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# Solution Studies of Systems with Polynuclear Complex Formation. 4. Heteronuclear Copper(II) Citrate Complexes with Nickel(II) or Magnesium(II)

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*The existence of heteronuclear complexes formed between citric acid, copper(II) and nickel(II) or magnesium(II) is demonstrated. The stoichiometry and stability of the complexes are reported. A volumetric example demonstrates the unexpectedly high stability of the Cu–Ni–citrate complex in comparison with the binary complexes and the interference of heteronuclear complex formation on citrate masking reactions. The paper also discusses the existence of heteronuclear cationic hydrolysis products.*

## Introduction

Polynuclear and heteronuclear complex formation in solution is an area of actual and potential importance and interest. Polynuclear species are frequently encountered in metal ion hydrolysis reactions [1]. The strong tendency of $OH^-(SH^-)$ and $O^{2-}(S^{2-})$ to form bridges between cations is an almost unique property among the simple ligands. A large number of heteropolyanions (of, *e.g.*, high-valent molybdenum-containing bridging $O^{2-}$ groups) have been both structurally and thermodynamically characterized [2]. Heteronuclear *cationic* hydrolysis products (with bridging $OH^-$ or $O^{2-}$ groups) have, however, been investigated to a far less extent, and a kinetic and synthetic approach has mainly been applied in these studies.

We have an interest in polynuclear complex formation in hydroxycarboxylate, mainly citrate, systems [3, 4, 5]. Our main concern is the bridge-bonding ability of the deprotonated alcoholic group of the ligand. The hydroxide ion has a similar bridge bonding ability, and the functional analogy between the quadruply ionized citrate ion and the hydroxide ion is obvious. The carboxylate groups of the citrate molecule may, however, modify the coordination sphere of the cation, so that steric reasons and different charge distributions will disturb a direct analogy in structure.

Sullivan *et al.* [6, 7] have demonstrated complex formation between $NpO_2^+$ and other cations such as U(VI), Th(IV), Fe(III), Al(III), Pb(II), Hg(II) and Hg(I), and have postulated the formation of MONpO bridges. These complexes can be regarded as mixed metal hdrolysis products. Later investigations of cation–cation interactions have mainly treated systems where one of the components is an oxocation [8], or both are oxocations [9, 10]. In a recent investigation Cannon *et al.* [11] reported mixed-metal binuclear complexes formed between $[Co(en)_2(OH)_2]^+$ (en = ethylenediamine) and divalent transition metal ions.

There are indications that mixed metal hydrolysis products of the type $Fe^{3+}–(OH)_x–Cu^{2+}$ may exist in solution, but, to the best of our knowledge, such systems have not been studied in any detail due to great experimental difficulties. The main problem is the early precipitation of the metal ions, placing a limit on the range of metal ion concentrations and pH over which the formation of hydroxide complexes can be studied in solution.

Mixed-ligand or ternary complexes commonly occur in metal ion solutions containing several kinds of ligands. The formation conditions are governed by factors such as stereochemical configurations, the type of bond formation between the metal ion and the ligands, interactions between the ligands, *etc.* [12]. A statistical effect also indicates ternary complexes [12].

The formation of mixed-metal complexes may be favoured by the factors mentioned above. The ability of hydroxycarboxylic acids such as citric, tartaric, malic and lactic acids to form heteronuclear complexes has been recognized in several systems [13], but thermodynamic data in the form of stability constants have not usually been reported. It is apparent that in at least one of the binary metal citrate systems polymeric species should be formed in order for heteronuclear complexes to exist [14].

The influence of electronic and magnetic interactions between the metal centers of homo- and heterobinuclear metal complexes was recently discussed at a EUCHEM conference [15], where the themes of the plenary lectures centred on ligand design and synthesis of bimetallic species, on chemical applications of bimetallic systems and the role of bimetallic centres in inorganic biochemistry. In this article we will make use of electronic effects in the absorption spectra caused by metal–metal interactions.

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Formation constants have recently been reported for heteronuclear complexes of quadruply ionized citrate with Cu(II)–Ni(II), Ni(II)–Zn(II) and Cu(II)–Zn(II) [16]. Citrate is widely used in analytical chemistry as a masking agent [17] and we wanted to confirm the composition of the heteronuclear copper-nickel citrate complex using a different experimental approach. An EDTA titration will illustrate the interference of heteronuclear complex formation on the citrate masking reaction. In addition we report the existence of a heteronuclear copper-magnesium citrate complex.

## 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$^{-1}$ $KNO_3$.

The potentiometric measurements were carried out with an Orion Research Model 801 pH/mV meter. A glass electrode was used for the pH measurements and the hydrogen ion concentrations were calculated from the readings using the relationship $-\log[H] = pH - 0.11$.

The spectrophotometric measurements were made with a GCA McPherson EU 700 spectrophotometer.

## Results and Discussion

Spectrophotometric measurements can be used to investigate the composition and stability of the heteronuclear citrate complexes. Spectral differences in the visible region were not recorded in the copper-nickel citrate system.

Many binuclear and polynuclear systems will display exchange-dependent spectral intensifications in the UV-region [18]. This means that the heteronuclear Ni–Cu citrate complex will have a different absorption spectrum. The high absorptivities necessitated difference spectra to be recorded. The difference measurements were achieved by placing two cuvets (with half the pathlength) containing the binary citrate complexes in the reference beam and the solution containing both metal ions in the sample beam. The solution in the three cuvets had the same pH value, total citrate and total metal ion concentrations.

A sharp absorbance maximum at *ca.* 310 nm was observed for the heteronuclear complex and the experiments shown in Figs. 1 and 2 were performed at this wavelength. The Job plot in Fig. 1 indicates the formation of a mixed metal complex containing equal numbers of copper and nickel atoms. Fig. 2 shows the pH dependence for the formation of the heteronuclear complex. The shape of the formation curve demonstrates that only one mol of hydroxide ion is consumed per mol of heteronuclear complex formed. Therefore, we consider it likely that the copper–nickel citrate complex contains two citrate molecules as ligands and the chemical composition is $CuNiH_{-2}L_2^{4-}$, where $H_3L$ denotes citric acid.

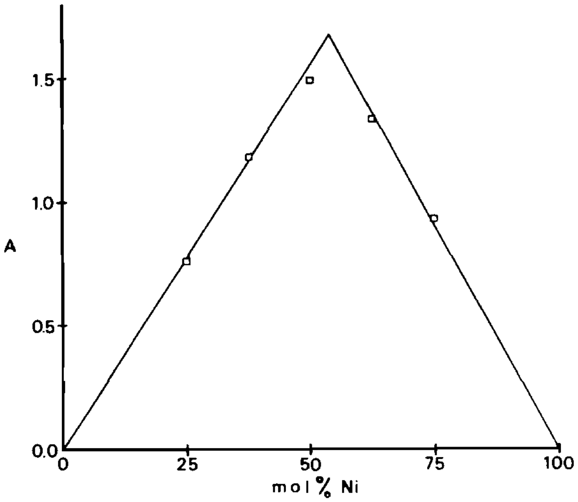

Fig. 1. Job plot for the copper-nickel-citrate system. Absorbance differences are measured at 310 nm. Total citrate concentration = 9 mml l$^{-1}$, sum of copper and nickel ions = 6 mmol l$^{-1}$. pH = 10.0.

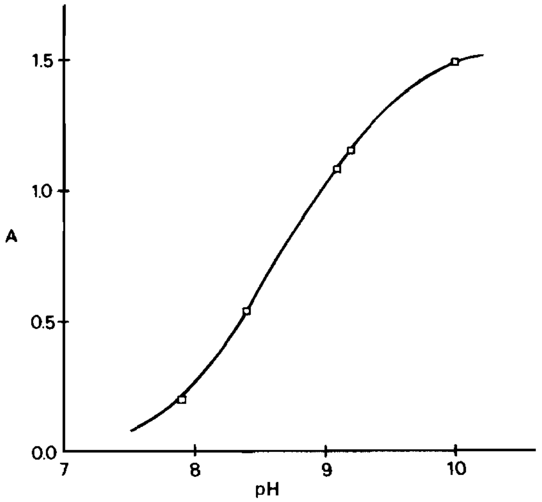

Fig. 2. pH-dependence for the formation of the mixed metal complex. Concentration of copper and nickel ions is 3 mmol l$^{-1}$, that of citrate is 9 mmol l$^{-1}$. Ionic strength = 0.1.

The pH-dependent reaction illustrated in Fig. 2 can be written $1/2Cu_2H_{-2}L_2^{4-} + NiL^- \rightleftarrows CuNiH_{-2}L_2^{4-} + H^+$. The formation constant $\beta_{11-22}$ of the reaction $Cu^{2+} + Ni^{2+} + 2L^{3-} \rightleftarrows CuNiH_{-2}L_2^{4-} + 2H^+$ can be calculated from the data shown in Fig. 2 and the reported stability constants for the formation of the complexes $Cu_2H_{-2}L_2^{4-}$, $NiL^-$, and $NiL_2^{4-}$ [3, 4]. The obtained value, $\log \beta_{11-22} = 1.37$, is in agreement with the value reported by Amico *et al.*, log $\beta_{11-22} = 1.55$ (25 °C, 0.1 mol $l^{-1}$ ($KNO_3$)) [16]. The latter value was calculated from a potentiometric titration recording pH and base consumption.

The considerable stability of the heteronuclear complex is illustrated in Fig. 3, where equimolar amounts of copper and nickel ions were titrated with EDTA at pH 8.9. The photometric titration curve consists of two linear portions with only one break point. The end point corresponds to the sum of copper and nickel ions. If a heteronuclear complex had not been formed, the photometric titration curve would have two break points as the difference between the stability constants of the copper and nickel EDTA complexes is several orders of magnitude. The example shows that the formation of heteronuclear complexes with hydroxycarboxylic acids will interfere in the masking reaction of the cations.

The formation of heteronuclear copper citrate complexes with zinc [16] and the alkaline earths [19] has been reported. The addition of magnesium ions to an alkaline solution of copper citrate results in a shift of the absorption maximum towards shorter wavelengths, indicating a distortion of the coordination sphere around the copper ion. An isosbestic point at *ca.* 720 nm indicates that a simple stoichiometry may be expected.

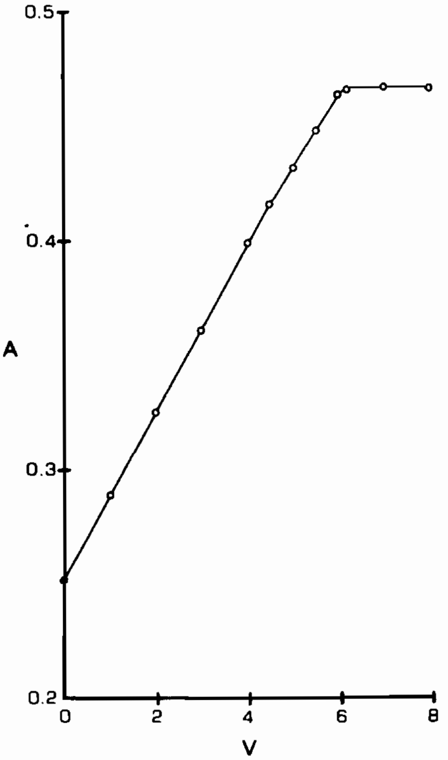

Fig. 3. Photometric titration of 50 ml of a solution containing copper and nickel ions in a concentration of 3.0 mml $l^{-1}$ and citrate 10 mmol $l^{-1}$ with a 49.0 mml $l^{-1}$ EDTA solution at pH 8.9. λ = 750 nm.

The Job plot in Fig. 4 reveals a 1:1 Cu:Mg ratio in the heteronuclear complex. The formation of the mixed-metal complex is pH-dependent as illustrated in Fig. 5. We may assume the following reaction to take place in the solution: $1/2Cu_2H_{-2}L_2^{4-} + MgL^- \rightleftarrows CuMgH_{-2}L_2^{4-} + H^+$. The average number of hydroxide ions bound to copper citrate, $\bar{n}_{OH}$, is defined in accordance with the equation. The value of the equilibrium constant of the above reaction can be calculated from the experimental data given in Fig. 5. The result is log K = –7.72. The value of the formation constant, log $\beta_{11-22} = -1.10$, is obtained assuming a value log $\beta_{11} = 3.73$ for the formation of magnesium citrate.

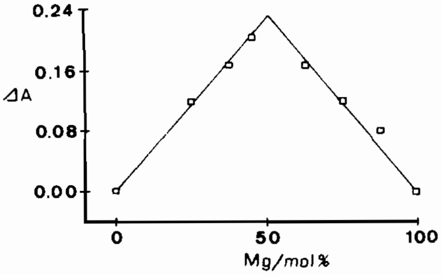

Fig. 4. Job plot for the copper-magnesium-citrate system. Absorbance differences are measured at 650 nm. Total concentration of citric acid = 100 mmol $l^{-1}$, the sum of copper and magnesium ions = 40 mmol $l^{-1}$. pH = 10.

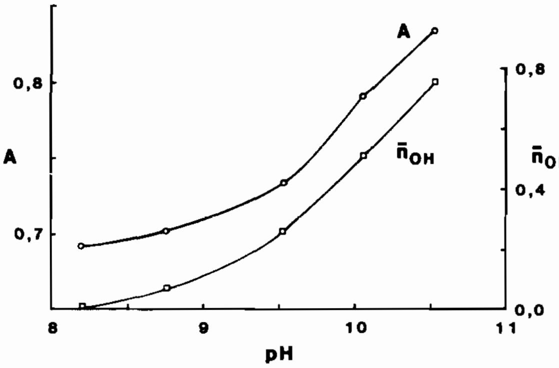

Fig. 5. pH-dependence for the formation of the mixed metal complex. Concentration of copper and magnesium ions is 20 mmol $l^{-1}$, that of citrate is 100 mmol $l^{-1}$. The absorbance is recorded at 650 nm. $\bar{n}_{OH}$ denotes the average number of hydroxide ions bound to each copper citrate dimer as defined in the text above.

The addition of calcium, strontium, or barium ions to a copper citrate solution results in the formation of mixed metal complexes. The heteronuclear complexes exist only at high pH-values, a higher pH-value being required for the formation of the copper–calcium citrate complex than for the corresponding magnesium complex, and still higher pH-values for the formation of the complexes with strontium and barium ions.

The present investigation shows that mixed metal complexes are frequently formed between copper citrate and other divalent cations. The general trend for their formation is in accordance with the hydrolytic behaviour of the cation (*e.g.*, in the form of the first hydrolysis step). Steric and electronic factors may also play a part, as shown by the low stability of the copper-zinc citrate complex.

In a larger context we stress that the general occurrence of mixed metal complexes with quadruply ionized citrate ions is a strong indication that mixed metal hydrolysis products may be observed in aqueous solutions. Experimental difficulties in their observation may be diminished by using complex-forming swamping electrolytes, so that the onset of hydrolysis starts at the same pH-value for both cations.

Mixed metal oxides are of great technical interest. The preparation of such materials can be performed by pyrolysis of heteronuclear citrate complexes. In this way different types of spinels have been prepared.

Examples of industrial relevance, pointing to further research in the area of mixed metal hydrolysis, are: corrosion studies, extraction of metals, and the production of paint [20].

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