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EPR Study of Copper(II) Heterodinuclear Citrate Complexes

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Abstract

A study of the EPR frozen solution spectra of copper(II) citrate heterodinuclear species containing Mg(II), Zn(II) or Pd(II) has been carried out. The comparison of the spin Hamiltonian parameters suggests that copper(II) is in a coordination environment considerably different from that found in the case of the copper(II) mono-citrate complex. These results have been interpreted considering that two possible sites with different arrangements of oxygen donors are accessible to copper: a square-planar geometry for copper(II) heterodinuclear species containing Mg(II) or Zn(II) or a tetragonally distorted octahedral geometry when the heterodinuclear species contains Pd(II).

Introduction

Metal complexes with citrate ion have been extensively studied in the past with the aim of ascertaining the biological and the physiological role of citrate. In fact, citrate is an intermediate in carbohydrate metabolism, is able to favour biosynthetic pathways, has a controlling action on several enzymes and has been considered important in calcium metabolism [1].

Some years ago the ability of forming heterodinuclear complexes, in particular, species with a general formula $[MCu(citrate)_2H_{-2}]^{4-}$ together with the homodinuclear species, $[M_2(citrate)_2H_{-2}]^{4-}$ and $[Cu_2(citrate)_2H_{-2}]^{4-}$, was detected by a thermodynamic study of the M–Cu–citrate system in aqueous solution at 25 °C and $I = 0.1$ mol dm^{-3}, Zn(II) or Ni(II) [2]. (H_{-2} refers to deprotonation of two citrate hydroxyl groups.)

Zn(II) or Ni(II) [2].

This paper deals with a frozen solution EPR study of the copper(II) heterodinuclear citrate complexes with diamagnetic metals (Zn(II), Mg(II) and Pd(II)), with the specific aim of obtaining information on the particular stereochemistry adopted by copper(II) in these heterodinuclear species. The particular purpose is to understand whether the coordination environment present around copper in the heterodinuclear species is similar to or different from that of the mono-citrate complex.

Experimental

Chemicals

All solutions were prepared in water by mixing the metal ions (nitrate salts) and citric acid and adjusting the pH of the resulting solution to a value about 7–8 (4–5 in the case of palladium(II)) with sodium hydroxide. In order to enhance the formation of the heterodinuclear species and to avoid the interference of minor species, an excess of the diamagnetic ion and of the citric acid was used. The calculations concerning the species distribution in the zinc–copper–citrate system were carried out by using the program DISDI [3]. This program allows the calculation of the species percentage versus pH, provided that analytical concentrations and formation constants are known. In Fig. 1 two species distribution diagrams are presented for the Zn(II) containing system in two extreme situations, the $[Cu^{2+}]:[Zn^{2+}]:[cit]$ ratios being 1:5:5 and 1:10:20, respectively. From Fig. 1b, it is possible to see that copper(II) homodinuclear complex formation has been reduced to negligible percentages.

Spectroscopic Measurements

EPR measurements were carried out on a Bruker ER 200 D spectrometer equipped with a standard low-temperature apparatus. Frozen solution spectra were run at the temperature of 140 K. The magnetic field was carefully measured every scan by means of a NMR gaussmeter (ER 035 M), which leaves markers

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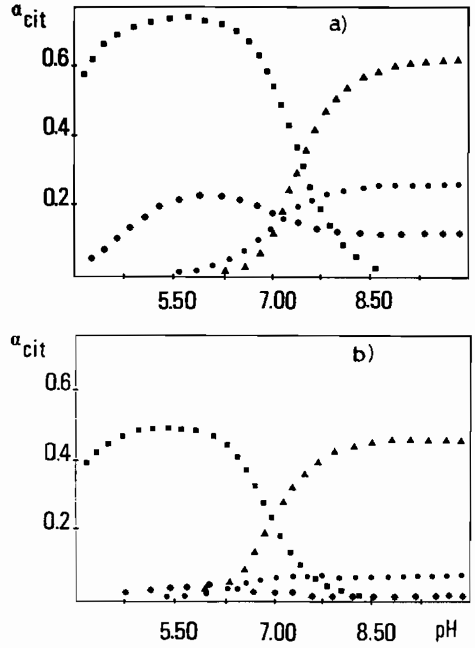

Fig. 1. Species distribution diagrams for the Zn(II)–Cu(II)–citrate system with $[Cu^{2+}] = 5$ mmol dm^{-3}: (a) $[Cu^{2+}]$:$[Zn^{2+}]$:[cit] = 1:5:5, $[CuZn(cit)_2H_{-2}] = 2.80$ mmol dm^{-3}, $[Zn_2(cit)_2H_{-2}] = 7.82$ mmol dm^{-3}, $[Cu_2(cit)_2H_{-2}] = 1.10$ mmol dm^{-3} at pH = 8.05; (b) $[Cu^{2+}]$:$[Zn_{2+}]$:[cit] = 1:10:20, $[CuZn(cit)_2H_{-2}] = 3.67$ mmol dm^{-3}, $[Zn_2(cit)_2H_{-2}] = 21.87$ mmol dm^{-3}, $[Cu_2(cit)_2H_{-2}] = 0.67$ mmol dm^{-3} at pH = 8.05; minor species in the low pH region have been omitted; ■ $[Zn(cit)]^-$, ● $[CuZn(cit)_2H_{-2}]^{4-}$, * $[Cu_2(cit)_2H_{2-}]^{4-}$, ▲ $[Zn_2(cit)_2II_{-2}]^{4-}$.

at preselected values, the klystron frequency being checked by using DPPH as reference ($g = 2.0036$). To improve resolution, methanol up to 10% was added to the aqueous solutions in which $^{63}Cu(NO_3)_2$ was dissolved (conc. = 5 mmol dm^{-3}). The EPR spectrum due to the copper(II) heterodinuclear species is not affected by the presence of the analogous homodinuclear zinc complex which is diamagnetic or of the homodinuclear copper complex [4] which has a low signal-to-concentration ratio. However, to reduce the amount of the copper(II) homodinuclear species, the Zn(II) or Mg(II) containing heterodinuclear species were studied by employing a $[Cu^{2+}]$:$[Zn^{2+}]$ = $[Mg^{2+}]$:[cit] 1:5:10 ratio, whereas for the Pd(II) a $[Cu^{2+}]$:$[Pd^{2+}]$:[cit] 1:1.6:4 ratio was used. The magnetic parameters did not show any concentration ratio dependence. The use of different ratios and pH values, though, may cause the appearance of a multi-species EPR spectrum, especially in the case of the heterodinuclear complex containing Pd(II). The spin Hamiltonian parameters were obtained by computing the experimental EPR spectra employing a general program written by Pilbrow and Winfield [5]. Spin Hamiltonian parameters are reported in Table 1. A minor species is contemporarily present in the EPR frozen solution spectrum of the Zn(II) containing dinuclear complex (see Fig. 3b). It probably is a dinuclear complex partially deprotonated owing to the difficulty of raising the solution pH because of the precipitation of Zn(II) hydroxide or Zn(II) hydrolytic species. Owing to the low pH value at which the formation of the Pd(II) containing heterodinuclear species occurs (it is important to avoid the formation of hydroxo-palladium(II) species) the EPR frozen solution spectrum is complicated by the presence of a certain amount of the mono-citrate copper(II) complex (see Fig. 3c).

Optical spectra in aqueous solution were recorded at room temperature with a Perkin-Elmer 330 double-beam spectrophotometer in quartz cells.

Results and Discussion

The EPR frozen solution spectra of the [Cu(cit)] and [Cu(l-mal)] species (l-mal = l-malate dianion) are shown in Fig. 2. They exhibit quite similar spin Hamiltonian parameters (see Table 1), thus suggesting that the two complexes have the same stereochemistry, the third citrate carboxylic group being probably not involved in the coordination. The species distribution study at 25 °C of copper(II) citrate and DL-malate systems [6, 7] indicated that below pH = 5 copper(II) mono-ligand complexes formed and that the third citrate carboxylic group is

TABLE 1. Spin Hamiltonian parameters (^{63}Cu) and optical data for copper(II) heterodinuclear species

Complex	$g_\parallel$	$A_\parallel$[a]	$g_\perp$	$A_\perp$[a]	λ (nm) (ε)[b]
[Cu(cit)]	2.368(1)	142(1)	2.080(3)	10(3)	750(42)
[Cu(l-mal)]	2.374(1)	140(1)	2.080(3)	10(5)	740(30)
Cu/$[Zn(l\text{-}mal)(H_2O)_2]\cdot H_2O$ [c]	2.425(1)	120(1)	2.089(1)	10(2)	
$[CuMg(cit)_2H_{-2}]^{4-}$	2.297(1)	173(1)	2.062(3)	12(3)	
$[CuZn(cit)_2H_{-2}]^{4-}$	2.297(1)	173(1)	2.062(3)	12(3)	725(50)
$[CuPd(cit)_2H_{-2}]^{4-}$	2.325(1)	161(1)	2.068(3)	7(3)	725(35)

[a] Units of coupling constants 10^4 cm^{-1}. [b] Errors on λ_{max} 2 nm, units of ε cm^{-1} mol^{-1} dm^3. [c] $g_z = g_\parallel$, $A_z = A_\parallel$, $g_\perp = 1/2(g_x + g_y)$, $A_\perp = 1/2(A_x + A_y)$ from ref. 8.

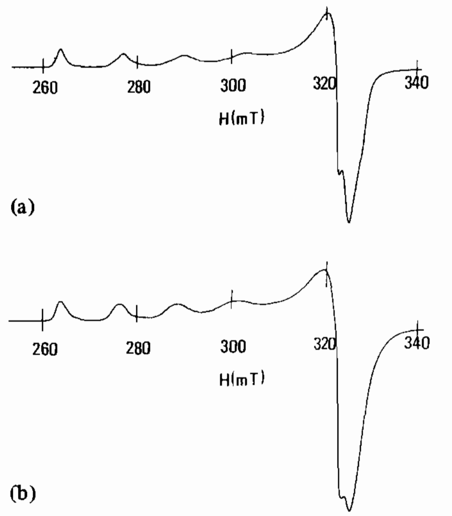

Fig. 2. Frozen solution EPR spectra of (a) [^{63}Cu(cit)] and (b) [^{63}Cu(l-mal)] in water–methanol mixture at 140 K. The aqueous solution pH was adjusted to a value of 4, before the addition of methanol.

protonated. However at low temperatures, varying the pH value from 4 to 5.5, another species appears in the frozen solution EPR spectrum of the copper(II)–citrate system. The spin Hamiltonian parameters of the latter did not differ appreciably from those found for the EPR spectrum at pH = 4 ($g_\parallel = 2.362(2)$, $A_\parallel = 148(2) \times 10^4$ cm^{-1}). These slight differences in $g_\parallel$ and $A_\parallel$ values can be attributed to the contribution of a possible species in which the third carboxylic group is deprotonated. Therefore, both [Cu(cit)] and [Cu(cit)]$^-$ contribute, with a different weight depending on the solution pH, to this frozen solution EPR spectrum. The similarity between [Cu(cit)] and [Cu(l-mal)] is quite important, since we have recently [8] reported a single crystal EPR study of copper(II) in zinc-l-malate trihydrate and, therefore, some of the conclusions about the stereochemistry assumed by copper(II) in the zinc-l-malate environment can be extended to the copper–citrate complex as well. This similarity is also evidenced by the diffractometric studies on crystals of magnesium, manganese(II) and iron(II) citrate, that form an isomorphous series, in which citrate behaves as a tridentate ligand, leaving the third carboxylate out of the coordination sphere of the central metal ion [1]. In particular, in the single crystal EPR study of the zinc-l-malate trihydrate doped with copper(II), we found that the direction of g_z points towards the hydroxyl oxygen, while the g_x and g_y directions lie in the plane which approximately contains the carboxylate oxygen–copper bonds. The $g_\parallel$ and $A_\parallel$ values observed in the solid state are different from those found in solution, while $g_\perp$ and $A_\perp$ are rather similar. Copper(II) complexes have a characteristic geometry (generally a tetragonally elongated octahedron) in solution, while in the solid state copper(II) is 'forced' to assume the coordination of the diamagnetic host, which, in the zinc-l-malate trihydrate, has a quite regular octahedron of oxygen atoms; obviously this situation is reflected by some differences of their magnetic parameters (see Table 1). Moreover, due to the rigidity of the crystal packing, the g tensor anisotropy is generally larger in the solid state than that found for the same complex in solution. Since the EPR frozen solution spectra yield spin Hamiltonian parameters, and not their directions, this comparison is extremely useful. In fact, based on it, even in solution, $g_\parallel$ can be reasonably assumed to point towards the hydroxyl oxygen and $g_\perp$ to lie in the plane of the carboxylate oxygen–copper bonds for both complexes.

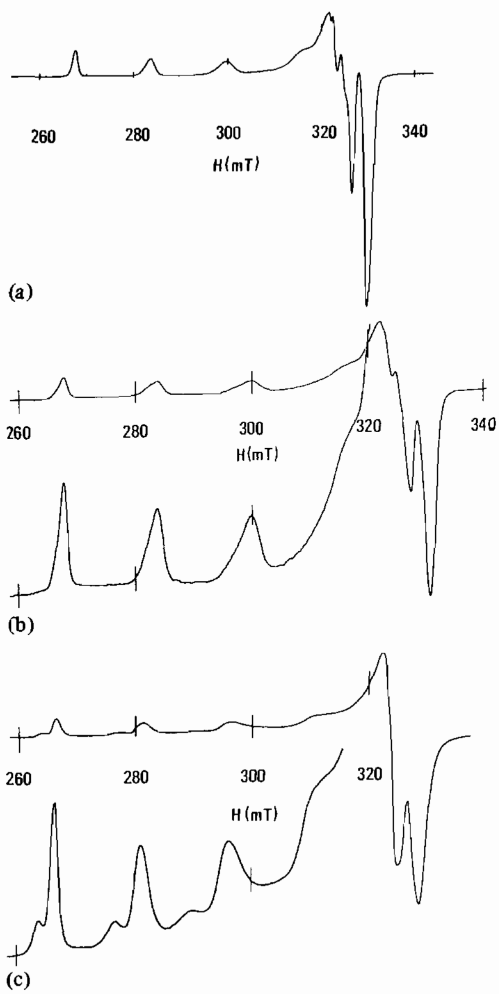

Fig. 3. Frozen solution spectra of copper(II)–citrate heterodinuclear species [^{63}CuM(cit)$_2$H$_{-2}$]$^{4-}$: (a) M = Mg(II), pH = 8.00; (b) M = Zn(II), pH = 7–8; (c) M = Pd(II), pH = 4.50, in water–methanol mixture at 140 K.

The EPR frozen solution spectra of the heterodinuclear species are presented in Fig. 3. They are considerably different from that of the mono-citrate species (see Table 1). Moreover, the spin Hamiltonian parameters pertaining to the heterodinuclear species with the Zn(II) and Mg(II) diamagnetic metals, are identical within experimental error, while the magnetic parameters associated with the heterodinuclear species containing Pd(II) are noteworthily different.

These results can be interpreted by taking into account that:

(1) In the copper(II) mono-citrate complex the hydroxyl oxygen atom is coordinated in its protonated form, while in the heterodinuclear species the presence of the diamagnetic ion promotes its deprotonation. This has a direct consequence: the heterodinuclear species is a negatively charged complex with respect to the mono-citrate complex; in other words, there is a contribution to the $g_{\parallel}$ and $A_{\parallel}$ shifts which comes from the deprotonation of hydroxyl oxygen atoms [9, 10].

(2) Two distinct sites are available to copper(II) within the heterodinuclear species framework, as pointed out by the differences in the magnetic parameters between the heterodinuclear species containing Zn(II) or Mg(II) and that containing Pd(II); if copper(II) kept its octahedral arrangement as in the mono-citrate complex (there is not much difference between the donor properties of water and carboxylate oxygen atoms apart from a contribution which can derive from the chelate effect) minor shifts would be expected in the $g_{\parallel}$ and $A_{\parallel}$ values, as found in the case of $[CuPd(cit)_2H_{-2}]^{4-}$, Therefore, the lower $g_{\parallel}$ and the higher $A_{\parallel}$ found for $[CuMg(cit)H_{-2}]^{4-}$ and $[CuZn(cit)H_{-2}]^{4-}$ seem to indicate that copper(II) is probably occupying a site with square-planar arrangement.

The optical data are also in agreement with such an interpretation; the electronic spectrum in the visible region for $[CuZn(cit)_2H_{-2}]^{4-}$ shows a shift of λ_{max} towards higher frequencies and an ϵ_{max} value a little higher than those associated with [Cu(cit)] and [Cu(l-mal)]. In the case of the heterodinuclear species with Pd(II) there is also a shift of λ_{max} towards higher frequencies, but the value of ϵ_{max} is lower than that of the copper(II) mono-citrate complex.

Complexes of hydroxy acids containing two different metals have been postulated in the past, especially to explain the inhibiting effect of chromium(III) on the analytical determination of copper(II) with 2,2′-biquinolyl. Irving and Tomlinson [11, 12] have hypothesized a possible structure for the heterodinuclear species $[CuCr(cit)_2H_{-2}]^{3-}$, which is reported in Fig. 4. Assuming this to be an adequate model for the arrangement of two citrate molecules around the two metal ions, i.e. the copper(II) and the diamagnetic ion, the trend of the paramagnetic parameters can be explained. It is well known that Pd(II) exclusively prefers a square-planar stereochemistry, while Zn(II) commonly has coordination numbers four, five and six and Mg(II) preferably shows a coordination number of six with oxygen ligands [13]. In this model both copper and the diamagnetic metal ions can occupy these two different sites: the former is surrounded by six oxygens in an octahedral situation, the latter by four oxygens in a square-planar arrangement. On the basis of what we have said before, the spin Hamiltonian parameters for the heterodinuclear species containing Zn(II) or Mg(II) suggest that copper(II) unquestionably occupies the square-planar site. On the contrary, in the case of the heterodinuclear complex with Pd(II), copper(II) is 'forced' to go to the six-coordinated site.

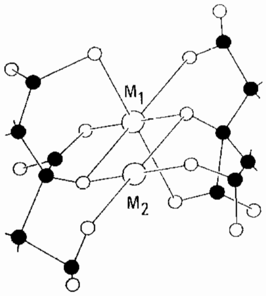

Fig. 4. A model for the possible arrangement of two citrate ions around two metal ions. M_1 and M_2 designate two sites with different geometry and coordination number.

The deprotonation of the two hydroxyl oxygen atoms in the copper(II) heterodinuclear species makes the Cu–O bonds stronger than the Cu–OH bond of the [Cu(cit)] complex, thus causing a shortening of the bond. Hence, while in the mono-citrate complex the distance of the Cu–OH bond is the longest one, the hydroxyl oxygen atom being located in an apical position (as one can see from the metal citrate diffractometric studies [1] and from our single crystal EPR work [8]), in the heterodinuclear species the deprotonated hydroxyl oxygen atoms occupy equatorial positions of the copper(II) coordination polyhedron.

Furthermore, it is important to make a comment about the deprotonation effect upon the $g_{\parallel}$ and $A_{\parallel}$ values. Deprotonation commonly occurs with changes in the complex stereochemistry, as, for instance, is shown by the soluble $[Cu(OH)_4]^{2-}$ complex, which is obtained by subsequently deprotonating the $[Cu(H_2O)_6]^{2+}$ complex. The former has an approximately square-planar geometry, whereas the latter has a tetragonally distorted octahedral one. Going from $[Cu(H_2O)_6]^{2+}$ to $[Cu(OH)_4]^{2-}$, $\Delta g_{\parallel}$ value of -0.148 and $\Delta A_{\parallel}$ value of 58×10^{-4} cm^{-1} have been found [10]. We would like to stress that, if a change in the copper(II) complex stereochemistry simultaneously occurs, attention must be paid before concluding that $g_{\parallel}$ and $A_{\parallel}$ shifts are due only to deprotonation of water or hydroxyl oxygen atoms. In the case of Pd(II)–Cu(II) heterodinuclear species, given the fact that there is no change in the stereochemistry of copper with respect to that of the Cu(II) mono-citrate complex, and given that the contribution of the carboxylate oxygen coordination is not very different from that of the water oxygen, then the shifts of the magnetic parameters ($g_{\parallel}$ and $A_{\parallel}$) represent changes due to the deprotonation of two hydroxyl oxygen atoms within a Cu(II) octahedral stereochemistry.

Finally, previous EPR studies [14] on heterometal ion hydroxycarboxylates in non-aqueous solutions have stressed the possibility that coupling between copper(II) ions occurs in some cases, because of the formation of species with a degree of polymerization higher than expected. Our present EPR results rule out this possibility, under the experimental conditions employed here. Our study stresses the importance of the diamagnetic ion in determining the particular stereochemistry of the copper(II) ion in the citrate heterodinuclear species.

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