[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MICHIGAN]

Citrate Complexes of Copper in Acid Solutions

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A method for identifying and obtaining instability constants of copper citrate coördination compounds in acid solution is described. The nature of the compound formed is determined primarily by the citrate-copper ratio and in a secondary manner by the age of the solution. The initial compound formed is $[\mathrm{Cu(HCit)(H_2Cit)^-}]$. If the citrate concentration is at least 30 times the copper(II) concentration, this compound is stable, but if the citrate–copper ratio is less than 30 the above complex adds copper(II) ion and liberates hydrogen ion. The addition of the cupric ion is a relatively slow process in solutions of low total copper concentration. The ultimate product appearing in solutions of very *low citrate–copper ratio* [1 to 2] is the insoluble solid $\mathrm{Cu_2[C_6H_4O_7.]}$

The following instability constants in solutions of ionic strength 3.0 have been obtained at 25°. For the process: $\mathrm{H^+ + [Cu(HCit)(H_2Cit)]^- \leftrightarrows Cu^{++} + 2H_2Cit^-}$, $K_3 = [\mathrm{Cu^{++}}][\mathrm{H_2Cit^-}]^2/[\mathrm{Cu(HCit)(H_2Cit)}][\mathrm{H^+}] = 1$. For the process at constant pH: $\mathrm{[Cu(HCit)(H_2Cit)]^- \leftrightarrows Cu^{++} + HCit^{=} + H_2Cit^-}$, $K_2 = [\mathrm{Cu^{++}}][[\mathrm{HCit^{=}}][\mathrm{HCit^-}]/[\mathrm{Cu(HCit)(H_2Cit)^-}] = 10^{-4}$. An *estimate* of the *thermodynamic value* at infinite dilution gives about 5×10^{-3} for K_3 and about 5×10^{-8} for K_2.

In the past metal–citrate coördination compounds have been formulated with the citrate ion ($\mathrm{Cit^{-3}}$) as the coördinated ligand. More recently the possibility of complex formation by mono or dihydrogen citrate ions in acid solution has been considered, but the problem has not been carefully examined. Ketelle, Boyd, Schubert, Richter and other members of the Oak Ridge Group who used acid citrate solutions as an elutriant for ion exchange columns in rare earth separations suggested that the dihydrogen and monohydrogen citrate anions might form coördination compounds with the rare earths.[1] In 1950 Meites[2] studied the polarography of solutions containing cupric and citrate ions at different pH values and interpreted the waves as indicating formation of copper complexes by both the mono and dihydrogen citrate ions; however, his data did not yield unambiguous results for the formulas of the compounds or even the identity of the coördinating groups, despite the fact that instability constants for complexes of unspecified composition were reported.

The present investigation resulted from an attempt to study the citrate–cupric ion–resin system, and had as its purpose identification of the coördination compounds formed between copper and citrate systems in acid solution and determination of their stability constants. The study was conducted at a constant pH value of 2.9 which represents the pH of potassium dihydrogen citrate in a magnesium sulfate salt solution of ionic strength 3.0[3] (see data for solutions 1a, 4a, 7a, 10a, Table II). Using the constants of Bates and Pinching[4] for citric acid, one calculates that a solution of $\mathrm{KH_2Cit}$ in water or a solution of a salt such as $\mathrm{MgSO_4}$ will contain 12% $\mathrm{H_3Cit}$, 76% $\mathrm{H_2Cit^-}$, 12% $\mathrm{HCit^{=}}$, and a negligible percentage of $\mathrm{Cit^{\equiv}}$. This unusual distribution results because the pK_2 for citric acid lies midway between the values for pK_1 and pK_3. If then a solution of cupric ion at the same pH as the $\mathrm{KH_2Cit}$ solution is added to the system, the identity of the complexing ligand may be established by the change in pH which results from complex formation. If $\mathrm{H_2Cit^-}$ is the coördinating species, no change in pH should result on addition of copper(II) ion; if $\mathrm{HCit^{=}}$ or $\mathrm{Cit^{\equiv}}$ is the coördinating species, the pH should drop as a result of coördination; and if $\mathrm{H_3Cit}$ is the coördinating group the pH should rise.

The above facts can be represented in more general terms by the equation

$$\mathrm{Cu^{++}} + n(\mathrm{H_2Cit^-}) \xrightleftharpoons{} \mathrm{Cu(H\bar{a}Cit)}_n^{n(\bar{a}-3)+2} + n\,(2-\bar{a})\mathrm{H^+} \qquad (1)$$

Because the concentrations of $\mathrm{H_3Cit}$ and $\mathrm{HCit^{=}}$ are equal in solutions of $\mathrm{KH_2Cit}$, the dihydrogen citrate ion used in equation 1 is replaced by the equilibrium shift without changing the ratio $\mathrm{H_3Cit/HCit^{=}}$ *i.e.*

$$\mathrm{H_3Cit + HCit^{=}} \xrightleftharpoons{} \mathrm{2H_2Cit^-} \qquad (2)$$

In equation 1, $\bar{a}$ equals the average number of hydrogen ions per coördinated citrate, and n equals the number of citrate groups coördinated per cupric ion. Then let

$[\mathrm{T{\cdot}Cu^{++}}]$ = concn. total copper added
$[\mathrm{T{\cdot}Cit}]$ = concn. total citrate added (all forms)
$[\mathrm{Cu^{++}}]$, $[\mathrm{H_2Cit^-}]$, $[\mathrm{HCit^{=}}]$, $[\mathrm{Cit^{\equiv}}]$, $[\mathrm{H_3Cit}]$ = respective concentrations of each species in system
$[\mathrm{KOH}]$ = milliequivalents of $\mathrm{OH^-}$ needed to bring 1 cc. of the system back to the original pH after adding cupric ion
$\bar{Z}$ = average number of hydrogens per citrate in citrate solutions at this pH ($\bar{Z}$ = very close to 2 for $\mathrm{KH_2Cit}$ solutions at pH of investigation)

The concentration of uncomplexed cupric ion can be determined in the solution by means of the copper electrode; pH can be followed with a glass electrode; and the value of KOH can be determined by titration with standard potassium hydroxide solution. Then

copper coördinated with citrate = $[\mathrm{T{\cdot}Cu^{++}}] - [\mathrm{Cu^{++}}]$
citrate coördinated with copper = $n([\mathrm{T{\cdot}Cu^{++}}] - [\mathrm{Cu^{++}}])$
free citrate = $[\mathrm{T{\cdot}Cit.}] - n([\mathrm{T{\cdot}Cu^{++}}] - [\mathrm{Cu^{++}}])$
hydrogen ion in complex = $\bar{a}n([\mathrm{T{\cdot}Cu^{++}}] - [\mathrm{Cu^{++}}])$
hydrogen ion on free citrate = $\bar{Z}([\mathrm{T{\cdot}Cit}] - n\{[\mathrm{T{\cdot}Cu^{++}}] - [\mathrm{Cu^{++}}]\})$
+
total hydrogen ion before addition $\mathrm{Cu^{++}}$ = $\bar{Z}[\mathrm{T{\cdot}Cit}] + [\mathrm{H^+}]$

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(1) B. H. Ketelle and G. E. Boyd, THIS JOURNAL, **69**, 2800 (1947).

(2) L. Meites, *ibid.*, **72**, 180 (1950).

(3) In a previous investigation of the effects of pH on the polarographic reduction of copper citrate complexes, Meites[2] neglected the effects of ionic strength in calculating solution composition from measured pH values. He calculated that a 0.5 M solution of citrate at a pH of 4.0 should contain 0.38 M $\mathrm{H_2Cit^-}$ ion. According to similar calculations a pH of 3.95 and an $\mathrm{H_2Cit^-}$ concn. of 0.38 M should be found in a 0.5 M $\mathrm{KH_2Cit}$ solution. The magnitude of the error due to neglecting activity effects is indicated by the fact that the pH of a 0.5 M $\mathrm{KH_2Cit}$ solution is actually 3.51 instead of 3.95; that of a 0.05 M $\mathrm{KH_2Cit}$ is 3.71 and the pH of all $\mathrm{KH_2Cit}$ solutions used in this investigation at a constant ionic strength of 3.0 is very close to 2.92 (Table II 1a, 4a, 7a, 10a).

(4) R. G. Bates and G. D. Pinching, THIS JOURNAL, **71**, 1274 (1949).

After a copper has been added and the *p*H has been restored to the original value by the addition of potassium hydroxide, the hydrogen balance is given by the equation

$$\text{Total H}^+ = [\text{H}^+ \text{ on free citrate}] + [\text{H}^+ \text{ in complex}] + [\text{H}^+ \text{ neutralized by KOH}] + [\text{H}^+] \quad (3)$$

or

$$\bar{Z}[\text{T·Cit}] + [\text{H}^+] = \bar{Z}([\text{T·Cit}] - n\{[\text{T·Cu}^{++}] - [\text{Cu}^{++}]\}) + \bar{a}n\{[\text{T·Cu}^{++}] - [\text{Cu}^{++}]\} + [\text{KOH}] + [\text{H}^+] \quad (4)$$

This may be solved for $\bar{a}$, the average number of H^+ per coördinated citrate, to give

$$\bar{a} = \frac{1}{n}\left[n\bar{Z} - \frac{[\text{KOH}]}{[\text{TCu}^{++}] - [\text{Cu}^{++}]}\right] \quad (5)$$

Since $\bar{Z}$ is known from the composition of the solution (*i.e.*, is very close to 2 in this investigation) and all terms other than $\bar{a}$ and n can be measured experimentally, $\bar{a}$ can be determined in terms of n, the number of citrate groups per cupric ion.

The n value may be determined as the slope of a straight line plot of log [Cu^{++}]/[Cu complex] against the log [free citrate]. The n value used to calculate the free citrate should be the n which appears as the slope at the point in question and is obtained by a series of approximations. The intercept of the line is equal to log K_1 where K_1 is defined as

$$K_1 = \frac{[\text{Cu}^{++}][\text{Citrate}]^n}{[\text{Cu}(\text{H}_{\bar{a}}\text{Cit})_n^{n(\bar{a}-3)+2}]} \quad (6)$$

Since concentrations have been measured experimentally, the true thermodynamic equilibrium constant would require suitable correction for activity coefficients. When n is known, $\bar{a}$ may be determined to establish the complete identity of the coordination compound.

Experimental

(a) Determination of $\bar{a}$, the Average Number of Hydrogen Ions per Citrate in the Coördination Compound.—Seventy-five cc. of 1 *M* KH_2Cit (prepared from reagent grade citric acid and potassium citrate) was diluted to 250 cc. with 1 *M* $MgSO_4$ [ionic strength of final solution = 3.1]. The *p*H of the solution was measured with a Beckman glass electrode. The *p*H of a 1 *M* $CuSO_4$ solution was then carefully adjusted with H_2SO_4 to give the same *p*H as the citrate solution. Two copper electrodes, prepared by depositing Cu on platinum flags (1-cm. square), were inserted in the citrate solution, and an external half-cell Hg/Hg_2SO_4/1 *M* $MgSO_4$ was connected to the system by means of a salt bridge (1 *M* $MgSO_4$).

A mechanical stirrer was placed in the system and the entire apparatus was thermostated at 25°. Increments of the one molar $CuSO_4$ solution were then added, with constant stirring, to the citrate solution; a drop in *p*H was noted; then the amount of standard KOH necessary to bring the *p*H back to the *original value* was added. When the *p*H was restored, the cupric ion concentration was determined by means of the copper electrodes. To determine cupric ion concentration under these conditions, a calibration curve was made by adding 1 *M* $CuSO_4$ to 200 cc. of 1 *M* $MgSO_4$ and then determining the potential of the cell Cu/Cu^{++}/1 *M* $MgSO_4/Hg_2SO_4/Hg$. A plot of the log of the copper concentration against the potential gave a straight line of slope 0.029 and intercept 0.353. The free Cu^{++} concentration could then be calculated from the equation

$$\log [\text{Cu}^{++}] = -\left(\frac{E - 0.353}{0.029}\right)$$

The data obtained were then used in equation 2 to calculate $\bar{a}$ in terms of n. Representative data are compiled in Table I. The values of the ratio [KOH]/[Cu complex] appear to be very close to 1 on the average at high ratios of citrate to cupric ion, but the values appear to rise toward 1.25 as the ratio of citrate to cupric ion becomes smaller than about 3.0. In the region where the ratio [KOH]/[Cu complex] is 1.0, $\bar{a}$, the average number of hydrogens per coördinated citrate, is given as $\bar{a} = (2n - 1)/n$. At smaller values of the citrate/cupric ion ratio, $\bar{a} = (2n - 1.25)/n$. The significance of these results will be considered later.

(b) Determination of n, the Average Number of Citrate Groups Coördinated per Cu^{++}.—Data obtained in the preceding investigation were not well suited to determination of n since the concentration of free citrate could not be conveniently varied over a wide range without adding an excess of copper. For this reason a separate set of solutions was prepared containing 3 different cupric ion concentrations and 4 different potassium dihydrogen citrate concentrations. Data obtained in part (a) indicated one hydrogen ion liberated for each cupric ion present. Accordingly one equivalent of KOH was added for each gram atom of Cu^{++}. The final ionic strength of each solution was adjusted to 3.0 with magnesium sulfate, the adjustment being based on a final total volume of 250 cc.[5] The validity of the measurement of $\bar{a}$ in part (a) is confirmed by the constancy of the *p*H throughout the series (see footnote *f*, Table II). Details are summarized in Table II.

Measurements of *p*H were made with a Beckman glass electrode and cupric ion was determined with a copper electrode. Since the precision of these measurements was to be higher than those of part (a) and since experimental conditions were different, the reliability of the copper electrode again required verification. A calibration curve giving cupric ion concentration *versus* potential was obtained by using a series of solutions containing varying concentrations of Cu^{++}, a constant *p*H of 3.0, and an ionic strength adjusted to 3.0 with $MgSO_4$ (*p*H effects negligible in absence of citrate). Either copper-plated platinum flags or recently polished copper wires could be used as electrodes. About 8 to 10 hours were allowed for the system to reach equilibrium before each potential measurement. A plot of the potential of the cell

$$\text{Cu}/(\text{Cu}^{++}, \text{SO}_4^{=})(\text{Mg}^{++}, \text{SO}_4^{=})//0.75\ M\ \text{MgSO}_4/\text{Hg}_2\text{SO}_4/\text{Hg}$$

against the log of the copper concentration is shown in Fig. 1.

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[5] Since the ionic strength is influenced somewhat by the process of complex formation and addition of KOH, it was desirable to correct for these effects using the data obtained in the determination of $\bar{a}$, the number of hydrogens per coördinated citrate. Preliminary plots of data from determination of $\bar{a}$ indicated a slope of between 1 and 2 for a plot of log [Cu^{++}]/[Cu complex] *versus* log [free citrate]. In the region where the citrate/cupric ion ratio is large, if $n = 1$, $\bar{a} = (2n - 1)/n = 1$. The following equation can then be assumed for the process

$$\text{Cu}^{++} + \text{H}_2\text{Cit}^- + \text{K}^+ + \text{SO}_4^{=} \longrightarrow \text{Cu(HCit)} + \text{K}^+ + \text{H}^+ + \text{SO}_4^{=}$$

$$\text{H}^+ + \text{K}^+ + \text{SO}_4^{=} + \text{K}^+ + \text{OH}^- \longrightarrow 2\text{K}^+ + \text{SO}_4^{=} + \text{H}_2\text{O}$$

The addition of $CuSO_4$ and KOH to a KH_2Cit + $MgSO_4$ solution will alter the ionic strength only by converting one formula weight of KH_2Cit to one formula weight of K_2SO_4 for each formula weight of $CuSO_4$ added. Final ionic strength may then be calculated from the equation

$$\mu = [\text{MgSO}_4]\cdot 4 + [\text{KH}_2\text{Cit}] - [\text{CuSO}_4] + \frac{2[\text{CuSO}_4] + 4[\text{CuSO}_4]}{2}$$

In computing the ionic strength secondary effects due to subsequent ionization of H_3Cit^- have been neglected. If n is assumed equal to 2, $\bar{a} = 3/2$ and the following equation is suggested:

$$\text{Cu}^{++} + \text{SO}_4^{=} + 2\text{K}^+ + 2\text{H}_2\text{Cit}^- \longrightarrow [\text{Cu(HCit)(H}_2\text{Cit)}]^- + 2\text{K}^+ + \text{H}^+ + \text{SO}_4^{=}$$

$$\text{H}^+ + \text{K}^+ + \text{SO}_4^{=} + \text{K}^+ + \text{OH}^- \longrightarrow 2\text{K}^+ + \text{SO}_4^{=} + \text{H}_2\text{O}$$

Ionic strength calculations are exactly the same since the compounds [K$^+$, H_2Cit^-] and [K$^+$, $\{Cu(HCit)(H_2Cit)\}^-$] cannot be distinguished in computing ionic strength.

TABLE I

75 cc. 1 *M* KH_2Cit; 175 cc. 1 *M* $MgSO_4$; initial ionic strength = 3.1; used 1 *M* $CuSO_4$ at *p*H 2.84; $\bar{Z} = 2$ for KH_2Cit; 1.702 *N* KOH; electrode system $Cu/Cu^{++}//1\ M\ MgSO_4/Hg_2SO_4/Hg$. Glass electrode checked at end with buffer = 4.00.

1 *M* $CuSO_4$, cc.	*p*H after Cu^{++} addition	KOH to restore *p*H (2.84), cc.	E.m.f. electrode 1	E.m.f. electrode 2	Total Cu^{++} concn.	Free Cu^{++} concn.[a]	Concn. complexed Cu^{++}	[KOH]	$\frac{[KOH]}{[Cu\ Complex]}$
0	2.84	0	0.4965	0.4957	....	....	....	....	..
0.320	2.82+	0.15	.4797	.4794	1.28×10^{-3}	4.57×10^{-5}	1.24×10^{-3}	1.03×10^{-3}	0.83
3.02	2.82[b]	1.00	.4538	.4539	1.19×10^{-2}	3.31×10^{-4}	1.16×10^{-2}	6.70×10^{-3}	.61
6.01	2.81[b]	3.02	.4454	.4455	2.32×10^{-2}	6.75×10^{-4}	2.25×10^{-2}	2.00×10^{-2}	.89
10.00	2.79[b]	5.56	.4390	.4391	3.76×10^{-2}	1.10×10^{-3}	3.65×10^{-2}	3.56×10^{-2}	.98
12.02	2.80	7.15	.4367	.4369	4.46×10^{-2}	1.29×10^{-3}	4.33×10^{-2}	4.52×10^{-2}	1.04
15.00	2.79	9.24	.4338	.4340	5.48×10^{-2}	1.62×10^{-3}	5.32×10^{-2}	5.73×10^{-2}	1.08
20.00	2.76	13.02	.4302	.4305	7.06×10^{-2}	2.24×10^{-3}	6.84×10^{-2}	7.85×10^{-2}	1.14
25.00	2.76	17.25	.4272	.4274	8.56×10^{-2}	2.82×10^{-3}	8.28×10^{-2}	1.00×10^{-1}	1.21
30.00	2.78	20.56	.4243	.4246	1.00×10^{-1}	3.59×10^{-3}	9.64×10^{-2}	1.16×10^{-1}	1.21
40.00	2.72	27.91	.4197	.4200	1.26×10^{-1}	4.90×10^{-3}	12.10×10^{-2}	1.49×10^{-1}	1.23

[a] Concn. Cu^{++} calculated from expression $\log [Cu^{++}] = -(E - 0.353)/0.029$ (see text). [b] Additional increments KOH between, so *p*H not as low as it would have gone.

TABLE II

COMPOSITION OF COPPER CITRATES

Sample	Molar concn. KH_2Cit	Molar[a] concn. $CuSO_4$	Molar concn. $MgSO_4$ for $\mu = 3.00$	Fresh solution							Aged solution—75 days			
				*p*H[a]	E_1	E_2	$\log \frac{[Cu^{++}]}{[Complex]}$	$[H_2Cit^-]^e$ (molar)	$[HCit^=]$ (molar)	$\log [HCit^=][H_2Cit^-]$	*p*H	*E*	$\log \frac{[Cu^{++}]}{[Complex]}$	$\log [HCit^=][H_2Cit^-]^e$
1a	0.500	0	0.625	2.98	....	....	.....	....	....	.....	...	.....	......	....
1	.500	4.96×10^{-3}	.622	2.97	0.4775	0.4778	−2.13[c]	0.372	0.059	−1.66	2.98	[d]	[d]	[d]
2	.500	9.92×10^{-3}	.620	2.98	.4702	.4700	−2.16	.364	.058	−1.67	2.97	0.4712	−2.20	−1.67
3	.500	4.96×10^{-2}	.600	2.94	.4491	.4491	−2.15	.305	.048	−1.83	2.98	.4505	−2.19	−1.83
4a	.300	0	.675	2.93	....	....	.....	....	....	.....	...	.....	......	....
4	.300	4.96×10^{-3}	.672	2.92	.4627	.4618	−1.61	.221	.035	−2.11	2.93	.4669	−1.75	−2.11
5	.300	9.92×10^{-3}	.670	2.92	.4544	.4545	−1.61	.214	.034	−2.14	2.88	.4580	−1.75	−2.25
6	300	4.96×10^{-2}	.650	2.90	.4366	.4360	−1.71	.154	.018	−2.56	2.86	.4360	−1.71	−2.53
7a	.100	0	.725	2.90	....	....	.....	....	....	.....	...	.....	......	....
7	.100	4.96×10^{-3}	.722	2.91	.4408	.4394	−0.78	.069	.011	−3.12	2.88	.4460	−1.04	−3.24
8	.100	9.92×10^{-3}	.720	2.91	.4318	.4324	− .83	.063	.010	−3.20	2.86	.4375	−1.03	−3.34
9	.100	4.96×10^{-2}	.700	2.90	.4095	.4090	− .72	.013[e]	.002[e]	−4.59[e]	2.76[b]	.4258[b]	−1.36[b]	....
10a	.050	0	.737	2.92[f]	....	....	.....	....	....	.....	...	.....	......	....
10	.050	4.96×10^{-3}	.735	2.97[f]	.4283	.4280	−0.23	0.033	0.005	−3.78	2.94	.4382	−0.70	−3.91
11	.050	9.92×10^{-3}	.732	2.95[f]	.4198	.4191	− .27	0.028	0.004	−3.95	2.90	.4267	− .60	−4.09
12	.050	4.96×10^{-2}	.712	3.01[f]	.4016	.4004	− .37	....[e]	....[e]	.....[e]	2.71	.4164	− .994[b]	....

[a] *p*H measured after one milliequivalent KOH had been added for each mmole $CuSO_4$. [b] Precipitate of $Cu_2[C_6H_4O_7]$ had formed in system. Ratio has little meaning. [c] $[Cu^{++}]$ calculated from expression: $-(E - 0.347)/0.0295 = \log [Cu^{++}]$. [d] Mold damage—solution discarded. [e] Calculation of total free citrate, $[H_2Cit^-]$ and $[HCit^=]$ based on an assumed value of 2 for *n*. Assumption confirmed in Fig. 2 for all solutions except 6, 9 and 12. [f] The *p*H in solutions 10, 11 and 12 is slightly higher than the control 10a. This results because 1 meq. KOH had been added for each millimole $CuSO_4$, and actually only about 50 to 75% of the Cu^{++} in these solutions coördinated to release H^+. In all other solutions essentially all of Cu^{++} added formed a complex.

Data fall on a straight line of slope 0.0295 and intercept 0.347. These data give a potential of 0.352 for the cell

$$Cu/0.75\ M\ CuSO_4/0.75\ M\ MgSO_4/Hg_2SO_4/Hg$$

Since the above cell has a negligible junction potential,[6] the value of 0.352 compares favorably with the value 0.351 obtained by Tourky and El Wakkad for the cell

$$Cu/0.75\ M\ CuSO_4/Hg_2SO_4/Hg$$

All potential measurements were made with duplicate electrodes. In general, the precision of the potential measurements was greatest in solutions of high citrate concentration.

As data of Table II indicate, *p*H and cupric ion determinations were made on all solutions within 72 hours after their preparation, then again after the solutions had been standing for about 75 days. In cases where the ratio of citrate to cupric ion was low, a marked change in potential was observed on standing and in those cases where the ratio was very low (2 or below), a precipitate settled out after about 3 weeks. In the latter case the *p*H of the resulting supernatant liquid dropped as the precipitate came out.

(c) Identity of the Precipitate Obtained when Solutions with a Very Low Citrate–Cupric Ion Ratio Were Allowed to Stand.—The blue precipitates obtained from solutions 9 and 12 (Table II) were filtered off, washed, dried at 100° under vacuum and analyzed. Data shown below correspond to the fomula $Cu_2(C_6H_4O_7)\cdot 0.7H_2O$.

	Theor.	Obsd.
Cu, %	38.75	38.36
H, %	1.64	1.62
C, %	22.00	22.60
O, % (by difference)	37.60	37.42

Interpretation of Results

(a) The Composition of Fresh Solutions.—A plot of the log $[Cu^{++}]/[Cu\ complex]$ against log

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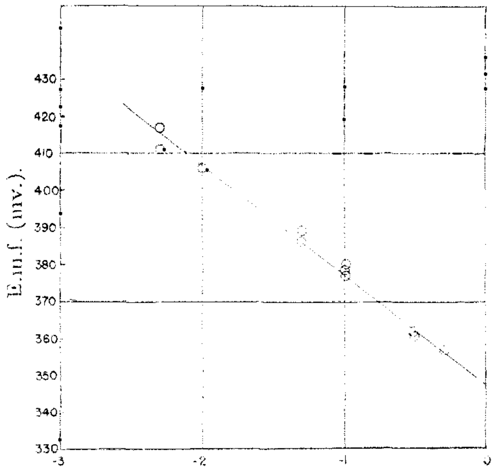
[6] G. N. Lewis and W. N. Lacey, THIS JOURNAL, **36**, 804 (1914).



log $[Cu^{++}]$.

Fig. 1.

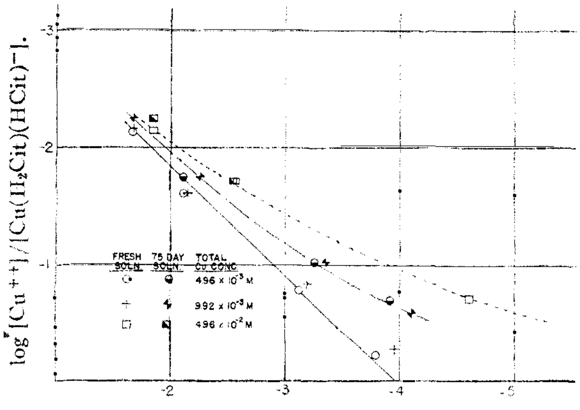
[Free Citrate] gives a straight line with a slope of approximately 2. The number of hydrogens per coördinated citrate is $(2n - 1)/2 = 3/2$. The equation for coördination compound formation then becomes

$$Cu^{++} + 2H_2Cit^- \rightleftarrows [Cu(HCit)(H_2Cit)]^- + H^+ \quad (7)$$

Since the dissociation of the complex under the conditions of constant pH used in this investigation can be represented as

$$[Cu(HCit)(H_2Cit)]^- \rightleftarrows Cu^{++} + H_2Cit^- + HCit^= \quad (8)$$

a plot of log $[Cu^{++}]/[Cu \text{ complex}]$ against log $[H_2Cit^-][HCit^=]$ should give a straight line of slope −1. Data from Table II plotted in Fig. 2 show that this is true for those cases where the total copper concentration is 0.01 molar or less.



log $[HCit^=][H_2Cit^-]$.

Fig. 2.

For higher copper concentrations the plot is not linear, indicating a change in n with the copper/citrate ratio. From the intercept of the straight line, one obtains a value of −3.98 ±0.06 for log K_2 at an ionic strength of 3.0 where K_2 is defined as

$$K_2 = [Cu^{++}][H_2Cit^-][HCit^=]/[Cu(H_2Cit)(HCit)^-] = 10^{-4} \quad (9)$$

To obtain the true K_2 at infinite dilution, suitable corrections for activity coefficients must be applied.[7]

Data for the series with a total copper concentration of 0.05 M indicate that the average n value is not constant in this region but drops from 2 toward 1 as the citrate–copper ratio decreases suggesting a new complex $[Cu(HCit)]_n$. Data obtained from the aged solution plus the eventual isolation from solutions 9 and 12 (Table II) of the solid compound $Cu_2(C_6H_4O_7)\cdot 0.7\ H_2O$ support this interpretation.

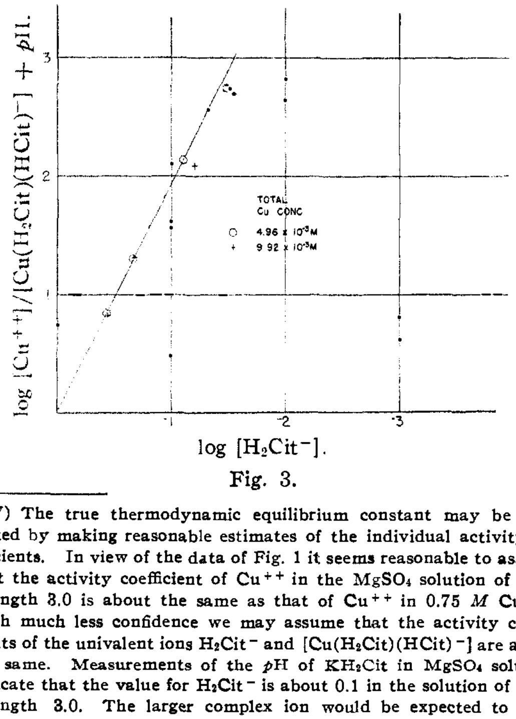
From equation 7 it can be shown that the pH dependence of the coördination process at high citrate–copper ratios is given by

$$\log [Cu^{++}]/[Cu(HCit)(H_2Cit)^-] + pH = \log K_3 - 2 \log[H_2Cit^-]$$

In Fig. 3 this relationship is illustrated. The expected slope of 2 is observed. From the intercept of the straight line the value of log K_3 at an ionic strength of 3.0 is 0.0 where

$$K_3 = [Cu^{++}][H_2Cit^-]^2/[Cu(HCit)(H_2Cit)^-][H^+] = 1$$

The thermodynamic constant would require inclusion of activity coefficients. Estimates such as those described in footnote 8 give a value for log K_3 of −2.3 at infinite dilution.



log $[H_2Cit^-]$.

Fig. 3.

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[7] The true thermodynamic equilibrium constant may be estimated by making reasonable estimates of the individual activity coefficients. In view of the data of Fig. 1 it seems reasonable to assume that the activity coefficient of Cu^{++} in the $MgSO_4$ solution of ionic strength 3.0 is about the same as that of Cu^{++} in 0.75 M $CuSO_4$. With much less confidence we may assume that the activity coefficients of the univalent ions H_2Cit^- and $[Cu(H_2Cit)(HCit)^-]$ are about the same. Measurements of the pH of KH_2Cit in $MgSO_4$ solution indicate that the value for H_2Cit^- is about 0.1 in the solution of ionic strength 3.0. The larger complex ion would be expected to have an activity coefficient only slightly larger than this. The activity coefficient of the divalent monohydrogen citrate ion can be estimated from pH measurements in the $MgSO_4$ solution as 0.01 if we assume the undissociated H_3Cit has a coefficient of 1. This value for the activity coefficient of monohydrogen citrate automatically compensates for citrate removed by complex formation with the large and nearly constant amount of Mg^{++} in the solution. Using these values

$$\log K_2 = \log \frac{[Cu^{++}][H_2Cit^-][HCit^=]}{[Cu(HCit)(H_2Cit)^-]} + \log \frac{\gamma_{Cu^{++}}\gamma_{H_2Cit^-}\gamma_{HCit^=}}{\gamma_{complex}}$$

$$\log K_2 = -3.98 - 3.3 = -7.3$$

$$K_2 = 5 \times 10^{-8}$$

Experimental determination of these activity coefficients is under consideration.

(b) Composition of Solutions Which Have Been Allowed to Age for 75 Days.—Data of Fig. 2 show that in those cases where the ratio of total citrate to total copper is large (30 or above), aging appears to have little detectable effect on the complex ion existing in the solution. On the other hand, in those cases where the ratio of total citrate to total copper is low, aging brings about a decrease in the average number of citrate groups bound to a given copper. This process culminates in the separation of the solid, $Cu_2(C_6H_4O_7)$, from solutions in which the ratio of the total citrate to total copper is 2 or below. The ion $[C_6H_4O_7^{-4}]$ represents the citrate group minus the hydroxyl hydrogen. In this solid the copper has replaced all acid hydrogens of the citrate as well as the hydroxyl hydrogen. If the process is represented by the equation

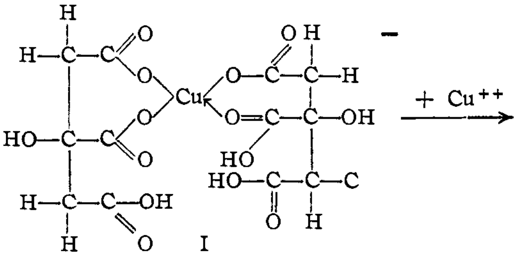
$$2[Cu(H_2Cit)(HCit)^-] \longrightarrow Cu_2(C_6H_4O_7) + 3H_2Cit^- + H^+$$

it is apparent that the *p*H should drop as the precipitate forms. Data of Table II, solutions 9 and 12, show a drop in *p*H during the aging period. Data of Table I also show that more than one hydrogen is liberated per copper when the citrate–copper ratio drops below 3.

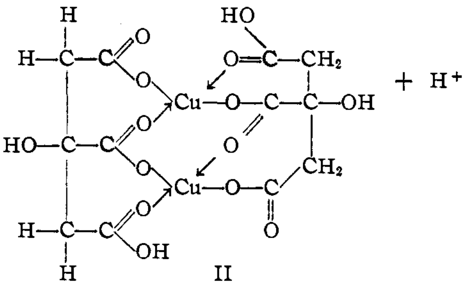
The velocity of the aging process appears to be influenced by the total copper concentration. In solutions where the total copper concentration was 0.05 molar, even the fresh solution showed significant amounts of such complexes as $[CuHCit]_n$, particularly in those cases where the ratio of total citrate to total copper was low (*i.e.*, 6 and below). In solutions where the total copper concentration was 0.01 or 0.005 *M*, the fresh solutions contained only the complex $[Cu(HCit)(H_3Cit)]^-$ at all citrate–copper ratios. As the aging process progressed, however, solutions with the lower citrate–copper ratios gave evidence of the presence of the complex $[CuHCit]_n$.

Discussion

The preceding data suggest that all of the ions present in the citrate solution, including the ion $[C_6H_4O_7]^{-4}$ can form coördination compounds with the cupric ion at a *p*H below 3. The initial complex, which appears to form rapidly in all solutions, involves the H_2Cit^- and the $HCit^=$ and can be formulated as a double chelate structure involving all four of the copper coördination positions. As the relative copper(II) ion concentration is increased, additional cupric ions coördinate to the citrate structure, liberating one hydrogen for each copper(II) ion coördinating. There are a number of points of attachment for copper ions. One mode of representation is indicated below.

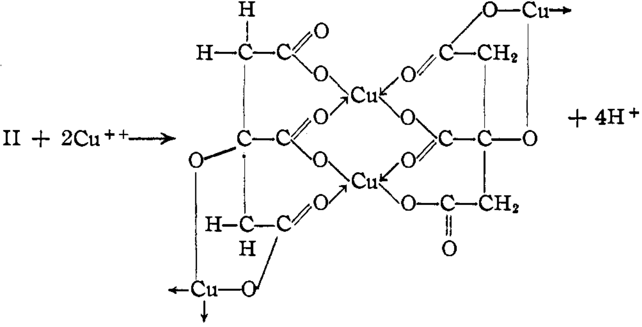


I



II

The addition of the second copper ion appears to be a relatively slow process, the rate of which is determined in part by the copper concentration. In the presence of a still larger copper concentration two additional copper(II) ions will coördinate to the citrate structure, liberating two hydrogens per copper in the process. This can be formulated as



The presence of coördination positions on the end coppers makes possible coördination of water and the formation of a crystalline solid $Cu_2C_6H_4O_7 \cdot 2H_2O$. Such a solid was isolated and the expected drop in *p*H was observed.

In view of the complexity of the citrate–copper system and the close relationship between composition of the coördination compound and the citrate–copper ratio, it is not surprising that ion exchange systems using citrate as the elutriant become much more complicated when large concentrations of the ion to be eluted are adsorbed on the resin. In such cases the elution process cannot be analyzed in terms of a single complex ion of citrate and metal. The existence of a single ionic species is much more probable when the metal ion concentration is low, thus giving a large citrate–metal ratio.

It is interesting to note that the precision of e.m.f. measurements in this investigation was greater in the presence of citrate. This might be interpreted as resulting from a cleaning of the electrode surface by the citrate solution; however, conclusive evidence on this point is not available.

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