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

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The complex formation in aqueous solution between the copper(II) ion and *meso*-tartaric 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_2T_2 respectively (T $=C_4H_4O_6^{2-}$), 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 polynuclear complexes are formed. In neutral solutions a complex $Cu_5T_4H_{-6}$ 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. Ramamoorthy and Manning[1] find a first and a second mononuclear complex while Ostacoli *et al.*,[2] besides mononuclear complexes, introduce a binuclear complex, $Cu_2T_2H_{-2}$ (T $=C_4H_4O_6^{2-}$). 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 $CuT.3H_3O$ can be precipitated from acid copper tartrate solutions, using either +-, *rac*- or *meso*-tartrate[7,8] and that solid phases containing a stoichiometric unit $Cu_4T_3H_{-5}$ can be prepared from neutralized copper +-, *rac*- and *meso*-tartrate solutions.[9,10,5] The solids of the latter kind as well as their solutions show the same reduction of the magnetic moment ($\mu_{eff}=1.48\mu_B$) 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*-tartaric 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 polynuclear 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
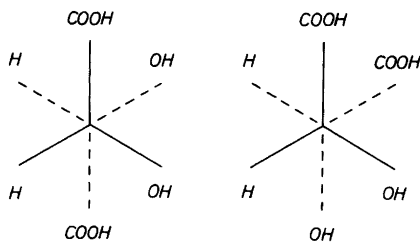
Fig. 1. Conformations of +-tartrate (right) and *meso*-tartrate (left) groups as found in the solid state.

solutions should be dominated by species having very weak magnetic interactions between metal centers.[17] 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.[8]

In a previous work[18] 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

$$S = \sum_i \left[w_{m,i}(E_{m,i}^{exp} - E_{m,i}^{cal})^2 + w_{h,i}(E_{h,i}^{exp} - E_{h,i}^{cal})^2 - w_{mh,i}(E_{m,i}^{exp} - E_{m,i}^{cal})(E_{h,i}^{exp} - E_{h,i}^{cal}) \right] \quad (1)$$

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.

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

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

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^o 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 β_{011} and β_{012}, *i.e.* the protolysis constants of the *meso*-tartaric acid, are determined separately. For the minimination process the FORTRAN subroutine STEPIT[19] has been used.

EXPERIMENTAL

Copper perchlorate, sodium perchlorate and *copper amalgam* are the same as used in Ref. 18. The *meso-tartaric acid, meso*-$C_4H_6O_6 \cdot H_2O$ (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.

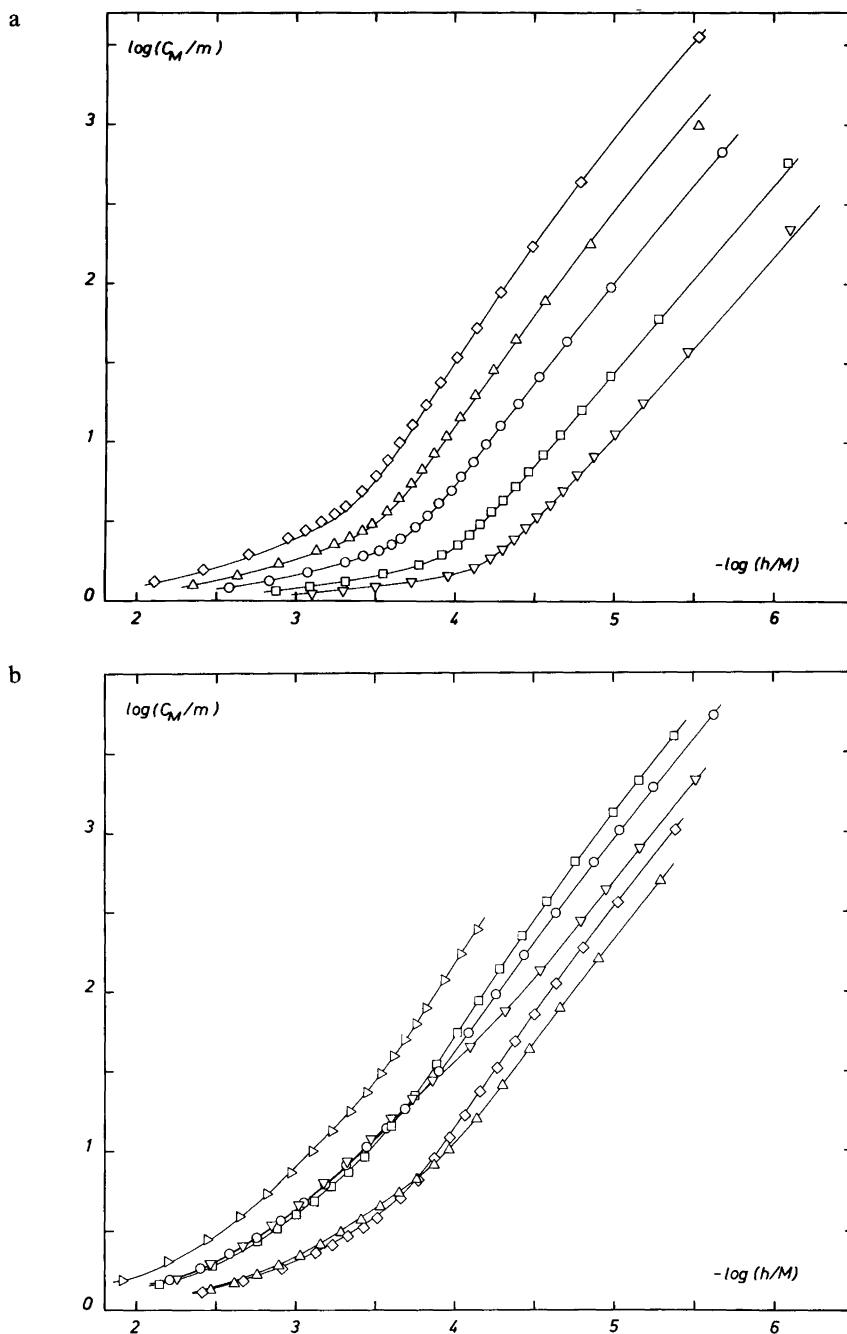
* Experimental data can be obtained from the author.

a

b

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 $C_M = C_T$, ($\bigtriangledown$) $C_M = C_T = 1$ mM; ($\square$) $C_M = C_T = 2$ mM; ($\bigcirc$) $C_M = C_T = 5$ 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; ($\bigtriangledown$) $C_M = 2$ mM, $C_T = 25$ mM; ($\Diamond$) $C_M = 5$ mM; $C_T = 10$ mM; ($\bigcirc$) $C_M = 5$ mM, $C_T = 25$ mM; ($\square$) $C_M = 10$ mM; $C_T = 25$ mM; ($\triangleright$) $C_M = 20$ mM, $C_T = 50$ mM.
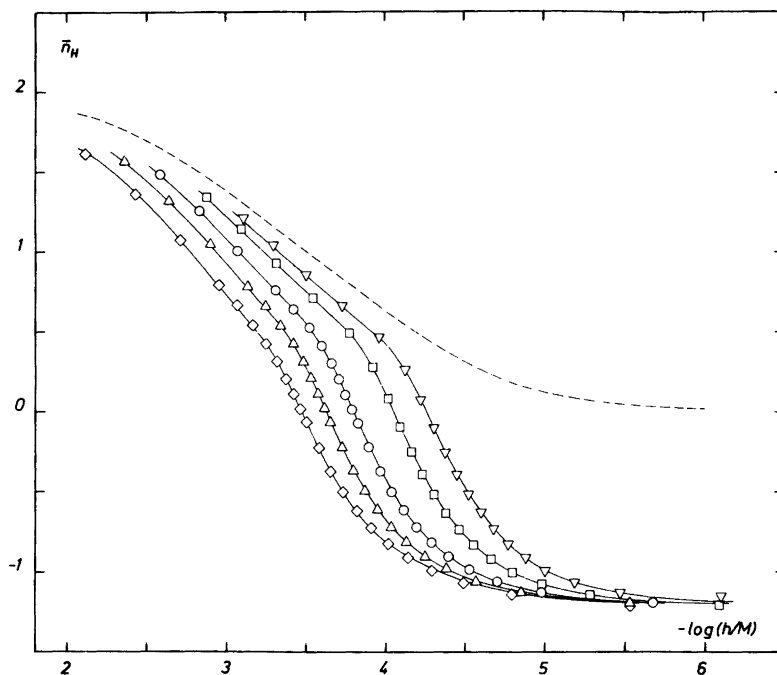
Fig. 3. $\bar{n}_H = (C_H - h)/C_T$ *versus* log h. The symbols are the same as in Fig. 2a. The dashed line represents the $\bar{n}_H$-function of *meso*-tartaric acid.

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,

$$K_{a1} = (1.314 \pm 0.006) \times 10^{-3} \text{ M}$$
$$K_{a2} = (7.52 \pm 0.02) \times 10^{-5} \text{ M}.$$

The constants are given with 99 % confidence intervals.

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.

Table 1. Stability constants of complexes Cu$_p$T$_q$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.

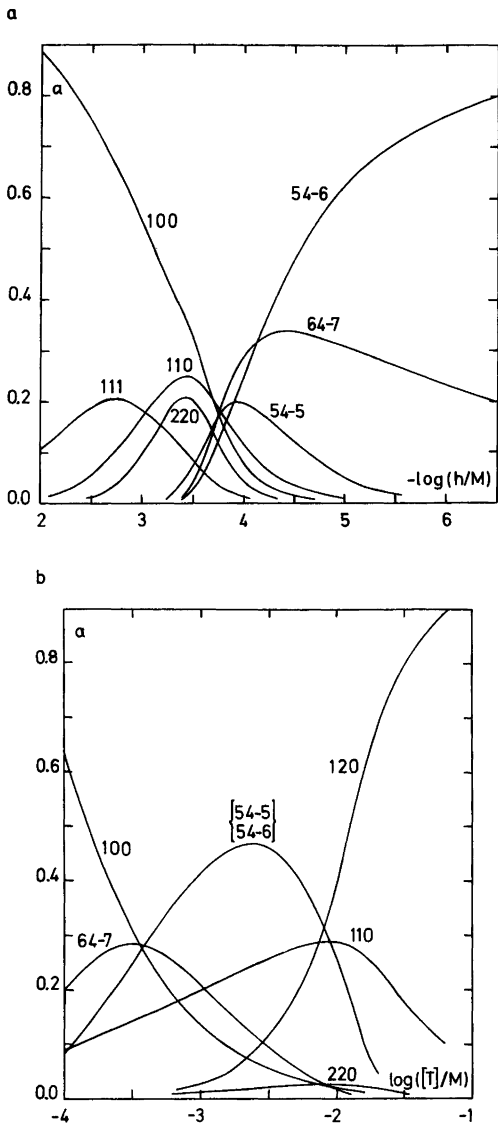| $p\ q\ r$	β_{pqr}		%
1 1 1	$(1.53 \pm 0.03) \times 10^6$	M^{-2}	40
1 1 0	$(1.41 \pm 0.05) \times 10^3$	M^{-1}	46
1 2 0	$(2.05 \pm 0.06) \times 10^5$	M^{-2}	92
2 2 0	$(3.3\ \pm 0.3)\ \times 10^8$	M^{-3}	33
5 4 -5	$(1.09 \pm 0.16) \times 10^4$	M^{-3}	22
5 4 -6	1.36 ± 0.08	M^{-2}	91
6 4 -7	$(1.64 \pm 0.13) \times 10^{-1}$	M^{-2}	52

Fig. 4. The relative distribution of copper amongst the different complexes. (a) *versus* log *h* when $C_M = C_T = 10$ mM; (b) *versus* log [T] when $C_M = 1$ mM and log $h = -4.5$.

Na$_2$T	NaHT	H$_2$T
16	−10	−17

As in the previous measurements, deviations of the sodium perchlorate concentration from one mol dm^{-3} and in some cases high tartrate(2−)

concentrations give the largest contributions to E_j.

The existence of several complexes have been tested. As in the case of copper +- 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 β_{110} and β_{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 +- 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 +- 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 +- 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

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 $Cu_5T_4H_{-6}$. From copper *meso*-tartrate solutions of a corresponding pH, solids containing the stoichiometric unit $Cu_{10}T_7H_{-12}$ have been prepared.[6] 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,[5] 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 $Cu_5T_4H_{-5}$ and $Cu_6T_4H_{-7}$ 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.* $Cu_4T_3H_{-4}$, 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.*,[2] 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_2T_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.[13] 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.

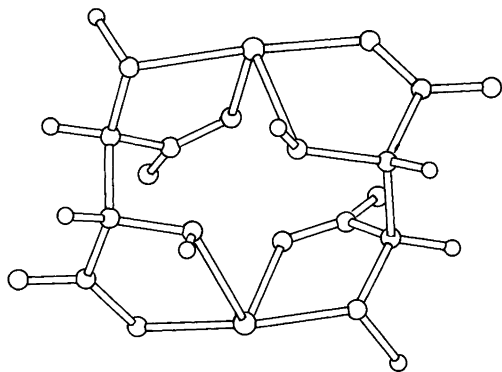| Reaction	K/M^{-1} (+)	K/M^{-1} (*meso*)	K_{meso}/K_+	No.
$T^{2-} + H^+ \rightleftarrows HT^-$	4.90×10^3	13.3×10^3	2.71	(1)
$HT^- + H^+ \rightleftarrows H_2T$	5.57×10^2	7.59×10^2	1.36	(2)
$Cu^{2+} + T^{2-} \rightleftarrows CuT$	4.3×10^2	14.1×10^2	3.31	(3)
$CuT + H^+ \rightleftarrows CuTH^+$	9.0×10^2	10.9×10^2	1.20	(4)
$HT^- + Cu^{2+} \rightleftarrows CuTH^+$	0.78×10^2	1.15×10^2	1.47	(5)
$CuT + T^{2+} \rightleftarrows CuT_2^{2-}$	0.57×10^2	1.45×10^2	2.54	(6)
$2\,CuT \rightleftarrows Cu_2T^2$	2.20×10^3	0.16×10^3	0.08	(7)

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 Cu_2T_2 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 very few reports on binuclear *meso*-tartrate complexes,[2,20,21] 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, $Cr_2T_2H_{-2}L_2$ and $NaCr_2T_2H_{-3}L_2$ (L = 1,10-phenanthroline or 2,2′-bipyridyl), to which a tartrate-bridged dimeric structure has been attributed for reasons based on spectrophotometric investigations.[21] Tapscott shows in his study of isomer stabilities of tartrate-bridged binuclear complexes[15] 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*-tatrate ion. The dimers, *i.e.* the ΔΔ- and ΛΛ-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,[15] though an inspection of molecular models makes it seem probable that these distances could be suf-

ficiently 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.[8]

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[3] 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 $Cu_5T_4H_{-6}$ may be conceived as the result of a polymerization principle of the same kind as that proposed for the formation of the octanuclear complex $Cu_8T_6H_{-10}$ in the copper +-tartrate system,[18,22] *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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