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Solution Studies of Systems with Polynuclear Complex Formation. 1. The Copper(II) Citrate System

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The complex formation between copper(II) and citrate ions (citric acid = H_3L) has been investigated in the pH range of 4.5 to 10 by means of combined pH and pCu measurements. The emphasis was on the formation of dimeric species and the concentration range chosen in the experiments favoured the formation of such species. The experimental data can be explained by the formation of the complexes $Cu_2H_{-1}L$, $Cu_2H_{-1}L_2^{3-}$, and $Cu_2H_{-2}L_2^{4-}$. The last complex is the predominating species even in very dilute neutral and weakly alkaline solutions containing an excess of ligand. A more highly polymeric fraction is observed in neutral solutions with an excess of metal ion.

Introduction

Citric acid (H_3L) plays an important role as ligand for transition metal ions in chemical reactions of biological, analytical, and technical interest. The ligand has been used as a masking reagent for most metal ions [1] preventing the precipitation of these ions as hydroxides or other slightly soluble salts. The metal chelates formed with triply ionized citrate are quite well characterized [2]. There seems, however, to be some disagreement about the composition and stability of the species formed with quadruply ionized citrate ion in neutral and alkaline solutions.

Copper(II) complexes with citric acid have been studied by several investigators. The results obtained in more recent articles are shown in Table I (some complexes proposed for the most acidic and alkaline regions have been omitted).

The main aim of the paper is to clarify the situation in neutral and alkaline solutions excluding, however, very alkaline solutions where decarboxylation of the ligand may occur. We are especially interested in the formation of dimeric species, as such species have been reported by some investigators but not by others. If there is an analogy in composition between the metal hydrolysis products and the complexes formed with quadruply ionized citrate, we may expect that the main hydrolysis product $Cu_2(OH)_2$ can be compared with the complex $Cu_2(OH)_2L_2$ or $Cu_2H_{-2}L_2$.

The existence of dimeric Cu(II)–citrate complexes was first suggested by Kahlenberg [3] in 1895 from freezing point and emf data. The suggestion was confirmed by Calame in 1898 [4]. Nevertheless, most of the stability constants given [2] are reported for mononuclear monoligand chelates. In 1957 Lefebvre [5] made a thorough reinvestigation of several Cu(II)–hydroxycarboxylate systems by means of combined pH and pCu measurements and found for the Cu–citrate system that dimeric species are the main species even in rather dilute solutions. At low pH values the dimers may break up into mononuclear chelates. The dominant species in the pH region of 5 to 11 was considered to be $Cu_2(OH)_2L_2$.

Rajan and Martell [6] investigated the Cu–citrate system using pH base consumption data and varied the total concentration of both the metal and the ligand ions. In this way, they were able to confirm the existence of dimeric species. Of the more recent investigations (see Table I) two favour the formation of the dimer $Cu_2H_{-2}L_2$, whereas two other studies explain their experimental data without introducing this species.

The present situation is somewhat uncertain as far as the existence of dimeric and also more highly polymeric species is concerned. We have chosen to use combined pH and pCu measurements in order to cut the 'experimental space', as the use of metal ion selective electrodes provides a simple and reliable method of studying the composition and stability of metal complexes [7, 8]. Dilution experiments can often be used to test metal chelate systems for the formation of dimeric and higher polymeric species. The method has been applied to both kinetic and equilibrium studies. Here, the dilution technique will be applied for establishing the degree of polymerization.

The formation of dimeric complexes has also been suggested on spectroscopic groups both for

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TABLE I. Equilibrium Data.

Reference	57-L	64-C	67-R	74-F	74-P	75-B	75-D
Temperature, °C	20	20	25	25	25	25	25
Ionic strength	1.0	0.1	1.0	0.1	0.5	2	0.1
Electrolyte	$NaClO_4$	$NaClO_4$	KNO_3	KNO_3	$NaNO_3$	$NaClO_4$	KNO_3
pH-range	2 to 12.5	3 to 7	3 to 10	2 to 11	not given	1 to 4.8	not given
	log β Values*						
CuL**	5.2	5.90	–	–	5.95	4.40	–
$CuH_{-1}L$	–	1.56	–	1.61	2.16	–	–
CuHL	–	9.10	–	9.31	8.68	–	9.47
CuH_2L	–	–	–	–	11.34	11.20	–
Cu_2L_2	12.8	–	13.2	14.72	–	–	14.60
$Cu_2H_{-2}L_2$	6.0	–	5.1	–	–	5.30	6.00
$Cu_2H_{-1}L_2$	–	–	–	–	–	–	10.75
$Cu_2H_{-2}L$	–	–	–	–	–	1.90	–
$Cu_2H_{-1}L$	–	5.03	–	–	–	–	–
Cu_2L	–	8.10	–	–	–	–	–
CuL_2	8.4	–	–	–	8.09	7.28	–
$CuHL_2$	–	–	–	–	–	11.78	–
CuH_2L_2	–	–	–	–	–	16.00	–

*$\beta_{p,q,r}$ is the stability constant for the general species $Cu_pH_qL_r$ defined by the reaction pCu + qH + rL $\rightleftharpoons$ $Cu_pH_qL_r$.
**Here, and elsewhere, charges are omitted.

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74-F: T. B. Field, J. L. McCourt and W. A. E. McBryde, *Can. J. Chem.*, *52*, 3119 (1974).
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aqueous and non-aqueous solutions [9, 10]. An estimate of the Cu–Cu distance in the complex $Cu_2H_{-2}L_2$ was made on the basis of ESR spectral data. The Cu–Cu separation in aqueous solution was proposed to be ≈3.1 Å, which is of interest as crystal structure data are not available in the literature. The short Cu–Cu separation may be achieved through coordination to the hydroxy group and carboxylic groups of the citrate anion utilizing the deprotonated hydroxy group as a bridging group.

The complex $Cu_2H_{-1}L$ is formed in acid solutions, even at pH ≈ 3 [11]. The crystal structure of the dihydrate, $Cu_2C_6H_4O_7 \cdot 2H_2O$, has been resolved [12]. The investigation shows a twisting of the copper coordination spheres in the crystal.

Experimental

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 0.1 mol/l (KNO_3).

The potentiometric measurements were carried out with an Orion Research Model 801 pH/mV meter. A Radiometer copper-ion selective Selectrode [13] was used for the pCu measurements. The linearity of the electrode was tested using various metal buffers and was found to be good. A glass electrode was used for the pH measurements and the hydrogen ion concentrations were calculated from the pH readings using the relationship $-\log[H] = pH - 0.11$.

Potentiometric titrations carried out at a constant pH value showed that the cupric and citrate ions mainly react in a ratio of 1:1 in neutral and weakly alkaline solutions [14]. The titration can be used for analytical purposes and the citrate solution was standardized in this way (HCO_3^-–CO_3^{2-} buffer) using the so called Gran functions for the equivalence point determination [15].

The spectrophotometric measurements were made with a GCA McPherson EU 700 spectrophotometer interfaced to a Monroe 1860 calculator. The memory capacity of the calculator was used for automatic baseline correction.

Citric acid forms weak complexes with potassium ions and the protonation constants of the ligand were taken from an investigation carried out under the same experimental conditions [2]: $\log K^H_{HL} = 5.65$, $\log K^H_{H_2L} = 4.30$, and $\log K^H_{H_3L} = 2.79$.

Theory and Results

Chelating agents L may be capable of forming dimeric species with metal ions M, *e.g.*, monomeric complexes of the formula ML, or M(OH)L, may form the new species, M_2L_2, or $M_2(OH)_2L_2$. Actually, this process or the formation of higher polynuclear species may occur more frequently than is generally realized. As an example, for complexes with coordinated water molecules we have the possibility of olation reactions. Many equilibrium studies are made without varying both the total concentration of metal and ligand ions, and the experimental data are explained with a model containing only monomeric chelates.

The concept of average ligand numbers or formation functions is usually introduced when dealing with stepwise equilibria [16]. For mononuclear complexes the average ligand number will not depend on the total concentration of metal ion [16], and the formation function will not change on dilution. It follows, that if constants for monomeric complexes are determined at various dilutions and the values obtained differ, then the occurrence of dimers or other polymeric species has to be carefully investigated.

The determination of stability constants of chelate complexes can be based on the concept of conditional constants [7, 8]. For such reactions a simple stoichiometry is common, whereas mixed acid and basic complexes are frequently observed. A very simple theory can be developed for cases where combined pH and pM (or pH and pL) measurements are possible. We will now extend the theory and consider the case where dimeric species are formed in solution.

Let us assume that the dimers have a 2:2 stoichiometry of the composition $M_2H_iL_2$, *i.e.*, a stepwise protonation or deprotonation of the dimer is allowed. We will further assume that the dimers predominate in the solution and that the solution contains an excess of ligand. The free metal ion concentration of the solution will then be determined by the conditional constant

$$K^{2M,2L'}_{(M_2L_2)'} = \frac{[(M_2L_2)']}{[M]^2[L']^2} = K^{2M,2L}_{M_2L_2}\,\alpha_{M_2L_2(H,OH)}/(\alpha_{L(H)})^2 \qquad (1)$$

where

$$[(M_2L_2)'] = \sum_{i=-r}^{s} [M_2H_iL_2] = [M_2(OH)_rL_2] + \ldots + [M_2(OH)_2L_2] + [M_2(OH)L_2] + [M_2L_2] + [M_2HL_2] + [M_2H_2L_2] + \ldots + [M_2H_sL_2] \qquad (2)$$

$$[L'] = \sum_{i=0}^{t} [H_iL] = [L] + [HL] + [H_2L] + \ldots + [H_tL] \qquad (3)$$

$\alpha_{L(H)}$ and $\alpha_{M_2L_2(H,OH)}$ denote distribution or α-coefficients and have their usual definitions [7]:

$$\alpha_{L(H)} = [L']/[L] = 1 + [H]K^{H}_{HL} + [H]^2K^{2H}_{H_2L} + \ldots \qquad (4)$$

$$\alpha_{M_2L_2(H,OH)} = [(M_2L_2)']/[M_2L_2] \qquad (5)$$

The mass balance equations will give:

$$[(M_2L_2)'] = \tfrac{1}{2}(C_M - [M']) \qquad (6)$$

$$[L'] = C_L - C_M + [M'] \qquad (7)$$

where C denotes total concentration and $[M']$ is the concentration of uncomplexed metal ion. If $[M']$ differs from [M] it is mostly a question of metal hydrolysis.

Substitution of (6) and (7) into (1) yields

$$\log K_{M_2L_2} + \log\alpha_{M_2L_2} = 2pM + 2\log\alpha_L + \log\frac{C_M - [M']}{2(C_L - C_M + [M'])^2} \qquad (8)$$

The equation shows that a dilution experiment can be used to test the existence of dimeric species in solution. A dilution by a factor of ten will diminish the pM value by 0.5 units (at a constant pH value and for fixed C_M:C_L ratio). A differentiation of eq. (8) yields for $[M'] \ll C_M$

$$\frac{dpM}{dpC_M} = -\frac{1}{2} \qquad (9)$$

When pM values are measurable the derivative dpM/dpC_M is an illustrative measure of the degree of polymerisation. Let us consider the more general case where the polymer $(ML)_m$ is the predominating species in solution. A differentiation of the corresponding expression will give

$$\frac{dpM}{dpC_M} = -\frac{m-1}{m} \qquad (10)$$

(or for the polymeric species M_mL_l we obtain $dpM/dpC_M = -(l - 1)/m$). It follows that for a trimer the differential quotient will be −2/3. If a monomer predominates, the value of dpM/dpC_M will be 0, as at an excess of the ligand the ratio [ML]/[L] will remain constant on dilution. If no complexation occurs the value of the derivative will be +1, *i.e.*, at a tenfold dilution pM will increase by one unit.

If the assumptions made above are not justified and no particular species will predominate in the solution, expression (10) will give a non-integral value of n. Lefebvre [5] has discussed this case in some detail, and more rigorous expressions have been derived on the basis of his concept of 'potentiometric surface'.

The copper(II) citrate system can be taken as an example to illustrate the outlined theory. Lefebvre [5] has investigated the system using a copper solid state electrode. The free metal ion concentration was measured in solutions containing an excess of the ligand. The results indicate that a dimeric species predominates at the pH values of 5.4, 5.0, and 4.6 ($dpCu/dpC_{Cu} \approx -1/2$). A plot of the pCu values obtained as a function of pH suggests that the composition of the dimer is $Cu_2(OH)_2L_2$.

We have carried out dilution experiments over a wider pH and concentration range. The solutions were mixed in the ratio $C_{Cu}:C_L = 1:2$ in order to maintain an excess of ligand in the solution. The results are given in Fig. 1 as a plot of pCu *vs.* pH. The curves have a slope of +1 and a spacing of −1/2 as a result of a tenfold dilution. Consequently, the dimer $Cu_2H_{-2}L_2$ is formed in neutral and alkaline solutions. (We prefer the notation $Cu_2H_{-2}L_2$ to $Cu_2(OH)_2L_2$ as we assume that the chelate contains the ligand in its quadruply ionized form).

A plot of the right-hand side of expression (8) *vs.* pH (not given) shows the formation of $Cu_2H_{-2}L_2$. The curves obtained for different dilutions will coincide in the pH range of 6 to 10 and have a slope of 2 indicating that two protons are dissociated per dimer formed. In acid solutions the slope of the plot will diminish in value and the curves will depart from each other. This means that the dimer may be protonated and/or will break up into simpler complexes.

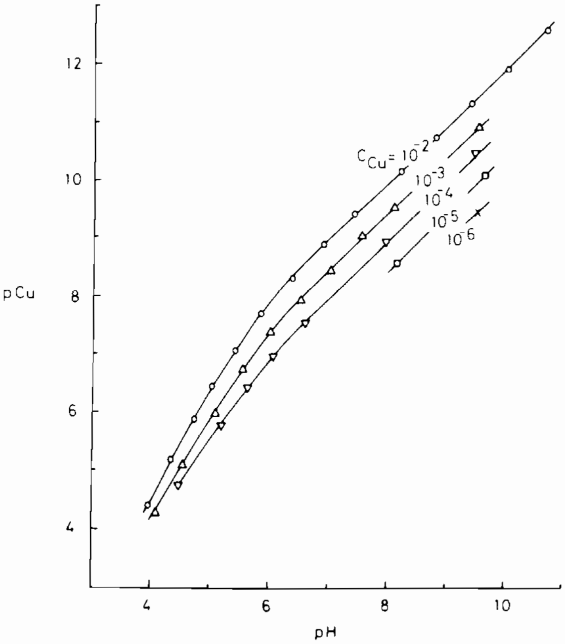

Fig. 1. Recorded pCu values of solutions with a $C_{Cu}:C_L$ ratio of 1:2 as a function of pH. All figures show only a part of the recorded experimental data points.

From the experimental data the dimerization constant of the reaction

$$2Cu^{2+} + 2L^{3-} \rightleftharpoons Cu_2H_{-2}L_2^{4-} + 2H^+ \qquad (11)$$

can be calculated by using the eqn. (8): $\log K^{2Cu,2L,-2H}_{Cu_2H_{-2}L_2} = \log \beta_{2,-2,2} = 5.80 \pm 0.07$.

The complexes formed in acid solution can be investigated by potentiometric titrations at constant pH values. Figure 2 shows titrations at pH 5.5, 5.0, 4.5, and 4.0, respectively. The upper part of the Figure shows the consumption of base as a function of added amount of citrate, whereas the lower part gives the recorded pCu values.

Figure 2 shows the formation of a complex with a Cu:citrate ratio of 2:1, which is deprotonated even at low pH values. The complex has the apparent com-

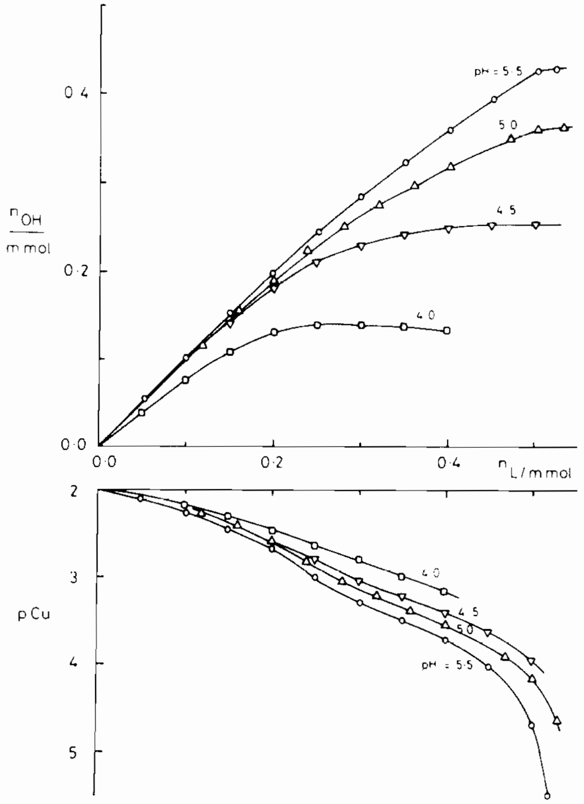

Fig. 2. Potentiometric titrations of 50 ml of a solution containing 0.010 mol/l copper ion with a 0.10 mol/l citrate solution. The pH value of the solution was kept constant at pH 5.5, 5.0, 4.5, and 4.0, respectively, by the addition of 0.050 mol/l NaOH solution. The upper half of the figure shows the consumption of base as a function of added amount of citrate, whereas the lower half gives the recorded pCu values.

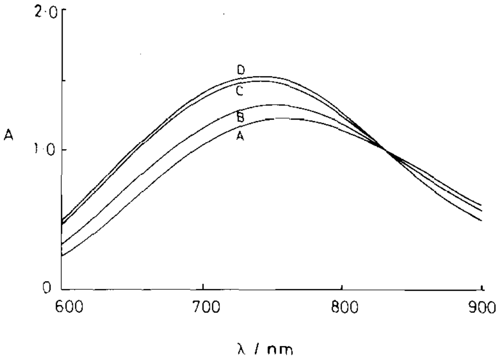

Fig. 3. Absorption spectra of copper(II) citrate solutions at pH 5.5. The solutions contain 0.03 mol/l copper(II) ions and varying concentrations of citrate ion: Curve A: 0.015 mol/l, B: 0.02 mol/l, C: 0.03 mol/l, and D: 0.06 mol/l, respectively.

position $Cu_2H_{-1}L$. Evidence for the existence of such a complex in solution comes also from spectrophotometric measurements [17]. The stability of the complex has been reported (see Table I).

The absorption spectra given in Fig. 3 show that at a pH of 5.5 we have two predominating chelates in solution. The two complexes show a slight modification of the coordination sphere around the cupric atom. A third species has, however, to be introduced in order to explain the experimental data of Fig. 2. Introduction of the complex CuL gave equilibrium constants exhibiting concentration dependence. The next step was to introduce the dimer Cu_2L_2. The value of $\log K_{Cu_2L_2}$ did not show systematic deviations at constant pH values, but was pH-dependent. The conclusion is that the species $Cu_2H_{-1}L_2$ is present in the solutions.

The data given in Fig. 2 (pH = 4.5, 5.0, and 5.5) can be explained by introducing the complexes $Cu_2H_{-2}L_2$, $Cu_2H_{-1}L_2$, and $Cu_2H_{-1}L$, but neglecting any mononuclear species. This is a result of the experimental conditions in the investigated part of the titration. The calculation of the equilibrium constants can be based on the mass balance expressions. The experimental data between the equivalence points were used for the calculation of the equilibrium constants:

$$\log K^{2Cu,2L,-H}_{Cu_2H_{-1}L_2} = \log\beta_{2,-1,2} = 10.82 \pm 0.02$$

$$\log K^{2Cu,L,-H}_{Cu_2H_{-1}L} = \log\beta_{2,-1,1} = 5.07 \pm 0.02$$

The potentiometric measurements have so far revealed that dimeric deprotonated chelates are formed in solutions containing an excess of the ligand. It does not follow that higher aggregates fail to form, and we now turn our interest to solutions with an excess of the metal ion. Earlier investigations have shown the existence of the species $Cu_2H_{-1}L$. A case in point is the iron(III) citrate system, where a discrete polymeric fraction of average molecular weight of (2.1 ± 0.1) 10^5 Daltons is observed in the buffer region from pH 8 to 9 [18]. The formation of the polymer, $Na[Fe_4O_4(OH)_{3.2}L]$, is accompanied by extensive dissociation of citrate ions. The remaining citrates are probably attached to the surface of a hydroxy–iron polymer preventing the particles from condensing. This polymeric species has been used as a model for the iron(III)–hydroxide polymer in the ferritin molecule [18].

We have carried out a series of titrations of citrate with Cu(II) ions at constant pH values. Figure 4 shows the titrations at pH 5.0, 6.0, 6.5, 7.0, and 9.0, respectively. The upper half of the Figure shows the consumption of base as a function of the amount of copper(II) ions added (a correction is made to the amount of free copper ions as recorded by the ion selective electrode), whereas the lower half gives the recorded pCu values.

Figure 4 shows that before the first equivalence point we have the formation of the complexes $Cu_2H_{-1}L_2$ and $Cu_2H_{-2}L_2$ in solution. These chelates

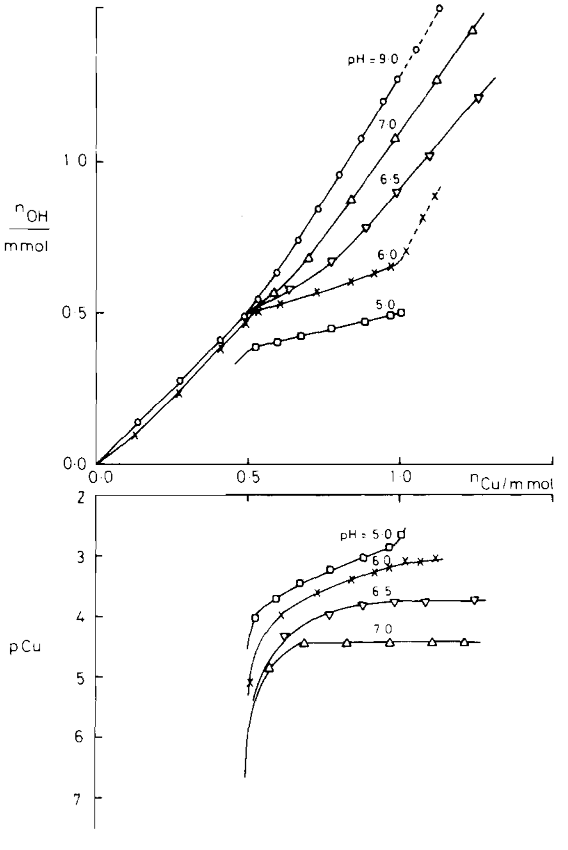

Fig. 4. Potentiometric titrations of 0.5 mmoles of citrate in 100 ml solution carried out at constant pH values of 9.0, 7.0, 6.5, 6.0 and 5.0, respectively. The figure shows the consumption of base and the recorded pCu values as a function of the amount of copper(II) ions added.

have been characterized above. After the equivalence point the complex $Cu_2H_{-1}L$ is formed at pH 5 and 6. At the latter p_H value we have to introduce an additional complex with bound hydroxide in order to explain the data. At the pH values 6.5, 7.0 and 9.0 we can expect the precipitation of copper(II) hydroxide, but this is not observed. The recorded pCu values reach an almost constant value soon after the first equivalence point, which indicates that polymeric species are formed in the solution. The nature of the polymer has not been investigated any further, but we expect a similarity to the polymer characterized in the iron(III) citrate system. In neutral solutions we were able to exceed a $C_{Cu}:C_L$ ratio of 2:1 without observable precipitation.

Discussion

The experiments have shown that dimeric species predominate in the copper(II) citrate system in the given concentration range. The complex $Cu_2H_{-2}L_2$ is the main hydrolysis product in neutral and weakly alkaline solutions containing an excess of the ligand. The dimer is of quite high stability as shown by the equilibrium constant of the reaction [19]

$$Cu_2(OH)_2^{2+} + 2L^{3-} \rightleftharpoons Cu_2(OH)_2L_2^{4-}; \log K = 16.8 \qquad (12)$$

The copper(II) citrate dimer is rather slow to dissociate. A rate constant of $1.2\ s^{-1}$ has been measured in stopped-flow experiments with EDTA as scavenger [20]. The apparent rate was independent of the EDTA concentration indicating a dissociative path as the rate determining step.

The main purpose of the present paper was to investigate dimeric and more highly polymeric copper(II) citrates, not mononuclear complexes. Accordingly, the concentration and pH range in the experiments was chosen to favour the formation of such species. A chemical consequence of the formation of the dimer $Cu_2H_{-2}L_2$ is that the metal ion concentration of a copper(II) citrate buffer will be a function of C_{Cu}, C_L, and pH.

We will further point out that citric acid may serve as a simple model for more complex ligands with only oxygen atoms as donor atoms. The humates, humic and fulvic acid, found in natural surface waters can be described chemically as polycarboxylic acids containing alcoholic and phenolic groups. The humates form stable complexes with cupric ions and humic acid has an ability to prevent the precipitation of iron(III) and copper(II) in the pH range of 5 to 11 [21].

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