

ording to the F test, and calculated titration curves with and without the additional species were just barely discernible. For several individual titration curves the calculation even failed to converge to physically sound, i.e. positive, values for all stability constants with the complete model.

Quite to the contrary, the results from the spectrophotometric titrations were always highly significant according to the F test. As shown in Figure 6 for one of the experiments with the amide, visual inspection also very clearly suggests the necessity of the complete model. These conclusions are even further substantiated by the reasonable spectra that are calculated for these minor species. Thus, while in no way ad-

vocating the abolition of potentiometric titrations, we are strongly in favor of also including the spectrophotometric variety whenever this is feasible. It is to be expected that the latter method will prove to be essential for establishing the correct chemical model in many cases.

Acknowledgment. We thank Ciba-Geigy Inc., Basel, Switzerland, for the elemental analysis. This work was supported by the Swiss National Science Foundation (Grants 2.452-0.79 and 2.213-0.81).

Registry No. 1, 4432-87-5; 2, 3216-99-7; 3, 92009-86-4; 4, 92009-87-5; 5, 58214-71-4; 6, 92009-88-6.

Contribution from the Department of Chemistry,
Åbo Akademi, SF-20500 Åbo 50, Finland

Solution Studies of Systems with Polynuclear Complex Formation. 5. Copper(II) and Cadmium(II) D-(+)-Tartrate Systems

KJELL BLOMQVIST and EBBE R. STILL*

Received December 9, 1983

The complex formation in aqueous solution between copper(II) or cadmium(II), respectively, and D-(+)-tartrate has been studied in the pH range of 4-11 in 0.5 mol L⁻¹ KNO₃ at 25 °C. The emphasis is on the alkaline region with the ligand in excess and on the formation of polynuclear, especially binuclear, complex species. A potentiometric method using glass and metal ion selective electrodes has been applied. The experimental data indicate the formation of mononuclear, binuclear, and more highly polymerized species. The evaluated stability constants are presented in Table I. The stabilities of the proton complexes of the ligand have been evaluated in the same ionic medium. The existence of heteronuclear copper-cadmium D-tartrate complexes has been probed spectrophotometrically by the lack of pairwise electronic excitations in the UV region.

Introduction

Metal tartrate complexes in solution exhibit manifold possibilities in composition and structure. The ligand contains two carboxyl and two hydroxyl groups, and the complexing agent may be expected to form chelate rings including one metal ion as well as bridges between several metal ions.^{1,2}

We have an interest in polynuclear complex formation in hydroxy carboxylate systems, with a main emphasis on citrate systems.³⁻⁵ The degree of polynuclearity of metal chelates seems to be governed mainly by the ligand as exemplified by the dimeric species of formulas M₂H₋₁L⁰, M₂H₋₁L₂³⁻, and M₂H₋₂L₂⁴⁻ formed in the copper(II) and cadmium(II) citrate systems (H₃L = citric acid).^{3,4}

Crystal structure investigations of various basic metal tartrates show discrete dimeric units in the solid state.^{1,2} It seems reasonable to assume that the same type of dimeric units also will appear in solution.

The existence of dimeric species in copper(II), lead(II), and antimony(III) tartrate solutions was first suggested by Kahlenberg⁶ in 1895 from freezing point depression and emf data, but these findings were opposed by later investigations.⁷ In 1957, Lefebvre⁸ made a reinvestigation of the cupric tartrate system by means of combined pH and pCu (= -log [Cu²⁺]) measurements and found evidence for an octanuclear complex,

Cu₈H₋₁₀T₆⁶⁻, (H₂T = tartaric acid) in neutral solutions, whereas in alkaline solutions there is an equilibrium, Cu₃H₋₆T₃⁶⁻ + 3T²⁻ ⇌ 3CuH₋₂T₂⁴⁻, which is dependent on the excess of ligand. The existence of the complexes Cu₈H₋₁₀T₆⁶⁻ and CuH₋₂T₂⁴⁻ was confirmed in a later investigation.⁹

The copper(II) tartrate complexes in acid and neutral solutions have been thoroughly investigated by Bottari et al.^{10,11} and by Johansson.¹²⁻¹⁴ According to the potentiometric studies, mononuclear and binuclear complexes are formed in weakly acidic solutions. In the copper(II) D-tartrate system the dimer Cu₂T₂⁰ undergoes a stepwise ionization reaction to form Cu₂H₋₁T₂⁻ and Cu₂H₋₂T₂²⁻ (pK values are 4.40 and 4.56) when the pH value of the solution is increased to neutrality.¹³ At the same time, an additional condensation takes place, yielding an octanuclear complex, Cu₈H₋₁₀T₆⁶⁻.

Studies of complex formation in the cadmium(II)-tartrate system are scarce.^{15,16} In an investigation of the alkaline pH range, the ionization of the CdT⁰ complex to CdH₋₁T⁻ and CdH₋₂T²⁻ was determined (pK values are 8.59 and 10.28 at 33 °C). It was assumed that the complexes formed are mononuclear.

The aim of the present paper was to investigate the metal chelates formed with triply as well as quadruply ionized tartrate. The investigation was carried out for two different

- (1) Tapscott, R. E.; Belford, R. L.; Paul, I. C. *Coord. Chem. Rev.* **1969**, *4*, 323.
- (2) Tapscott, R. E. *Transition Met. Chem. (N.Y.)* **1982**, *8*, Chapter 3.
- (3) Still, E. R.; Wikberg, P. *Inorg. Chim. Acta* **1980**, *46*, 147, 153.
- (4) Grenthe, I.; Wikberg, P.; Still, E. R. *Inorg. Chim. Acta* **1984**, *91*, 25.
- (5) Blomqvist, K.; Still, E. R. *Inorg. Chim. Acta* **1984**, *82*, 141.
- (6) Kahlenberg, L. Z. *Phys. Chem. Stoichiomet. Verwandtschaftsl.* **1895**, *17*, 577.
- (7) Reihlen, H.; Hezel, E. *Liebigs Ann. Chem.* **1931**, *487*, 213.
- (8) Lefebvre, J. J. *Chim. Phys. Phys.-Chim. Biol.* **1957**, *54*, 601.

- (9) Petit-Ramel, M.; Blanc, C. M. *J. Inorg. Nucl. Chem.* **1972**, *34*, 241.
- (10) Bottari, E.; Liberti, A.; Rufolo, A. *Inorg. Chim. Acta* **1969**, *3*, 201.
- (11) Bottari, E.; Vicedomini, M. *J. Inorg. Nucl. Chem.* **1971**, *33*, 1463.
- (12) Johansson, L.; Larsson, R. *Chem. Scr.* **1975**, *7*, 67, 102.
- (13) Johansson, L. *Acta Chem. Scand., Ser. A* **1980**, *A34*, 495.
- (14) Johansson, L. Ph.D. Thesis, Lund, Sweden, 1979.
- (15) Sillén, L. G.; Martell, A. E. *Spec. Publ.—Chem. Soc.* **1964**, *No. 17*; **1972**, *No. 25*.
- (16) IUPAC, "Stability Constants of Metal Ion Complexes"; Pergamon Press: Oxford, 1979; Part B.

Table I. Stability Constants of Complexes $M_pH_qT_r$ Formed in Metal D(+)-Tartrate Solutions at 25 °C and Ionic Strength 0.5 mol L⁻¹ (KNO₃)^a

<i>p</i>	<i>q</i>	<i>r</i>	reaction	log β _{<i>pqr</i>} ± 3σ	
0	1	1	H ⁺ + T ²⁻ ⇌ HT ⁻	3.72 ± 0.01	
0	2	1	2H ⁺ + T ²⁻ ⇌ H ₂ T	6.36 ± 0.03	
				log β _{<i>pqr</i>} ± 3σ	
<i>p</i>	<i>q</i>	<i>r</i>	reaction	Cu ²⁺	Cd ²⁺
1	1	1	M ²⁺ + H ⁺ + T ²⁻ ⇌ MHT ⁺	5.5 ± 0.1	
1	0	1	M ²⁺ + T ²⁻ ⇌ MT ⁰	2.5 ± 0.1	1.6 ± 0.1
1	0	2	M ²⁺ + 2T ²⁻ ⇌ MT ₂ ²⁻		3.0 ± 0.2
2	0	2	2M ²⁺ + 2T ²⁻ ⇌ M ₂ T ₂ ⁰	8.7 ± 0.1	4.6 ± 0.2
2	-1	2	2M ²⁺ + 2T ²⁻ ⇌ M ₂ T ₂ ⁰	4.5 ± 0.1	
2	-2	2	M ₂ H ₋₁ T ₂ ⁻ + H ⁺	0.1 ± 0.1	-8.6 ± 0.2
2	-2	2	2M ²⁺ + 2T ²⁻ ⇌ M ₂ H ₋₂ T ₂ ²⁻ + 2H ⁺		
2	-3	2	2M ²⁺ + 2T ²⁻ ⇌ M ₂ H ₋₃ T ₂ ³⁻ + 3H ⁺	-7.0 ± 0.1	-18.3 ± 0.1
2	-4	2	2M ²⁺ + 2T ²⁻ ⇌ M ₂ H ₋₄ T ₂ ⁴⁻ + 4H ⁺	-17.3 ± 0.1	
8	-10	6	8M ²⁺ + 6T ₆ ⁶⁻ ⇌ M ₈ H ₋₁₀ T ₆ ⁶⁻ + 10H ⁺	-7.5 ± 0.2	

^a Stated errors are equal to 3 standard deviations. ^b The stability constant β_{*pqr*} for the general species M_{*p*}H_{*q*}T_{*r*}^{2*p*+*q*-2*r*} (M = Cu²⁺, Cd²⁺) is defined by the equation $pM^{2+} + qH^+ + rT^{2-} \rightleftharpoons M_pH_qT_r^{2p+q-2r}$.

cations with differing hydrolytic behavior in order to compare how closely the ionization of the metal tartrate follows the binary hydrolysis of the aquo cation. Our choices were Cu²⁺ and Cd²⁺, as for both metal ions reasonably well-functioning metal ion selective electrodes are available.

Experimental Section

All chemicals were of reagent grade and were used as received. The experiments were carried out at 25 ± 0.1 °C in solutions of ionic strength 0.5 mol L⁻¹ (KNO₃).

The potentiometric measurements were carried out with two Orion Model 801 pH/mV meters. A Radiometer metal ion selective SELECTRODE^R was used for the pCu and pCd measurements. The linearity of the electrode was tested by using various metal buffers and was found to be good. The E_M^0 value of the electrode was measured in the metal ion solution before the addition of the ligand and was checked after the titration. A glass electrode was used for the pH measurements, and the hydrogen ion concentration was calculated from the pH readings by using the relationship $-\log [H^+] = \text{pH} - 0.14$.

All the calculations were performed with the aid of a programmable pocket calculator of the type HP-41 CV.

Results

Tartaric acid forms weak complexes with potassium ions, and the protonation constants were determined in the same ionic medium. The results are given in Table I.

The data required to analyze the equilibria in a system containing polynuclear species must involve variables measured over a wide concentration range. We have chosen to use combined pH and pM measurements as variables, since the determination of the free metal ion concentration provides a convenient method of studying the formation of polynuclear metal complexes.^{3,17}

The evaluation of the stability constants follows the theory outlined in an earlier article.³ A short presentation is given below: Let us assume that the predominant species in solution are dimers of the composition M₂H_{-*i*}T₂^{*i*-}; i.e., a stepwise ionization of the dimer is allowed. The free metal ion concentration in a solution containing an excess of the ligand will then

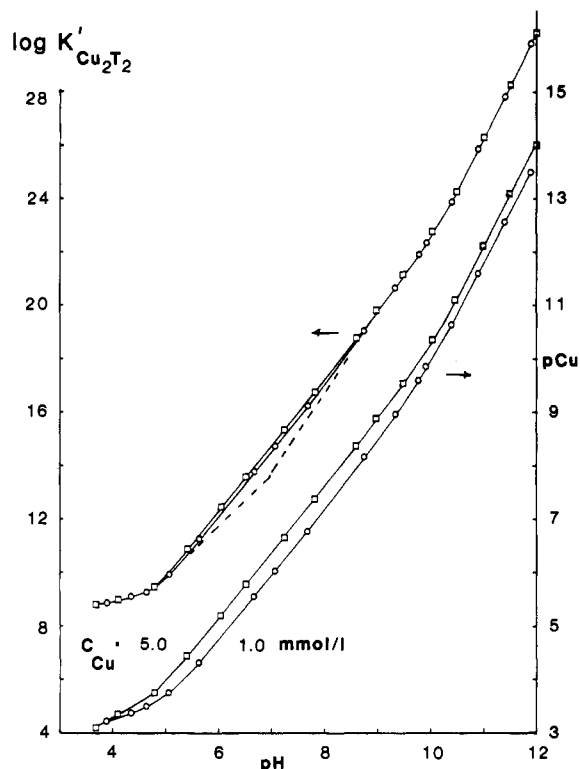


Figure 1. Lower curves: Recorded pCu values vs. pH for solutions with a C_{Cu}:C_T ratio of 1:2, C_{Cu} = 5.0 and 1.0 mmol/L, respectively. Upper curves: log K'_{Cu₂T₂} as a function of pH.

be determined by the conditional constant (all charges are omitted)

$$K^{2M,2T'}_{(M_2T_2)'} = \frac{[(M_2T_2)']}{[M]^2[T']^2} = K^{2M,2T}_{M_2T_2} \alpha_{M_2T_2(H,OH)} / (\alpha_{T(H)})^2 \quad (1)$$

where

$$[(M_2T_2)'] = \sum_i [M_2H_{-i}T_2] \quad (2)$$

$$[T'] = \sum_i [H_iT] \quad (3)$$

$\alpha_{T(H)}$ and $\alpha_{M_2T_2(H,OH)}$ denote distribution or α coefficients and have their usual definitions:

$$\alpha_{T(H)} = [T']/[T] = 1 + [H]K^{HT} + [H]^2K^{2HT} \quad (4)$$

$$\alpha_{M_2T_2(H,OH)} = [(M_2T_2)']/[M_2T_2] \quad (5)$$

Substitution of the mass balance equations (*C* denotes total concentration)

$$[(M_2T_2)'] = \frac{1}{2}(C_M - [M]) \quad (6)$$

$$[T'] = C_T - C_M + [M] \quad (7)$$

into eq 1 yields

$$\log K'_{M_2T_2} = \log K^{2M,2T'}_{M_2T_2} + \log \alpha_{M_2T_2} = 2\text{pM} + 2 \log \alpha_T + \log \frac{(C_M - [M])/2}{(C_T - C_M + [M])^2} \quad (8)$$

Equation 8 shows that a dilution experiment can be used to test the existence of dimeric species in solution. A differentiation of the equation yields for $[M] \ll C_M$

$$\text{dpM}/\text{dp}C_M = -1/2 \quad (9)$$

More generally we obtain³ for the polymeric species M_{*m*}T_{*i*}

$$\text{dpM}/\text{dp}C_M = -(i-1)/m \quad (10)$$

In both cases we assume a constant pH value and a fixed C_M:C_T ratio.

(17) Rossotti, F. J. C.; Rossotti, H. "The Determination of Stability Constants"; McGraw-Hill: New York, 1961.

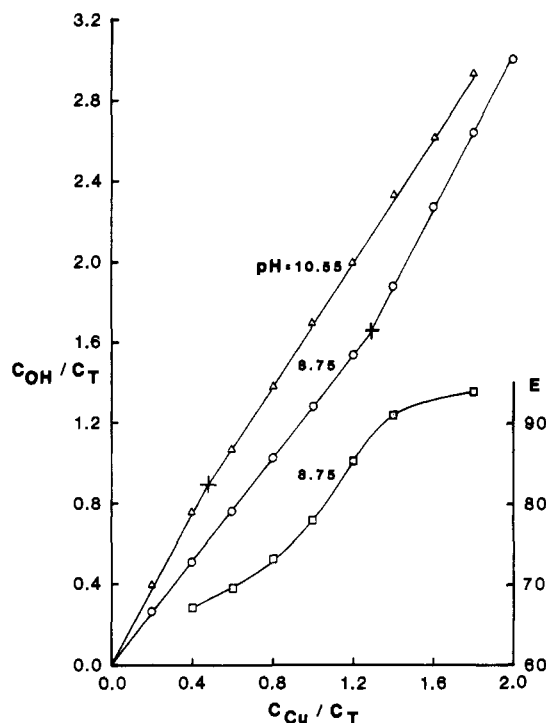


Figure 2. Potentiometric titration of a 10 mmol/L D-tartrate solution with a 200 mmol/L cupric salt solution. The pH was kept constant at 8.75 and 10.55, respectively, by addition of a 200 mmol/L NaOH solution. The upper half of the figure shows the consumption of base as a function of added amount of copper, whereas the lower half gives recorded emf values of the ion-selective electrode.

If mononuclear complexes coexist in solution, we have to introduce additional terms in the mass balance equations.

In the copper(II) D-tartrate system the solutions were mixed in the ratio $C_{Cu}:C_T = 1:2$. The results are given in Figure 1 as a plot of pCu vs. pH. The curves have a spacing, $dpCu/dpC_{Cu} = -1/2$, indicating the formation of a dimer, and a slope that is a function of pH. The calculated value of $\log K'_{M_2T_2}$ (eq 8) is also given as a function of pH.

A more elaborate analysis of the plot in Figure 1 shows the following features: In acid solutions with a pH value of 3–4 we have an equilibrium between the dimer $Cu_2T_2^0$ and the mononuclear complexes CuT^0 and $CuHT^+$ with the dimer predominating. When the pH value of the solution exceeds 4, the dimer starts to ionize to $Cu_2H_2T_2^-$ and $Cu_2H_2T_2^{2-}$. In the pH 5–9 region a further polymerization is taking place. The slopes of the plots of $\log K'_{Cu_2T_2}$ vs. pH (the plots shown for the two solutions do not coincide in this pH region as $dpCu/dpC_{Cu}$ amounts to -0.55) indicate a complex with a $Cu:OH$ ratio of 1:1.25. At pH values exceeding 9 the plots coincide again, yielding evidence for a continued ionization to $Cu_2H_3T_2^{3-}$ and $Cu_2H_4T_2^{4-}$.

The composition of the polymeric species was checked by a titration at a constant pH value of 8.75. The breakpoint at $C_{Cu}:C_{OH}:C_T = 4:5:3$ shown in Figure 2 indicates that the complex is either tetranuclear $Cu_4H_5T_3^{3-}$ or the octanuclear $Cu_8H_{10}T_6^{6-}$ reported earlier.^{8,13} According to eq 10 the tetranuclear complex will have a spacing of -0.50 , whereas the value for the octanuclear one will be -0.625 . The obtained result of -0.55 gives indication for the octanuclear one. In our rather dilute solutions considerable amounts of the dimers $Cu_2H_2T_2^{2-}$ and $Cu_2H_3T_2^{3-}$ are in equilibrium with the higher polymer. In the model used to explain our experimental data we have introduced only the complex $Cu_8H_{10}T_6^{6-}$ as a better fit is obtained with the octanuclear complex than with the tetranuclear one.

Figure 2 shows also a pH-static titration performed at pH

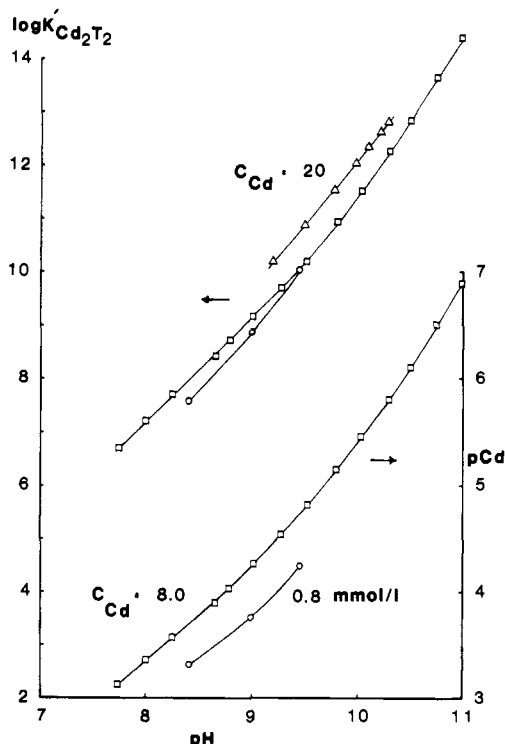


Figure 3. Lower curves: Recorded pCd values of solutions with a $C_{Cd}:C_T$ ratio of 1:5 as a function of pH. $C_{Cd} = 8.0$ and 0.8 mmol/L, respectively. Upper curves: $\log K'_{Cd_2T_2}$ vs. pH. Included is also a titration with $C_{Cd} = 20$ mmol/L and $C_T = 40$ mmol/L.

10.55. The breakpoint at $C_{Cu}:C_T = 0.5$ and $C_{OH}:C_T = 0.95$ indicates the complex $CuH_2T_2^{4-}$ reported earlier.^{8,9} The base consumption at $C_{Cu}:C_T = 1.0$ is $C_{OH}:C_T = 1.75$, which is consistent with the equilibrium $Cu_2H_3T_2^{3-} \rightleftharpoons Cu_2H_4T_2^{4-} + H^+$.

The pH-static titrations shown in Figure 2 can be carried out to a $C_{Cu}:C_T$ ratio of ca. 2.0 before the onset of cupric hydroxide precipitation. The result indicates a complex that may be formulated $(Cu_2H_3T)_n^{n-}$ with n probably greater than 1.

The stabilities of the mononuclear complexes CuT^0 and $CuHT^+$ have been evaluated from data obtained in the acid pH region for solutions with a low concentration of cupric ions. In the final refinement of the constants of the dimeric species account has to be taken of the mononuclear complexes in the acid pH region and the octanuclear complex in neutral solutions.

The obtained stability constants together with the errors at 95% confidence level are presented in Table I.

The composition of the complexes formed in the cadmium D-tartrate system should be very similar to those found in the corresponding cupric system. The ionic radius of the Cd^{2+} ion is about 50% bigger than the radius of the Cu^{2+} ion, and, as a consequence, we can expect a lower stability of the cadmium complexes.

The solubility of the cadmium tartrates in neutral solutions is rather low, and a fairly narrow concentration range with the ligand in excess is accessible to experimental measurements. The Cd-selective electrode (used in emf titrations of neutral solutions) may be prone to systematic errors in the E^0 determination, and the model with the complexes CdT^0 , $Cd_2T_2^0$, and CdT_2^{2-} should be considered tentative.

Figure 3 shows the formation of dimeric species in alkaline solutions. At low concentrations of metal ion and ligand, the dimer $Cd_2H_2T_2^{2-}$ seems to be partly dissociated into mononuclear species. At higher concentrations ($C_{Cd} = 20$ mmol/L, $C_T = 40$ mmol/L) the plot gives some indication of a further

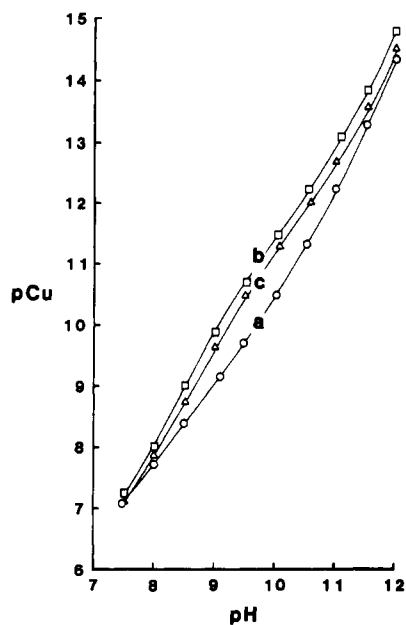


Figure 4. Influence of ammonia on recorded pCu values vs. pH of solutions. Total concentrations in mmol/L: (a) $C_{Cu} = 5.0$, $C_T = 10.0$, $C_{NH_3} = 0.0$; (b) $C_{Cu} = 5.0$, $C_T = 10.0$, $C_{NH_3} = 50.0$; (c) $C_{Cu} = 1.0$, $C_T = 2.0$, $C_{NH_3} = 50.0$.

condensation complex with a Cd:H ratio of 1:-1.25, which may correspond to the octanuclear cupric complex.

Potentiometric titrations at constant pH value (carried out as a titration of the ligand in 10 mmol/L concentration with a cadmium ion solution and measuring the consumption of base) gave the following values of the consumption of base per cadmium ion:

pH	8.0	9.0	10.0	10.7
mol of OH^- /mol of Cd^{2+}	0.92	1.04	1.18	1.36

The results are in agreement with Figure 3. The obtained stability constants are presented in Table I.

Crystal structures of binuclear D-tartrates show a rather open coordination sphere of the cations, and the remaining coordination positions may easily be filled by bidentate ligands such as 2,2'-bipyridyl or 1,10-phenanthroline forming a 2:2:2 complex.¹⁸ We want to report some preliminary titration results indicating ternary cupric-tartrate-ammonia complexes in solution. Figure 4 shows the combined pCu-pH data obtained for solutions with constant concentration of ammonia (curves b and c). The deviation from the titration plot of a solution with no ammonia (curve a) and the spacing occurring on dilution can be interpreted in terms of a polymeric ternary complex. The response of the cupric-selective electrode (containing Ag_2S and CuS) is, however, not well characterized in solutions containing ammonia, and the system awaits a closer spectroscopic investigation.

Discussion

The aim of the present work was to clarify the composition of the polymeric cupric D-tartrate complexes formed in neutral and weakly alkaline solutions. Our interest was mainly focused on solutions containing a moderate excess of the ligand, but some remarks will be made for solutions containing an excess of metal ion. In addition we wanted to carry out the investigation for the corresponding cadmium system as the Cd^{2+} ion has a considerably greater ionic radius and hence a smaller polarizing power than that of the Cu^{2+} ion.

Table II. Compilation of Proposed Cupric D-Tartrate Complexes and Their Stability Constants (Given as $\log \beta$ Values)

ref	7	9, 10	12, 13	this work
temp, °C	20	25	25	25
ionic strength	1.0	1.0	1.0	0.5
electrolyte	$NaClO_4$	$NaClO_4$	$NaClO_4$	KNO_3
pH range		3.7-7	2-6	4-12
$CuHT^+$		5.45 ± 0.05	5.58 ± 0.01	5.5 ± 0.1
CuT^0	3.2	2.70 ± 0.03	2.63 ± 0.03	2.5 ± 0.1
$CuH_{-1}T^-$		-2.6 ± 0.3		
CuT_2^{3-}		4.00 ± 0.03	4.38 ± 0.02	
$CuH_{-2}T_2^{4-}$	-6.8			exists
$Cu_2T_2^0$		8.58 ± 0.05	8.60 ± 0.01	8.7 ± 0.1
$Cu_2H_{-1}T_2^-$			4.20 ± 0.02	4.5 ± 0.1
$Cu_2H_{-2}T_2^{2-}$		-0.24 ± 0.20	-0.35 ± 0.03	0.1 ± 0.1
$Cu_2H_{-3}T_2^{3-}$		-7		-7.0 ± 0.1
$Cu_2H_{-4}T_2^{4-}$				-17.3 ± 0.1
$Cu_3H_{-6}T_3^{6-}$	-23.7			
$Cu_8H_{-10}T_3^{6-}$	-6.9		-7.38 ± 0.05	-7.5 ± 0.2
$Cu_6H_{-7}T_4^{3-}$			-5.52 ± 0.05	

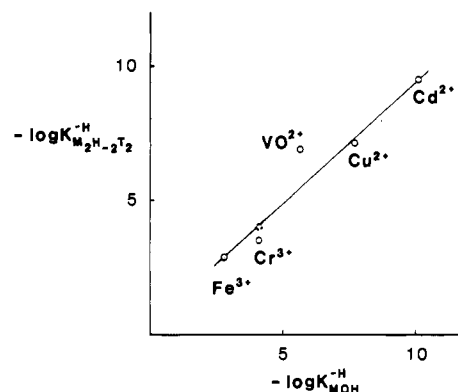


Figure 5. The third ionization constant of the binuclear tartrate complexes as a function of the first binary hydrolysis step. The equilibrium constants are defined in the text.

Equilibrium studies of metal tartrates in alkaline solutions are scarce. Information obtained from spectroscopic¹⁹⁻²¹ and solid-state^{1,2,22} studies points to the existence of dimeric species with a 1:1 metal:tartrate ratio in solution. Our potentiometric studies can be interpreted in terms of dimeric species of the type $Cu_2H_{-i}T_2^{i-}$ ($i = 0-4$). A compilation of results obtained in more recent investigations^{8,11,13} is given in Table II. A comparison shows the general consensus about the composition and stability of the complexes formed in weakly acid and neutral solutions, whereas the situation is more uncertain in alkaline solutions.

The dimeric tartrate complexes $M_2T_2^{(4-2n)-}$ ($n =$ charge of the cation) can be considered as tetrabasic acids, and the alcoholic groups of the ligand will be deprotonated with increasing pH of the solution. An example is the cupric D-tartrate system with the acidity constants 4.2, 4.4, 7.1, and 10.3 (see Table I). The differences in the ionization constants can be attributed to the polarizing power of the cation and to intramolecular as well as intermolecular hydrogen bonding. The influences on the acidity caused by a strong intramolecular hydrogen bond²³ and by intermolecular hydrogen bonds¹⁴ have been pointed out earlier. We want to stress that the polarizing power of the cation is operative in the ionization of the tartrate complexes. The effect of the cation can be illustrated by a comparison of the first hydrolysis step of the cation

(19) Chasteen, N. D.; Belford, R. L. *Inorg. Chem.* **1970**, *9*, 169.

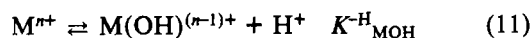
(20) Smith, T. D.; Pilbrow, J. R. *Coord. Chem. Rev.* **1974**, *13*, 173.

(21) Treptow, R. S. *Inorg. Chem.* **1970**, *9*, 2583.

(22) Prout, C. K.; Carruthers, J. R.; Rossotti, F. J. C. *J. Chem. Soc. A* **1971**, 3336.

(23) Robbins, G. L.; Tapscott, R. E. *Inorg. Chem.* **1976**, *15*, 154.

(18) Ortega, R. B.; Tapscott, R. E.; Campana, C. F. *Inorg. Chem.* **1982**, *21*, 2517.



and the third ionization step of the metal tartrate complexes

$$M_2H_{-2}T_2^{(6-2n)-} \rightleftharpoons M_2H_{-3}T_2^{(7-2n)-} + H^+ \quad K^{-H}_{M_2H_{-2}T_2} \quad (12)$$

The result of the comparison is given in Figure 5, where literature data have been used for the binary hydrolysis constants,²⁴ as well as for the D-tartrate complexes of ferric ion,²⁵ chromic ion²³ [a study of (phen)₂Cr₂H₋₂T₂ (phen = *o*-phenanthroline and H₂T = mesotartaric acid) and corrected for the influence of the ternary ligand], and vanadyl ion.²⁶ Figure 5 shows a good correlation between the two ionization constants, with the vanadyl system being an exception. Equilibrium studies²⁶ show that the species (VO)₂H₋₃T₂³⁻ is present to only a small extent in any pH region due to an immediate further ionization. The absence of this species in the vanadyl D-tartrate system may be due to the well-known trans effect operative in oxocation systems and is an indirect indication of the intramolecular hydrogen bond being formed in other metal tartrate systems.

We wanted to confirm the existence of polymerized species in alkaline solutions by a spectroscopic method. Our choice was to show the existence of mixed Cu(II)/Cd(II) D-tartrate species by difference UV spectroscopy⁵ (with the technique of that ref). For polymerized complexes there is the possibility of spin-spin interactions giving rise to simultaneous pair electronic excitations²⁷ due to an exchange-dependent mechanism.²⁸ In heteronuclear tartrate complexes we may expect geometrical distortions arising from the different coordination geometries of the cations (such a deformation has been observed in mixed As(III)/Sb(III) tartrate complexes²⁹). Difference spectra were recorded for tartrate solutions of pH \approx 9.05 containing the metal ions in differing Cu:Cd ratios. A sharp absorption peak at ca. 319 nm is observed with a de-

creased absorption for the mixed complex. A Job plot failed to give conclusive results regarding the composition of the heteronuclear complex(es) present at this pH value but gave strong evidence that such species are formed in solution and that polynuclear complexes are present in at least one of the binary metal tartrate systems.

The polynuclear complexes formed in alkaline solutions with an excess of cupric ions and denoted as (Cu₂H₋₃T)_nⁿ⁻ seem to have a rather open structure so that a stepwise addition of cupric ions is possible. Figure 2 shows good metal buffer capacity of the solution for C_{Cu}:C_T ratios close to 2. Our conclusion is that the value of *n* will be greater than 1.

In this context we want to refer to the measurements performed by Johansson^{12,14} at pH 4.40 including solutions with an excess of cupric ions. Both potentiometric and CD data are best described in terms of a predominating complex Cu₈H₋₈T₄. The CD spectrum of this complex resembles that of Cu₂H₋₃T⁻ reported²¹ at pH 9.8, whereas the spectrum of Cu₈H₋₁₀T₆⁶⁻ differs considerably.¹⁴ A possibility is that the Cu₈H₋₈T₄ complex at pH 4.40 will ionize into a complex Cu₈H₋₁₂T₄⁴⁻ at higher pH values. The CD spectra show that the structures of Cu₈H₋₁₀T₆⁶⁻ and (Cu₂H₋₃T)_nⁿ⁻ must be quite different.

The Cu₈H₋₁₀T₆⁶⁻ complex formed in neutral solutions is of considerable stability. The potential jump shown in Figure 2 indicates that the octamer is a predominating species over a wide range of tartrate concentrations, and a rather compact structure with respect to further addition of tartrate ions may be suggested. The octamer is formed in the same pH range as Cu₂H₋₂T₂²⁻ and Cu₂H₋₃T₂³⁻. The deprotonated alcoholic groups of the ligand may promote the polymerization reaction by acting as bridges between cupric ions. From the composition of the involved species we will, however, suggest that the octamer in addition will contain OH⁻ bridges.

The structure of the cage formed by the cupric ions in the octameric complex is of crystallographic interest, as is the use of this special topology in other chemical reactions.

Acknowledgment. We thank Dr. Lennart Johansson, Lund, Sweden, for valuable comments on the paper. This work is part of a program financially supported by the Academy of Finland.

(24) Baes, C. F., Jr.; Mesmer, R. E. "The Hydrolysis of Cations"; Wiley-Interscience: New York, 1976.

(25) Timberlake, C. F. *J. Chem. Soc.* **1964**, 1229.

(26) Pettit, L. D.; Swash, J. L. M. *J. Chem. Soc., Dalton Trans.* **1978**, 286.

(27) Schuger, H. J.; Rossman, G. R.; Barraclough, C. G.; Gray, H. B. *J. Am. Chem. Soc.* **1972**, *94*, 2683.

(28) Lohr, L. L., Jr. *Coord. Chem. Rev.* **1972**, *8*, 241.

(29) Marcovich, D.; Tapscott, R. E. *J. Am. Chem. Soc.* **1980**, *102*, 5712.