Complex Formation with
Triethylenetetraminehexaacetic Acid

I. Iron Chelates

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The interaction of triethylenetetraminehexaacetic acid with ferric and ferrous ions was studied by redox-potential measurements, pH-titrations, spectrophotometry, and polarographic measurements. The following mononuclear species exist in aqueous solutions: Fe(III)TTHA, Fe(III)HTTHA, Fe(III)H$_2$TTHA, Fe(III)(OH)TTHA, Fe(III)(OH)$_2$TTHA, Fe(II)TTHA, Fe(II)HTTHA, Fe(II)H$_2$TTHA, Fe(II)H$_3$TTHA, Fe(II)(OH)TTHA, Fe(II)(OH)$_2$TTHA. The equilibrium constants for the different mononuclear chelate forms have been calculated. The existence of a binuclear ferric chelate with the formula Fe$_2$(III)(TTHA)(OH)$_2$ and a ferrous chelate with the formula Fe$_2$(II)TTHA have been demonstrated, and possible structures have been formulated.

Triethylenetetraminehexaacetic acid is one of the synthetic amino acids which have become increasingly valuable as reagents in analytical chemistry. Although the compound was synthetized about ten years ago,[1] very little information concerning its properties has been published. Iron complexes are of special interest as potential sources of iron for the treatment of iron chlorosis in agriculture, and because of the interesting chemical properties of the chelates, which can form protonated species as well as products of hydrolysis. TTHA has ten possible coordinating centers, and polynuclear compounds are highly probable.

EXPERIMENTAL

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

A standard solution of ferric iron was made by dissolving reagent grade ferric nitrate in water containing dilute perchloric acid in order to prevent hydrolysis. The stock solution was standardized by titration with standard ethylenediaminetetraacetic acid,

salicylic acid being used as an indicator. The determination of the excess free acid in
this ferric solution could not be performed by direct titrations, as hydrolysis occurs
during the titration and no end-point at a defined composition could be obtained. There-
fore, a 1:1 ferric-EDTA solution was made, and this was titrated with standard NaOH
solution to pH = 4.5. In this case no hydrolysis is possible in the pH-range measured.
The excess acid is thus equivalent to the added NaOH minus an amount corresponding
to neutralization of two hydrogen ions per ferric chelate.

The solutions containing ferrous iron were made up by direct addition of carefully
weighed quantities of ferrous ammonium sulphate (reagent grade). To prevent air oxida-
tion to the ferric state, this was the last component to be added. Oxygen-free nitrogen
was bubbled through the solution prior to addition and during the measurements. The
ferrous ammonium sulphate was tested to make sure it contained no ferric iron or free
acids. The water content was determined by analysis, and the necessary correction made.
For exchange studies, the reagent N,N'-ethylenebis-[2(o-hydroxyphenyl)]glycine was
used. The product was obtained from Fluka A. G., Switzerland, in purum quality. The
remaining chemicals were of reagent grade.

Methods. All the data were obtained at 25.0 ± 0.1°C and the ionic strength was kept
close to 0.1 by addition of sodium perchlorate. The titrations were performed with
0.1 M CO_2-free NaOH solutions. The pH values were determined with a Beckman Zero-
matic pH-meter or a Radiometer automatic titrator. The Radiometer Polarograph
PO4 was used for the polarographic measurements, and a Vernier Potentiometer was
used to measure redox potentials. All solutions were thoroughly degassed with oxygen-
free nitrogen gas at least 10 min prior to the measurements. For studies of the redox
potentials of the ferric/ferrous chelates, a platinum electrode was inserted in the vessel
containing equimolar quantity of Fe(II) and Fe(III) with an excess of TTHA.
The potentials were measured at zero current (with a Multiflex galvanometer) *vs.* a satu-
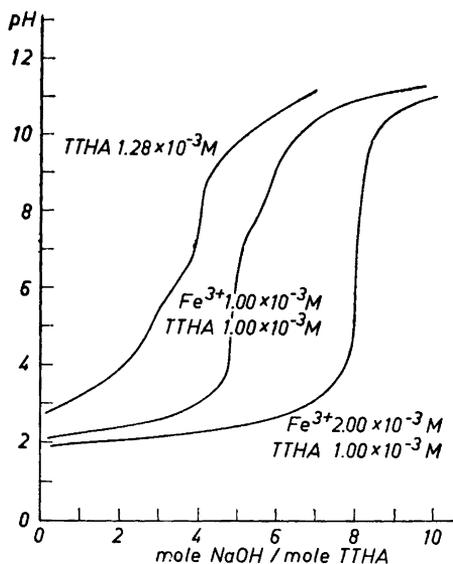rated calomel electrode connected to the solution with a KCl-agar bridge.

Fig. 1. Titration curves of TTHA alone and in the presence of one and two equivalents of trivalent iron (0.1 M $NaClO_4$, 25°C).
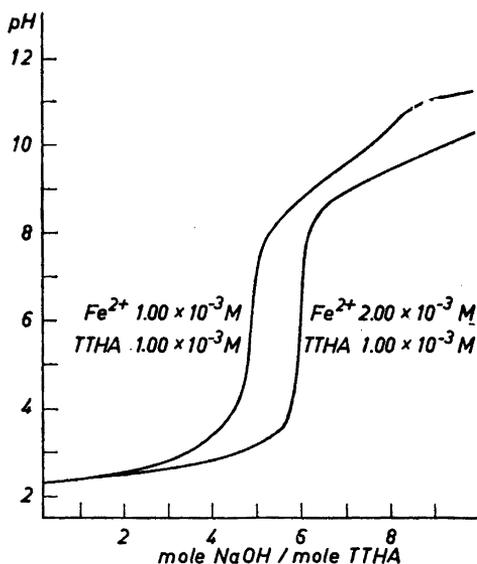
Fig. 2. Titration curves of TTHA in the presence of one or two equivalents of bivalent iron (0.1 M $NaClO_4$, 25°C).

EXISTENCE AND COMPOSITION OF THE CHELATES, pH TITRATION DATA

Titration data of TTHA, alone and in the presence of one and two equivalents of ferric iron are indicated in Fig. 1. Measurements with a great excess of ferric ions could not be performed as hydroxides are precipitated already at very low pH-values.

The system Fe(III)TTHA in ratio 1:1. Comparison of the titration curve of TTHA alone and in the presence of ferric ions indicates that the complex formation takes place even prior to the addition of base.

A steep inflection occurs at 5 equivalents of base per equivalent of the amino acid. This indicates formation of 1:1:1 protonated ferric chelate according to:
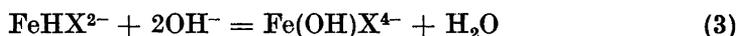
$$H_6X + 5OH^- + Fe^{3+} = FeHX^{2-} + 5H_2O \qquad (1)$$

Here H_6X is the free TTHA acid.

Further addition of sodium hydroxide results in an increase of the pH without any well-developed inflection. But a well-developed buffer region is formed. This indicates overlapping inflections due to:
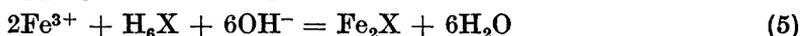
$$FeHX^{2-} + OH^- = FeX^{3-} + H_2O \qquad (2)$$

and possibly

$$FeHX^{2-} + 2OH^- = Fe(OH)X^{4-} + H_2O \qquad (3)$$
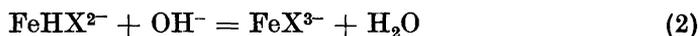
although the formation of $Fe(OH)X^{4-}$ and $Fe(OH)_2X^{5-}$ is not proved by these experiments.

The existence of the diprotonated chelate FeH_2X^- is highly probable, but no inflection corresponding to four equivalents of NaOH was observed. However, this is believed to be due to a strong overlapping with the inflection corresponding to the formation of the monoprotonated chelate, as discussed later.

With the metal ions in a ligand ratio of 2:1, a quite different titration curve was obtained. A very steep inflection occurred at 8 equivalents of the base per equivalent of ligand. No other inflections were observed. This might be due to:

$$2Fe^{3+} + H_6X + 8OH^- = Fe_2(OH)_2X^{2-} + 6H_2O \qquad (4)$$

although overlapping reactions are possible:

$$2Fe^{3+} + H_6X + 6OH^- = Fe_2X + 6H_2O \qquad (5)$$

$$2Fe^{3+} + H_6X + 7OH^- = Fe_2(OH)X^- + 6H_2O, \textit{ etc.} \qquad (6)$$

Alternative reactions. The above indicates the ready formation of the two species $FeHX^{2-}$ and $Fe_2(OH)_2X^{2-}$ with solutions of ferric ion to ligand ratio 1:1 and 2:1 respectively. However, the following, alternative reaction might occur in the 2:1 solution when 8 moles of base per ligand are added:

$$2Fe^{3+} + H_6X + 8OH^- = FeHX^{2-} + H_2O + Fe(OH)_3 \qquad (7)$$
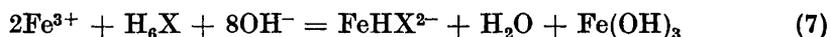
A possible, though improbable reaction in the solution with metal to ligand ratio 1:1 is

$$Fe^{3+} + H_6X + 5OH^- = \tfrac{1}{2}Fe_2(OH)_2X^{2-} + 4H_2O + \tfrac{1}{2}H_4X^{2-} \qquad (8)$$
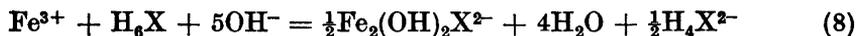
A formation of protonated, uncomplexed ligand H_4X^{2-} according to eqn. 8 corresponds to the titration curve of TTHA alone at two moles of base per mole of ligand. The buffering capacity is here considerable because of the overlapping formation of different protonized species. That is in contrast to the sharply defined inflection at 5 moles of NaOH for the 1:1 curve, indicating that reaction 1 is the probable one.

Reaction 7 would give rise to precipitation. As no precipitation occurred until pH exceeded 9, and the inflection at 8 moles of base is very steep, reaction 4 seems to be the most important one. This also fits very well into structural possibilities as treated later in this paper.

The system Fe(II)TTHA. Titration curves of mixtures of ferrous iron and TTHA in mole ratio 1:1 and 2:1 are indicated in Fig. 2. In the case of the curve from 1:1 solutions, only one very steep inflection is observed when 5 moles of base were added. This might be due to:

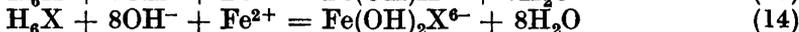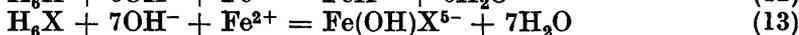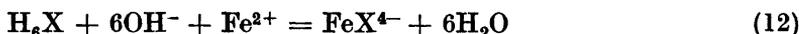$$H_6X + 5OH^- + Fe^{2+} = FeHX^{3-} + 5H_2O \qquad (9)$$

In the absence of other acid-base reactions, the buffering capacity beyond this titration point would have to be lower than that actually observed on the titration curve. This must be due to reactions occurring simultaneously. On the acid side of the inflection, the following reactions are proposed:

$$H_6X + 4OH^- + Fe^{2+} = FeH_2X^{2-} + 4H_2O \qquad (10)$$

and possibly

$$H_6X + 3OH^- + Fe^{2+} = FeH_3X^- + 3H_2O \qquad (11)$$

and on the basic side:

$$H_6X + 6OH^- + Fe^{2+} = FeX^{4-} + 6H_2O \qquad (12)$$
$$H_6X + 7OH^- + Fe^{2+} = Fe(OH)X^{5-} + 7H_2O \qquad (13)$$
$$H_6X + 8OH^- + Fe^{2+} = Fe(OH)_2X^{6-} + 8H_2O \qquad (14)$$

Reaction 14 would be the cause of the slight, perhaps not significant increase of the slope of the titration curve at 8 moles of NaOH per mole of TTHA.

An entirely different titration curve is obtained with two equivalents of ferrous ions per equivalent of ligand. The main inflection occurs at 6 moles of base which would correspond to the formation of a binuclear complex:

$$2Fe^{2+} + H_6X + 6OH^- = Fe_2X^{2-} + 6H_2O \qquad (15)$$

The overlapping formation of complexes containing hydrogen or hydroxyl ions might occur when less or more base is added.

Possible formation of polymer complex compounds. Polymerization through the formation of diol compounds has been reported to be an intermediate step in the hydrolysis and precipitation of ferric hydroxide,[2] and recently diol formation has been shown also to occur with ferric chelates.[3]

The tendency toward such reactions, however, is expected to decrease as the stability and polydentity of the ligand increase, which would indicate that polymerization of the present chelate should not occur. To verify this, the fact was utilized that, upon addition of base to equivalent quantities of ferric iron and TTHA, the pH should in case of solely monomer reactions be a function only of the number of equivalents of base added per equivalent of TTHA, but might change with the concentration of the complex if polymerization occurs. For example, a dimerization:

$$2Fe(OH)X^{4-} = Fe_2(OH)_2X_2^{8-} \tag{16}$$
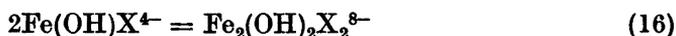
would shift the equilibrium

$$FeX^{3-} + OH^- = Fe(OH)X^{4-} \tag{17}$$
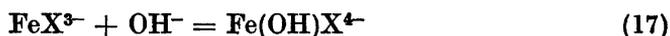
further to the right, and result in a lowering of the pH in this buffer region, which corresponds approximately to 6.5 equivalents of base added, with increasing concentration of chelates.

A solution of 5×10^{-4} moles of TTHA and equimolar quantities of Fe^{3+} with 6.5 equivalents of NaOH was prepared. To the mixture was added 0.1 M $NaClO_4$ until all the solid phase was dissolved. The volume had then reached 45 ml. After equilibrium was obtained, the pH was measured as 8.20. The mixture was further titrated with 0.1 M $NaClO_4$ solution. When the original 45 ml solution (corresponding to 7.34×10^{-3} M) had been diluted ten times, the pH value had not changed; all the observed values were within pH = 8.20 ± 0.02. This indicates within the experimental error, that no diol polymerization occurs.
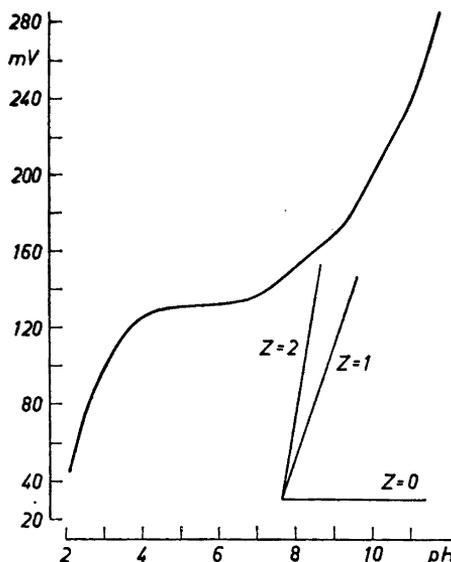

Fig. 3. Redox-potentials of a system with equimolar quantities of bi- and trivalent iron and excess of TTHA, measured with a platinum electrode *vs.* a saturated calomel electrode (1.00×10^{-3} M Fe^{3+}, 1.00×10^{-3} M Fe^{2+}, 7.00×10^{-3} M TTHA, 0.1 M $NaClO_4$, 25°C).

STUDIES WITH REDOX POTENTIAL MEASUREMENTS

By means of the cell,

Pt | Fe^{III} complex, Fe^{II} complex, TTHA ¦ Agar KCl bridge | sat. calomel electrode,

potentials were measured with equimolar quantities of the two kinds of ions and with excess of TTHA. The results are indicated in Fig. 3.

With the following assumed general equation

$$Fe(II)H_iX \rightarrow Fe(III)H_jX + (i-j)H^+ + e^- \tag{18}$$
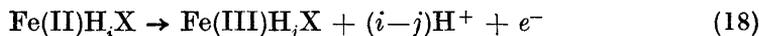
the electrode potentials are given by

$$E = E° - 0.059 \log \frac{[Fe(III)H_jX]}{[Fe(II)H_iX]} + 0.059(i-j)pH \tag{19}$$

when $E°$ is the standard potential.

(Formation of hydroxyl complexes might be included in the equations by taking i and j to be negative).

If the main reactions only are considered, the ratio of the concentration term in eqn. 19 is unity and the slope is

$$\frac{dE}{dpH} = 0.059(i-j) = 0.059 Z \tag{20}$$

The theoretical slope is indicated in Fig. 3. As seen in that figure, the potential is markedly dependent on the pH of the solution. It is of interest to notice that the slope is always positive, indicating $i > j$, and thus that the tendency of proton association (hydroxyl dissociation) of bivalent iron complexes exceeds that for the trivalent ones — which also is expected, considering the charges of the ions.

In the pH range between approximately 4.5 and 6.5, the potential is *ca.* 130 mV, nearly independent of pH. Comparisons with the titration curves (Figs. 1 and 2) indicate that the monohydrogen complexes are the main species and that, consequently, the most probable electrode reaction is

$$Fe(II)HX^{3-} \rightarrow Fe(III)HX^{2-} + e^- \tag{21}$$
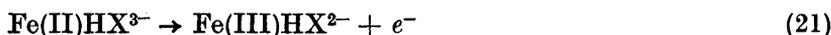
Between pH = 3.5 and 4.5, overlapping reactions occur, but from pH = 3.5 to 2.5 the slope increases, corresponding to $Z = 1$. The corresponding probable main electrode reaction is thus:

$$Fe(II)H_2X^{2-} \rightarrow Fe(III)HX^{2-} + H^+ + e^- \tag{22}$$
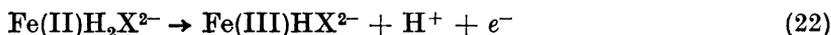
At still lower pH values, the slope increases to a value corresponding approximately to $Z = 2$ thus:

$$Fe(II)H_3X^- \rightarrow Fe(III)HX^{2-} + 2H^+ + e^- \tag{23}$$

(Two other electrode reactions, with the chelates all containing one more hydrogen atom, are alternatives to eqns. 22 and 23).

From pH = 6.5 to about pH = 9.5, overlapping electrode reactions occur. Based on a comparison of the titration curves, it appears that on increasing pH from 6.5, the species Fe(III)X occurs with the electrode reaction

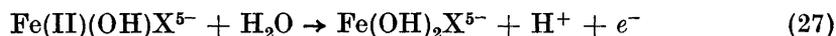$$Fe(II)HX^{3-} \rightarrow Fe(III)X^{3-} + H^+ + e^- \tag{24}$$
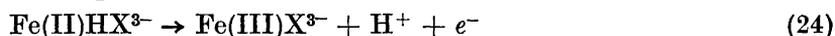
The small, though significant, decrease of the slope of the potential curve at pH near 9 is in agreement with the titration curves, the most probable (zero slope) electrode reaction being

$$Fe(II)X^{4-} \rightarrow Fe(III)X^{3-} + e^- \tag{25}$$

At further increasing pH values, hydroxyl chelates and normal chelates co-exist. The slope increases again due to the competing reaction

$$Fe(II)X^{4-} + H_2O \rightarrow Fe(OH)X^{4-} + H^+ + e^- \tag{26}$$
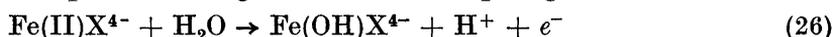
and at pH values exceeding 9.5 this, or possibly

$$Fe(II)(OH)X^{5-} + H_2O \rightarrow Fe(OH)_2X^{5-} + H^+ + e^- \tag{27}$$

is the probable electrode reaction.

Polarographic and EMF measurements. Direct polarographic measurements are difficult to perform because of irregularities in the polarographic waves. An EMF method which makes use of a mercury indicator electrode (like that described by Reilly,[13] for example) is convenient for studies of highly stable complexes, but in the case of TTHA the method could not be utilized, as it was impossible to obtain valid potential data. This is probably due to slightly soluble mercury complexes and film formation on the mercury surface.[14]

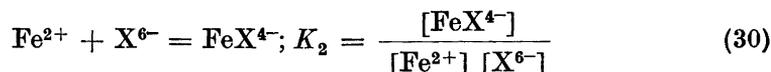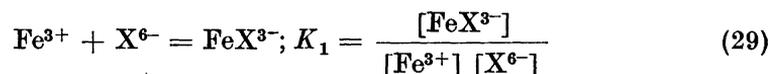### DETERMINATION AND CALCULATION OF STABILITY CONSTANTS

1:1 Chelates. The acid dissociation constants of TTHA have been reported by Grimes *et al.*[4] to be

2.46	2.52	4.00	5.98	9.35	10.33

for pk_1 to pk_6, respectively, in accordance with the definition

$$H_6X = H_5X^- + H^+; \quad k_1 = \frac{[H^+][H_5X^-]}{[H_6X]} \quad etc. \tag{28}$$
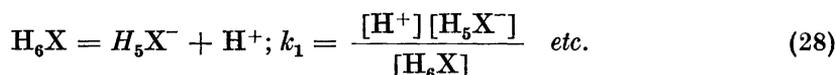
To describe the equilibrium species, the constants are defined as follows: Total dissociation reactions:

$$Fe^{3+} + X^{6-} = FeX^{3-}; \quad K_1 = \frac{[FeX^{3-}]}{[Fe^{3+}][X^{6-}]} \tag{29}$$

$$Fe^{2+} + X^{6-} = FeX^{4-}; \quad K_2 = \frac{[FeX^{4-}]}{[Fe^{2+}][X^{6-}]} \tag{30}$$

Hydrolysis:

$$FeX^{3-} + H^+ = FeHX^{2-}; \quad K_{Fe(III)HX} = \frac{[FeHX^{2-}]}{[H^+][FeX^{3-}]} \tag{31}$$

$$FeHX^{2-} + H^+ = FeH_2X^-; \quad K_{Fe(III)H_2X} = \frac{[FeH_2X^-]}{[H^+][FeHX^{2-}]} \tag{32}$$

$$FeX^{3-} + OH^- = Fe(OH)X^-; \quad K_{Fe(III)(OH)X} = \frac{[Fe(OH)X^{4-}]}{[OH^-][FeX^{3-}]} \tag{33}$$

$$Fe(OH)X^{4-} + OH^- = Fe(OH)_2X^{5-}; \quad K_{Fe(III)(OH)_2X} = \frac{[Fe(OH)_2X]}{[OH^-][Fe(OH)X^{3-}]} \tag{34}$$
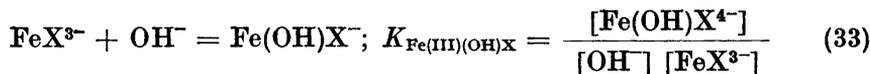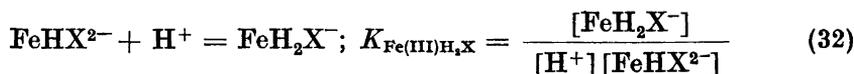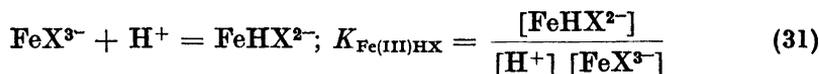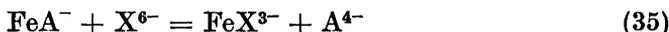
The stability constants of the hydrolytic ferrous chelates are defined by similar expressions.

A direct calculation of the stability constants K_1 and K_2 with any accuracy is not possible because their numerical values are too high. The complexes do not dissociate to measurable extents even in the most acid solutions. For this reason, indirect methods are necessary. The stability constants of the ferrous chelates of the related complexing agents EDTA and DTPA (diethylene-triaminepentaacetic acid) might be determined with the direct method. This is possible as the numerical values of the constants are lower than for the TTHA chelate.

In the case of ferric complexes, the concentration of free ferric ions must be kept very low in order to prevent precipitation or formation of products of hydrolysis, e.g. $Fe(OH)^{2+}$, which would cause large errors in the calculations of the stability constants. Except in very acid solutions, it is therefore advisable to employ a method not involving the measurement of uncomplexed ferric ions.

N,N'-Ethylenebis-2(o-hydroxyphenyl)glycine (EHPG) forms a very stable complex with trivalent iron. The logarithmic stability constant (log K_{FeEHPG}) has previously [5] been determined to be 33.86. This chelate is very stable against the formation of hydroxyl or protonated complexes even in very alkaline or acid solutions. As this complex has an intense red colour at 480 mμ (molar extinction with 4 cm light path is 2.05×10^4), this reagent is well suited for exchange studies as the degree of exchange easily might be measured. The quantity of the total ferric ion bound to EHPG might also be determined by polarographic measurements.

Solutions with different quantities of TTHA, EHPG and trivalent iron were prepared. They were all deficient in iron, compared with the amount of the complexing agents present. Different quantities of sodium hydroxide were added. The colour had stabilized after a week, and was stable for a longer period. With H_4A designating the EHPG acid, the following reaction occurs:

$$FeA^- + X^{6-} = FeX^{3-} + A^{4-} \tag{35}$$

As the proton dissociation constants of the ligands, the amounts of reagents added, the pH of the solution, and the concentration of FeA^- are known,

the stability constant was calculated in the following way. Due to the occurrence of protonated TTHA complexes the exchange reaction is

$$\text{FeA}^- + \text{X}^{6-} + i\text{H}^+ = \text{FeH}_i\text{X} + \text{A}^{4-} \tag{36}$$

(The protonating of the uncomplexed ligands is omitted for brevity).

Hydroxyl complexes are included with negative i. When the total amounts of ligands added are C_X and C_A and when the ratio of iron combined with EHPG and that combined with TTHA is designated R, then

$$1/R = \frac{K_1[\text{X}^{6-}]}{K_{\text{FeEHPG}}[\text{A}^{4-}]} \cdot \sum_i K_{\text{FeH}_i\text{X}} \cdot [\text{H}^+]^i \tag{37}$$

$$K_1 \cdot \sum_i K_{\text{FeH}_i\text{X}} \cdot [\text{H}^+]^i = K_{\text{FeEHPG}} \cdot \frac{1}{R} \cdot \frac{[\text{A}^{4-}]}{[\text{X}^{6-}]} \tag{38}$$

R is found from spectrophotometric or polarographic measurements. The amounts of A^{4-} and X^{6-} might be calculated with knowledge of the acid dissociation constants. For EHPG these are reported to be 6.54, 8.64, 10.24, and 11.68 for pk_1 to pk_4, respectively.[6] If α denotes the ratio of the amount of uncomplexed ligand in all degrees of hydrolysis to the amount of completely dissociated ligand, the following expression is valid:

$$K_1 \cdot \sum_1 \cdot K_{\text{FeEHPG}} [\text{H}^+]_i = F([\text{H}^+]) = K_{\text{FeEHPG}} \cdot \frac{\alpha_{\text{TTHA}}}{\alpha_{\text{EHPG}}} \cdot \frac{1}{R} \cdot \frac{C_A}{(R+1)C_X - C_A} \tag{39}$$

(For the present measurements $C_A = C_{\text{Fe}^{3+}}$ in order to facilitate the calculations.) The α's vary with the pH of the solution and might be calculated as the dissociation constants of the two ligands are known. Eqn. 39 is thus a power series. All 1:1 stability constants of 1:1 TTHA-Fe^{3+} complexes might be determined by means of an extrapolation method, similar to the method described by Leden [7] or by Fronæus,[8] but as the stability constants for the hydrolysis of the FeH$_i$X chelates are determined independently later in this paper, $\sum K_{\text{FeH}_i\text{X}} [\text{H}^+]^i$ is known and a direct calculation of K_1 was possible. The result is presented in Table 1. As the stability constant of the EHPG

Table 1. Stability constants for the Fe(II) and Fe(III) chelates of TTHA (25°C, 0.1 M NaClO$_4$).

Constants	log K	Constants	log K
K_1	29.4	K_2	17.1
—	—	$K_{\text{Fe(II)H}_2\text{X}}$	<2
$K_{\text{Fe(III)H}_2\text{X}}$	2.60	$K_{2\text{Fe(II)H}_2\text{X}}$	3.25
$K_{\text{Fe(III)HX}}$	7.51	$K_{\text{Fe(II)HX}}$	8.67
$K_{\text{Fe(III)(OH)X}}$	4.20	$K_{\text{Fe(II)(OH)X}}$	4.98
$K_{\text{Fe(III)(OH)}_2\text{X}}$	3.50	$K_{\text{FE(II)(OH)}_2\text{X}}$	4.19
$K_{\text{Fe}_2\text{(III)X}}$	—	$K_{\text{Fe}_2\text{(II)X}}$	10.2
$K_{\text{Fe}_2\text{(III)X(OH)}}$	—	$K_{\text{Fe}_2\text{(II)X(OH)}}$	5.27
$K_{\text{Fe}_2\text{(III)X(OH)}_2}$	2.9	$K_{\text{Fe}_2\text{(II)X(OH)}_2}$	5.18

complex is much higher than that of TTHA, a higher excess of the latter complexing agent was necessary. This also eliminated the possibility of formation of complexes with metal-to-ligand ratio 2:1.

The stability constants of hydrolyzed bi- and trivalent 1:1 complexes of iron were determined from the titration data using Bjerrum's method.[9] Hydrogen or hydroxyl ions are considered as ligands which react with the ferric or ferrous complexes. In the present study the dissociation of the complexes to metal and free ligands was assumed to be negligible. The stability constants were corrected by successive approximations as outlined by Carlson et al.,[10] making use of a computer programme that repeats the approximation until, if possible, the relative change in the constants between two cycles is lower than 0.001. The results are presented in Table 1.

The constant K_2 was determined from the redox potential data. The standard potential of the ferricferrous couple

$$\text{Fe(II)} \rightarrow \text{Fe(III)} + e^- \tag{40}$$

is taken to be -0.771 V $vs.$ N.H.E. or -0.529 V $vs.$ S.C.E. In order to avoid complications when competing reactions are considered, the calculations were performed from data obtained from solutions with pH values corresponding to slopes which yield integer Z values. In the region between pH = 4.5 and 6.5, the electrode reaction is given by eqn. 21 and the potential is

$$E = E° - 0.059 \log \frac{[\text{Fe(III)HX}^{2-}]}{[\text{Fe(II)HX}^{3-}]} \tag{41}$$

If K_1 is known, it is therefore possible to determine K_2 by means of the dissociation constants of the hydrogenated complexes.

The dissociation constants of the 1:1 iron TTHA complexes are included in Table 1.

2:1 Compounds. As the number of bonding groups in TTHA is high, formation of hinuclear chelates is expected. The formation constants might be calculated as given below if no appreciable amount of chelate is assumed to be present in the solution. Knowledge of the acid-base properties of the binuclear chelates is also necessary for the calculations. With a great excess of metal ions these constants could easily be obtained. Due to hydroxide precipitation, it is, however, virtually impossible to maintain an excess of metal ions, and the main binuclear products were for the mole ratio 2:1, assumed to be $\text{Fe}_2(\text{II})\text{X}$ or $\text{Fe(III)(OH)}_2\text{X}$, in solutions containing less than 6 equivalents of added base.

In such cases the following equations are valid for trivalent iron:

$$C_\text{M} = [\text{Fe}^{3+}] + \sum[\text{FeH}_i\text{X}] + 2[\text{Fe}_2(\text{OH})_2\text{X}^{2-}] \tag{42}$$

$$C_\text{TTHA} = \sum[\text{FeH}_i\text{X}] + [\text{Fe}_2(\text{OH})_2\text{X}^{2-}] \tag{43}$$
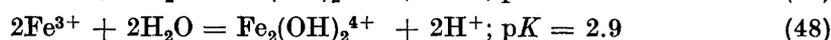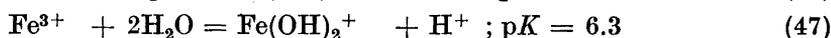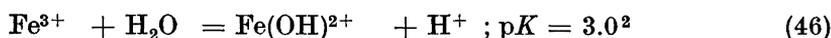
$$(6-a)C_\text{TTHA} - [H^+] + [\text{OH}^-] = i \sum[\text{FeH}_i\text{X}] - 2[\text{Fe}_2(\text{OH})_2\text{X}^{2-}] \tag{44}$$

(In the case of bivalent iron, the similar equations are valid, but in eqns. 42 and 43 the last terms are then altered to Fe_2X^{2-} and in eqn. 44 the last
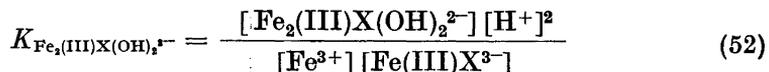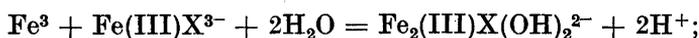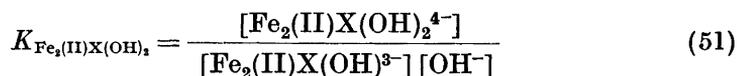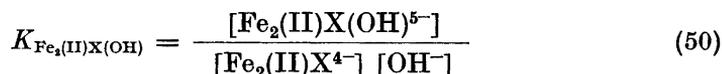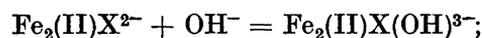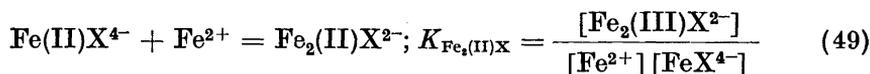
term is dropped). Even in a moderately acid solution of iron salts in water, partial hydrolysis occurs, and polynuclear complexes such as diol compounds exist. The stability constants obtained are corrected for this effect using equilibrium constants previously reported:

$$Fe^{2+} + H_2O = Fe(OH)^+ + H^+; \quad pK = 9.5 \text{ [11]} \tag{45}$$
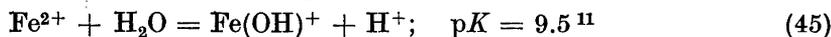
(This is reported to be the only hydrolysis reaction apart from the formation of ferrous hydroxide).

$$Fe^{3+} + H_2O = Fe(OH)^{2+} + H^+ ; pK = 3.0 \text{ [2]} \tag{46}$$

$$Fe^{3+} + 2H_2O = Fe(OH)_2^+ + H^+ ; pK = 6.3 \tag{47}$$

$$2Fe^{3+} + 2H_2O = Fe_2(OH)_2^{4+} + 2H^+; pK = 2.9 \tag{48}$$

In order to describe the binuclear equilibrium species, the constants are defined as follows:

$$Fe(II)X^{4-} + Fe^{2+} = Fe_2(II)X^{2-}; \quad K_{Fe_2(II)X} = \frac{[Fe_2(III)X^{2-}]}{[Fe^{2+}][FeX^{4-}]} \tag{49}$$

$$Fe_2(II)X^{2-} + OH^- = Fe_2(II)X(OH)^{3-};$$

$$K_{Fe_2(II)X(OH)} = \frac{[Fe_2(II)X(OH)^{5-}]}{[Fe_2(II)X^{4-}][OH^-]} \tag{50}$$

$$Fe_2(II)X(OH)^{3-} + OH^- = Fe_2X(OH)_2^{4-};$$

$$K_{Fe_2(II)X(OH)_2} = \frac{[Fe_2(II)X(OH)_2^{4-}]}{[Fe_2(II)X(OH)^{3-}][OH^-]} \tag{51}$$

$$Fe^3 + Fe(III)X^{3-} + 2H_2O = Fe_2(III)X(OH)_2^{2-} + 2H^+;$$

$$K_{Fe_2(III)X(OH)_2^-} = \frac{[Fe_2(III)X(OH)_2^{2-}][H^+]^2}{[Fe^{3+}][Fe(III)X^{3-}]} \tag{52}$$

From the titration curves, the compounds $Fe_2(III)X$ and $Fe_2(III)X(OH)$ do not exist in measurable quantities under the reported experimental conditions. The stability constants obtained are reported in Table 1.

The accuracy of the constants reported in Table 1 were checked from the maximum deviation in the series of measurements. The hydrolytic constants (reported with two decimals) are within ± 0.1 log units. Log $K_1 = 29.4 \pm 0.24$. K_2 was calculated as a function of K_1, but as the deviation in the potential measurements was very small, log $K_2 = 17.1 \pm 0.25$. The stability constants of the 2:1 complexes are within ± 0.2 log units.

DISCUSSION

The coordination number of ferrous or ferric iron is, almost without exception, equal to six. The maximum number of donor groups in the TTHA molecule is ten. If all the possible donor groups in a TTHA molecule participate
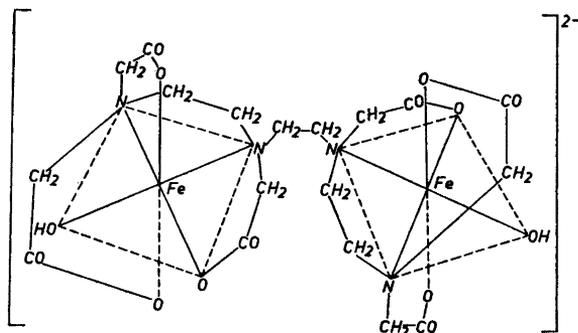
Fig. 4. Possible structural formula for the 2:1 $Fe_2X(OH)_2^{2-}$ chelate.

in the complex formation with two metal ions, a deficiency of two donor groups appears. These positions might be occupied by ligands present in the solution. The titration data of the 2:1 ferric complex show that two hydroxyl ions are very firmly bonded to the molecule. This observation corresponds with the structural formula shown in Fig. 4. In the case of the 2:1 ferrous complex, the titration data indicate that the dihydroxyl compound is not formed in appreciable quantities. It is not likely that the ferrous ions are in 5-coordination in that instance, and the most probable explanation is therefore that a coordination with two water molecules occurs. This difference between Fe(II) and Fe(III) complexes might be explained by the difference in electrical charges of the two ions. In the case of 1:1 chelates, it was also observed that
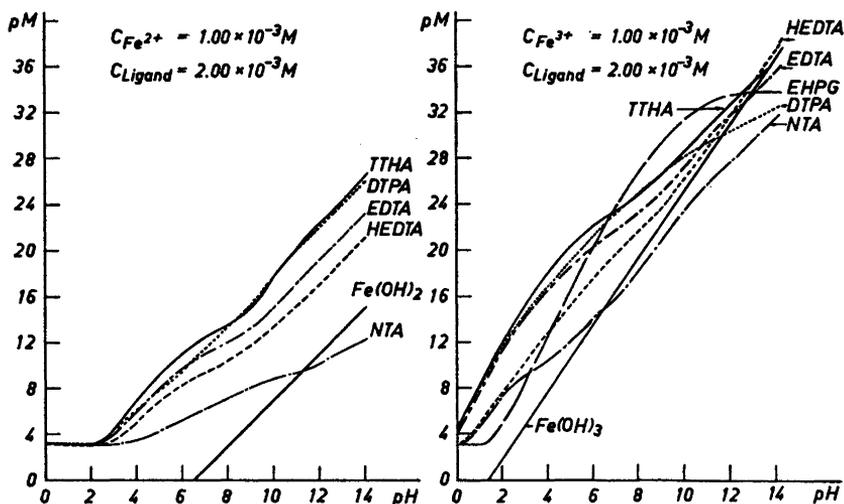

Fig. 5. pM as a function of pH for ferric or ferrous chelates of TTHA and related ligands. The straight lines represent precipitation of the hydroxides (1.00×10^{-3} M iron ions, 100 % excess of the ligands).

the tendency towards formation of protonated complexes of bivalent iron exceeds that of the trivalent, as reported above. That the tendency towards formation of protonated complexes decreases with decreasing number of iron ions in the molecule is also expected. With trivalent iron a possible 3:1 chelate would, *e.g.*, be $Fe_3(OH)_iX$ ($i \leq 8$). Attempts at preparation of this complex failed, due to precipitation of hydrolysis products. The reagent DTPA (H_5A), with one amino group and two carboxyl groups less than TTHA forms stable 1:1 complexes with ferric and ferrous iron,[12] but 2:1 complexes with ferric iron have never been reported. By analogy to TTHA, an expected formula might be $Fe_2A(OH)_i$ ($i \leq 4$). The author's attempts to prepare this compound did not succeed. As also would be the case with the hypothetical 3:1 Fe^{3+}/TTHA, precipitation took place. The coordination groups available for bonds in the third iron ion in the case of TTHA and the second iron ion in the case of DTPA will not result in bonds strong enough to counteract the precipitation of hydroxide.

To describe the pH dependence of the formation of ferric or ferrous chelates of TTHA with excess of ligand present, Fig. 5 represents pM *vs.* pH curves, where pM = —log [Fe]. Similar curves are given for some related complexing agents. The straight lines in the figure represent the limit for precipitation of $Fe(OH)_3$ or $Fe(OH)_2$.

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