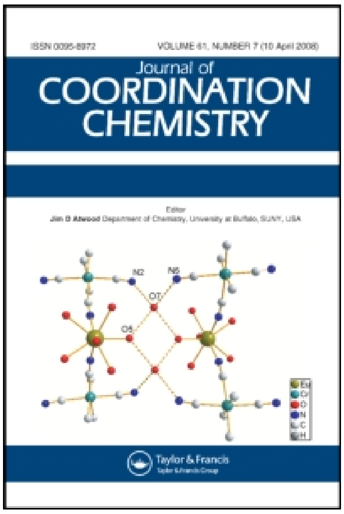

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Tamas Kiss[a]; Henryk Kozlowski[b]; Giovanni Micera[c]; Liliana Strinna Erre[c]
[a] Department of Inorganic and Analytical Chemistry, Kossuth Lajos University, Debrecen, Hungary [b] Institute of Chemistry, University of Wroclaw, Wroclaw, Poland [c] Dipartimento di Chimica, Universitá di Sassari, Sassari, Italy

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COPPER(II) COMPLEXES OF 2,3-DIHYDROXYBENZOIC ACID

TAMAS KISS

Department of Inorganic and Analytical Chemistry, Kossuth Lajos University, 4010 Debrecen, Hungary

HENRYK KOZLOWSKI

Institute of Chemistry, University of Wroclaw, Joliot-Curie 14, 50-383, Wroclaw, Poland

GIOVANNI MICERA* and LILIANA STRINNA ERRE

Dipartimento di Chimica, Università di Sassari, Via Vienna 2, 07100 Sassari, Italy

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The interaction of copper(II) with 2,3-dihydroxybenzoic acid (2,3-DHB) in aqueous solution has been investigated by means of potentiometric and spectroscopic (EPR and electronic absorption) measurements. The complex formation equilibria in the Cu(II)–2,3-DHB system are distinctly different from those already observed with analogous ligands such as 3,4-DHB and 2,*x*-DHB (*x* = 4, 5 and 6) which form catechol- and salicylic-like complexes, respectively. The position of the three binding sites allows 2,3-DHB to exhibit both the salicylic and catechol coordination types. Besides monomeric species, oligonuclear complexes are formed in which the carboxylate groups are responsible for the metal bridging.

Keywords: Copper(II), 2,3-dihydroxybenzoic acid, stability constants, oligomers

INTRODUCTION

Our recent studies on the binding ability of the dihydroxybenzoic acids have shown that deprotonated phenolic functions are very effective binding sites for cupric ions especially when the two hydroxyls are in *ortho* positions (catechol-like coordination).[1,2] Carboxylic groups can play an important role in metal ion binding at low pH or in cases when the two hydroxyls are not properly situated.[1–5] The 2,*x*-dihydroxybenzoic acids (*x* = 4, 5 and 6), in which one of the phenolic groups is in an *ortho* position to the carboxyl function while the other one cannot form catechol-like chelate rings, behave as salicylic acid ligand.[2] The formation of the (COO^-, O^-) chelates, however, leads to stable species indicating that such a bonding mode could be also of importance in natural systems, *e.g.*, in soil organic matter. 2,3-Dihydroxybenzoic acid (2,3-DHB) has three potential binding functions on three adjacent ring carbons and as such it could be a good model to study the possibility of competitive chelate formation by two pairs of donors, (O^-, O^-) and (COO^-, O^-), with varying pH and metal-to-ligand molar ratios. In this paper we present results of potentiometric and spectroscopic studies of the copper(II)–2,3-DHB system in aqueous solution.

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* Author for correspondence.

EXPERIMENTAL

Potentiometric studies

Stability constants for proton and copper(II) complexes were determined by pH-metric titrations 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 0.75:1, 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. The titrations were performed in the pH range 2.6 to 11.0, unless precipitation occurred earlier. 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 calibrated by the method of Irving *et al.*,[6] so the pH-metric 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.[7]

Spectroscopic Studies

Absorption spectra were recorded on a Beckman Acta MIV spectrophotometer and EPR spectra were measured on a Varian E 9 spectrometer (X band) at 110 K. The measurements were performed under argon with concentrations of samples similar to those used in the potentiometric studies.

RESULTS AND DISCUSSION

Proton complexes

2,3-Dihydroxybenzoic acid (2,3-DHB, AH_2) has two measurable proton dissociation constants (Table I). The very weak acidity of the third proton may be attributed to electrostatic attraction of the nearby negative charges as well as to a hydrogen bond between the hydroxyl and carboxyl functions. The pK values obtained in this work are close to those presented by Aplincourt *et al.*,[8] except for the third dissociation constant which we found to be above 14 (Table I). The weak acidity of the second hydroxyl group was proved by pH-spectroscopic titration. The UV absorption of the ligand remains unchanged in the pH region 11.0–13.2, indicating the lack of deprotonation of the phenolic hydroxyl group.

Copper complexes

The equilibria existing in the Cu(II)–2,3-DHB system are distinctly different from those found with the other 2,x-DHB ligands (x = 4, 5 or 6),[2] which form salicylate-type complexes, or with 3,4-DHB, which behaves as a catechol derivative. The considerable differences are seen in the shapes of the potentiometric curves of solutions at a ligand-to-metal molar ratio of 2:1 (see Figure 1). The potentiometric curve of the copper(II)–3,4-DHB system shows a sharp pH jump at $m = 6$, indicating the dissociation of three protons (from two phenolic OH and one COOH groups) of the ligand and suggesting pure (O^-, O^-) coordination. The titration curve of the copper(II)–2,4-DHB system shows no significant pH jump, but rather a smooth and

TABLE I
Proton (pK) and copper(II) (log β) stability constants with 2,3-DHB acid.

Species	Model Ia	Model Ib	Model II	Ref. 8
pK(COOH)		2.66 ± 0.02		2.70
pK(3-OH)		9.80 ± 0.02		9.76
pK(2-OH)		>14		13.00
CuAH	11.86 ± 0.13	11.71 ± 0.16	11.78 ± 0.20	
CuA	7.56 ± 0.03	7.65 ± 0.03	7.73 ± 0.02	
$CuAH_{-1}$	—	1.90 ± 0.03	1.96 ± 0.02	
$CuAH_{-2}$	9.09 ± 0.09	9.10 ± 0.09	9.01 ± 0.11	
CuA_2H_{-2}	−4.80 ± 0.03	−4.84 ± 0.03	−4.82 ± 0.04	
$Cu_2A_2H_{-1}$	13.06 ± 0.03	12.48 ± 0.14		
$Cu_2A_2H_{-2}$	6.75 ± 0.03			
$Cu_3A_2H_{-2}$	10.15 ± 0.36	10.45 ± 0.20		
Δcm^3	$9.75 \cdot 10^{-3}$	$1.18 \cdot 10^{-2}$	$1.48 \cdot 10^{-2}$	
$\log(K_1/K_2)$		8.64	8.74	
$pK(CuAH_{-1})$		10.97	11.00	
Cu + HA = CuA + H	−2.24	−2.15	−2.07	−2.33
$CuA + HA = CuA_2 + H$				−3.38
$pK(CuA_2)$				−9.57
$pK(CuA_2H_{-1})$				−8.57

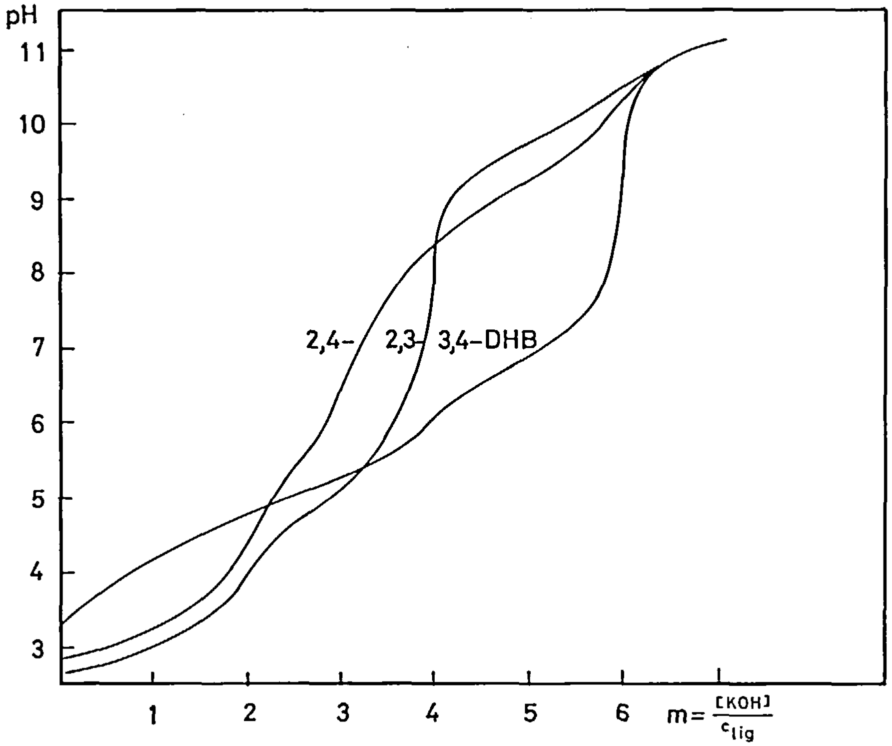


FIGURE 1 Titration curves for the copper(II)-2,3-DHB, -2,4-DHB and -3,4-DHB systems at a ligand-to-metal ration of 2:1.

continuous increase indicating a weaker salicylate-type (O^-, COO^-) coordination and an overlap of the complex formation reaction with the dissociation of the non-coordinating phenolic OH in position 4. In the case of copper(II)-2,3-DHB system a flatter titration curve and a sharp pH jump at $m = 4$ is observed suggesting strong metal ion coordination (stronger than that of the salicylate-type) but without the dissociation of all of the acidic groups of the ligand. These results confirm the expectations that the arrangement of the carboxylic and the two phenolic hydroxyls on the three neighbouring ring carbons makes 2,3-DHB behave as both salicylic acid and catechol ligands.

TABLE II

Spectroscopic data for Cu(II) complexes of 2,3-DHB.[a]

Species	$g_{\parallel}$	ESR $A_{\parallel}$, $10^{-4}\,cm^{-1}$	Absorption λ, nm (ε)	Coordination mode of ligand
CuAH	2.363	154		COO^-
CuA	2.324	168[b]	740(62)[d] 415(185)[e]	$\{COO^-, 2\text{-}O^-\}$
CuA_2H_{-2}	2.239	201	600(169)[d] 420(640)[e]	$2 \times \{2\text{-}O^-, 3\text{-}O^-\}$
$Cu_2A_2H_{-1}$[c]	2.313 2.296	168 176	715(87)[d] 415(375)[e]	$\{2\text{-}O^-, 3\text{-}O^-, COO^-\} + \{2\text{-}O^-, COO^-\}$
$Cu_2A_2H_{-2}$	2.307	165	675(120)[d] 430(570)[e]	$\{2\text{-}O^-, 3\text{-}O^-, COO^-\}$

[a] ε Values were calculated for the total Cu(II) concentration for pH at which the respective species is a major complex. [b] The same parameters were found for equimolar Cu(II) complexes of 2,x-DHB (x = 4, 5 or 6) with well established salicylic-like coordination (ref. 2). [c] This complex contains two different Cu(II) chromophores (see Scheme 1). [d] = d-d Transition. [e] = Phenolate oxygen-to-Cu(II) charge transfer transition (see refs. 1, 2, 11, 12); ε in units of $M^{-1}\,cm^{-1}$.

The titration curves for the copper(II)–2,3-DHB system were evaluated by assuming several models, some of which are collected in Table I. The spectroscopic data for the respective complexes are shown in Table II. Two basic sets of species were tried in the computation, *i.e.*, with or without the assumption of polymeric species (models I and II, respectively). Other possible species, *e.g.*, CuA_2, CuA_2H_{-1}, Cu_2AH_{-1}, *etc.*, were also assumed but they were rejected by the computer program. It can be seen in Table I that the fitting parameter, Δcm^3 (the average difference between the measured and calculated titration curves)[7] is not good if only monomeric species are assumed. The first complex found in all models and seen by EPR spectroscopy is the species with carboxyl coordination only and which is usually found in this kind of systems.[2,9] The EPR parameters (Table II) are those typical of this type of coordination. In a previous paper[2] we have pointed out that the potentiometric determinability of these species is poor, since only minor pH effects are produced by copper(II) carboxyl binding in this pH range. Therefore, the assignment of mono- or bis-carboxylate coordination to the formed species is purely indicative. At pH above 5 the complex CuA, or, more precisely, $Cu(HAH_{-1})$ with salicylate-type (COO^-, O^-) coordination is formed. The equilibrium constant characteristic of the process $Cu^{2+} + HA^- = CuA + H^+$ is in good agreement with that of salicylic acid or its derivatives.[2] According to Model II, at higher pH the complexes $CuAH_{-1}$ and CuA_2H_{-2} are formed. In these species the binding mode is presumably of the catechol-type (O^-, O^-). The mixed bonding mode (COO^-, O^-; O^-, O^-) in the species CuA_2H_{-2} can be excluded, since EPR and absorption spectra clearly show pure (O^-, O^-) donor sets. However, in this case the coordination of the second ligand should be very much hindered because the value of log[K(CuA)/K(CuA_2)] is 8.7 compared to that of *ca* 3 expected for true (O^-, O^-) coordination.[1,11] Similarly, the very weak acidity, pK($CuAH_{-1}$) *ca* 11, of a water molecule coordinated in the equatorial plane of the complex $CuAH_{-1}$ is unlikely.

In order to obtain a more reasonable description of the system and to improve the quality of fit of the titration curves, the formation of various polymeric species, similar to those found in the other copper(II)–DHB systems,[2,9] was also assumed (Models Ia and Ib). In this manner the fitting was improved by about 50% and fell within the limits of experimental error. It was found that the species $Cu_2A_2H_{-2}$ could be substituted by its corresponding monomeric form $CuAH_{-1}$ (Model Ib) in the calculation with a decrease of the goodness of fit. If, however, both the monomeric and dimeric species were assumed, the monomeric species was rejected giving the same result as for Model Ia.

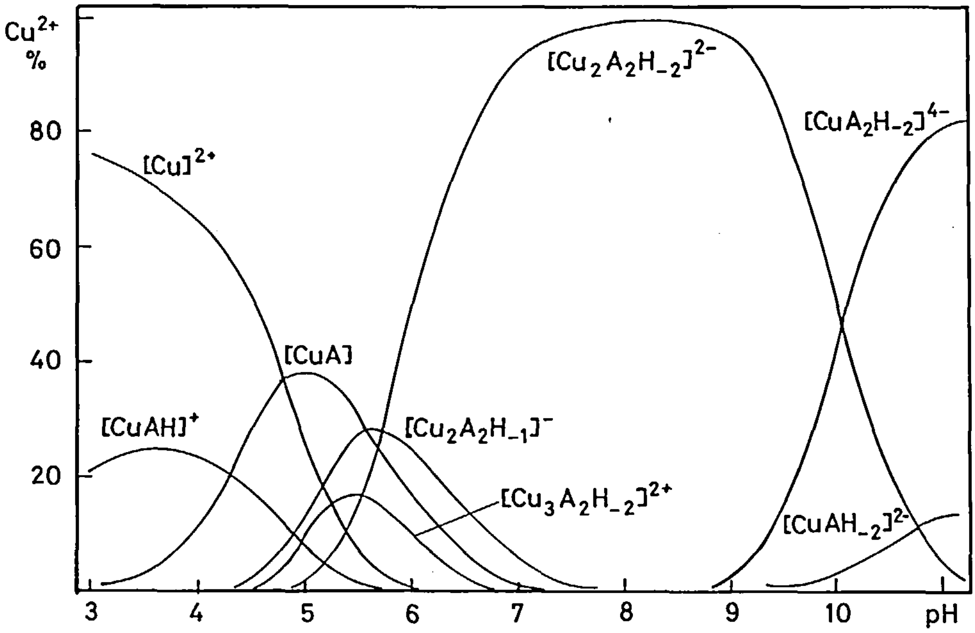
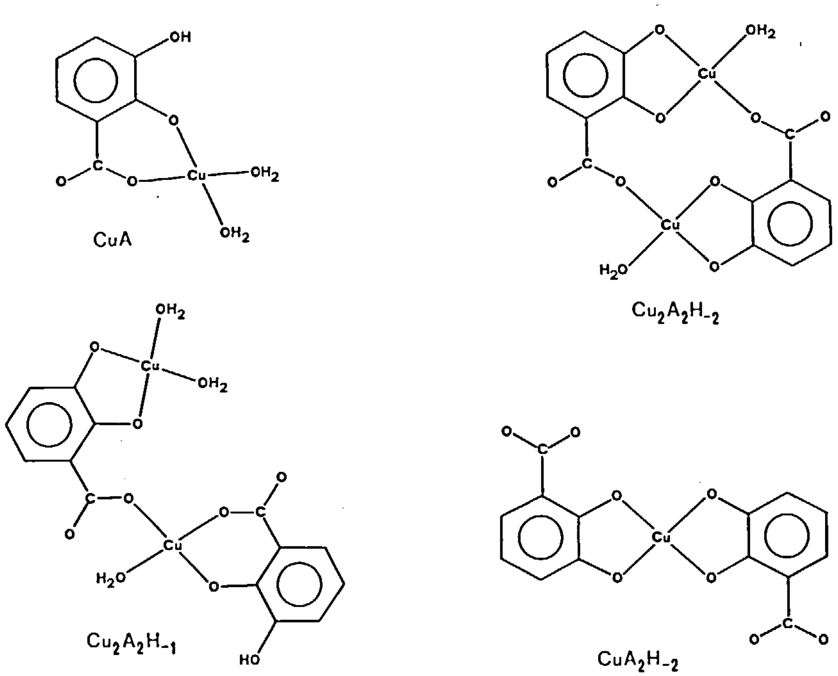


FIGURE 2 Concentration distribution curves for the complexes formed in the copper(II)–2,3-DHB system; $C_{Cu} = 0.002\ mol\ dm^{-3}$, $C_{ligand} = 0.004\ mol\ dm^{-3}$.

The concentration distribution curves of the species formed according to Model Ia are depicted in Figure 2. It can be seen in the figure that, beside the monomeric species, a dimer, $Cu_2A_2H_{-1}$, is formed around pH 5. The bridging group between the two chelated copper(II) ions is presumably a carboxylate group (see Scheme 1). The spectroscopic results are in good agreement with such a dimeric structure as the EPR and absorption spectral data are very close to those obtained for analogous



SCHEME 1

coordination in the case of 3,4-DHB system.[1] The deprotonation of the phenolic group of the second DHB ligand leads to formation of the other dimeric species $Cu_2A_2H_{-2}$. The EPR spectra indicate that both the metal ions in the dimer are bound to the same or very similar donor set. The formation of the latter dimeric species causes the shift of the d–d transition towards higher energy from 715 nm at pH 5.8 ($Cu_2A_2H_{-1}$ major species) to 675 nm ($Cu_2A_2H_{-2}$ major species). This energy shift could be explained by the change from salicylic-like to catechol-like coordination for the second metal ion in the dimeric unit. The resulting structure is also presented in Scheme 1. The considerably higher stability of $Cu_2A_2H_{-2}$ when compared to the respective complex of 3,4-DHB[1] in which only one carboxylate could be involved in the bridging of two metal ions supports the hypothesis that in the present case both carboxylate groups are involved in metal bridging. The examination of molecular models shows that such a structure, as presented in Scheme 1, is sterically possible only for the 2,3-DHB ligand. The formation of such a closed structure introduces, however, some hindrance which is substantiated by the slight decrease of the hyperfine structure parameter $A_{\parallel}$ ($165 \times 10^{-4}\,cm^{-1}$) when compared to the data obtained for the "open" dimer of the 3,4-DHB ligand ($176 \times 10^{-4}\,cm^{-1}$). The increase of pH above 9.5 leads to hydrolysis of the dimeric form and two monomeric species are formed: $CuAH_{-2}$ in equimolar solutions and CuA_2H_{-2} complex in solutions with excess ligand (Fig. 2). Both complexes have catechol-like coordination as found in the case of 3,4-DHB. The high stability of the dimer $Cu_2A_2H_{-2}$ formed by 2,3-DHB disfavours (O^-, O^-) coordination. In fact, the species CuA_2H_{-2} is formed at pH about 3 units higher than the respective complexes in the Cu(II)–3,4-DHB system. The formation of the monomeric

CuA_2H_{-2} complex indicated by the potentiometric data is followed precisely also by the EPR and absorption spectra (for parameters, see Table II). The results obtained in this paper are in distinct disagreement with the conclusions presented in an earlier work[8] in which the authors assumed only the formation of monomeric species with stoichiometries similar to other 2,*x*-DHB systems. The tendency of copper(II) to form oligonuclear complexes with the ligands having a catechol-type of donor set and carboxylate as the third function was however shown to be evident in several other systems.[1,10] The comparison of the data obtained here with those reported, *e.g.* for the 3,4-DHB system, seems to present reasonable arguments for the formation of dimeric species with 2,3-DHB as well.

It must be mentioned that the EPR spectra do not indicate dimer formation unequivocally. For example, in the "closed" dimer the magnetic coupling between the copper centres should be strong enough to cause a seven-line splitting of the ESR signals (see, *e.g.* ref. 11). Nevertheless, the variation of the spectral parameters with pH and a number of assigned species corresponds exactly to the potentiometric findings presented in Fig. 2 (Table II). The previous study on the 2,*x*-DHB ($x = 4$, 5 and 6) has shown that the transition of salicylic-type mono-chelate to salicylic-type bis-chelate coordination distinctly increases the $A_{\parallel}$ value[2] (from 168 to $176 \times 10^{-4}\,cm^{-1}$), while in the case presented here the transformation of the two consecutive complexes between pH 5 and 8 leads to a slight but measurable decrease of this value (Table II). In both the cases mentioned above the $g_{\parallel}$ value decreases as predicted for the substitution of water or carboxyl binding for the phenolate oxygen coordination. Thus, the coordination equilibria existing in the Cu(II)-2,3-DHB as well as in the 3,4-DHB system (see ref. 1) are distinctly different than in the case of the Cu(II)-2,*x*-DHB systems in which salicylic-type coordination is forced by the donor positions in the ligand molecules.

CONCLUDING REMARKS

The coordination mode of ligands having two phenolic and one carboxylate functions on the aromatic ring depends strongly on the positions of the respective donors. Although all ligand functions may be involved in metal ion binding, the most effective is catechol-like coordination. The system studied here as well as the earlier (on diphenolic acids) shows clearly the tendency of cupric ions to form oligonuclear complexes with ligands possessing a catechol function and a carboxylate group.[1,10] The carboxyl groups, which act as bridges between the monomeric units, can be removed from the coordination sphere by phenolic groups in basic media.

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