

bach and Ackermann.⁷⁾ AC₃OH is commercially available. AC₄OH and AC₅OH, which are new compounds, were synthesized and purified by our own method which will be reported elsewhere in detail.⁸⁾ Potentiometric titrations were carried out at 25 ± 0.1 °C and I = 0.10 (KNO₃) for standardized solutions involving Cu(NO₃)₂ and ligands by the usual method. Reproducibility of the results were checked by repeating titrations. The stability constants, β_{pqr}, defined in Eq. 1 were calculated by the method of nonlinear least-squares with the computer program SUPER-QUAD⁹⁾ (charges are omitted for simplicity)

$$\beta_{pqr} = \frac{[\text{Cu}_p\text{L}_q\text{H}_r]}{[\text{Cu}]^p[\text{L}]^q[\text{H}]^r} \quad (1)$$

where L denotes one of the above-mentioned aminopolycarboxylic acid ligands, and where p, q, and r are the numbers of Cu(II), L, and proton(H), respectively, in the complex Cu_pL_qH_r which will hereafter be expressed as pqr.

Typical titration curves for the proton-AC₃OH and Cu(II)-AC₃OH systems are shown in Fig. 1. Analyses of these data gave the following values of log β_{pqr} with estimated standard deviations in parentheses: 014, 20.809(9); 013, 18.872(6); 012, 16.344(2); 011, 9.418(2); 111, 18.70(2); 110, 15.97(2); 210, 20.11(2); 21-1, 14.40(2); 21-2, 7.69(2); 21-3, -3.95(2). The values of log β_{pqr} for the other ligand systems were also determined in the same way.⁸⁾ All the complex species of 011, 012, 013, and 014 are not concerned in the deprotonation of the alcoholic OH group. The species distributions shown in Fig. 2 were calculated from all these β_{pqr} values. The equilibrium constants for the main species of 21r are listed in Table 2. Interestingly, only in the case of AC₅OH, 21-2 is most stably formed from 210 at a step, as is also shown in Fig. 2C.

The species distribution curves for the 2:1 Cu(II)-AC₃OH, -AC₄OH, and -AC₅OH systems are quite different from those for the 2:1 Cu(II)-AC₃, -AC₄, and -AC₅ systems, respectively, as exemplified by comparison between those systems of AC₅OH (Fig. 2C) and AC₅ (Fig. 2D). This fact indicates that complex formation is largely dependent upon the presence of an alcoholic OH group in the ligands and, after all, upon its deprotonation and bridging-type coordination, suggesting that the possible structures of 210, 21-1, and 21-2 are schematically shown as in Fig. 3. This is strongly supported by ESR spectroscopy. In aqueous solutions at room temperature, the 210 species is usually ESR-detectable, while the 21-1 and 21-2 species are apparently ESR-silent, because of line-broadening effects due to fairly strong spin-exchange interaction between the μ-alkoxo and/or μ-hydroxo bridged Cu(II) ions. Magnetic susceptibility measurements by the so-called Evans

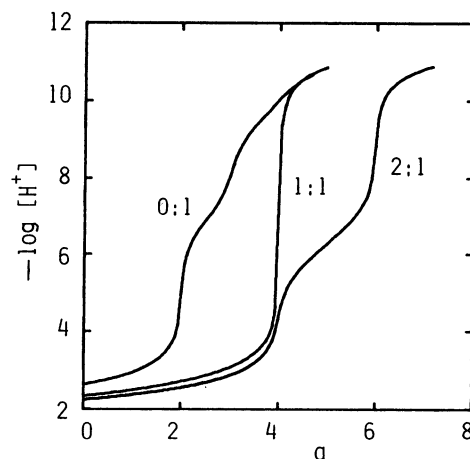


Fig. 1. Typical titration curves for proton-L system (0:1), 1:1 Cu(II)-L system (1:1), and 2:1 Cu(II)-L system (2:1): L = AC₃OH; [L] = 1.444 mM (1 M = 1 mol dm⁻³); a = moles of KOH added per mole of L.

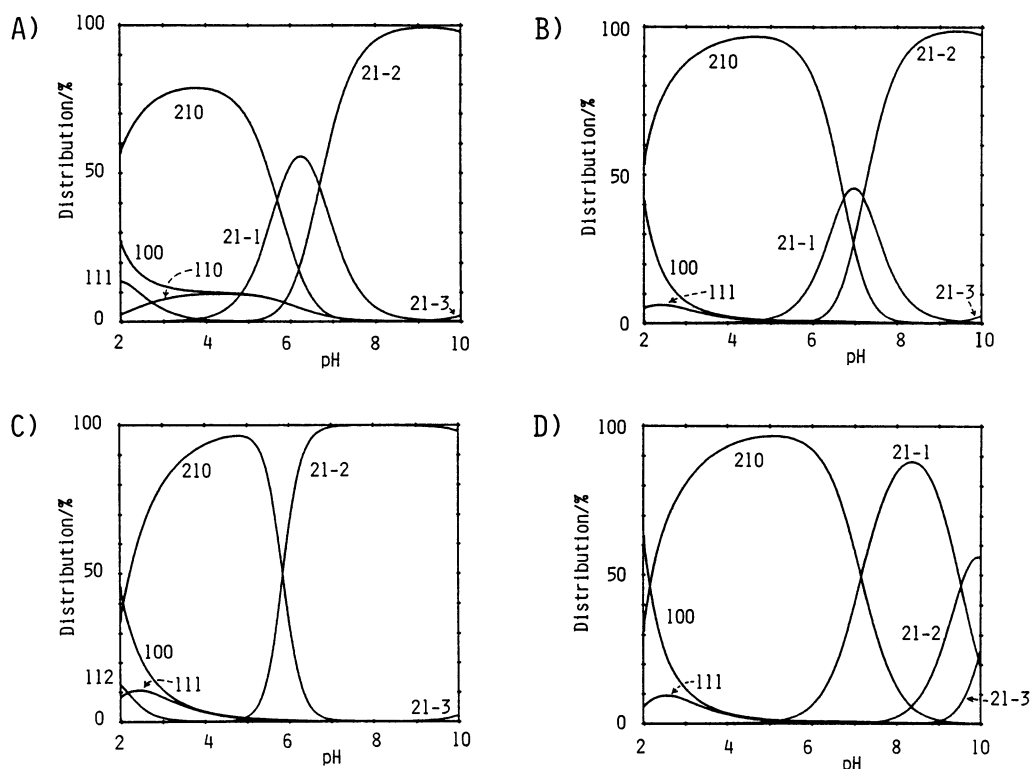


Fig. 2. Species distributions as a function of pH: A, 2:1 Cu(II)-AC₃OH system; B, 2:1 Cu(II)-AC₄OH system; C, 2:1 Cu(II)-AC₅OH system; D, 2:1 Cu(II)-AC₅ system (ligand concentrations, 1.5 mM). Numbers pqr in the figures express the complex Cu_pL_qH_r (see text).

method have revealed that the apparently ESR-silent species have subnormal magnetic moments.⁸⁾ The apparent ESR intensity, I , varies with pH according to the equations of $1/I = K_1K_2/[H^+]^2 + K_1/[H^+] + 1$ for the AC₃OH and AC₄OH systems and of $\log(1/I - 1) = 2 \text{ pH} + \log K_3$ for the AC₅OH one. Such ESR data for the AC₃OH system are shown in Fig. 4 for information. Equally- and narrowly-spaced seven hyperfine lines of the room-temperature ESR spectrum in the figure afford clear evidence for the formation of 210.⁸⁾ The equilibrium constants thus determined by this ESR method are listed in parentheses in Table 2. They are in satisfactory agreement with those determined potentiometrically, giving strong evidence to warrant our conclusion shown in Fig. 3.

Figure 2 shows that the alcoholic OH groups of the binuclear copper(II) complexes of AC₃OH, AC₄OH, and AC₅OH deprotonate at pH < 6 to form μ -alkoxo bridges. Especially for the first one, the deprotonation occurs at pH < 5.5, probably due

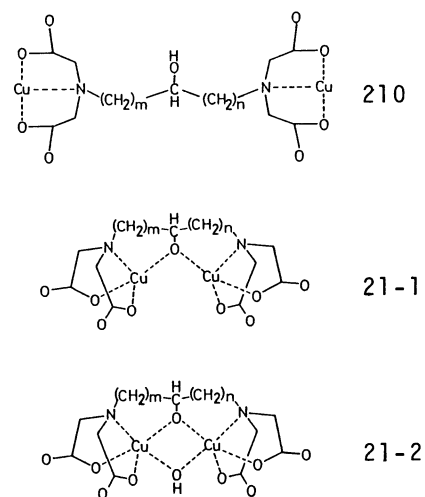


Fig. 3. Schematic illustrations of the complex structures of 210, 21-1, and 21-2.

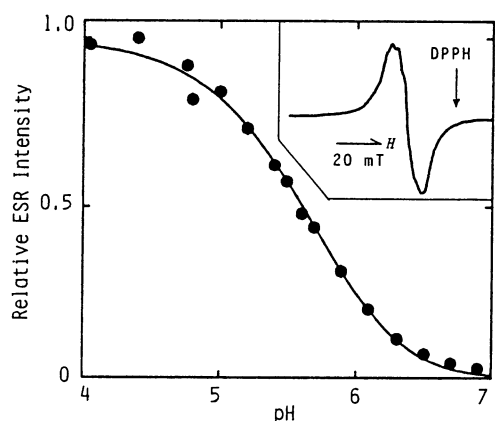
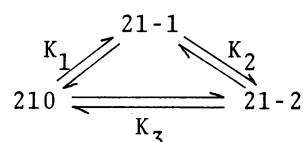


Fig. 4. pH dependence of the intensities of room-temperature ESR spectra for the 2:1 Cu(II)-AC₃OH (10 mM) system. The insert shows a room-temperature ESR spectrum observed at pH 5.2.

Table 2. Equilibrium Constants^{a, b)} for the Main Complex Species of 21r

Ligand	pK ₁	pK ₂	pK ₃
AC ₃ OH	5.71(5.68)	6.71(6.33)	12.42(12.01)
AC ₄ OH	6.75(6.80)	7.21(7.61)	13.96(14.41)
AC ₅ OH	—	—	11.74(11.35)

a) The equilibrium constants of K₁, K₂, and K₃ are defined in the following:



b) Numbers in parentheses express the equilibrium constants determined by the ESR method (see text).

to double chelating effects in the formation of two 5-membered chelating rings involving the bridging oxygen atom. On the other hand, Fig. 2C shows that the last complex forms μ -alkoxo and μ -hydroxo double bridges at a step at pH 5.8, suggesting that two 6-membered chelating rings in this complex are sterically favorable to the formation of μ -hydroxo bridging. This is also considered as a promoting effect of μ -alkoxo bridging on the formation of μ -hydroxo one, and vice versa, giving a model for biological active sites which show functional cooperativity. Interestingly, molecular conformations of the above binuclear complexes largely change upon the formation of μ -alkoxo and/or μ -hydroxo bridges. It has been first demonstrated in this study that two copper(II) ions located near an alcoholic OH group have a potential to deprotonate the OH group easily at pH < 6 to form a μ -alkoxo bridge.

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