Potentiometric and Spectroscopic Studies on Cu(II) Complexation to Aminophosphonic Acid, 1-(3-Pyridyl)-1-(n-butylamino)-methanephosphonic Acid

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Abstract

The results are reported of a potentiometric and spectroscopic study of the copper(II) complexes of aminophosphonic acid containing a pyridyl side chain. The aminophosphonic acid coordinates similarly to carboxyl amino acids, forming chelate MA and MA_2 species. Stable MAH species with only a phosphonic group coordinated to the metal ion exist at lower pH. The pyridyl side chain was found to be noneffective in the interaction with Cu(II) ion.

Introduction

The main interest in aminophosphonic acids as ligands derives from the fact that they are phosphorus analogues of amino acids. Similarly to amino acids they have been found in many living organisms [1–4]. Some of the pyridine derivatives of aminophosphonic acids, e.g., *N*-[2-(3-methylpyridyl)]-aminomethylenediphosphonic acid and its salts, were found to be effective herbicides [5, 6]. The metal complexes with phosphonic amino acids have been studied mostly in the solid state [7–11]. The X-ray structures have shown that at lower pH range the main coordination site derives from the phosphonic donor [9, 10], while at higher pH chelate formation with involvement of amino group was also found [11]. A typical feature of most of these complexes is their polymeric structure, though monomeric species are also formed [12]. The solution studies are quite limited; the major potentiometric data were presented by Woźniak and Nowogrocki [13].

In this communication we present the spectroscopic and potentiometric data for a Cu(II)–aminophosphonic acid system containing a pyridyl side chain as a possible competitive nitrogen donor site for cupric ions.

Experimental

1-(3-pyridyl)-1-(n-butylamino)-methanephosphonic acid hydrochloride was obtained by the method described in ref. 14. $CuCl_2 \cdot 2H_2O$ was the source of copper ion.

For spectroscopic studies, solutions with metal ion concentrations of 0.005 mol dm^{-3} and with 1:5 and 1:10 copper ion to ligand molar ratios were used. Electronic paramagnetic resonance (EPR) spectra were taken on JEOL JES-ME-3X spectrometer at liquid nitrogen temperature and at 9.25 GHz. The absorption spectra were recorded on a Hitachi 356 spectrophotometer at room temperature.

In the potentiometric studies, ligand concentrations of 0.004 and 0.006 mol dm^{-3} were used and metal ion to ligand molar ratios of 1:2 to 1:5 were employed. Measurements were made with a Radiometer pHM 64 pH-meter with a GK 2322 C combined calomel–glass electrode and an ABU 13 automatic burette. All pH-metric titrations were carried out at 25 °C at an ionic strength of 0.20 mol dm^{-3} KCl. Details on the method for computer evaluation of the data and on the potentiometric procedure used were the same as in ref. 15.

Results and Discussion

In the pH range studied (2.5–11), 1-(3-pyridyl)-1-(n-butylamino)methanephosphonic acid (PPA) behaves as tribasic acid H_3A with protonation constants $pK_i = 3.47$, 5.22 and 9.45 (see Table I for log β values). Two of the higher values correspond

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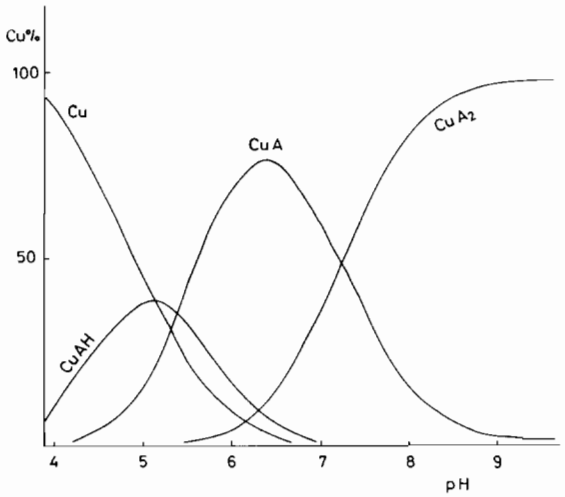

Fig. 1. Species distribution for Cu(II):PPA 1:5 solutions.

TABLE I. Formation Constants of Complexes of PPA with H^+ and Cu^{2+} (25 °C, $I = 0.20$ M KCl) and Spectroscopic Characterization of the Species (1:5 metal ion to ligand molar ratio); $\beta_{pqr} = [M_pA_qH_r][M]^{-p}[A]^{-q}[H]^{-r}$ [a]

Species	$\log \beta_{pqr}$	d–d transition λ_{max} (nm)		EPR	
				$A_\parallel$ (G)	$g_\parallel$
HA^{1-}	9.45(1)				
H_2A	14.67(1)				
H_3A^{1+}	18.13(1)				
MA	6.88(1)	690	65	174	2.261
MA_2^{2-}	11.67(1)	618	90	152	2.287
MAH^{1+}	12.25(1)				

[a]Standard deviations are given in parentheses.

well to the proton dissociation constants found for simple aminophosphonic acids [13] for the $PO_3H^- \rightleftarrows PO_3^{2-} + H^+$ and $RNH_2^+ \rightleftarrows RNH + H^+$ ionization reactions, respectively. The third ionization constant, 3.47, corresponds to the dissociation of pyridyl nitrogen.

With copper(II) PPA forms three species, MAH, MA and MA_2, for which stability constants are given in Table I. The absorption and EPR spectra easily distinguish two of these species, MA and MA_2. The d–d transition energy found for the MA species around 690 nm corresponds well to one-nitrogen coordination [16, 17], and ~620 nm for the MA_2 species seems to support two nitrogens bound to the cupric ion. In both cases the high stability constants (see Table I and ref. 13) and the X-ray study [11] clearly indicate the formation of a chelate ring in which the phosphonic oxygen as well as the nitrogen are bound to the metal ion.

The MAH complex formed at a lower pH range than the species in which ligand is monodentately bound to the metal ion via the phosphonic group oxygen(s). Such coordination was found in several structures for the species which crystallized at such pH ranges [9, 10, 12]. Though polymeric structures were usually found in the solid state, they do not seem to be formed at the low concentrations of the solutions used in this study.

Thus, phosphonic amino acid may interact with cupric ion in a manner similar to carboxyl amino acid with formation of chelate ring. The major difference in the coordination mode is found at the lower pH range in which the phosphonic group (in contrast to carboxylate [18]) may interact with cupric ion as a monodentate ligand with formation of a very stable complex species. The pyridyl side chain was found to be noneffective in the interaction with cupric ion due to steric hindrance effect.

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