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Electron Spin Resonance Study of 2,6-Dihydroxybenzoate Copper(II) Complexes

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Much current interest is devoted to elucidate the nature and the extent of the interaction between metal ions and naturally occurring ligands, such as fulvic and humic acids, which take part in either storage or transport of trace metal ions in soil [1, 2]. Although the structure of such polyelectrolytes is not well-defined, all the models agree that the potentially active groups in the metal binding are those of aromatic hydroxycarboxylic acids [3–6]. In order to model the metal-humate and -fulvate interactions using simple compounds, we have undertaken the investigation of metal complexes formed by dihydroxybenzoic acids in both solution and solid state.

From acidic aqueous solutions containing Cu^{2+} and 2,6-dihydroxybenzoate ions a green crystalline complex, $[Cu(H_2A)_2(H_2O)_2]$,** was isolated [7]. The X-ray analysis revealed that the ligand is coordinated to copper(II) only through a monodentate carboxylate bond. As such a complex, or the corresponding solution species, is not the only possible one, we have investigated the composition of copper(II)-2,6-dihydroxybenzoate aqueous solutions over a wide pH range. ESR and electronic spectroscopies were used to obtain information on the system.

Experimental

Crystalline $[Cu(H_2A)_2(H_2O)_2]$ was obtained as described elsewhere [7]. The ESR spectra were recorded on a Varian E 9 spectrometer (X-band) at 110 K. DPPH was used as standard field marker. The electronic spectra were recorded on a Beckman Acta M IV spectrophotometer using 1-cm quartz cells. Aqueous solutions of $[Cu(H_2A)_2(H_2O)_2]$, adjusted to selected pH values, were used. The pH measurements were made using an Orion Model 901 pH-meter. Dimethyl sulphoxide was added (50% by volume) to assure the formation of good glasses at low temperatures. The final copper(II) concentration was about 5 m*M*.

Results and Discussion

In frozen dry dimethyl sulfoxide $[Cu(H_2A)_2(H_2O)_2]$ gives an ESR spectrum attributable to a single species with axial symmetry ($g_\parallel = 2.378$, $g_\perp = 2.074$, $A_\parallel = 147 \cdot 10^{-4}$ cm^{-1}). Compared to the solid $[Cu(H_2A)_2(H_2O)_2]$ complex, which is characterized by a lower $g_\parallel$ value ($g_\parallel = 2.311$, $g_\perp = 2.076$), the solution species is believed to be axially coordinated by solvent molecules. In aqueous solution over pH range 2.5–6.5, diluted with dimethyl sulfoxide, more than one species is observed (Figs. 1–3). The solvated ion is easily distinguished by its small $A_\parallel$ ($134 \cdot 10^{-4}$ cm^{-1}) and distinctive $g_\parallel$ (2.410) values [8]. Moreover a species (denoted as *1*) exhibiting ESR parameters very close to those of $[Cu(H_2A)_2(H_2O)_2]$ dissolved in dry dimethyl sulfoxide, is also detected. Over the pH range 2.5–3.5 only the signals of the free ion and *1* are observed. As the pH is raised, the complex *1* vanishes to give a species, namely *2*, which is in equilibrium with the free ion at pH 5.5–6.0. In neutral media the species *2*, which shows higher $A_\parallel$ ($163 \cdot 10^{-4}$ cm^{-1}) and smaller $g_\parallel$ (2.333) values than those of *1*, becomes the only kind of copper(II) complex in solution. This species is stable until pH ~ 7.5, when the signals of a new species, denoted *3*, ($g_\parallel = 2.305$, $g_\perp = 2.068$, $A_\parallel = 172 \cdot 10^{-4}$ cm^{-1}, $A_\perp$ =

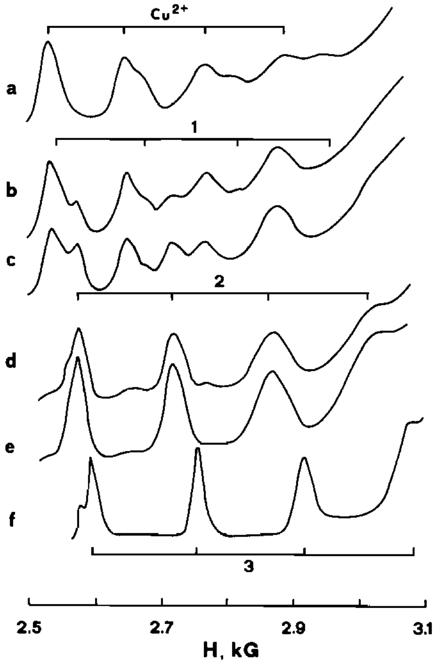

Fig. 1. $g_\parallel$ region of the ESR spectra (110 K) of ~10 m*M* aqueous solutions of $[Cu(H_2A)_2(H_2O)_2]$ at (a) pH 3.1, (b) pH 4.0, (c) pH 4.5, (d) pH 5.5, (e) pH 6.2, (f) pH 9.5 diluted 1:1 with dimethyl sulfoxide.

**H_2A and HA indicate the monoanion $C_6H_3(OH)_2COO^-$ and the dianion $C_6H_3(OH)(O^-)COO^-$, respectively.

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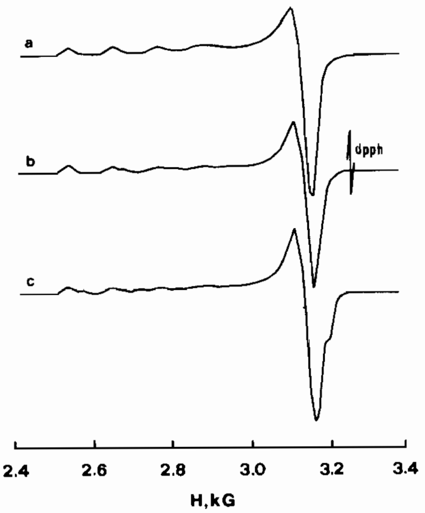

Fig. 2. ESR spectra (110 K) of ~10 m*M* aqueous solutions of $[Cu(H_2A)_2(H_2O)_2]$ at (a) pH 2.5, (b) pH 3.1, (c) pH 4.0 diluted 1:1 with dimethyl sulfoxide.

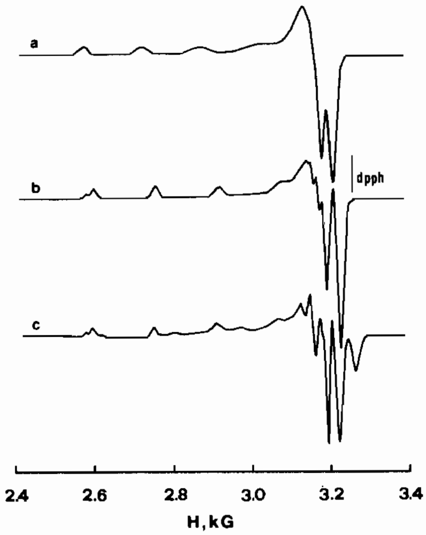

Fig. 3. ESR spectra (110 K) of ~10 m*M* aqueous solutions of $[Cu(H_2A)_2(H_2O)_2]$ at (a) pH 6.5, (b) pH 9.5, (c) pH 12.7 diluted 1:1 with dimethyl sulfoxide.

$17 \cdot 10^{-1}$ cm^{-1}), appear. More basic solutions enhance the transition *2* → *3*, which is almost complete at pH 9.5. Further addition of NaOH (pH > 12.5) leads to the formation of $[Cu(OH)_4]^{2-}$, which is identified by the $A_\parallel$ value ($186 \cdot 10^{-4}$ cm^{-1}) as well as the distinctive 'overshoot' band in the g ~ 2.0 spectral region [9].

The electron spectroscopy data concerning the copper(II)-2,6-dihydroxybenzoate system are given in Fig. 4, where the pH-dependence of the *d–d* band energy is shown. As the pH is raised, a shift of the absorption maximum to higher frequencies is observed. However, clearly evident are two 'plateau' regions, corresponding to the stepwise formation of the species *2* and *3*, respectively.

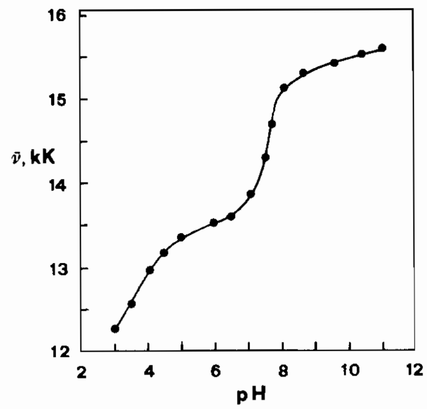

Fig. 4. *d–d* absorption maximum of ~10 m*M* aqueous solutions of $[Cu(H_2A)_2(H_2O)_2]$ over the pH range 3–11 diluted 1:1 with dimethyl sulfoxide.

Thus it appears that both ESR and electronic spectra are consistent with a sequence of pH-dependent equilibria, according to the scheme:

$Cu^{2+} \rightleftarrows 1 \rightleftarrows 2 \rightleftarrows 3 \rightleftarrows [Cu(OH)_4]^{2-}$

By a comparison with the analogous copper(II)–salycylate system [10], *2* is believed to be a chelate [Cu(HA)] complex (solvent molecules completing the ion coordination), whereas *3* corresponds to the square-planar bis chelate $[Cu(HA)_2]^{2-}$ anion as well as the species generated after deprotonation of the residual phenolic groups. On the other hand, the species *1*, likely involving only carboxylate bonds between ligand molecules and copper(II) ion, is never found as a major component of the system.

Despite possible differences between the models examined here, and the natural systems, some observations seem pertinent to an understanding of the complexation mechanisms concerning trace metal ions in the soil environment. In moderately acid media a single Cu(II) species is never detected. In fact, the easy displacement of phenolic hydrogens by copper(II) allows the formation of 1:1 neutral chelates in addition to the 'acetate like' species. Both mechanisms take place at pH values which are of significance in nature. Besides, it must be considered that in the irregular structure of the humic and fulvic macromolecules carboxylic groups without *ortho* phenolic substitutions are also involved. This is supported by previous reports [11, 12] which give evidence for at least two metal binding sites (pH-dependent) in humic and fulvic ligands. The availability of different binding mechanisms in soil macromolecules is of interest especially in view of their biological significance. Thus metal-organic interactions of different stability are inferred, their extent being dependent on the pH and the nature of the ions. They could be mechanisms controlling the cationic movement in soil: chelation is likely favouring storage and scavenging of ions, whereas carboxylate or outer-sphere complexation (the latter detected in some M(II)-2,6-dihydroxy-benzoate complexes [7]) allows easier transfer of the ions towards soil components able to act through similar binding mechanisms [13, 14].

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