

Complex Formation and Stereoselective Effects in the Copper(II) +- and *rac*-Tartrate Systems in Acid and Neutral Aqueous Solution

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The complex formation in aqueous solution between copper(II) ion and tartaric acid in the +- and *rac*-forms (+-tartrate = *R,R*-tartrate) has been studied in the acid and neutral pH-range at 25 °C. A potentiometric method with the use of glass- and copper amalgam electrodes has been applied. A formal ionic strength equal to 1 mol dm⁻³ was maintained by the addition of sodium perchlorate.

Experimental data were analyzed as to the complexes formed and their stability constants. At pH < 4 both of the systems are characterized by an equilibrium between mononuclear and binuclear species, CuTH, CuT, CuT₂ and Cu₂T₂ and Cu₂T₂H₋₁, respectively (T=C₄H₄O₆²⁻). At increasing pH up to neutrality the hydrolysis of the dimers continues to Cu₂T₂H₋₂ but at the same time an additional condensation takes place.

From a comparison of the stability constants of the complexes in the two systems it is concluded that the +- and -- enantiomers of Cu₂T₂ are stereospecifically formed in the copper *rac*-tartrate system. In the case of Cu₂T₂H₋₁ and Cu₂T₂H₋₂ the formation of the enantiomers is still favoured but increasing amounts of *rac*-isomers are formed. The ratio between the amounts of the enantiomeric species and the *rac*-isomer of CuT₂ is close to that statistically expected if structural effects are absent.

Some differences in the formation of the polynuclear complexes at pH > 4 are discerned. The predominating complex in neutral solutions has in both of the systems studied the stoichiometric formula Cu₄T₃H₋₅ but is in the +-tartrate system best represented by Cu₈T₆H₋₁₀ while for the description of the *rac*-tartrate system only Cu₄T₃H₋₅ is needed.

There are several reports on stereoselective effects in the complex formation between the copper(II)

ion and optically active and racemic tartrate.¹ Copper(II) +-tartrate and copper(II) *rac*-tartrate in alkaline solutions exhibit colour differences that are discernible with the naked eye. ESR spectra from solutions of the latter kind have been interpreted on the basis of the predominance of a dimeric unit,^{2,3} [Cu₂-+-TH₋₂--TH₋₂]⁴⁻. This unit has also been identified in an X-ray study⁴ of Na₂Cu-*rac*-C₄H₄O₆·5H₂O. The absence of the corresponding Cu₂(+-TH₋₂)₂ or Cu₂(--TH₋₂)₂ dimers is supported by the fact that ESR-spectra of alkaline copper +-tartrate reveal no dimeric units² and that attempts to precipitate the corresponding solid phase from alkaline copper(II) +-tartrate solutions give substances with variable compositions.⁴ These observations are in accordance with the prediction by Tapscott *et al.* in their review on tartrate-bridged binuclear complexes,⁵ that the *rac*-isomer is more stable than corresponding +- and -- isomers if the coordination geometry is tetragonal.

It is well-established that weakly acid copper(II) tartrate solutions contain binuclear complexes as well.⁶⁻⁹ However, absorption¹ and ESR² spectra of acid copper(II) +- and *rac*-tartrate solutions do not differ. This would indicate that only +- and -- dimers are formed in the acid copper *rac*-tartrate solution. Yet, the possibility of *rac*-isomers with spectral characteristics identical with the +- and -- isomers remains.

A determination of the stability constants of the complexes present in acid copper(II) +- and *rac*-tartrate solutions under exactly the same experimental conditions could give a definite answer to the question of stereoselectivity of the complex formation in these solutions. A great many equi-

librium studies of the copper(II) tartrate system have been performed but only two of them form a basis for a direct comparison between the two systems. Fronæus¹⁰ determined from potentiometric measurements the stability constants of the mononuclear complexes and found a difference in the values of the stability constants of the first complex, CuT. Such a difference is not expected but must reflect any other divergent behaviour of the two systems. Simeon *et al.*¹¹ who used a polarographic method, described their measurements with only one complex, the 1:1 complex, and found no difference in the complex formation between the +- and *rac*-tartrate systems in the pH-range 2–5.

Another region of interest is the pH-range 5–8. At pH about 4 a further polymerization beyond the binuclear complexes begins and results in a large pH jump when 1.25 mol OH⁻/mol Cu(II) is added.^{12,13} Again, no differences between +- and *rac*-tartrate may be discerned either from ESR¹⁴ spectra or from magnetic susceptibility¹⁴ measurements. From neutral copper(II) +- and *rac*-tartrate solutions solid phases containing the stoichiometric unit Cu₄T₃H₃²⁻ have been prepared.^{12,15,16} However, there is a remarkable difference between the copper +- and *rac*-tartrate solution as to the solubility of these solids.¹⁵

In the present work the complex formation between the copper(II) ion and +-tartrate as well as *rac*-tartrate has been studied under the same experimental conditions. The concentrations of the free ions Cu²⁺ and H⁺ have been determined simultaneously by a titration procedure using copper amalgam and glass electrodes. The solutions were made from copper(II) perchlorate, tartaric acids and sodium hydroxide and with an ionic medium of sodium perchlorate creating a formal ionic strength equal to 1 mol dm⁻³. The study was limited to the acid and neutral pH-range, a region of reliable behaviour of the amalgam electrode.

METHOD OF CALCULATION

With T representing the tartrate ion, C₄H₄O₆²⁻, a copper(II) tartrate complex may be written [Cu_pT_qH_r]^{2(p-q)+r}. In the following the charges will generally be omitted. *r* will take both positive and negative values, a negative value means that protons have been lost or hydroxide ions coordinated. If the free concentrations of the copper(II), tartrate and hydrogen ions are represented by

m, *t*, and *h* the stability constant is defined by eqn. (1).

$$\beta_{pqr} = \frac{[\text{Cu}_p\text{T}_q\text{H}_r]}{m^p t^q h^r} \quad (1)$$

Assuming constant activity factors the β_{pqr} 's are real constants. By the use of eqn. (1) the total concentrations of copper, tartrate and hydrogen ions, C_M, C_T and C_H, may be expressed as functions of the free concentrations *m*, *t* and *h*. To each set of total concentrations there are two simultaneously measured electromotive forces (emf's), whose values in mV units are related to corresponding free concentrations by eqns. (2) and (3), where E_j is a

$$E_m = E_m^0 - S_m \ln m + E_j \quad (2)$$

$$E_h = E_h^0 - S_h \ln h + E_j \quad (3)$$

correction term which is supposed to have approximately the same value in the two expressions.¹⁷ Its meaning will be discussed later.

The calculation of the stability constants is entirely done by means of a numerical method in which the least square function [eqn. (4)] is mini-

$$S = \sum_i [w_{m,i} (E_{m,i}^{\text{exp}} - E_{m,i}^{\text{cal}})^2 + w_{h,i} (E_{h,i}^{\text{exp}} - E_{h,i}^{\text{cal}})^2 - w_{mh,i} (E_{m,i}^{\text{exp}} - E_{m,i}^{\text{cal}}) (E_{h,i}^{\text{exp}} - E_{h,i}^{\text{cal}})] \quad (4)$$

mized by varying the β_{pqr} parameters.

Weighing. The weights in eqn. (4) are given by eqns. (5)–(7), where *c* is an arbitrary constant and

$$w_{m,i} = \frac{c}{\text{var}(E_{m,i}) (1 - \rho_{mh,i}^2)} \quad (5)$$

$$w_{h,i} = \frac{c}{\text{var}(E_{h,i}) (1 - \rho_{mh,i}^2)} \quad (6)$$

$$w_{mh,i} = \frac{2c\rho_{mh,i}}{[\text{var}(E_{m,i})\text{var}(E_{h,i})]^{1/2} (1 - \rho_{mh,i}^2)} \quad (7)$$

$\rho_{mh,i}$ the correlation coefficient ($\rho_{mh,i} = \text{cov}(E_{m,i}, E_{h,i}) / [\text{var}(E_{m,i}) \text{var}(E_{h,i})]^{1/2}$).

It is difficult to assign adequate values to the moments – especially the covariance – directly from the experimental emf data, so they are obtained from an analysis of the origins of the errors and the rules for propagation of errors.¹⁸

For the minimization process the FORTRAN subroutine STEPIT¹⁹ has been used, completed

with routines necessary for the fitting of data for STEPIT and for the calculation of the function S . The mathematical expressions used for the calculation of the weights include the stability constants, the parameters to be varied. As the calculation of the weights is a rather time-consuming process, the weights are calculated with the start values of the parameters and are retained throughout the run. Restarting the run and recalculating the weights from the new set of parameters make it possible to check that the set of weights is consistent with the final values of the parameters. In order to avoid an ungainly large number of unknown parameters the E° -values and the protolysis constants of the tartaric acid, β_{011} and β_{012} , are determined separately.

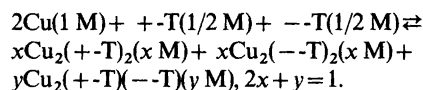
For the entire concentration region used the copper(II) concentration is low enough and the formation of tartrate complexes sufficiently strong so that hydrolysis of the copper(II) ion²⁰ can be neglected.

At very low total copper concentrations the disproportionation reaction, $\text{Cu(am)} + \text{Cu}^{2+} \rightleftharpoons 2\text{Cu}^+$, would interfere.¹⁰ With an oxygen donor ligand such as the tartrate ion it is supposed, however, that there is no further stabilization of the Cu(I) state and that the amount of Cu(I) is smaller than it would be in solutions with no tartrate present. In the series with the lowest copper concentration, 1 mM, and at a low pH – the most unfavourable concentration range in this sense – the amount of Cu(I) is estimated to about 1.5 % of the total copper concentration.

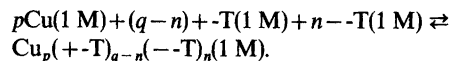
The correction term E_j in eqns. (2) and (3) represents the deviation from a constant value E° which may be the result of liquid junctions or media effects. Irrespective of the origins of the effects it is reasonable to suppose that any departure from the pure ionic medium of one molar sodium perchlorate will contribute more or less to E_j . In this work E_j is hypothetically considered as a sum of contributions from each kind of electrolyte that makes up the complex solution. As a linear relationship is often found within wide concentration ranges between E_j and the concentration of a species that replaces the inert salt,^{21,22} E_j is approximated as a sum of linear terms. The sum includes a term accounting for the deviation of the sodium perchlorate concentration itself from 1 mol dm^{-3} . Only species with high concentration are expected to give marked contributions to E_j . As the copper concentration is not very high the concentra-

tions of the complexes are low and their contributions to E_j may be disregarded. The linear coefficients of the correction terms of the other electrolytes that are present in the complex solution may be determined separately.

A complex $\text{Cu}_p\text{T}_q\text{H}_r$ in the copper(II) *rac*-tartrate system is either a pure +-tartrate complex formed together with the analogue --enantiomer or if $q \geq 2$ a complex with both +- and --tartrate ligands, *i.e.* a mixed complex. (When the numbers of +-tartrate and --tartrate ligands are equal, the notation *rac*-isomer or *rac*-complex is used in this text.) The two kinds of complexes may exist together in the *rac*-tartrate system and each species with the formula $\text{Cu}_p\text{T}_q\text{H}_r$ will contribute to the experimentally determined stability constant. The formation of mixed complexes is revealed in a comparison of this stability constant with the corresponding one of the copper(II) +-tartrate system. However, in such a comparison it must be kept in mind that, since the racemic system is treated as a one-ligand system in the calculations according to the description above, the compared constants do not refer to the same standard state as for the free ligand and the complexes formed. If we take the complex Cu_2T_2 as an example, the constant β_{22} determined from calculations on the racemic system will represent the free energy change of the reaction



Let us denote with $\beta_{pq}^{q-n,n}$ the stability constant of the complex $\text{Cu}_p(+\text{T})_{q-n}(-\text{T})_n$, which represents the free energy change in the normal standard state *e.g.*



The relations between a constant β_{pq} of the *rac*-system calculated in the way described and the number of $\beta_{pq}^{q-n,n}$ constants are then easily shown to be as eqns. (8) and (9),

$$\beta_{pq} = \sum_{n=0}^{q-1} (1/2)^{q-1} \beta_{pq}^{q-n,n}, \quad q \text{ odd} \quad (8)$$

and

$$\beta_{pq} = (1/2)^q \beta_{pq} + \sum_{n=0}^{q-1} (1/2)^{q-1} \beta_{pq}^{q-n,n}, \quad q \text{ even} \quad (9)$$

The upper limit of summation is explained by the identity between $\beta_{pq}^{q-n,n}$ and $\beta_{pq}^{n,q-n}$.

$\beta_{pq}^{q,0}$ is obtained from the measurements on the copper(II) + tartrate system. Thus, for complexes with $q \leq 3$ the individual $\beta_{pq}^{q-n,n}$ values can be calculated from eqns. (8) or (9) and can be used for a direct comparison. Hence it is seen that the formation of *rac*-complexes implies for the β_{pq} constant of the *rac*-system that $\beta_{pq} > (1/2)^{q-1} \cdot \beta_{pq}^{q,0}$.

The formation of a *rac*-complex is statistically favoured.²³ When comparing the constants in order to search for stereoselective effects of structural origins the $\beta_{pq}^{q-n,n}$ value should be divided by a statistical factor, $R = \binom{q}{n}$.²⁴

EXPERIMENTAL

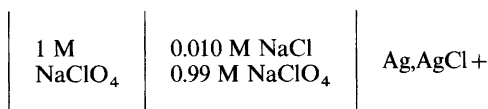
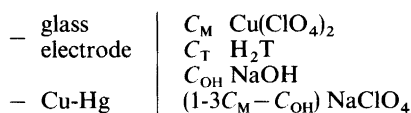
Chemicals. Copper(II) perchlorate, $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (BDH), was recrystallized once. The prepared stock solution was analyzed for copper by electrolytical deposition. The amount of free acid was determined to be 2.04×10^{-3} mol H^+ /mol Cu^{2+} by potentiometric titration.

The *racemic tartaric acid*, $\text{rac-C}_4\text{H}_6\text{O}_4 \cdot \text{H}_2\text{O}$ (Fluka, *purum*) was recrystallized three times (m.p. 202–204 °C).

The *optically active tartaric acid*, $+-\text{C}_4\text{H}_6\text{O}_4$ (Merck *p.a.*) was used without further purification. The concentrations of the stock solutions of the two acids were determined by alkalimetric titration.

Sodium perchlorate was prepared by the neutralization of perchloric acid (Baker *p.a.*) with sodium carbonate (Merck *p.a.*) and sodium hydroxide to pH = 7. Precipitated impurities were filtered off and the perchlorate was crystallized as $\text{NaClO}_4 \cdot \text{H}_2\text{O}$. The amount of protolytic impurities was analyzed potentiometrically in a 1.000 M solution. The protolyte present corresponds in total to 1.5×10^{-5} M OH^- . The preparation of the *copper amalgam*, ca. 2%, has been described in Ref. 25.

Method. The emf's of the following two cells were measured at 25 °C.



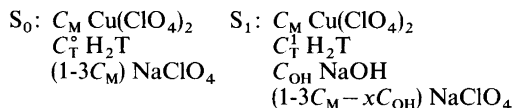
All other factors apart from the glass and amalgam electrode were the same for the two cells during the titration procedure. The glass electrode was a Jena U 9201 and its emf was read with a precision of ± 0.1 mV from a Radiometer PHM 52 digital potentiometer. The slope of this measuring device, S_h in eqn. (3), was determined as 25.54 mV. Before and after each titration the glass electrode was checked in a buffer solution of constant pH.

The emf of the amalgam electrode cell was measured with a Norma potentiometer and by the use of a Kipp en Zonen Galvanometer as a zero instrument. The emf could be read with ± 0.01 mV precision. For S_m in eqn. (2) the theoretical value 12.85 mV was used.

The emf's were usually stable after a few minutes, but a little slower response was discerned in the *rac*-system in the region of rapid change of pH.

The reference electrode was prepared according to Brown.²⁶

The composition of the left half-cell solution was changed during the titration by adding an increasing volume of a solution S_1 to 20 ml of a start solution S_0 . The solutions S_0 and S_1 had the following compositions



In most of the series $C_T^+ = C_T^- \cdot x$ in the expression of the sodium perchlorate concentration of solution S_1 has normally been chosen equal to 1 but in a couple of series with high tartrate concentration the sodium perchlorate concentration is further reduced ($x = 1.47$).

Before the titration a stream of oxygen-free nitrogen, premoistened in a 1.00 M sodium perchlorate solution was passed through the solutions for half an hour. During the titration the same nitrogen stream was bubbled through the titration vessel.

The protolysis constants of the acids were determined under the same experimental conditions as above. The hydrogen ion concentration was measured with the glass electrode in titration series with constant concentration of the acid and varying amounts of sodium hydroxide or perchloric acid.

MEASUREMENTS AND RESULTS

As to the concentration ranges, the principal aim has been to study and compare the formation of binuclear complexes or any further condensation products in weakly acid or neutral solutions

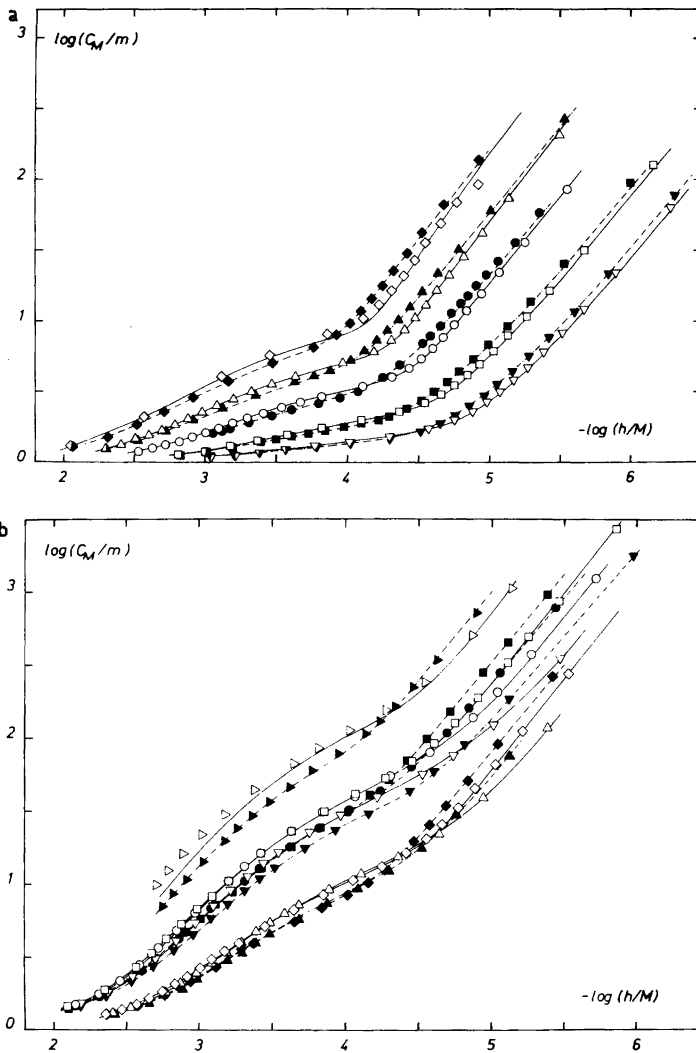


Fig. 1. $\log C_M/m$ versus $\log h$. In each series C_M and C_T are constant. Open symbols represent the copper +-tartrate system and filled symbols the copper *rac*-tartrate system. The lines represent values calculated from the constants of Table 1. (a) Series with $C_M = C_T$, (∇) $C_M = C_T = 1$ mM; (\square) $C_M = C_T = 2$ mM; (\circ) $C_M = C_T = 5$ mM (\triangle) $C_M = C_T = 10$ mM; (\diamond) $C_M = C_T = 20$ mM. (b) Series with $C_T > C_M$, (\triangle) $C_M = 2$ mM, $C_T = 10$ mM; (∇) $C_M = 2$ mM, $C_T = 25$ mM; (\diamond) $C_M = 5$ mM, $C_T = 10$ mM; (\circ) $C_M = 5$ mM, $C_T = 25$ mM; (\square) $C_M = 10$ mM, $C_T = 25$ mM; (\triangleright) $C_M = 20$ mM, $C_T = 50$ mM.

equimolar in copper(II) and tartrate or with a moderate excess of tartrate. The corresponding series divide into two groups, one with $C_M = C_T$ (Figs. 1a and 2) and the other with $C_T > C_M$ (Fig. 1b). In each of this kind of series C_M and C_T are constant while pH is changed from 2.5 to about 7. In the case of *rac*-tartrate the ratio $C_H/C_M = -1.25$ is not

reached because of the onset of precipitation which occurs even at low copper concentration (< 5 mM) in the sodium ion medium. Otherwise, the upper limit of C_M is set by the low solubility of the neutral copper tartrate. At unfavourable pH values the solutions are supersaturated even at low values of C_M but only at $C_M = 20$ mM does the onset of

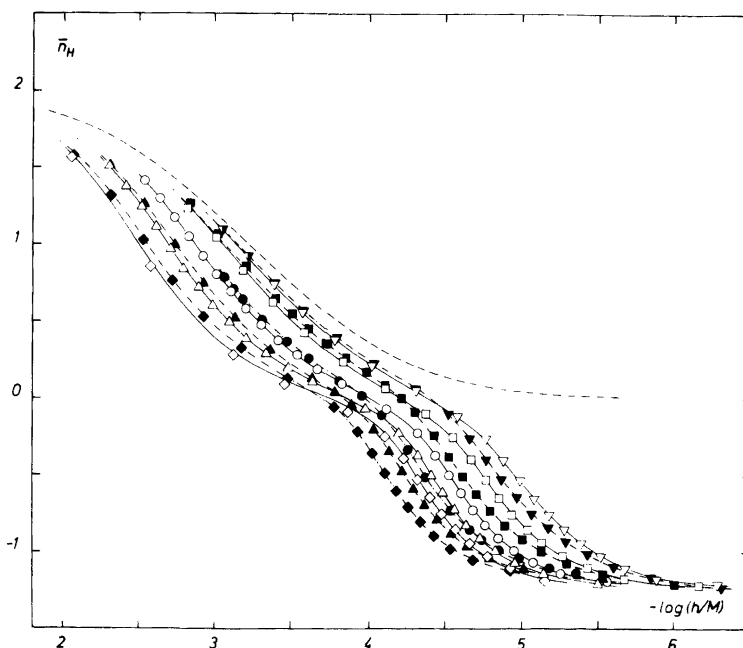


Fig. 2. $\bar{n}_H = (C_H - h)/C_T$ versus $\log h$. The symbols are the same as in Fig. 1a. The dashed line represents the \bar{n}_H -function of +- (or rac-) tartaric acid.

precipitation disturb the execution of the titration. As the formation of binuclear complexes begins at very low copper concentrations, series with C_M as low as 1 mM have been performed. The tartrate concentration in these two groups of series does not exceed 50 mM. In a couple of series with low copper(II) concentrations, 1 and 2 mM, C_T was varied up to about 100 mM at $\text{pH} \approx 4.5$ ($[T]/[HT] \approx 7$) with the intention of obtaining data for the characterization of the mononuclear complexes. Higher concentrations of tartrate have been avoided as an extreme substitution of perchlorate with the doubly charged tartrate ion will probably cause serious changes of the medium.

Protolysis constants. For the measurement of the protolysis constants, titration series with $C_T = 5, 10, 25,$ and 50 mM and varying pH were performed. The constants were calculated numerically. The following constants were obtained.

+ - tartaric acid	$K_{a_1} = (1.809 \pm 0.008) \times 10^{-3}$ (M)
	$K_{a_2} = (2.043 \pm 0.009) \times 10^{-4}$ (M)
rac-tartaric acid	$K_{a_1} = (1.807 \pm 0.007) \times 10^{-3}$ (M)
	$K_{a_2} = (2.048 \pm 0.007) \times 10^{-4}$ (M)

The constants are given with 99 % confidence intervals. No significant divergence between the protolysis constants of the two acids is observed. No indication of association between +- and -- tartrate ions of the racemic acid could be detected in the examined concentration region.

Emf-corrections. When determining E_m° of the copper amalgam electrode it was observed that E_m° varied linearly with the copper(II) concentration in the examined range up to 100 mM if the correction term E_j was not regarded. The slope of the variation depends, however, on the way the ionic medium is maintained. The slopes are $-26.9, -15.8,$ and -6.9 mV M^{-1} , respectively, when ($[\text{Cu}^{2+}] + [\text{Na}^+] = 1$ M, $[\text{ClO}_4^-] = 1$ M and finally the formal ionic strength $I = 1$ M. These observations are consistent with the hypothesis of E_j as a sum of linear terms and make it possible to calculate the linear emf correction coefficients of copper and sodium perchlorate. The emf correction coefficients of the tartrate species were obtained from three titration series on tartrate buffers of different total concentrations, and the correction coefficients were calculated from the titration data assuming

that the protolysis constants are real constants throughout the titration range.

The separately determined emf correction coefficients are summarized as follows:

NaClO ₄ -9	Cu(ClO ₄) ₂ -34	HClO ₄ 49
Na ₂ T 11	NaHT -3	H ₂ T -13 mV M ⁻¹

In the calculations on the complex solutions the emf correction, E_j , amounts to at most 3.6 mV. The greatest part of this derives from the often rather large deviation of the sodium perchlorate concentration from 1 mol dm⁻³ but the influence of high tartrate(2-) concentrations may also be important in some titration series. An attempt to estimate the contribution to the emf correction from the complexes by guessing reasonable values of their correction coefficients showed that this contribution should be very modest (≈ 0.1 mV).

An inspection of the data obtained* does not readily reveal what complexes are formed except that both systems exhibit a potential jump, when C_H/C_M approaches -1.25, which indicates that complexes that are at least tetranuclear are formed. In order to find a model to describe the data, the existence of a large number of complexes has to be tested. As the presence of coexisting complexes, including polynuclear as well as hydrolyzed species, is expected, the difficulty in finding a unique model significantly better than all others, must be recognized.

In the present calculations the search for a set of complexes to describe the experimental data started with a set conjectured from the stoichiometric composition of the solutions and the results from earlier investigations.^{7,27,28} The continued choice of complexes was governed by the result of the preceding calculations in order to improve the fit of data in different regions and to test complexes with compositions similar to those earlier accepted. As to the degree of condensation, complexes of increasing values of p , q and r were introduced as long as the sum of least squares was significantly reduced. Complexes with a low overall concentration are especially hard to identify correctly, or systematic errors may even be interpreted as such complexes. As a consequence, complexes which appear in the calculations with a presence less than 10–15 %

relative to the total copper concentration, have been omitted from the final sets of complexes. Otherwise the effect on the sum of S in eqn. 4 and the magnitude of the variances have been the criteria in deciding to adopt or omit a given complex.

In the final calculation of the constants and their variances the series with $C_M=20$ mM have been omitted. As mentioned above the precipitation of copper tartrate began to interfere in these series. The calculations of the +tartrate system show discrepancies in the most critical pH-range of these series that cannot be eliminated by the introduction of a new complex. For the sake of uniformity the 20 mM series of the *rac*-tartrate system were omitted too in the final calculation, but in this case the obtained constants describe the data of these series quite well.

When $C_H/C_M \geq 0$ corresponding to a pH lower than 4.0–4.5 the systems can be described with mono- and binuclear complexes, mainly CuTH, CuT and Cu₂T₂. At this low pH there is, however, a considerable hydrolysis of the binuclear complex Cu₂T₂ into Cu₂T₂H₋₁ and even Cu₂T₂H₋₂. The calculations give no evidence that complexes more condensed than the binuclear are formed in this area.

When the pH is increased the hydrolysis of the binuclear complexes continues but soon the formation of more condensed species becomes predominant. The hydrolysis of CuT into CuTH₋₁ in this pH-range²⁷ cannot be traced. When C_H/C_M approaches -1.25 the pH increases rapidly to about 8 and at the same time $[Cu^{2+}]$ is reduced in a corresponding way, indicating an almost quantitative formation of complexes with the ratio of Cu:H equal to 1:-1.25. The calculations give the best fit to the experimental data if the species formed up to this equivalence point have the stoichiometric relation Cu:T:H equal to 4:3:-5. A close examination of the area of the pH jump – without sodium perchlorate – showed that in the case of *rac*-tartrate the change of pH is less than in the case of +tartrate and that the titration curve is not quite so steep. Small amounts of more hydrolyzed complexes are obviously formed in the *rac*-system and the formation of the 4:3:-5 complex is not completely quantitative.

The 4:3:-5 complex is earlier reported as Cu₄T₃H₋₅²⁹ or Cu₈T₆H₋₁₀.²⁸ The potentiometric data of this study give some indication of both of these complexes being present in the +tartrate system. The sum of least squares, S , is 16 % lower

* Experimental data can be obtained from the author.

when both complexes are present compared to the case with only $\text{Cu}_8\text{T}_6\text{H}_{-10}$ present. The introduction of a trimer, $\text{Cu}_{12}\text{T}_9\text{H}_{-15}$, brings no improvement. Recordings of absorption and circular dichroism spectra³⁰ of copper +-tartrate solutions with $C_{\text{H}}/C_{\text{M}} = -1.25$ and C_{M} varying from 2 to 100 mM show, however, that Beer's law is perfectly obeyed which is a strong indication that only one complex is present. The best fitting of data is then obtained if $\text{Cu}_8\text{T}_6\text{H}_{-10}$ is applied and if the formation of this complex is preceded by another, less hydrolyzed, complex *viz.* $\text{Cu}_6\text{T}_4\text{H}_{-7}$. If $\text{Cu}_8\text{T}_6\text{H}_{-10}$ is exchanged for $\text{Cu}_4\text{T}_3\text{H}_{-5}$, S is increased with 24%. The formation of an octanuclear complex is supported by the results of an X-ray investigation on a concentrated copper +-tartrate solution.³⁰

For the description of the *rac*-tartrate system only a tetranuclear 4:3:-5 complex is required, but also in this case there are indications of appreciable amounts of some other species in the range $-1.25 < C_{\text{H}}/C_{\text{M}} < -1.00$. This species is best characterized as $\text{Cu}_6\text{T}_5\text{H}_{-7}$, but it must be pointed out that complexes with a similar stoichiometric composition may fit almost as well.

In earlier works the existence of the complex Cu_2T_3 has been claimed.^{7,9} The reported stability constants are assigned values large enough for the complex to be present in the solutions with excess of tartrate. The preliminary calculations do not exclude the existence of this species, but its calculated stability constant has very low statistical significance and its presence is not needed for the

description of data. The same may be said of the complex CuT_3 which would possibly appear at high values of C_{T} in the series with varying C_{T} .

In all about 75 complexes have been tested. Table 1 shows the complexes which were finally chosen to describe the complex formation in the acid and neutral region of the copper(II) +- and *rac*-tartrate systems. The two sets of complexes describe corresponding systems with practically the same degree of precision. Where relevant, stability constants of single *rac*-complexes calculated according to eqn. 9 are given in Table 1.

It may be noted that the values of some constants are rather sensitive to changes of the model of description and may be somewhat more uncertain than would be inferred from the stated errors. As might be expected, some constants show a large correlation, *e.g.* $\rho_{110,220}$ is equal to -0.87 in the +-tartrate system and -0.74 in the *rac*-system. The relative distribution of Cu(II) amongst the different complexes is shown in Fig. 3 for two different compositions of the systems.

DISCUSSION

Complexes and corresponding stability constants of the present work are in particular instances in good agreement with some earlier investigations. However, different authors have examined the complex formation in different concentration ranges and thus consider different sets of complexes.

Table 1. Stability constants of complexes $\text{Cu}_p\text{T}_q\text{H}_r$, formed in acid and neutral copper +- and *rac*-tartrate solutions calculated from data of potentiometric measurements at 25 °C and ionic strength 1.00 M with NaClO_4 as neutral salt. Stated errors are equal to three standard deviations. The percentages state the maximum presence of complexes relative to the total amount of copper in the concentration region used for the calculation.

p	q	r	Copper +-tartrate	%	Copper <i>rac</i> -tartrate	%	<i>rac</i> -complexes from eqn. (9)
1	1	1	$(3.84 \pm 0.14) \times 10^5$	31	$(3.70 \pm 0.15) \times 10^5$	32	M^{-2}
1	1	0	$(4.3 \pm 0.3) \times 10^2$	23	$(4.5 \pm 0.3) \times 10^2$	30	M^{-1}
1	2	0	$(2.44 \pm 0.14) \times 10^4$	59	$(2.36 \pm 0.11) \times 10^4$	68	$(4.6 \pm 0.5) \times 10^4$ M^{-2}
2	2	0	$(4.00 \pm 0.13) \times 10^8$	67	$(2.04 \pm 0.08) \times 10^8$	58	$(0.2 \pm 0.4) \times 10^8$ M^{-3}
2	2	-1	$(1.60 \pm 0.08) \times 10^4$	29	$(0.98 \pm 0.10) \times 10^4$	23	$(0.7 \pm 0.4) \times 10^4$ M^{-2}
2	2	-2	$(4.4 \pm 0.2) \times 10^{-1}$	66	$(3.0 \pm 0.4) \times 10^{-1}$	32	$(3.1 \pm 1.6) \times 10^{-1}$ M^{-1}
4	3	-4			$(3.4 \pm 0.5) \times 10^{-1}$	15	M^{-2}
4	3	-5			$(1.42 \pm 0.14) \times 10^{-5}$	81	M^{-1}
6	4	-7	$(3.0 \pm 0.3) \times 10^{-6}$	33			M^{-4}
6	5	-7			$(1.1 \pm 0.2) \times 10^{-2}$	56	M^{-3}
8	6	-10	$(4.2 \pm 0.5) \times 10^{-8}$	66			M^{-3}

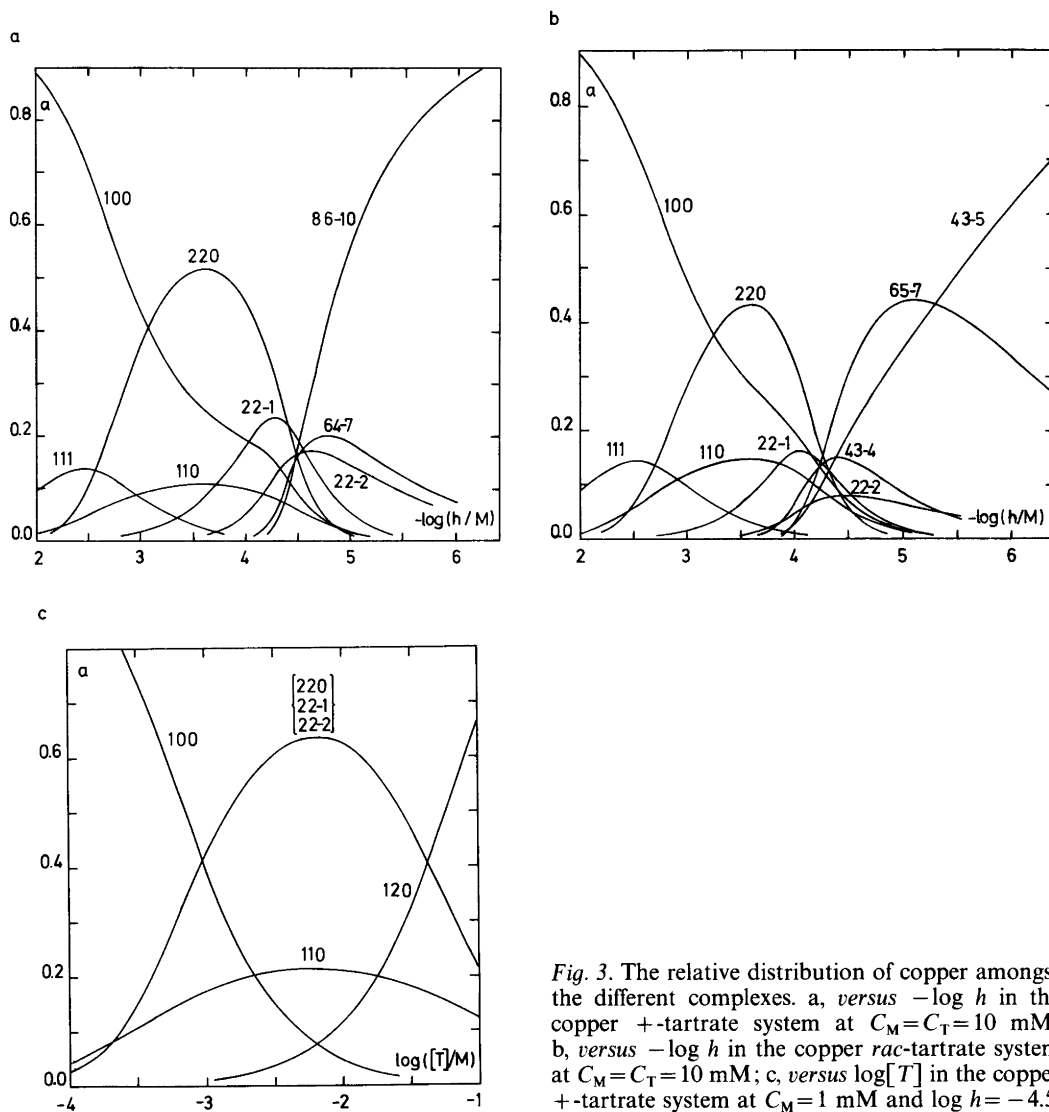


Fig. 3. The relative distribution of copper amongst the different complexes. a, versus $-\log h$ in the copper + tartrate system at $C_M = C_T = 10$ mM; b, versus $-\log h$ in the copper *rac*-tartrate system at $C_M = C_T = 10$ mM; c, versus $\log [T]$ in the copper + tartrate system at $C_M = 1$ mM and $\log h = -4.5$.

The view of the systems as mainly built up by CuT and Cu_2T_2 in acid and equimolar solutions⁶⁻⁸ is confirmed in this work. The absence of more condensed species in this pH range has been shown to be valid in an increased concentration area up to the limit set by the solubility of the copper tartrate. The stability constants of the complexes CuT and Cu_2T_2 show small differences from the corresponding values of Bottari *et al.*⁷ As should be expected, the values of the stability constants obtained for the complexes CuTH and CuT do not

differ significantly between the two systems. The magnitude of β_{111} is surprising as it implies that the neutral species CuT is as strong a base — or even stronger — as the negatively charged hydrogen tartrate ion HT^- (CuT : $k = 900$; HT^- : $k = 560$ (M^{-1}), $k = k_b/k_w$).

As soon as a complex contains more than one tartrate group there are possibilities for the formation of diastereomers of this complex in the *rac*-tartrate system. The stability constant of the *rac*-complex $\text{Cu}(+-\text{T})(--\text{T})$ is about twice as large as

that of $\text{Cu}(+-\text{T})_2$. Recognizing the statistical factor $R=2$ for this complex, it turns out that the greater stability of the *rac*-complex is of statistical origin.

The stability constants of the Cu_2T_2 complex show that the formation of this complex in *rac*-tartrate solutions is practically stereospecific in favour of pure $++-$ and $--$ -complexes. A stereoselectivity of the same sort has been deduced for the corresponding nickel tartrate complex, Ni_2T_2 , from pressure-jump kinetic studies by Hoffman *et al.*^{31,32}

In the case of $\text{Cu}_2\text{T}_2\text{H}_{-1}$ and $\text{Cu}_2\text{T}_2\text{H}_{-2}$, the calculated constants indicate that *rac*-complexes are formed but that the $++-$ and $--$ -complexes are still favoured. $\text{Cu}_2\text{T}_2\text{H}_{-1}$ and, to a greater extent, $\text{Cu}_2\text{T}_2\text{H}_{-2}$ are formed in the region where the continued polymerization takes place. It is difficult to exactly establish the most suitable model of the complex formation in this region. Due to inadequacies in the adopted models, the stability constants of these two complexes may be somewhat more uncertain than is suggested from the stated errors. However, the results of the testing of various models in the preliminary calculations do not place the existence of the *rac*-complex of $\text{Cu}_2\text{T}_2\text{H}_{-2}$ in question whereas the existence of

the corresponding $\text{Cu}_2\text{T}_2\text{H}_{-1}$ complex is more uncertain.

The tartrate-bridged binuclear structures, the occurrence of which has been established for many crystal structures of metal tartrates,^{4,5,33} and which are evidently present in some alkaline metal tartrate solutions,^{2,34} have also been used in the discussion of the binuclear tartrate complexes formed in acid solution.^{9,32}

In an assessment of the conformation angles and the strain induced in the central carbon-carbon bond of the tartrate ions when a tartrate-bridged binuclear complex is formed, Tapscott³⁵ has shown that the tetragonal coordination geometry with a square planar arrangement of the chelate rings is most favourable for a *rac*-complex (Fig. 4a). A $++-$ or $--$ -complex with tetragonal geometry should imply a somewhat higher conformational energy,³⁶ ca. 5 kJ mol^{-1} , than that of the *rac*-complex. However, the conformational energy is lowered if the coordinative bonds to the *trans*-positioned hydroxyl oxygens form an angle less than 180° . A minimum of the conformational energy would be reached when the chelate rings are arranged in a manner somewhere between a trigonal bipyramidal (Fig.

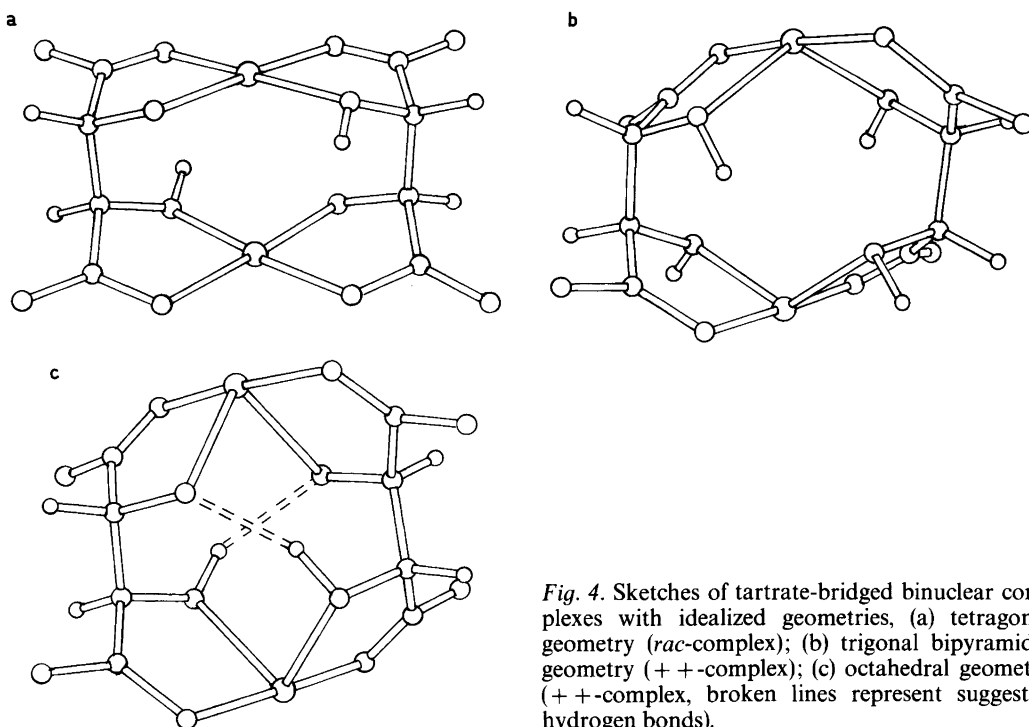


Fig. 4. Sketches of tartrate-bridged binuclear complexes with idealized geometries, (a) tetragonal geometry (*rac*-complex); (b) trigonal bipyramidal geometry ($++-$ complex); (c) octahedral geometry ($++-$ complex, broken lines represent suggested hydrogen bonds).

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Received February 22, 1980.