*Inorganica Chimica Acta, 138* (1987) 31–34

# Cupric Complexes with 3,4-Dihydroxybenzoic Acid

KRYSTYNA GEREGA, HENRYK KOZŁOWSKI*
*Institute of Chemistry, University of Wrocław, Joliot-Curie 14, 50-383 Wrocław, Poland*
TAMAS KISS
*Institute of Chemistry, Kossuth University, 4010-Debrecen, Hungary*
GIOVANNI MICERA, LILIANA STRINNA ERRE
*Istituto di Chimica Generale ed Inorganica, Università di Sassari, Via Vienna 2, 07100 Sassari, Italy*
and FRANCO CARIATI
*Dipartimento di Chimica Inorganica e Metallorganica, Università di Milano, 20133 Milan, Italy*

(Received February 11, 1987)

## Abstract

Potentiometric and spectroscopic results indicated that 3,4-dihydroxybenzoic acid is a very effective ligand for cupric ions and the coordination equilibria formed are relatively complicated. In dilute aqueous solutions the bidentate catechol part of the ligand studied predominates as the binding site for metal ion although the carboxyl group may also participate in the metal ion binding leading to creation of the dinuclear species. More concentrated solutions yield a trimeric complex molecule ($Cu_3A_2$) with one metal ion bound to four phenolate oxygens and two others bound to the respective carboxylates.

## Introduction

The bioavailability to plants of metal ions, either essential or toxic, is strongly influenced by chelating agents which may be present in the soil. Of special interest are the phenolic ligands which are known to be present in the root exudates and may participate in the transport process of e.g. iron from the surrounding soil or nutrient solution to the roots [1].

Phenolic ligands are also important as the constituents of more complicated humic and fulvic acids, which are the main ligands taking part in the transport and accumulation of the nutrient ions [2].

Solid state studies have shown that a low pH carboxylate was main donor in the formed complexes with several 2,*x*-dihydroxybenzoic acids ($x = 4, 5, 6$) while the phenolate oxygens remained protonated [3–5].

Different behaviour was found for 3,4-dihydroxybenzoic acid for which, in the case of Cu(II) ion, the polynuclear species with $Cu_3A_2$ unit was isolated. The preliminary results suggested completely deprotonated ligand to be present in the complex formed, which may indicate involvement of all its donors in the metal ion binding. Since the complex was not suitable for X-ray analysis, to clarify this system we have undertaken a detailed solution study and the results are presented in this work.

The earlier solution study on the Cu(II) caffeic acid solution have shown the complexity of this kind of system [6] and that is why we have performed both potentiometric and spectroscopic experiments.

## Experimental

### *Potentiometric Studies*

Stability constants for complexes with $H^+$ and copper(II) were determined by pH-metric titration of 25 $cm^3$ samples. The concentration of the ligand in the samples was 0.004 or 0.002 mol $dm^{-3}$. Metal-to-ligand molar ratios of 1.5:1, 1:1, 1:2 and 1:4 were used in the titrations, and the ionic strength was adjusted to 0.2 mol $dm^{-3}$ with KCl in each sample. The titrations were performed over the pH range 3–9 (or until precipitation) with KOH solution of known concentration (*ca.* 0.2 mol $dm^{-3}$). The dissociation constant of the second phenolic hydroxy group of the ligand was determined at a concentration of 0.08 mol $dm^{-3}$. The pH was measured with a Radiometer pHM 64 instrument with G2040B glass and K4040 Calomel electrodes. Since the ligand tends to undergo oxidation, all measurements were performed in a TTA 80 titration unit in an argon atmosphere. The electrode system was

---

*Author to whom correspondence should be addressed.

0020-1693/87/$3.50

calibrated by the method of Irving *et al.* [7], so the pH-meter readings could be converted into hydrogen ion concentrations. In all cases the temperature was 25 °C. The calculations of the stability constants were made with the PSEQUAD computer program [8].

### *Spectroscopic Studies*

Absorption spectra were recorded on a Beckman UV240 spectrophotometer and EPR spectra were measured on a Jeol JES-ME-3X spectrometer at 120 K and 9.15 GHz. All spectroscopic measurements were carried out under argon and the concentrations were the same as used in the potentiometric titrations.

The solid state complex was obtained by adding an aqueous solution of copper(II) acetate to a warm solution of ligand. For all metal-to-ligand molar ratios (0.5–1.5) a dark red precipitate was formed almost immediately. *Anal.* Calc. for $Cu_{1.5}C_7H_9O_7$: C, 27.98; H, 3.00; $H_2O$, 17.98. Found: C, 27.45; H, 2.84; $H_2O$, 19.0%. The techniques and the instrumentation used in the study of the solid state complex have been described elsewhere [3–5].

## Results and Discussion

### *The Complex Formation in Diluted Solution*

Calculated protonation and Cu(II) complex formation constants are given in Table I. The literature data for the respective catechol complexes are also presented. The species distributions of the copper(II) complexes formed with 3,4-dihydroxybenzoic acid (DHB) at metal-to-ligand molar ratios of 1:1 and 1:2 as a function of pH are presented in Figs. 1 and 2.

TABLE I. Formation Constants of the Cu(II)–3,4-Dihydroxybenzoic Acid and Cu(II)–Catechol Complexes at 25 °C and $I = 0.2$ mol dm$^{-3}$ (KCl), in log units. $B = [Cu_pA_qH_r]/[Cu]^p[A]^q[H]^r$

| Species | (*pqr*) | DHB | Catechol[a] |
|---|---|---|---|
| HA | (011) | 13.1 | 13.0 |
| $H_2A$ | (012) | 21.77 | 22.28 |
| $H_3A$ | (013) | 26.02 | |
| CuAH | (111) | 19.22 ± 0.03 | |
| CuA | (110) | 13.95 ± 0.05 | 13.82 |
| $CuAH_{-1}$ | (11−1) | 6.32 ± 0.04 | |
| $CuA_2$ | (120) | 25.02 ± 0.04 | 24.69 |
| $Cu_2A$ | (210) | 16.50 ± 0.2 | |
| $Cu_2A_2$ | (220) | 30.00 ± 0.17 | |
| $Cu_2A_3$ | (320) | 41.30 ± 0.2 | |
| log *K*(CuA)/*K*($CuA_2$) | | 2.88 | 2.95 |
| $CuAH \rightleftharpoons CuA + H$ | | −5.27 | |
| $CuA \rightleftharpoons CuAH_{-1} + H$ | | −7.63 | |
| $CuA + A \rightleftharpoons CuA_2$ | | 11.07 | 10.87 |
| $CuA + Cu \rightleftharpoons Cu_2A$ | | 2.55 | |
| $Cu_2A + A \rightleftharpoons Cu_2A_2$ | | 13.50 | |
| $Cu_2A_2 + A \rightleftharpoons Cu_2A_3$ | | 11.30 | |

[a]See ref. 9.

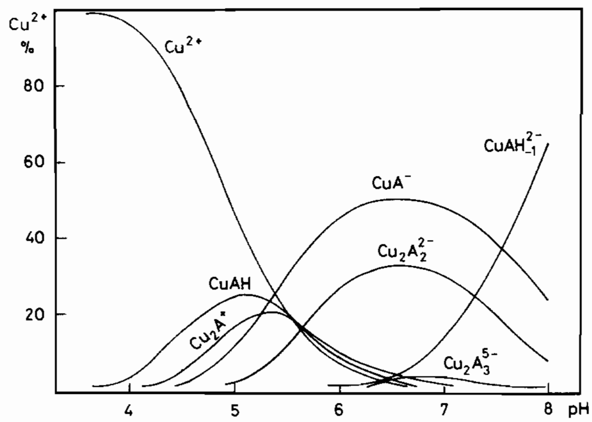


Fig. 1. Species distribution in the Cu(II)–3,4-dihydroxybenzoic acid system as a function of pH in equimolar solution.

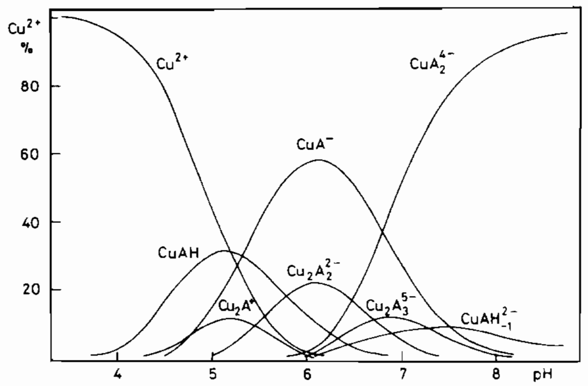


Fig. 2. Species distribution in the Cu(II)–3,4-dihydroxybenzoic acid system as a function of pH in a 1:2 metal-to-ligand molar ratio solution.

DHB has three protonation constants log *K*(1) = 13.1 (HA), 8.77 ($H_2A$), and 4.25 ($H_3A$). They correspond to the two deprotonations of phenolate and carboxyl groups, respectively. These values are in good agreement with the data obtained for catechol and other 3,4-dihydroxyphenyl derivatives [9–11].

The titration data for the Cu(II)–DHB solutions were evaluated at first assuming the coordination of the phenolic hydroxy groups only. The coordination of these groups is easily seen by their characteristic charge-transfer bands observed around 440 nm, which could be assigned to the phenolate oxygen to Cu(II) transitions [9, 12] (Table I). The fit, however, between the experimental and calculated data was bad, especially for 1.5:1 and 1:1 metal ion-to-ligand

TABLE II. Spectroscopic Data for Cu(II)–3,4-Dihydroxybenzoic Acid Complexes

| Species | EPR | | Absorption λ (nm) (ε) |
|---|---|---|---|
| | $A_{\|}$ (gauss) | $g_{\|}$ | |
| CuA | 165 | 2.292 | 737$^a$ (50)$^c$<br>430$^b$ (120)$^c$ |
| $CuAH_{-1}$ | 167 | 2.286 | 680$^a$ (53)$^d$<br>430sh (190)$^d$ |
| $CuA_2$ | 190 | 2.254 | 645$^a$ (60)$^e$<br>365$^b$ (400)$^e$ |
| dinuclear<br>$\{Cu_2A_2 + Cu_2A\}^f$ | 155<br>165 | 2.325<br>2.286 | |

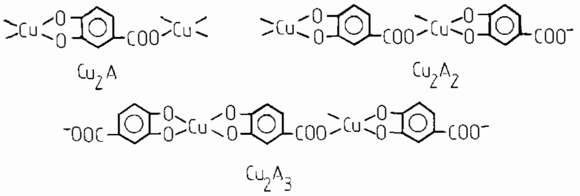
[a] d–d transitions. [b] Phenolate oxygen to Cu(II) charge-transfer transitions. [c] Calculated for equimolar solution at pH 6.2 for total Cu. [d] Calculated for equimolar solution at pH 9. [e] Calculated for 1:2 (M:A) solution at pH 10. [f] From 1.5:1 (M:A) and equimolar solutions at pH = 6, the overlapped spectra are observed when $Cu_2A_2$ and $Cu_2A$ are the major species according to the potentiometric species distribution.

molar ratios (fitting parameter 0.0204 cm$^3$ for 369 experimental points [8]). In the next step we have assumed carboxylate involvement as well as the formation of polymeric species. The best fitting of the experimental data with those calculated (0.0113 cm$^3$) was obtained for the set of species presented in Table I. This set of complex species corresponds basically to that proposed earlier for the Cu(II)–caffeic acid system [6]. The presence of two different cupric binding sites in the complexes formed at pH above 5, *i.e.* at the region where dimeric forms are suggested by potentiometric data, is also seen in the EPR spectra. They consist of two or three overlapped sets of lines and their intensity depends on pH and metal-to-ligand molar ratio (Table II). There are two EPR spectra observed at pH > 10 for the 1:1 molar ratio solutions with $A_{\|} = 167$ gaus [G] and $g_{\|} = 2.286$, and $A_{\|} = 188$ G and $g_{\|} = 2.252$. The spectrum with the latter parameters is also observed for the other molar ratio solutions at high pH range and it corresponds well to the $CuA_2$ species. The formation of this complex in equimolar solution is possible as some precipitation was observed at pH around 7–8, most likely of $Cu(OH)_2$. The former spectrum observed for the equimolar solution corresponds to the $CuAH_{-1}$ species in which metal ion binds ligand via two deprotonated phenolate oxygens. The assignments of the other EPR spectra are given in Table II. The formation of the CuA and $CuA_2$ species as the major complexes in 1:1 and 1:2 molar ratio solutions is also supported by the intensity of the phenolate oxygen to metal charge-transfer transition which is almost doubled in the latter case when compared to the previous one (in both cases ε is calculated with respect to the metal ion concentration).

The EPR parameters of the $CuAH_{-1}$ species are almost the same as those found in equimolar solution for CuA complex (Table II). This indicates clearly that the coordination sets in both species are very similar, *i.e.* the former complex is formed by deprotonation of a water molecule in the CuA species. The coordination modes in the complexes formed can be also concluded from the stability constants and the species distributions given in Table I and Figs. 1 and 2:

(1) Because of the significant difference in the ability to form a complex between the bidentate catechol part of the molecule and the monodentate carboxylate, mainly $\{O,O\}$ (two phenolate oxygens), coordinated monomeric complexes, *i.e.* CuAH, CuA and $CuA_2$, are formed in the system studied. In the CuAH species the carboxylate group is protonated. The deprotonation constant of this complex (p$K$ = 5.27) is about one order higher than that of the free ligand due to the strong electron-releasing effect of the phenolate groups. The stepwise stability constants of the CuA and $CuA_2$ complexes and their $\log(K_1/K_2)$ values are in good agreement with those obtained for the Cu(II)–catechol system. This proves again the $\{O,O\}$ coordination mode in the complexes studied. $CuAH_{-1}$ seems to be really the mixed hydroxo complex, as suggested above.

(2) Without ligand excess the carboxylate may also be involved in the metal ion binding and polynuclear species of various stoichiometries are formed, e.g. $Cu_2A$, $Cu_2A_2$ or $Cu_2A_3$. The spectroscopic results and the stability constants given in Table I suggest the binding modes for these species as presented in Scheme 1.

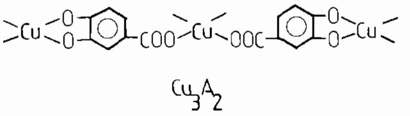


Scheme 1.

The equilibrium constant for the reaction CuA + Cu ⇌ $Cu_2A$ (log $K$ = 2.55) is about one order of magnitude higher than $\log K_{CuB} = 1.5$ for benzoic acid (HB) [13]. This stability increase can be explained by the increase in the basicity of the carboxylate in the coordinated DHB molecule (see above log $K$ for CuAH). The stepwise stability constants for the coordination of a second and a third ligand molecule, forming $Cu_2A_2$ (log $K$ = 13.5) or $Cu_2A_3$ (log $K$ = 11.3) species, respectively, agree well with those obtained for the monomeric complexes assuming $\{O,O\}$ coordination modes.

The solid state complex obtained from more concentrated solutions seems to be also a polynuclear species having a $Cu_3A_2$ unit. The reflectance absorption spectra show a very broad d–d transition band centered around 770 nm and the charge-transfer band at 450 nm. Although the latter transition indicates involvement of the phenolate oxygens in the metal ion binding (see e.g. Table II), the relatively low d–d transition energy when compared to, e.g., $CuA_2$ may indicate that in the trimeric unit cupric ions may exist bound mostly with carboxylic or water oxygens (the energy of the d–d transition for cupric aquo ion is around 840 nm, and for the CuA species in which two sites are occupied by phenolate oxygens it is equal to 737 nm, see above).

Thermogravimetric measurements are consistent with a water release occurring in two different steps. In the first step (25–75 °C) two water molecules are lost, while in the second step (75–120 °C) the remaining four water molecules are removed from a trimeric unit. The pH of the solution from which the precipitate was obtained was around 4. According to the potentiometric results, in this pH range there are two complex species in equilibrium, CuAH and dinuclear $Cu_2A$, with coordination modes as given in Scheme 1. The simple reaction of these two complexes leads to formation of a trinuclear complex, *i.e.* $CuAH + Cu_2A \rightleftharpoons Cu_3A_2 + H^+$, with coordination mode as given in Scheme 2. The water molecules removing mode (2 + 4) and the spectroscopic features of the trimeric species are easily understood when such a structure is assumed for the trinuclear species. The EPR spectra of this complex consists of a very broad featureless band at $g$-2, supporting its polymeric structure.



Scheme 2.

The study presented above, as well as those performed earlier, clearly indicate that two adjacent phenolate functions of the dihydroxybenzoic moiety are a very potent donor set, able to form complex species even at acidic pH (>4). The high metal concentrations may lead to formation of the polynuclear species but additional donor species (even weakly binding, e.g. carboxylate (for Cu(II) ions)) must be present. Thus, the metal ion may cause the aggregation of organic matter which may yield humic substances.

## Acknowledgements

This work was financially supported by the Polish Academy of Sciences (Project 01.12) and Consiglio Nazionale delle Ricerche (Rome).

## References

1 R. A. Olsen, J. C. Brown, J. H. Bennett and D. Bloom, *J. Plant Nutrition, 5*, 433 (1982).
2 M. Schnitzer and S. U. Khan, 'Humic Substances in the Environment', Dekker, New York, 1972.
3 F. Cariati, L. Erre, G. Micera, A. Panzanelli, G. Ciani and A. Sironi, *Inorg. Chim. Acta, 80*, 57 (1983).
4 G. Micera, L. Strinna Erre, P. Piu, F. Cariati, G. Ciani and A. Sironi, *Inorg. Chim. Acta, 107*, 223 (1985).
5 G. Micera, L. Strinna Erre, F. Cariati, G. Ciani and A. Sironi, *Inorg. Chim. Acta, 108*, L1 (1985).
6 P. W. Linder and A. Voye, *Rev. Port. Quim., 27*, 337 (1985).
7 H. Irving, M. G. Miles and L. D. Pettit, *Anal. Chim. Acta, 38*, 475 (1967).
8 L. Zekany and I. Nagypal, in Leggett (ed.), 'Computational Methods for the Determination of Stability Constants', Plenum, New York, 1985.
9 A. Gergely and T. Kiss, *Inorg. Chim. Acta, 16*, 51 (1976).
10 T. Kiss and A. Gergely, *Inorg. Chim. Acta, 36*, 31 (1979).
11 A. Gergely, T. Kiss, Gy. Keak and I. Sovago, *Inorg. Chim. Acta, 56*, 35 (1981).
12 H. Kozlowski, M. Bezer, L. D. Pettit, M. Bataille and B. Hecquet, *J. Inorg. Biochem., 18*, 231 (1983) and refs. therein.
13 D. D. Perrin, 'Stability Constants of Metal Ion Complexes', Part B, Pergamon, Oxford, 1979.