Complex Formation in the Copper(II) meso-Tartrate System in Acid and Neutral Aqueous Solution

LENNART JOHANSSON

Inorganic Chemistry I, University of Lund, Chemical Center, P.O. Box 740, S-220 07 Lund 7, Sweden

The complex formation in aqueous solution between the copper(II) ion and meso-tartraric acid has been studied in the acid and the 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 one 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 $< 4$ the system is characterized by an equilibrium between mono- and binuclear species, CuT, CuTH and CuT$_2$, and Cu$_2$T$_2$ respectively (T $=\text{C}_4\text{H}_6\text{O}_{6}^{2-}$), though the binuclear complex does not play such an important role as the binuclear complexes in the copper +- and rac-tartrate systems.

At pH $> 4$ polymeric complexes are formed. In neutral solutions a complex Cu$_3$T$_2$H$_{-6}$ is formed almost quantitatively.

Whereas the complex formation between +- and rac-tartrate and various metal ions has been subject to much attention, the studies on the complex formation of the meso-tartrate ion are relatively few. For the copper(II) meso-tartrate system there are only two investigations reported on a quantitative determination of complexes formed in aqueous solution. Both of them concern the acid pH-range. Ramamorthy and Manning$^1$ find a first and a second mononuclear complex while Ostacoli et al.$^2$ besides mononuclear complexes, introduce a binuclear complex, Cu$_3$T$_2$H$_{-2}$ (T $=\text{C}_4\text{H}_6\text{O}_{6}^{2-}$). The stability constants of the mononuclear complexes are larger than the corresponding ones in the copper +-tartrate system. It is also noted from a comparison of protolysis constants that the meso-tartrate ion shows a greater basicity than the +-tartrate ion.$^1,2$

Much of the work on the copper meso-tartrate system concerns the characterization of solids precipitated from solutions at different values of pH$^3-6$. The similarity as to the composition of these solids compared to +- and rac-tartrates prepared under similar conditions is emphasized.$^3,4$ For the pH-region used in this work, it is observed that the trihydrates CuT.3H$_2$O can be precipitated from acid copper tartrate solutions, using either +- , rac- or meso-tartrate$^7,8$ and that solid phases containing a stoichiometric unit Cu$_4$T$_3$H$_{-5}$ can be prepared from neutralized copper +- , rac- and meso-tartrate solutions.$^8,10,5$ The solids of the latter kind as well as their solutions show the same reduction of the magnetic moment ($\mu_{\text{eff}} = 1.48\mu_B$) and similar ESR-spectra$^{11}$ indicating polymeric units with copper ions linked by exchange interactions.

Besides the difference in configuration, it has been shown from diffraction investigations on the crystal structures of meso-tartraric acid$^{12}$ and various meso-tartrates$^{8,13,14}$ that the meso-tartrate molecule takes a staggered conformation with the carboxyl groups in an adjacent position whereas the +-tartrate molecule places them in a transoid position (Fig. 1). Considering those differences in configuration and conformation it seems hardly probable that the meso-tartrate ion would show a behaviour equivalent to the +- and rac-tartrates in the formation of polymeric complexes. As shown by Tapscott$^{15}$ the formation of tartrate-bridged binuclear complexes, which are prevalent in many +- and rac-tartrate compounds,$^{16}$ should be less favourable for meso-tartrate. In accordance with this, ESR-measurements on acid copper meso-tartrate solutions indicate that these
solutions should be dominated by species having very weak magnetic interactions between metal centers. The crystal structures of the trihydrates display similar conditions in that the meso-tartrate structure is built up from copper tartrate chains whereas in the +tartrate structure a typical tartrate-bridged dimer can be discerned.

In a previous work a comparative study of the copper + and rac-tartrate systems in acid and neutral aqueous solution was performed by the use of a potentiometric method. In the present work that study is extended to the copper meso-tartrate system in order to produce a basis for a comparison of the meso-tartrate system to the other two systems under equivalent conditions. Consequently the experimental arrangements are the same as in the previous work, i.e. the concentrations of the free ions Cu^{2+} and H^{+} are determined simultaneously by the use of a copper amalgam and a glass electrode and a common reference electrode. The measurements were performed at 25 °C as titrations in a sodium perchlorate medium and with an ionic strength equal to 1 mol dm^{-3}.

METHODS

The mathematical treatment of measured data is the same as that of Ref. 18. Therefore those matters will be recapitulated briefly and for details the reader is referred to the previous paper.

The stability constants of the complexes used for the description of data are calculated by minimizing the sum

\[ S = \sum_l \left[ w_{m,l} (E_{m,l}^{\text{exp}} - E_{m,l}^{\text{cal}})^2 \right] + \sum_i \left[ w_{h,i} (E_{h,i}^{\text{exp}} - E_{h,i}^{\text{cal}})^2 \right] - \sum_{m,h,i} \left[ (E_{m,i}^{\text{exp}} - E_{m,i}^{\text{cal}})(E_{h,i}^{\text{exp}} - E_{h,i}^{\text{cal}}) \right] \]  \hspace{1cm} (1)

The emf's \( E_m \) and \( E_h \) are related to the free concentrations of Cu^{2+} and H^{+} according to eqns. (2) and (3), where \( E_j \) is a correction term.

\[ E_m = E_m^w - S_m \ln m + E_j \]  \hspace{1cm} (2)

\[ E_h = E_h^w - S_h \ln h + E_j \]  \hspace{1cm} (3)

As the emf's are measured simultaneously there will be a considerable correlation between them in some concentration regions which is the reason for the addition of the third term in eqn. (1). The weights of eqn. (1) have been calculated analytically from the expressions accounting for the relations between the emf's and the variables which are considered as sources of error. The values of \( E^w \) in eqns. (2) and (3) have been determined separately. The correction term, \( E_j \), has been approximated to a sum of linear terms, each term representing an electrolyte of the complex solution. The terms representing the complex electrolytes are supposed to be negligible as the total copper concentration is low. The values of \( \beta_{011} \) and \( \beta_{012} \), i.e. the protolysis constants of the meso-tartraric acid, are determined separately. For the minimization process the FORTRAN subroutine STEPIT has been used.

EXPERIMENTAL

Copper perchlorate, sodium perchlorate and copper amalgam are the same as used in Ref. 18. The meso-tartraric acid, meso-C_4H_6O_6.H_2O (Fluka purum) was recrystallized three times (m.p. 146-148 °C). The preparation of the solutions and the measuring procedure were identical with those of Ref. 18. Stable emf's were obtained after a few minutes.

MEASUREMENTS AND RESULTS

The concentration region covered is the same as in the previous work. The measurements are confined to the acid and neutral pH range. The series measured * are illustrated in Figs. 2 and 3. As was the case in the previous work, two series with low copper(II) concentration, 1 and 2 mM, and the tartrate concentration varying up to 100 mM were performed in addition to the series shown in Fig. 2.

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* Experimental data can be obtained from the author.
Fig. 2. Log $C_M/m$ versus log $h$. In each series $C_M$ and $C_T$ are constant. The lines represent values calculated from the constants of Table 1. (a) Series with $C_M = C_T$: (▲) $C_M = C_T = 1$ mM; (□) $C_M = C_T = 2$ mM; (○) $C_M = C_T = 5$ mM; (△) $C_M = C_T = 10$ mM; (◇) $C_M = C_T = 20$ mM. (b) Series with $C_T < C_M$: (△) $C_M = 2$ mM; $C_T = 10$ mM; (▲) $C_M = 2$ mM; $C_T = 25$ mM; (◇) $C_M = 5$ mM; $C_T = 10$ mM; (○) $C_M = 5$ mM; $C_T = 25$ mM; (□) $C_M = 10$ mM; $C_T = 25$ mM; (▷) $C_M = 20$ mM; $C_T = 50$ mM.

The protolysis constants of meso-tartaric acid were calculated numerically from data measured under the same experimental conditions as the other measurements. The following constants were obtained,

\[ K_{s1} = (1.314 \pm 0.006) \times 10^{-3} \text{ M} \]

\[ K_{s2} = (7.52 \pm 0.02) \times 10^{-5} \text{ M} \]

The constants are given with 99% confidence intervals.

\textit{Emf corrections.} Emf correction coefficients from Ref. 18 were used except for the coefficients of the meso-tartrate species which were determined in the same way as in Ref. 18. The following coefficients (mV M\(^{-1}\)) were obtained.

\textbf{Table 1.} Stability constants of complexes Cu\(_n\)T\(_n\)H\(_r\) formed in acid and neutral copper meso-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 region used for the calculations.

<table>
<thead>
<tr>
<th>p</th>
<th>q</th>
<th>r</th>
<th>(\beta_{ppr})</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>1</td>
<td>(1.53 \pm 0.03) \times 10^6</td>
<td>40</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>0</td>
<td>(1.41 \pm 0.05) \times 10^3</td>
<td>46</td>
</tr>
<tr>
<td>1</td>
<td>2</td>
<td>0</td>
<td>(2.05 \pm 0.06) \times 10^5</td>
<td>92</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>0</td>
<td>(3.3 \pm 0.3) \times 10^8</td>
<td>33</td>
</tr>
<tr>
<td>5</td>
<td>4</td>
<td>-5</td>
<td>(1.09 \pm 0.16) \times 10^4</td>
<td>22</td>
</tr>
<tr>
<td>5</td>
<td>4</td>
<td>-6</td>
<td>1.36 \pm 0.08</td>
<td>91</td>
</tr>
<tr>
<td>6</td>
<td>4</td>
<td>-7</td>
<td>(1.64 \pm 0.13) \times 10^{-1}</td>
<td>52</td>
</tr>
</tbody>
</table>
concentrations give the largest contributions to $E_j$.

The existence of several complexes have been tested. As in the case of copper $\pm$- and rac-tartrate systems, it appears that polynuclear as well as hydrolyzed complexes are formed and the same difficulties to find an exclusive set of complexes for the description of the data is experienced. For this reason the existence of complexes with a low concentration — less than $10-15\%$ relative the total copper concentration — is considered as very uncertain and such complexes are consequently omitted.

In the series with the highest copper concentration, 20 mM, the onset of a precipitation of copper tartrate — as in the $+$-tartrate system — disturbed the measurements. A small discrepancy in the fitting of the data in the most critical pH-range of these series is attributed to the precipitation. The stability constants presented in Table 1 are obtained from calculations at which the 20 mM series have been omitted. It should also be noted that there is a considerable correlation between the calculated values of some constants, especially between $\beta_{110}$ and $\beta_{220}$ ($\rho_{110,220} = -0.83$). The relative distribution of Cu(II) amongst the different complexes is shown in Fig. 4 for two different compositions of the system.

As for the copper $\pm$- and rac-tartrate systems the meso-system is described in acid solutions in terms of mono- and binuclear complexes viz. CuTH, CuT and Cu$_2$T$_2$. The mononuclear complexes are, however, more stable than corresponding $+$-tartrate complexes and — contrary to the situation in the $\pm$- and rac-tartrate systems — they are more abundant than the binuclear complexes. An exclusion of the binuclear complex will, however, make the sum of the least squares about six times larger.

The continued polymerization accompanying the increase of pH starts somewhat earlier in the meso-tartrate system. At pH 4 complexes containing more than two copper ions are already predominant. Ostacoli et al. $^2$ report a hydrolyzed binuclear complex, Cu$_2$T$_2$H$_2$, but the existence of hydrolyzed binuclear complexes cannot be verified from the data of this study. The formation of such complexes is probably depressed by the early appearance of the more condensed species. As in the $\pm$- and rac-systems there is a rapid change of pH — however not so large as that of the $+$-tartrate system — when equimolar copper meso-tartrate solutions are neutralized, but it appears

\begin{tabular}{ccc}
Na$_2$T & NaHT & H$_2$T \\
16 & -10 & -17
\end{tabular}

As in the previous measurements, deviations of the sodium perchlorate concentration from one mol dm$^{-3}$ and in some cases high tartrate(2-)
earlier and is practically completed when $C_H/C_M = -1.20$. The calculations show that the change of pH corresponds to an almost quantitative formation of the complex $\text{Cu}_5\text{T}_4\text{H}_{-6}$. From copper meso-tartrate solutions of a corresponding pH, solids containing the stoichiometric unit $\text{Cu}_9\text{T}_7\text{H}_{-12}$ have been prepared. However, the addition of a complex with that composition to the set of complexes does not improve the fitting of the data. The formation of complexes with the ratio Cu:T:H equal to 4:3:5, which are important in the + - and rac-systems and to which corresponding solids have been prepared in the meso-tartrate system, cannot be established with acceptable statistical significance from the present data, nor excluded.

As was the case in the + - and rac-systems appreciable amounts of some other species appear in the range $-1.20 < C_H/C_M < 0$. They have been characterized as $\text{Cu}_9\text{T}_4\text{H}_{-5}$ and $\text{Cu}_9\text{T}_4\text{H}_{-7}$, but the difficulty of a unique choice of complexes for description of the data in this pH-range has to be admitted. None of the two complexes may be excluded without increasing the value of $S$ considerably (twice and seven times respectively), but especially the first one may be exchanged for a complex with similar composition, e.g., $\text{Cu}_9\text{T}_4\text{H}_{-4}$, without any appreciable change of $S$.

**DISCUSSION**

A comparison with the single study of the copper meso-tartrate system performed under similar experimental conditions as this study, viz. that of Ostacoli et al., shows a consistency in the predominance of the mononuclear complexes in acid solutions and a fairly good agreement between the stability constants of CuTH and CuT. However the description of the data of this work requires the introduction of the binuclear complex Cu$_2$T$_2$ even if this complex takes a less important part of the complex formation than the corresponding complex in the + - and rac-systems.

The fact that the mononuclear copper meso-tartrate complexes are stronger than their + - tartrate analogues, and the greater basicity of the meso-tartrate(2-) ion can be understood by considering the difference in conformation. The conformation according to Fig. 1, which is the conformation found in crystal structures of meso-tartrate, is the most favourable conformation of a meso-tartrate ion if oxygen-oxygen distances are considered. All other conformations will lead to oxygen oxygen distances shorter than two van der Waals radii. The adjacent position of the two negatively charged carboxyl groups should, however, imply the presence of greater coulombic repulsions than in the + - tartrate ion with the carboxyl groups in the transoid position. Whatever conformation the free meso-tartrate ion takes in aqueous solution the coordination of a positive ion -- in this case Cu$^{2+}$ or H$^+$ -- and the formation of a complex in which the meso-tartrate ion takes the conformation shown in Fig. 1, will lead to a decrease of repulsive energy. The result will be an increase of the free energy change of the complex formation reaction. When equilibrium constants of reactions that involve an uncoordinated tartrate(2-) ion are compared (Table 2, reactions Nos. 1, 3 and 6) it turns out that the meso-tartrate constants are about three times greater than the corresponding constants of the + - tartrate system. Then it would be expected that much of the repulsive energy is released and that the difference between the two systems is less when a second ion is coordinated to the remaining carboxyl group.

**Table 2.** Equilibrium constants of some corresponding copper + - and meso-tartrate reactions. Constants of the + -tartrate reactions are taken from Ref. 18.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$K/M^{-1}$ (+)</th>
<th>$K/M^{-1}$ (meso)</th>
<th>$K_{meso}/K_+$</th>
<th>No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{T}^2^- + \text{H}^+ \rightleftharpoons \text{HT}^-$</td>
<td>$4.90 \times 10^3$</td>
<td>$13.3 \times 10^3$</td>
<td>2.71</td>
<td>(1)</td>
</tr>
<tr>
<td>$\text{HT}^- + \text{H}^+ \rightleftharpoons \text{H}_2\text{T}$</td>
<td>$5.57 \times 10^2$</td>
<td>$7.59 \times 10^2$</td>
<td>1.36</td>
<td>(2)</td>
</tr>
<tr>
<td>$\text{Cu}_2^+ + \text{T}^2^- \rightleftharpoons \text{CuT}$</td>
<td>$4.3 \times 10^2$</td>
<td>$14.1 \times 10^2$</td>
<td>3.31</td>
<td>(3)</td>
</tr>
<tr>
<td>$\text{CuT} + \text{H}^+ \rightleftharpoons \text{CuTH}^+$</td>
<td>$9.0 \times 10^2$</td>
<td>$10.9 \times 10^2$</td>
<td>1.20</td>
<td>(4)</td>
</tr>
<tr>
<td>$\text{HT}^- + \text{Cu}^2^+ \rightleftharpoons \text{CuTH}^+$</td>
<td>$0.78 \times 10^2$</td>
<td>$1.15 \times 10^2$</td>
<td>1.47</td>
<td>(5)</td>
</tr>
<tr>
<td>$\text{CuT} + \text{T}^2^- \rightleftharpoons \text{Cu}_2\text{T}_2^2^-$</td>
<td>$0.57 \times 10^2$</td>
<td>$1.45 \times 10^2$</td>
<td>2.54</td>
<td>(6)</td>
</tr>
<tr>
<td>$2 \text{CuT} \rightleftharpoons \text{Cu}_2\text{T}_2$</td>
<td>$2.20 \times 10^3$</td>
<td>$0.16 \times 10^3$</td>
<td>0.08</td>
<td>(7)</td>
</tr>
</tbody>
</table>
Fig. 5. Sketch of a tartrate-bridged meso,meso-dimer with an idealized octahedral geometry.

Reactions Nos. 2, 4 and 5 in Table 2 are examples of such reactions and it appears that the constants of the meso-tartrate reactions are only a factor 1 to 1.5 greater than the corresponding (+)-tartrate constants.

Although the stability constants of Cu₃T₃ are about the same size in the copper meso- and (+)-tartrate systems, a comparison of the dimerization constants (reaction No. 7 in Table 2) shows that the tendency to form binuclear complexes is much less pronounced in the meso-tartrate system. There are rather few reports on binuclear meso-tartrate complexes, which could, of course, be a consequence of the small number of studies on meso-tartrate systems. Among the few binuclear meso-tartrate complexes reported there are two chromium(III) complexes, Cr₂T₂H₄L₂ and NaCr₂T₂H₄L₂ (L = 1,10-phenanthroline or 2,2'-bipyridyl), to which a tartrate-bridged dimeric structure has been attributed for reasons based on spectrophotometric investigations. Tapscott shows in his study of isomer stabilities of tartrate-bridged binuclear complexes that two meso,meso-dimers can certainly be formed without disturbing the conformation or introducing strain in the central carbon-carbon bond of the meso-tartrate ion. The dimers, i.e. the ΔΔ- and ΔΔ-enantiomers, have to take an octahedral coordination and the asymmetric carbon atoms of the chelate rings at one and the same metal ion must take opposite configurations (Fig. 5). However, in dimers of this kind there are rather short distances either between opposed hydroxyl or between opposed carboxyl groups, though an inspection of molecular models makes it seem probable that these distances could be sufficiently increased by a small increase of the angle between the chelate rings without violating the demands of a proper conformation. However, it may also be noted that the carboxyl oxygens are cis-coordinated which in unhydrolyzed dimers is supposed to be unfavourable from an electrostatic point of view. The lower tendency for dimerization observed in the copper meso-tartrate system compared to the (+)- and rac-systems would be understood against the background of the objections raised against the formation of the meso,meso-tartrate dimers as would the difference between the crystal structures of the copper + - and meso-tartrate trihydrates mentioned in the introduction.

Notwithstanding his statement that the (+)- and meso-tartaric acids behave completely similar in relation to the copper(II) ion in the formation of various solids, Reihlen presents a copper tartrate with the ratio Cu:T:H equal to 5:4:—:6 only in the case of meso-tartaric acid.

The formation of the complex Cu₅T₄H₁₀ may be conceived as the result of a polymerization principle of the same kind as that proposed for the formation of the octanuclear complex Cu₉T₈H₁₀ in the copper + -tartrate system, i.e. a copper ion joins two tartrate-bridged dimers via two hydroxyl groups at each dimer. In the case of meso-tartrate it may be noted, however, that the meso,meso-dimer turns all the four hydroxyl groups to one side of the dimer and the four carboxyl groups to the other (Fig. 5). Thus, an association of the kind mentioned has to cease when two dimers are joined, i.e. when a complex with five copper and four tartrate ions is formed, provided that the terminal carboxyl groups cannot bring about a further polymerisation.

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REFERENCES

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