analysis the mole ratio of Hg and TTHA in the white precipitate was found to be 2.09; thus the sparingly soluble product may be this Hg_2H_2X chelate. With three moles of Hg^{2+} per mole of TTHA, precipitates, perhaps of the compound Hg_3TTHA, occurred even in moderately acid solutions. The analogous compound, Ag_4EDTA is also reported to be slightly soluble.[18]

DISCUSSION

The stability constants of the mononuclear mercury(II) complexes with NTA, EDTA and DTPA have previously been reported.[12,13,19] The binuclear complexes of these reagents are now investigated in this laboratory to make comparative studies possible. The stability constant data are presented in Table 1. The stability constant of the 1:1 TTHA complex exceeds the corresponding value for the EDTA compound with 3.5 pK units, but is 1.4 pK units lower than the stability constant of the Hg-DTPA chelate. A hydroxyl chelate exists for the EDTA complex, but is reported to be non-existent in the case of DTPA.[12] In the present investigation the corresponding compound is not found to be present within the limits of experimental error under the experimental conditions used.

Anderegg and co-workers[12] have correlated these observations with the particular tendency for mercury and two nitrogen atoms to form a complex with a linear arrangement. This is impossible in the case of the mononuclear EDTA complex, and therefore hydroxyl, NH_3, and chloro complexes *etc.* may be formed instead. This is in contrast to the DTPA complex where the linear arrangement is possible and no free coordination site is available for mixed ligand or polynuclear complex formation. It is reasonable to assume that the mercury ion also exists in the favourable linear arrangement in the TTHA complex.
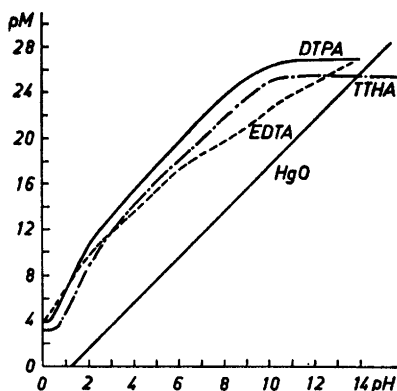
Fig. 3. Plots of pM *vs.* pH for 1:1 mercury chelates of TTHA and related ligands. The straight line represents precipitation of HgO. (1.00 × 10^{-3} M; Hg^{2+}, 100 % excess of the ligands).

The higher stability constants for the DTPA and TTHA complexes relative to the EDTA complex may be explained by assuming that mercury ions obtain the stable linear coordination through nitrogen atoms in the DTPA and TTHA complexes. The decrease of the stability constant of the TTHA complex compared to the one with DTPA might be due to the higher number of groups in the TTHA molecule which are not bound to mercury. The entropy change will be of a more positive value for the complex formation with DTPA than that for TTHA. If the bond energies are approximately equal for the two complexes, ($\Delta H_1 \approx \Delta H_2$), the difference in entropy change from the DTPA- to the TTHA complex is about 2.8 *e.u.* (calculated from the stability constants of the complexes).

The tendency to form protonated complexes increases as expected with increasing number of carboxylic acid groups in the molecule. In contrast to DTPA and EDTA, a biprotonated TTHA-chelate exist. (With nitrilotriacetic acid, no protonated species have been reported). A comparison of the magnitudes of the step stability constants of the hydrogen complexes gives considerably smaller difference between the EDTA and DTPA than between the DTPA and TTHA complexes. This is explained by assuming that the mercury atom in the EDTA complex, in contrast to the DTPA and TTHA complexes, is not coordinated to the EDTA coordination sites only, but that some of its coordination sites are bound to solvent particles. Thus carboxylate groups will be available for proton association.

To illustrate the stability of the mercury-TTHA chelate, $-\log [Hg^{2+}] =$ pM is plotted in Fig. 3 *vs.* the pH of solutions containing excess of the ligand. For comparison, curves for DTPA and EDTA chelates are also given.

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