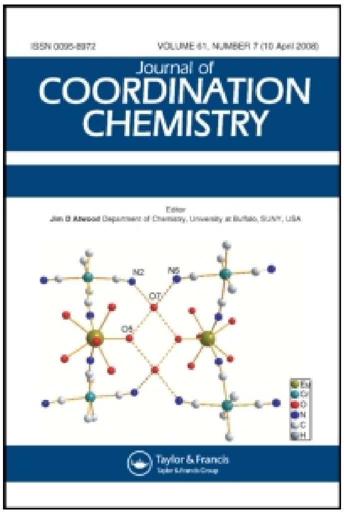

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Coordination of Copper(II) to Polyaminopolycarboxylic Acids in Aqueous Solution

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COORDINATION OF COPPER(II) TO POLYAMINOPOLYCARBOXYLIC ACIDS IN AQUEOUS SOLUTION

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The formation of copper(II) complexes in aqueous solution has been followed by EPR and electronic absorption spectroscopy for a series of polyaminopolycarboxylic ligands, namely ethylenediaminotetraacetic (EDTA), *N*-(2-hydroxyethyl)ethylenediamino-*N*,*N'*,*N'*-triacetic (HEDTA), ethylenediaminodiacetic (EDDA), iminodiacetic (IDA), and nitrilotriacetic (NTA) acids. The species in complex formation have been identified and structures proposed by previous studies have been examined and discussed on the basis of the spectroscopic data.

Keywords: Copper, multidentates speciation, stability constants

INTRODUCTION

The coordination of heavy metal ions to polydentate polyaminopolycarboxylic ligands is of considerable interest. Because of the extensive use and the fairly strong complexing properties of this class of compounds, their presence in the environment may have implications for metal ion transport and accumulation processes.

While the structures of many of their complexes have been elucidated in the solid state (*e.g.*, refs. 1–7), similar information on corresponding species in solution, which may be different, is much less available. It is however necessary to understand the bonding modes of these compounds and their possible ternary interactions with metal ions and biological or other natural surfaces. We report here a spectral examination, performed by EPR and electronic absorption spectroscopy, on copper(II) complexes formed in aqueous solution by the polyaminopolycarboxylic acids ethylenediaminotetraacetic (EDTA), *N*-(2-hydroxyethyl)ethylenediamino-*N*,*N'*,*N'*-triacetic (HEDTA), ethylenediaminodiacetic (EDDA), iminodiacetic (IDA), and nitrilotriacetic (NTA) acids (see Scheme).

The investigation is preliminary to a study aimed at the identification of the complex species formed by simultaneous adsorption of the ligands and the metal ion on inorganic soil components.

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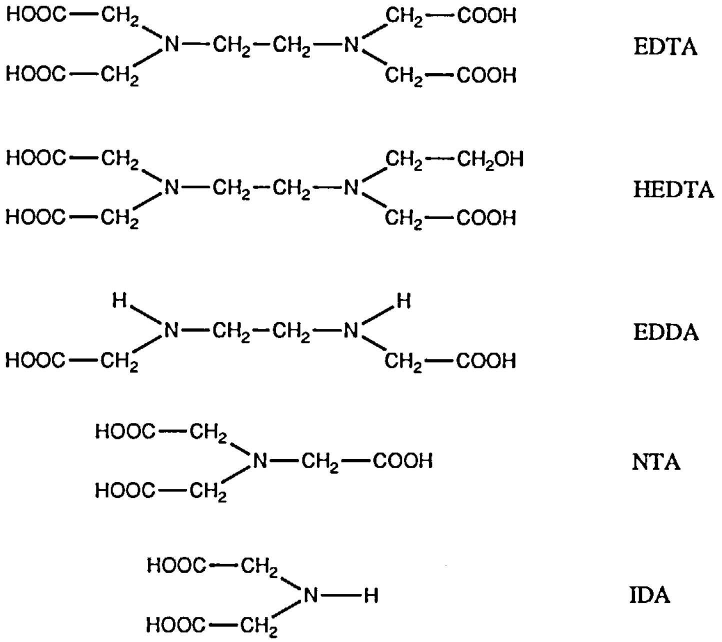

Scheme

EXPERIMENTAL

The ligands ethylenediaminotetraacetic (EDTA), *N*-(2-hydroxyethyl)ethylenediamino-*N*,*N*′,*N*′-triacetic (HEDTA), ethylenediaminodiacetic (EDDA), iminodiacetic (IDA), and nitrilotriacetic (NTA) acids were purchased from Aldrich. Aqueous solutions of $CuSO_4$ (1×10^{-3} M) and ligands at varying molar ratios were examined as a function of pH. The ionic strength was adjusted to 0.1 ($KClO_4$). X-Band EPR spectra were recorded at 120 K with a Varian E9 spectrometer on frozen solutions after addition of ethylene glycol to ensure good glass formation. Electronic spectra were measured with a Uvidec Jasco 610 spectrophotometer.

RESULTS AND DISCUSSION

Cu(II)-EDTA

Over the pH range 3–11, signals attributable to two principal species are observed by EPR (Table I). The first (**I**) is predominant around pH 3, whereas the second (**II**) becomes more pronounced as the pH and/or the ligand-to-metal molar ratio is raised. In any case, in the presence of an excess of ligand, **II** becomes almost the sole species around pH 4.5. EPR analysis shows that **I** exhibits $g_{\parallel}$ and $A_{\parallel}$ values which are higher and lower, respectively, than those of **II**. As reported by potentiometric and polarographic studies, see ref. 8, two main species, $CuLH^-$ and CuL^{2-}, are formed in the Cu(II)–EDTA system over the pH range 3–11 in the presence of an excess of ligand. The former involves a ligand molecule having an undissociated carboxyl group (LH^{3-}) whereas the latter involves the fully deprotonated form of EDTA (L^{4-}). Therefore, the number of species detected by EPR is fully consistent with the above reports. However, it is also evident that the transformation of $CuLH^-$ (I) into CuL^{2-} (II) is followed by a detectable rearrangement of the metal chromophore. In fact, it appears that the ligand donor set, which is of the (2 N, 3 COO^-) type, in $CuLH^-$ actually imposes distorted five-coordination around the metal ion (as suggested by the EPR parameters which are distinctive of such a geometry). Upon deprotonation and coordination of the fourth carboxylate group, the donor set changes into that of the (2 N, 4 COO^-) type, yielding a tetragonal species. Similar conclusions about the species distribution in the analogous Ni(II) and Fe(II) complex systems were also reached by use of ^{13}C and ^{17}O NMR and Mössbauer spectroscopies, respectively.[9,10] On the other hand, the interpretation of the spectral trend by assuming an equilibrium between a hexacoordinate and a pentacoordinate form of the complex CuL^{2-}, the latter involving an uncoordinate carboxylate,[11] is less convincing because only a single set of EPR signals is found after the deprotonation of the fourth carboxylic group (pK value ~3, according to stability data for the complexes).

TABLE I
EPR parameters for the complexed species.

Ligand	Species	$g_\parallel$	$A_\parallel$ (10^{-4} cm^{-1})	M:L molar ratio and donor set
EDTA	I	2.328	155	1:1 (2 N, 3 COO^-)
	II	2.288	159	1:1 (2 N, 4 COO^-)
	III	2.320	130	1:1 (2 N, 3 COO^-, OH^-)
HEDTA	IV	2.311	162	1:1 (2 N, 2 COO^-)
	V	2.253	170	1:1 (2 N, 3 COO^-)
	VI	2.272	164	1:1 (2 N, 3 COO^-, CH_2O^-)
	VII	2.313	144	1:1 (2 N, 3 COO^-, OH^-)
EDDA	VIII	2.263	182	1:1 (2 N, COO^-)
	IX	2.251	181	1:1 (2 N, 2 COO^-)
	X	2.233	190	1:2 (4 N, 2 COO^-)
IDA	XI	2.296	171	1:1 (N, 2 COO^-)
	XII	2.269	179	1:2 (2 N, 4 COO^-)
NTA	XIII	2.309	160	1:1 (N, 3 COO^-)
	XIV	2.303	145	1:1 (N, 3 COO^-, OH^-)
	XV	2.261	190	1:1 (N, 3 COO^-, 2 OH^-)
	XVI	2.334	155	1:2 (2 N, 3 COO^-)
	XVII	2.264	180	1:2 (2 N, 4 COO^-)

A further species (III) is observed in the Cu(II)–EDTA system above pH 11 and the extent of its formation becomes more significant as solution basicity is increased. The spectral changes, and particularly the significant decrease in the $A_\parallel$ value (Table I), are consistent with the presence of a hydroxo group in the apical position of a (2 N, 3 COO^-, OH^-)-coordinate species of the $CuLH_{-1}{}^{3-}$ type formed by hydrolysis.[8,12,13] The *d–d* absorption maxima of both **I** and **II** fall around 730 nm; the latter complex, however, has a higher extinction coefficient (*ca* 100 M^{-1} cm^{-1}). On the other hand, the formation of **III** is revealed by a remarkable decrease in intensity of the *d–d* absorption band (ε *ca* 47 M^{-1} cm^{-1}).

Cu(II)–HEDTA

HEDTA (H_3L) behaves similarly to EDTA. Deprotonation of the three carboxylate groups is complete above pH 4 and yields CuL^- (**V**), while between pH 2 and 3 the monoprotonated species CuLH (λ_{max} *ca* 720 nm) is predominantly formed (**IV**); see potentiometric data in ref. 8. Also, **IV** (involving two nitrogens and two carboxylates) has parameters of somewhat distorted five-coordination, where a solvent molecule is the fifth donor (see Table I). Instead, **V** (λ_{max} *ca* 710 nm), which involves two nitrogens and three carboxylates in metal coordination, has a more tetragonal geometry (square pyramidal). Two further species are observed above pH 11; the first (**VI**) has spectral parameters similar to those of **II**, whereas the second (**VII**) is more similar to the hydrolysed species **III**. Therefore the complex **VII** may be assigned as that formed by deprotonation of a water molecule bound to the metal ion. Species **VI** may be formed by the deprotonation and coordination of the hydroxyethyl group which acts as the sixth donor as does the fourth carboxylate in the Cu–EDTA complex.[8] The formation of the two latter species shifts the *d–d* absorption maximum toward 700 nm.

Cu(II)–EDDA

In this system too, the EPR spectra exemplify several main complexes. The first of them (**VIII**) is formed at pH ~2.5, where it coexists together with the aquaion, and becomes predominant over the pH range 4–10 in solutions with a 1:1 ligand-to-metal molar ratio. With increasing pH, the species is transformed into a further complex (**IX**) with only a minor change in spectral parameters. EPR data for these species are typical of a copper(II) chromophore containing two nitrogen atoms (*e.g.*, the 1 : 1 complex of *N,N'*-dimethylethylenediamine[14]). On this basis, a similar structure, where the copper ion is bound to two N atoms of a chelating molecule, together with the oxygens from carboxylates, can be assigned to the species. The difference in the two species could be the number of metal-bound carboxylates (one or two for **VIII** and **IX**, respectively). Both these species, which have been identified previously by potentiometric measurements with glass and ion-specific electrodes,[15] show *d–d* absorption maxima around 670–680 nm. At higher ligand-to-metal molar ratios, different behaviour is observed. Species **VIII** and **IX** are again observed in acid media, but above pH 7 a new complex (**X**) is stable. This species exhibits $g_\parallel$ and $A_\parallel$ values remarkably lower and higher, respectively, than those of **VIII** and **IX** and has an absorption maximum at 630 nm. This spectral trend suggests the in-plane coordination of further strong N-donor atoms to the metal ion. Therefore, the spectral data assign the third complex as a species with a 1:2 M:L molar ratio, where four nitrogens coordinate the metal ion and possibly the carboxylate oxygens are the axial donors. This complex too has been confirmed by spectrophotometric titrations.[16]

Cu(II)–IDA

EPR spectra show the existence of two main species. At a 1:1 metal-to-ligand molar ratio, complex formation begins at a pH as low as 2.5 to yield the first species (XI). However, precipitation takes place at about pH 6 in solutions at the 1:1 ligand-to-metal molar ratio. The EPR parameters of **XI** (λ_{max} *ca* 730 nm) are consistent with the presence of only a single nitrogen donor in the Cu(II) coordination sphere, *e.g.*, they compare well with those of the mono(α-amino acidate)Cu(II) complexes in solution.[17] These findings are in accordance with thermodynamic studies (see ref. 18 and references therein), which show that the 1:1 species formed by the fully deprotonated ligand is predominantly formed over the acid pH range. A second species (XII), which is favoured in basic media at ligand-to-metal molar ratios higher than 2 : 1, exhibits EPR and absorption parameters (λ_{max} *ca* 675 nm) which are near to those of the 1 : 1 M : L complexes of EDDA. Therefore, two nitrogens from two ligand molecules and two carboxylate oxygens are the donor atoms in the metal plane of **XII**, with two other carboxylates in the apical positions.

Cu(II)-NTA

Several species have been observed in this system by EPR. In solutions with a 1:1 ligand-to-metal molar ratio a species (XIII), characterized by a broad absorption band with λ_{max} at *ca* 825 nm, predominates between pH 3 and 8. As reported previously,[19,20,21] this species is the 1:1 M:L complex CuL^-, involving coordination by a fully deprotonated ligand (L^{3-}). The spectral data, particularly involving the energy of the absorption maximum, suggest that the ligand really acts as tetradentate and that one of its chelating arms produces a rather strong apical interaction at the metal ion. However, hydrolysis takes place in basic solution and two further species, namely the monohydroxo complex $CuLOH^{2-}$ (XIV) and the dihydroxo species $CuL(OH)_2{}^{3-}$ (XV), coexist between pH 9 and 11. These complexes too have been previously detected by equilibrium studies in solution.[19] The formation of hydrolysed species is revealed in the electronic spectra by two *d-d* bands at 880 and 760 nm, which have been assigned to the mono- and di-hydroxo species, respectively. On the whole, the data indicate that a distorted five-coordination may be assigned to **XIV**, while **XV** is strongly tetragonally elongated, probably due the involvement of the strongest donors (2 OH^- groups and a N atom) in the metal plane, the weaker carboxylate groups completing hexacoordination. In solutions at a 1:2 metal-to-ligand molar ratio, **XIII** is again observed in equilibrium, up to pH 7, with another complex (XVI) exhibiting λ_{max} *ca* 770 nm. A final species (XVII) is formed in basic media (λ_{max} *ca* 720 nm). With increasing L/M ratios, **XVII** becomes more favoured even in acidic media where it coexists with only minor amounts of **XIII** and **XVI**. The spectral trend indicates that **XVII** is the bis-chelated complex where two nitrogen atoms and four oxygens from carboxylates are coordinated to the metal ion. Also, **XVI** is a complex involving two ligands bound to copper(II). However, the $g_{\parallel}$ and $A_{\parallel}$ values are again distinctive of a five-coordinate chromophore. This suggests that two different forms of the ligand are bound to the metal ion. A plausible hypothesis is that the species is formed by the simultaneous coordination of a terdentate (N, 2 COO^-) and a bidentate (N, COO^-) molecule. A nitrilotriacetato(–1) ligand coordinated to Cu(II) in the latter mode has been observed in the solid complex $[Cu(H_2NTA)_2]\cdot 2H_2O$ by X-ray crystal structure measurements.[2] Actually, in this complex, each H_2NTA molecule acts as terdentate by coordinating apically with an unionized carboxyl group and the resulting geometry is tetragonal. The deprotonation and coordination of one of the apical carboxylic groups could rearrange the chromophore and lead to the distorted structure observed in **XVI**.

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