Solution Equilibrium and EPR Study of the Dinuclear Copper(II) Complexes of Aminopolycarboxylic Acids with an Alcohol OH Group in the Alkyl Chain Linkage

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Dinuclear copper(II) complexes of 2-hydroxy-1,3-diaminopropane-, 2-hydroxy-1,4-diaminobutane-, and 3-hydroxy-1,5-diaminopentane-*N,N,N′,N′*-tetraacetic acids (AC$_3$O, AC$_4$O, and AC$_5$O) have been investigated by potentiometric titration, EPR and other spectroscopies. It has been confirmed that two or three different kinds of dinuclear complex species are formed in every ligand system, depending on the pH. In the complexes formed in the low-pH region, the two copper ions are coordinated independently by the two iminocarboxyl groups and have a weak magnetic dipolar interaction. In all of the three ligand systems the dinuclear complexes deprotonate the alcohol OH groups at low pH values (below 6) to form μ-alkoxo between the two copper ions. For AC$_3$O and AC$_4$O systems, the formation of μ-alkoxo and μ-hydroxo-double bridged complexes follows as the pH increases, while the AC$_5$O system forms a double-bridged complex at a step from the non-bridged complex at pH 5.8. These mono-μ-alkoxo bridged and double-bridged complexes have fairly strong spin exchange interactions between the paramagnetic centers through the bridges. The length of the methylene linkage plays a role in determining the complex structures and magnetic interactions between the paramagnetic centers.

Dinuclear copper complexes have found increasing interest in many fields of chemistry.[1] Copper ions play important roles in a number of enzyme systems,[2] and coupled copper active sites are present in a wide variety of them.[3] Many studies are being carried out to develop dinuclear copper complex models for them. Especially, oxygen (hydroxo, alkoxo, and phenoxo) bridged dinuclear complexes are being fully investigated.[1–4]

The exchange interaction between paramagnetic centers has been extensively studied during the last few decades. As a result, a magneto-structural correlation for hydroxo-bridged dinuclear copper complexes has been established.[5] Despite such intensive investigations, however, there still remains much uncertainty concerning the structures and equilibria of dinuclear complexes in solutions. Since their formation in aqueous solutions is dependent upon the stability constants of the hydrolysis of copper(II) ions such investigations become complicated.[6] Although the hydrolysis of metal ions has been receiving much attention for many years, there still remains much uncertainty concerning the estimated structures, and no corroborative evidence for the estimated structure has been provided by any method.[6] In a previous study, we investigated the formation of dinuclear copper(II) complexes with 3,12-bis(carboxymethyl)-6,9-dioxa-3,12-diazatetradecanedioic acid (H$_4$egta) in aqueous solutions by the EPR method.[7] We showed in the investigations that a complemental use of the potentiometric titration and EPR spectroscopy is very useful for investigating the equilibria and structures of dinuclear copper(II) complexes in aqueous solutions.

Alkoxo-bridged dinuclear copper(II) complexes, as well as hydroxo-bridged ones, have been widely studied in solids. However, no structural information concerning them in aqueous solultions has been obtained. Few attempts have been reported concerning the design and synthesis of the ligands which coordinate to metal ions with deprotonated alcohol groups in aqueous solutions. In this respect it must be noted that the alcohol OH group has a very high pK_a value (>16). However, there have been a few papers which show that some copper(II) mononuclear complexes with alkoxide coordination are formed, even in the low-pH range.[8] This fact has urged us to consider the possibility that the alcohol OH groups function as bridging ligands in aqueous solutions to form dinuclear copper(II) complexes.

Our purpose was to study the effects of alcohol OH groups on metal-binding and their bridging affinities in dinuclear copper(II) complexes using several new ligands, and to investigate the nature of the coordinating alkoxo-bridges in aqueous solutions by EPR and potentiometric titration. The ability of metal ions to displace the alcohol OH protons and, thus, to produce metal chelates of higher stability is greatly influenced by the steric arrangements of the alcohol OH group and the other functional groups in the multidentate ligands.

For the purpose we designed ligands which have an alcohol OH group on the alkyl chain linkage of the aminopolycarboxylic acids with different chain lengths. The synthesized ligands are 2-hydroxy-1,4-diaminobutane-*N,N,N′,N′*-tetraacetic acid (AC$_4$O), and 3-hydroxy-1,5-diaminopentane-*N,N,N′,N′*-tetraacetic acid (AC$_5$O). We studied the equilibria and structures of complexes of the ligands at different pH in aqueous solution. We compared them with those of the aminopolycarboxylic acids without alcohol OH groups in order to clarify the role of the alcohol OH group.

Experimental

The reagents used were of the highest grade.

Syntheses of Ligands. 2-Hydroxy-1,4-diaminobutane-*N*,*N*,*N*′,*N*′-tetraacetic acid (AC_4O) was synthesized by the condensation of 4-equivalent of bromoacetic acid with 1-equivalent of 1,4-diaminobutan-2-ol,[9] which was synthesized as follows: 1,4-Dibromobutan-2-ol (from Aldrich) was added drop by drop to dimethylformamide (150 mL) containing sodium azide (8.2 g) with stirrinig. The solution was heated (80—85 °C) for three hours, and then allowed to come to room temperature. Upon extracting the mixture with diethylether, the ether layer was washed with water, giving 1,4-diazidobutan-2-ol; IR: $\bar{\nu}_{NNN}=2100\ cm^{-1}$. The diazide (3.5 g) was hydrogenated in a Parr hydrogenation vessel containing methanol (200 mL) and platinum dioxide catalyst (0.2 g) at 3 $kg\ cm^{-2}$ for 20 h. Removal of the catalyst and the solvent left a colorless liquid which, upon distillation, gave 1,4-diaminobutan-2-ol; bp: 90—95 °C at 0.2 Torr (1 Torr=133.322 Pa), yield: 80% (1.86 g).

Bromoacetic acid (7.4 g) was dissolved in water (5 mL) and cooled to 5 °C. NaOH (2.29 g) dissolved in water (5 mL, 5 °C) was added portionwise with stirring to the solution while keeping the temperature below 10 °C. 1,4-diaminobutan-2-ol was then added, and the mixture was kept at 50 °C for 1.5 h. During this period, NaOH (2.29 g), dissolved in water (10 mL), was added to keep the pH at about 10. After the addition was completed, the solution was gradually heated up to 90 °C and kept there. Barium chloride (6.5 g) dissolved in water (15 mL) was added to this solution; the mixture was stirred vigorously for one hour. During this period white $Ba_2(Hac_4o)$ was precipitated out of the solution (AC_4O=H_5ac_4o). This precipitate was filtered off, washed with warm water, and dried under reduced pressure. Two equimolar amounts of H_2SO_4 were added to a suspended aqueous solution of the solid, and $BaSO_4$ was removed by filtration. The filtrate was concentrated and the pH adjusted to 2.5 with HCl. By adding a small amount of methanol, and cooling to 0 °C, AC_4O was precipitated; the precipitate was recrystallized from hot water four times. Yield: 70% (3.00 g). Anal. Calcd for $C_{12}H_{22}N_2O_{10}$ (monohydrate): C, 40.68; H, 6.26; N, 7.91%. Found: C, 40.63; H, 6.39; N, 7.79%.

3-Hydroxy-1,5-diaminopentane-*N*,*N*,*N*′,*N*′-tetraacetic acid (AC_5O) was prepared from 1,5-diaminopentan-3-ol,[10] bromoacetic acid, and barium hydroxide by a procedure similar to that employed for AC_4O. Yield: 50%, Anal. Calcd for $C_{13}H_{22}O_9$: C, 44.57; H, 6.33; N, 8.00%. Found: C, 44.65; H, 6.39; N, 7.92%.

1,3-diaminopropanetetraacetic acid (AC_3) was synthesized by the method of Weyh and Hamm.[9c] 1,4-diaminobutane-*N*,*N*,*N*′,*N*′-tetraacetic acid (AC_4) and 1,5-diaminopentane-*N*,*N*,*N*′,*N*′-tetraacetic acid (AC_5) were prepared by using a modified method of Schwarzenbach and Ackermann.[9a]

2-hydroxy-1,3-diaminopropane-*N*,*N*,*N*′,*N*′-tetraacetic acid (AC_3O) was obtained from Dojindo Laboratories, and recrystallized from hot water.

Potentiometric Measurements. Potentiometric measurements were made by adding standardized KOH solutions (0.1011 M)[11] to 0.0014—0.0017 M ligand solutions with or without equal or twice of copper(II) nitrate. The experimental solutions were maintained at 25.0±0.1 °C and protected from air with humidified, prepurified N_2. The KOH solution was delivered using a 10 ml Kyoto Electronics APB 118 auto piston burette with a constricted tip under the surface of the solution. The pH of the solution was measured with a Denki Kagaku Keiki IOC-10 pH meter. All of the solutions were prepared from freshly boiled double-distilled water; ionic strength (I) was maintained at 0.10 with KNO_3; 13.792 was used as the pK_w value. The stability constants, β_{pqr} (defined in Eq. 1), were calculated by the method of nonlinear least-squares with the computer program SUPERQUAD[12] (charges are omitted for simplicity):

$$p\mathrm{Cu} + q\mathrm{L} + r\mathrm{H} \rightleftharpoons \mathrm{Cu}_p\mathrm{L}_q\mathrm{H}_r \qquad (1)$$

and

$$\beta_{pqr} = \frac{[\mathrm{Cu}_p\mathrm{L}_q\mathrm{H}_r]}{[\mathrm{Cu}]^p[\mathrm{L}]^q[\mathrm{H}]^r}\ , \qquad (2)$$

where L denotes one of the aminopolycarboxylic acid ligands; p, q, and r are the numbers of Cu(II), L, and proton (H), respectively, in the complex $Cu_pL_qH_r$ (hereafter expressed as pqr).

Electron Paramagnetic Resonance Measurements. A JEOL JES-FE2XG EPR spectrometer was used to measure EPR spectra over the temperature range 77 K to room temperature; a Varian E112 was used for measurements at temperatures from 5 to 60 K. All of the sample solutions were prepared by dissolving ligands and mixing a copper(II) perchlorate solution whose concentration was determined by titration; the ionic strength was adjusted by the addition of sodium perchlorate. The real intensities of the EPR spectra were obtained by double integration of the observed first-derivative spectra.[13] The intramolecular spin exchange interaction energy, J, was evaluated from the temperature dependence of the spectral intensity.[14] A computer simulation of the EPR spectra was carried out by a method using a point-dipole approximation.[15]

Nuclear Spin Resonance Measurements. The ^1H NMR spectra were measured on a JEOL JNM-FX90Q NMR spectrometer. For measurements of the ligands, the solutions were prepared by dissolving the ligands (about 0.05 M) with NaOD in D_2O, and then adding 3-(trimethylsilyl)-1-propane-sulfonic acid (DSS) for a reference peak. The magnetic susceptibilities of the complexes were measured at 25 °C in aqueous solutions containing 2% *t*-butyl alcohol as an indicator by the Evans method.[16]

Electronic Absorption Spectral Measurements. All sample solutions were prepared using a procedure similar to that in the EPR measurements. The spectra were measured at 25 °C using a Shimadzu UV-240 spectrophotometer.

pH adjustiments were carried out throughout this work without using any buffer.

Results and Discussion

NMR Spectra and Solution Equilibria of Ligands.

NMR spectral data of AC_4O and AC_5O are presented in Table 1. AC_5O shows the expected singlet, triplet, and two multiplets, corresponding to symmetrically sub-

Table 1. NMR Spectra of Ligands[a,b)]

Ligand	δ (ref. to DSS)	Relative integration	Type peak[c)]	Assignment
AC_3O	2.60	3.9	m	$-NCH_2-$
	3.80	1.0	m	$-NCH_2C\underline{H}(OH)-$
	3.20	7.9	s	$-NC\underline{H}_2CO_2-$
AC_4O	1.58	2.0	dt	$-NCH_2C\underline{H}_2CH(OH)-$
	2.60	4.1	m	$-C\underline{H}_2CH(OH)CH_2C\underline{H}_2-$
	3.78	1.0	m	$-CH_2C\underline{H}(OH)CH_2-$
	3.18	7.8	d	$-NC\underline{H}_2CO_2-$
AC_5O	1.62	3.9	dt	$-NC\underline{H}_2-$
	2.64	3.9	t	$-NCH_2C\underline{H}_2-$
	3.80	1.0	q	$-NCH_2CH_2C\underline{H}(OH)$
	3.16	8.0	s	$-NC\underline{H}_2CO_2-$

a) pD=pH+0.4=12. b) 0.1 M solutions in D_2O at 25.0 °C. c) Key: s=singlet; d=doublet; t=triplet; q=quintet; m=multiplet.

stituted acetate and 1,5-pentanediamine-3-ol.[17] On the other hand, AC_4O shows doublet signals for the acetate protons, reflecting the unsymmetrical structure of 1,4-diaminobutan-2-ol, or the different environments of the two ends of the molecule.

A potentiometric equilibrium measurement of AC_5O with an added standard base gives an equilibrium curve similar to the one of AC_4, or AC_5[18] with losses of two protons from carboxyl groups in the acidic region and two protons from imino groups in the basic region (Fig. 1).[9a,19] On the other hand, in the case of AC_4O, two protons are lost in the acidic region and the two imino protons are lost in a stepwise sequence similar to the case of AC_3O and AC_3.[19–21] These features indicate that the alkoxo protons are not released when the pH is between pH 2 and pH 11 in the absence of metal ions. The calculated protonation constants are given in Table 2. The β_{012} and β_{011} values, which reflect the addition of a proton to the imino groups, become larger as the methylene bridge becomes longer, and show large differences from the inherent values of imino groups.[19e,22] These values for AC_3O, AC_4O, and AC_5O are smaller than those for the corresponding aminocarboxylic acids havinig no alcohol OH group in the alkyl chain linkage (AC_3, AC_4, and AC_5). It is known that the inductive effect decreases with increasing number of carbon atoms in the alkyl chains. The changes in the basicities of the imino groups increase with the reduction of the inductive effect of the alcohol OH group, producing differences between the sum of the β_{012} and β_{011} values for the aminopolycarboxylic acids having the alcohol OH group and those for the corresponding aminopolycarboxylic acids having no alcohol OH group.[23]

Solution Equilibria of Copper Complexes. The potentiometric curves for the systems of the 1 : 1 molar ratio of copper(II) ion with AC_5,[9a,19] AC_4O, and AC_5O have inflections after three and four protons are removed (Fig. 1). On the other hand, AC_3, AC_4, and AC_3O have only one inflection after four protons are removed.[20,21] These features indicate that the alcoholic protons of the methylene linkages in AC_3O, AC_4O, and AC_5O are not released under these conditions. For systems with a 2 : 1 molar ratio of the metal ion to the ligand, however all of the potentiometric equlibrium curves are different from one another. For AC_3 and AC_4 systems, after inflection (pH>7), a precipitate of copper hydroxide is formed.[6c,24] For AC_5 system, however, there are many inflections in a (moles of KOH added per mole of L) over range 6 to 8 (Fig. 1-c).[18] On the other hand, the AC_3O, AC_4O, and AC_5O systems all have inflections at a=4 and 6, and form no precipitation. These facts indicate that complex formation is largely dependent upon the presence of an alcohol OH group in the ligands and, after all, upon its deprotonation and coordination, as mentioned later.[21] The 21-n species, therefore, correspond to alkoxo-coordinated species. Analyses of the above-mentioned titration curves gave the values of log β_{pqr} listed in Table 2. Plots of the species distribution fractions vs. pH are presented in Fig. 2 for systems of 2 : 1 and 1 : 1 molar ratio of copper(II) ion to AC_4O, and for systems of 2 : 1 molar ratio of copper(II) ion to AC_3O and AC_5O, respectively. The 2 : 1 system is comparatively simple, with the initial formation of a dinuclear complex (210 species) without any alcohol deprotonation. Above pH 6, alkoxo-coordinated complexes are predominantly formed by deprotonation and successive hydroxo complex formation as the pH increases. Interestingly, only in the case of the AC_5O system, is the 21-2 species extensively formed from the 210 species at a step. The 1 : 1 system, however, is surprisingly complicated. As can be seen from the species distribution curve, the dinuclear 210 species is initially formed along with the protonated mononuclear chelate species (111) in the low-pH region. In the middle-pH range, although the 1 : 1 complex is predominant it is converted at a higher pH to alcohol-deprotonated dinuclear species (21-2).

Figure 3 shows the EPR spectra of a fluid solution for the 2 : 1 molar ratio of copper(II) ion with AC_3O, AC_4O, and AC_5O at a pH of about 5 as well as the spectrum for a 1 : 1 molar ratio with the AC_3O system. A comparison between the 2 : 1 and 1 : 1 systems can also be made in terms of the EPR spectra. All of the EPR spectral line shapes observed for the 1 : 1 copper-ligand systems depend on the pH in the range of 2 to 6, but are

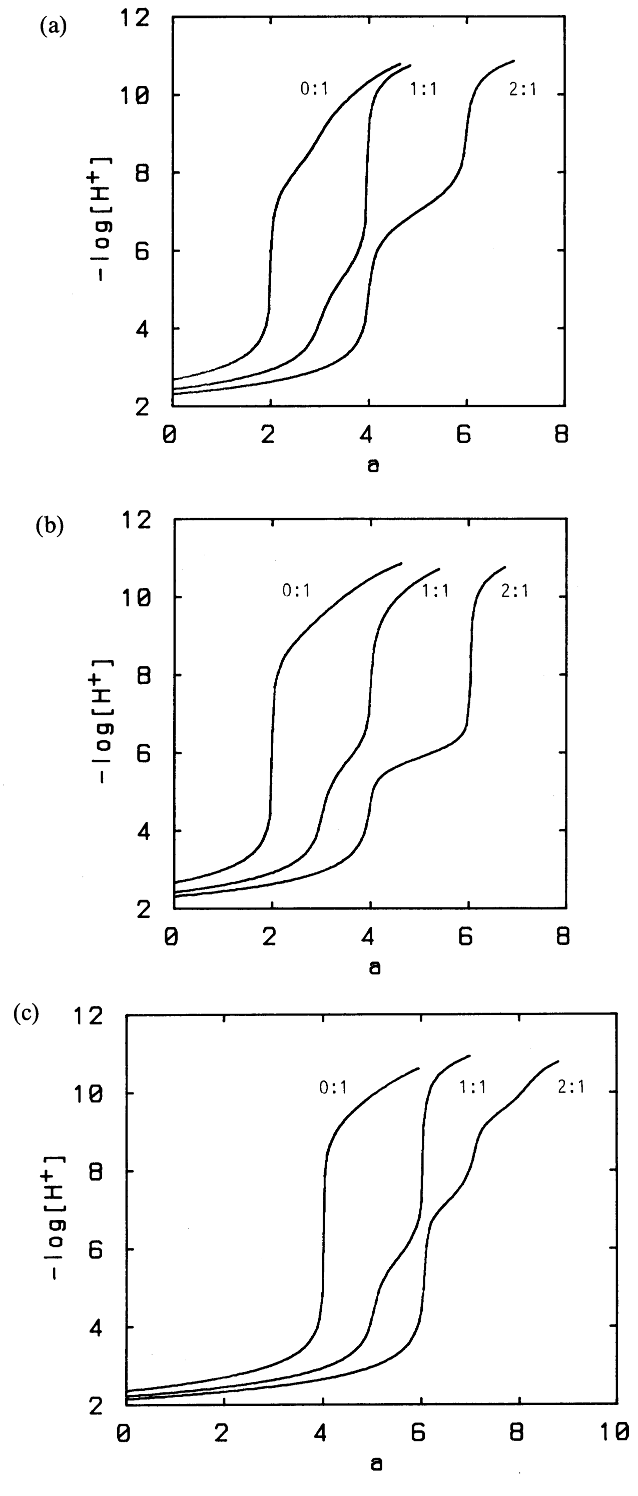

Fig. 1. Potentiometric equilibrium curves (25.0 °C, I=0.1 (KNO$_3$)) for proton–L (0:1), 1:1 Cu(II)–L (1:1), and 2:1 Cu(II)–L (2:1) systems: (a), L=AC$_4$O, [L]=1.375 mM; (b), L=AC$_5$O, [L]=1.511 mM; (c), L=AC$_5$, [L]=1.502 mM; a=moles of KOH added per mole of L.

independent of pH in the range 6 to 10 . Judging from the spectral pattern of the four equally separated hyperfine lines and species distribution analyses, all of these spectra observed in the pH 6 to 10 range can be assigned to the 1 : 1 mononuclear copper(II) complexes, expressed as 110.

By contrast, the EPR spectral intensities of the 2 : 1 systems depend on the pH without any change in the line shape. Based on the species distribution plots, all of the spectra obtained here are attributed to the 210 species, which have the structure shown in Fig. 4 (vide infra). Especially, the seven-line equally- and narrowly-spaced hyperfine spectra[7,24] are observed for the AC$_3$O system. Quasi-mononuclear spectral patterns are observed for the AC$_4$O and AC$_5$O systems analogous to Cu$_2$(egta) and Cu$_2$(edta), which have copper–copper distances of 5.5 Å and 5.6 Å, respectively.[7,26] As shown in Fig. 5, the EPR spectral intensities of the 2 : 1 complexes of copper(II) with ligands containing an alcohol OH group in aqueous solutions gradually decrease as the pH increases from 5 to 8, and become zero at pH 9. On the other hand, one can see that the pH range in which the EPR intensity decreases corresponds well to that for a concentration increase of the 21-1 and/or 21-2 species, as shown in Fig. 2. The decrease in the EPR intensity can therefore be attributed to the formation of dinuclear complexes which are EPR silent in a fluid solution, due to a line broadening effect of a strong spin-exchange interaction through the alkoxo and/or hydroxo bridges.[7] The formation of such dinuclear species is supported by the following magnetic susceptibility data as well as the frozen solution EPR spectra (shown later).

An inspection of Table 3 and Fig. 2 shows that μ_{eff} for the AC$_3$O system is small compared to the spin only value (1.73 B.M.) in the pH range where the 21-1 and 21-2 species are dominant; for the AC$_4$O system, it is small in the pH range where the 21-1 species is dominant, and becomes large in the pH range where the 21-2 species is mainly formed. The μ_{eff} value for the AC$_5$O system is small in the pH range where the 21-2 species is dominant. For the AC$_3$O system, the μ_{eff} value in a high-pH region is obviously subnormal and indicative of the presence of a strong antiferromagnetic interaction in the 21-1 and/or the 21-2 species. The value in a neutral pH region for the AC$_4$O system is obviously small compared to those for ordinary mononuclear species or weakly coupled dimers, and is also indicative of the presence of an antiferromagnetic interaction through the alkoxo bridge in the 21-1 species. On the other hand, the value in a high-pH region is large compared to the value in a low-pH region, indicating that the 21-2 species has an weak antiferromagnetic or ferromagnetic interaction. For the AC$_5$O system the value in a high-pH region indicates that the 21-2 species has an antiferromagnetic interaction. The spin exchange interactions in dinuclear copper(II) complexes have been extensively studied.[5] Hatfield and Hodgson have shown that hydroxo-bridged dinuclear complexes have strong spin exchange interactions through the bridges.[27] By analogy, it is more likely to consider that all of the 21-1 and 21-2 species have such bridged structures as those shown in

Table 2. Stability Constants (log β_{pqr})[a,b] and Equilibrium Constants

Cu	L	H	log β_{pqr}					
p	q	r	AC_3O	AC_4O	AC_5O	AC_3	AC_4	AC_5
0	1	4	20.81(1)	22.71(1)	24.01(1)	23.19(1)	24.50(1)	25.22(1)
0	1	3	18.87(1)	20.62(1)	21.85(1)	21.13(1)	22.27(1)	22.84(1)
0	1	2	16.34(1)	18.01(1)	19.19(1)	18.50(1)	19.61(1)	20.15(1)
0	1	1	9.42(1)	9.94(1)	10.19(1)	10.47(1)	10.55(1)	10.63(1)
1	1	2	—	—	23.14(11)	—	—	—
1	1	1	18.70(2)	19.38(4)	20.97(6)	21.13(3)	20.85(2)	21.42(5)
1	1	0	15.97(2)	14.59(2)	15.40(4)	18.40(3)	17.08(1)	16.17(3)
2	1	0	20.11(2)	21.00(3)	22.15(7)	20.87(7)	22.05(1)	22.58(4)
2	1	-1	14.40(2)	14.25(3)	—	—	14.12(3)	15.41(4)
2	1	-2	7.69(2)	7.04(3)	10.41(7)	—	—	5.87(4)
2	1	-3	−3.95(2)	−4.52(5)	−1.22(9)	—	—	−4.49(5)
pK_1			5.71(5.74)[c]	6.75(6.80)[c]	—	—	—	—
pK_2			6.71(6.66)[c]	7.21(7.61)[c]	—	—	—	—
pK_3			12.42(12.40)[c] 11.05[d]	13.96(14.41)[c]	11.74(11.35)[c]	—	—	—

a) The equilibrium constants of K_1, K_2, and K_3 are defined in the following. b) Values in the parentheses denote standard deviations. c) Numbers in the parentheses express the equilibrium constants determined by the EPR method (see text). d) The number expresses the equilibrium constant determined by the photometric titration (see text).

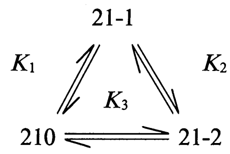

Fig. 4.

As mentioned above, the EPR spectra observed for the three systems are all attributed to the 210 species. Based on this assignment, changes in the EPR intensity with pH can be calculated by using Eqs. 3 to 5 for the AC_3O and AC_4O systems, and by Eqs. 6 to 7 for the AC_5O system.

$$1/I_{\mathrm{epr}} = A[K_1K_2/[\mathrm{H}^+]^2 + K_1/[\mathrm{H}^+] + 1], \qquad (3)$$

where

$$K_1 = [21\text{-}1][\mathrm{H}^+]/[210] = \beta_{21\text{-}1}/\beta_{210} \qquad (4)$$

and

$$K_2 = [21\text{-}2][\mathrm{H}^+]/[21\text{-}1] = \beta_{21\text{-}2}/\beta_{21\text{-}1}. \qquad (5)$$

Further,

$$1/I_{\mathrm{epr}} = A'[K_3/[\mathrm{H}^+]^2 + 1], \qquad (6)$$

where

$$K_3 = [21\text{-}2][\mathrm{H}^+]^2/[210] = \beta_{21\text{-}2}/\beta_{210}. \qquad (7)$$

In Eqs. 3 and 6, I_{epr} denotes the EPR intensity at a specific spectral position; A and A' are proportionality constants. K_1, K_2, and K_3 are the formation constants expressed by Eqs. 4, 5, and 7. The formation constants determined by these equations using the least-squares method are listed in parentheses in Table 2. Since they are in satisfactory agreement with those determined potentiometrically, they also give strong evidence to warrant our conclusion in Fig. 4.

The absorption spectra for the solution of 2 : 1 molar ratio of copper(II) to AC_5O and the change in the spectral intensity at 350 nm with increasing pH are given in Fig. 6. The spectra in a high pH region give a shoulder-like band at 350 nm which is attributed to charge transfer transitions from the non-bonding orbital of bridging oxygen to the vacant copper d-orbitals, indicating that 21-2 species has a μ-alkoxo bridge.[10b,28] However, the spectra for the AC_3O and AC_4O system do not show such bands. According to the CPK molecular model analysis, the 21-2 species of the AC_5O has only a planar dinuclear structure around the copper ions. Judging from these results, a planar structure may force sp^2 hybridized orbitals to be formed at the bridging oxygen, leaving one p-orbital as a nonbonding orbital; the CT band thus appears in a relatively lower frequency region, showing a shoulder. As mentioned above, equilibrium exists at between 210 and 21-2 species in this system. The equilibrium constants were determined by the changes in the spectral intensity at 350 nm. The absorbance at 350 nm (A_{350}) is given by

$$A_{350} = C_t[\mathrm{H}^+]^2/(K_3 + [\mathrm{H}^+]^2)(\varepsilon_{210} + K_3\,\varepsilon_{21\text{-}2}/[\mathrm{H}^+]^2). \qquad (8)$$

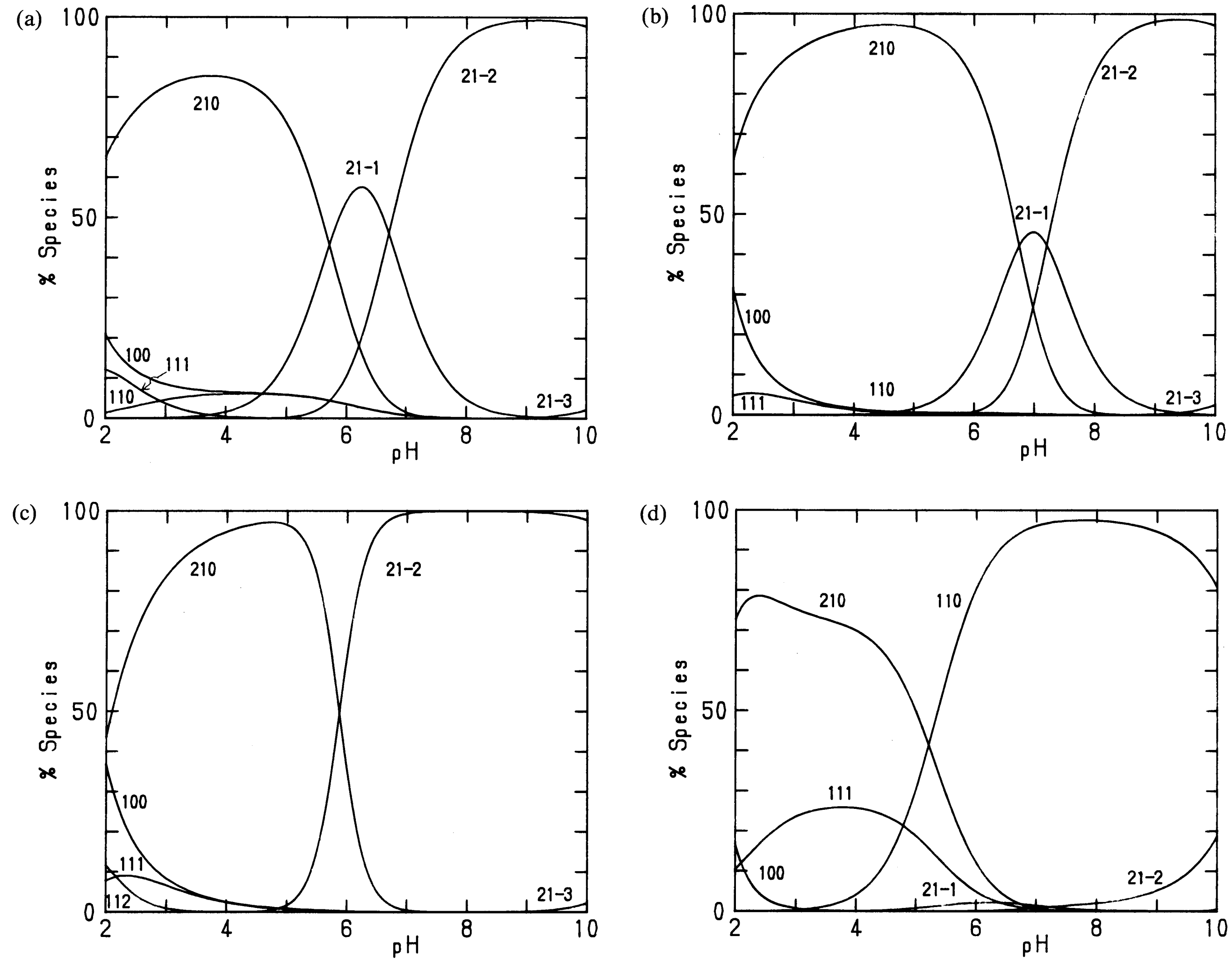

Fig. 2. Species distributions as a function of pH: (a) 2:1 Cu(II)–AC$_3$O system; (b) 2:1 Cu(II)–AC$_4$O system; (c) 2:1 Cu(II)–AC$_5$O system; (d) 1:1 Cu(II)–AC$_4$O system.

In this equation, C_t is the total concentration of dinuclear species, i.e. half of the total concentration of the copper(II) ion; ε_{210} and $\varepsilon_{21\text{-}2}$ are the molar absorption coefficients for the 210 and 21-2 species, which were determined from the absorbance pH 4 and pH 10 to be 45.2 cm^{-1} M^{-1} and 256 cm^{-1} M^{-1}, respectively. The equilibrium constant, K_3, obtained by this method, as listed in Table 2, is also in satisfactory agreement with those determined by potentiometry and EPR method.

Figures 2 a—c show that the alcohol OH groups of the dinuclear copper(II) complexes of AC$_3$O, AC$_4$O, and AC$_5$O deprotonate at pH$<$6 to form a μ-alkoxo bridge. Especially for the AC$_3$O complex, deprotonation occurs at pH$<$5.5, probably due to double chelating effects in the formation of two 5-membered chelating rings involving the bridging oxygen atom. On the other hand, Fig. 2-c shows that the AC$_5$O complex forms μ-alkoxo and μ-hydroxo double bridges at a step at pH 5.8, suggesting that two 6-membered chelating rings in this complex are sterically favorable to the formation of μ-hydroxo-μ-alkoxo double bridges. However, this may also be explained as a promoting effect of μ-alkoxo bridging on the formation of μ-hydroxo one, and vice versa. Interestingly, molecular conformations of 210-type complexes, which have two copper ions coordinated by the iminoacetato groups, respectively, change largely upon the formation of μ-alkoxo and/or μ-hydroxo bridges connecting the two copper ions (Fig. 4). It was demonstrated above that two copper(II) ions located near an alcohol OH group have a potential to deprotonate the OH group easily at pH$<$6 to form a μ-alkoxo bridge. In our previous study[29] it was found that when hydrogen peroxide is added to blue aqueous solutions of the dinuclear copper(II) complexes of AC$_3$O, AC$_4$O, and AC$_5$O at pH$>$7, only the solution of the AC$_4$O complex produces an intense green color, which is attributed to the formation of a peroxide bridged dinuclear complex. This fact also indicates that the reactivity and nature are strongly dependent upon small structural variations of the dinuclear complexes, such as

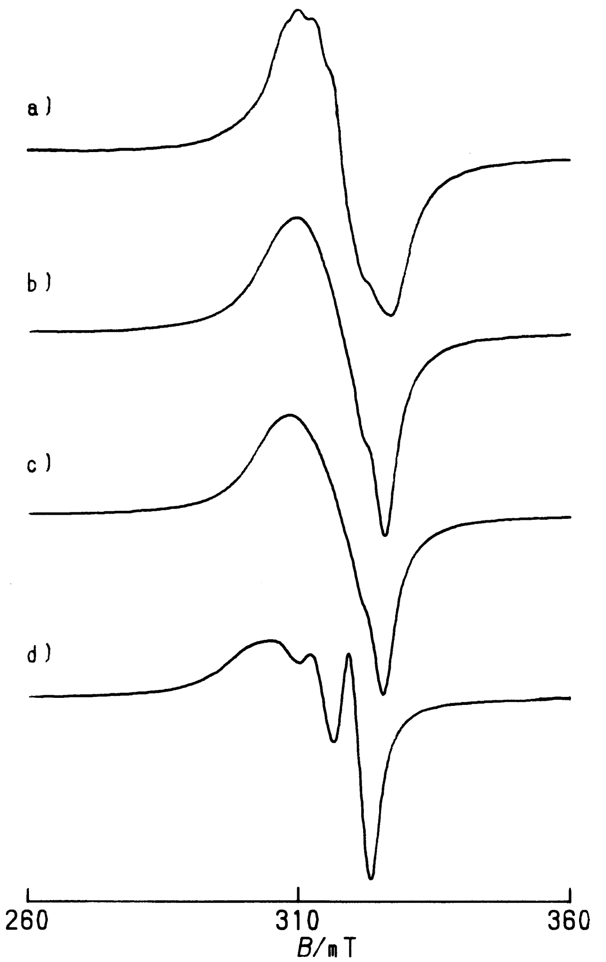

Fig. 3. EPR spectra in fluid aqueous solutions at pH 5 (25.0 °C, $[Cu(ClO_4)_2]=5.04$ mM, $I=0.50$ ($NaClO_4$), $\nu=9.187$ GHz); (a) 2:1 Cu(II)-AC_3O system: (b) 2:1 Cu(II)-AC_4O system; (c) 2:1 Cu(II)-AC_5O system; (d) 1:1 Cu(II)-AC_4O system.

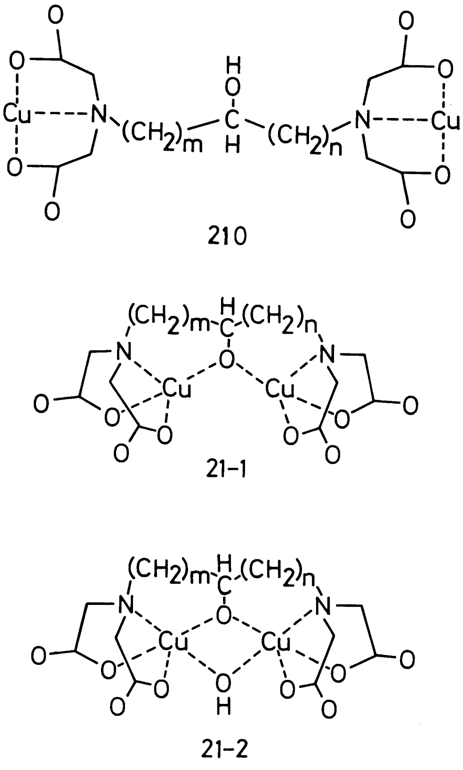

Fig. 4. Schematic illustration of the complex structures of the 210, 21-1, and 21-2 species. H_2O ligands are omitted for simplicity.

Table 3. Effective Magnetic Moments for 2:1 Cu(II)-L Aqueous Solutions at 25 °C and Different pH's[a)]

Ligand	pD[b)]	μ_{eff}/B.M.
AC_3O	4.45	1.82
	6.56	1.66
	8.68	1.61
AC_4O	4.92	1.84
	6.22	1.77
	7.03	1.71
	7.93	1.73
	8.56	1.83
	9.85	1.85
AC_5O	4.03	1.84
	5.11	1.74
	6.50	1.70
	8.84	1.68

a) $[Cu(II)]=2.50\times10^{-2}$ M; [Cu(II)]/[ligand]=2. b) pD= pH+0.4.

changes in the relative positions and asymmetrical environments of the two copper(II) ions.

Frozen Solution EPR Spectra and the Structures of Dinuclear Complexes. Frozen solution EPR spectra of dinuclear copper(II) complexes are useful to identify species found in solution in comparison with fluid solution EPR spectra and species distribution analyses. They are also useful for obtaining structural information concerning the complexes. The EPR spectra observed for the 2 : 1 copper-ligand solutions at 77 K are shown in Figs. 7 to 9. Two kinds of spectra were observed for the AC_3O system. Based on species distribution analyses, the EPR spectra observed in the high- and low-pH regions are attributed to the 21-2 and 210 species, respectively. For the AC_4O system, two kinds of spectra were observed, which are attributed to the 210 and 21-1 species, respectively. On the other hand, only one spectrum attributed to the 210 species was observed for the AC_5O system. These results indicate that the 21-1 species of the AC_3O and the 21-2 species of the AC_4O and AC_5O are of EPR-silent oxygen-bridged types due to large zero-field splittings.[30)]

All of the spectra observed for the 210 species show weak absorption at a low field of about 0.15 T and a strong one in the region around $g=2$, indicating that the spectra apparently come from a triplet state due to a weak spin-spin interaction between copper atoms.[14,15,25,31,32)] The structures of all the 210 species have been analyzed by computer simulations of the EPR spectra; in the analyses the coordinate of dimers was taken to be of a parallel-planar type with structural parameters of r and ξ (r, the Cu–Cu distance; ξ, the angle between the Cu–Cu

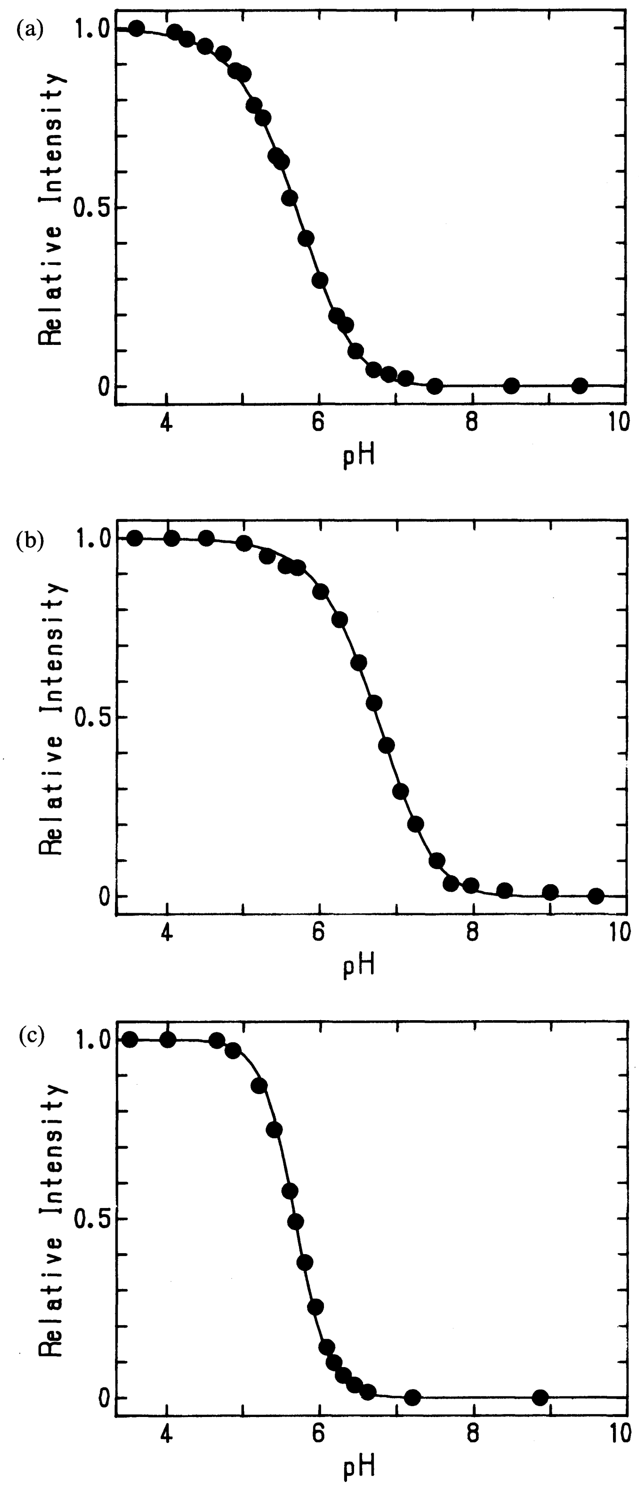

Fig. 5. pH dependence of the intensities of fluid solution EPR spectra for 2:1 Cu(II)-L systems: (a), AC_3O system; (b), AC_4O system; (c), AC_5O system. The solid lines indicate the calculated spectral intensity changes (see text).

direction and the normal to the molecular plane) and a point-dipole approximation being used.[14] As a result, r=4.9 Å and ξ=5° were determined for the AC_3O system. The simulation spectrum is shown in Figs. 7-b and 8-b. These values of r and ξ indicate that this complex has such a compact form as exemplified by the Cu_2(egta), which has a copper–copper distance of 5.5 Å. This structure is likely to exist when the ether-type oxygens are far away from the copper atoms. On the other hand, for the 210 species of the AC_3O, the compact form may be realized when the alcohol OH group weakly coordinates at the apical position of each copper atom of the $CuNO_3$ (one tertiary amino nitrogen, two calboxylic oxygen and coordinated water oxygen) type chromophore (Fig. 4).

On the other hand, the spectral patterns of the $\Delta M_s=2$ transitions for the 210 species of the AC_4O and AC_5O are greatly different from those of the usual parallel planar type with two identical copper ions with respect to the $\boldsymbol{A}$ and $\boldsymbol{g}$ tensors. These facts indicate that they have nonparallel axis alignments for the copper(II) ions,[7,31] and that their structures can not be estimated by the approximation used above. However, since the intensity ratio of the forbidden $\Delta M_s=2$ transitions to the allowed $\Delta M_s=1$ one has been revealed to depend only on r, it is possible to estimate the copper–copper distance by the ratio.[32] In the present case, the ratios for the AC_4O and AC_5O system are 7.5×10^{-4} and 4.3×10^{-4}, respectively and, thus, the copper–copper distance for the AC_4O and for the AC_5O system could be estimated to be 5.5 and 6.1 Å, respectively[32a] using

$$r=[(21/I_r)(9.1/\nu)^2]^{1/6}, \tag{9}$$

where r is expressed in units of Å, I_r is the relative intensity, and ν is the microwave frequency in units of GHz. The r values, thus obtained, for the 210 species are useful for selecting the correct structure from two possible types: An open configuration which has minimum steric repulsion, as exemplified by Mg_2(egta) in a crystal,[33] and a compact configuration like that seen in AC_3O. The obtained r values indicate that these are of a compact type, although their structures are different from that of the AC_3O system. It is now clear that the methylene linkage plays an important role in determining the structure.

For the AC_3O system, the EPR spectrum observed at pH 9.8 shows broad signals at magnetic fields of 0.05 T and 0.5—1.0 T, in addition to a sharp signal with a weak absorption intensity at around 0.3 T, which can be assigned to the residual 110 species (Fig. 9a). As mentioned above, the triplet-state spectrum is attributed to the 21-2 species. The spectral pattern shows that the 21-2 species has a much larger zero-field splitting parameter, $|D|$ (about 0.6 cm^{-1}) than that of 210, also suggesting that this complex is of such a bridged type, as shown in Fig. 4.[6f]

For the AC_4O system, the EPR spectrum observed at pH 7.5 shows signals at magnetic fields of 0.15 T and 0.3—0.4 T due to a triplet state; it can be assigned to the 21-1 species, based on distribution analyses (Fig. 9b). The spectral pattern shows that since the 21-1 species also

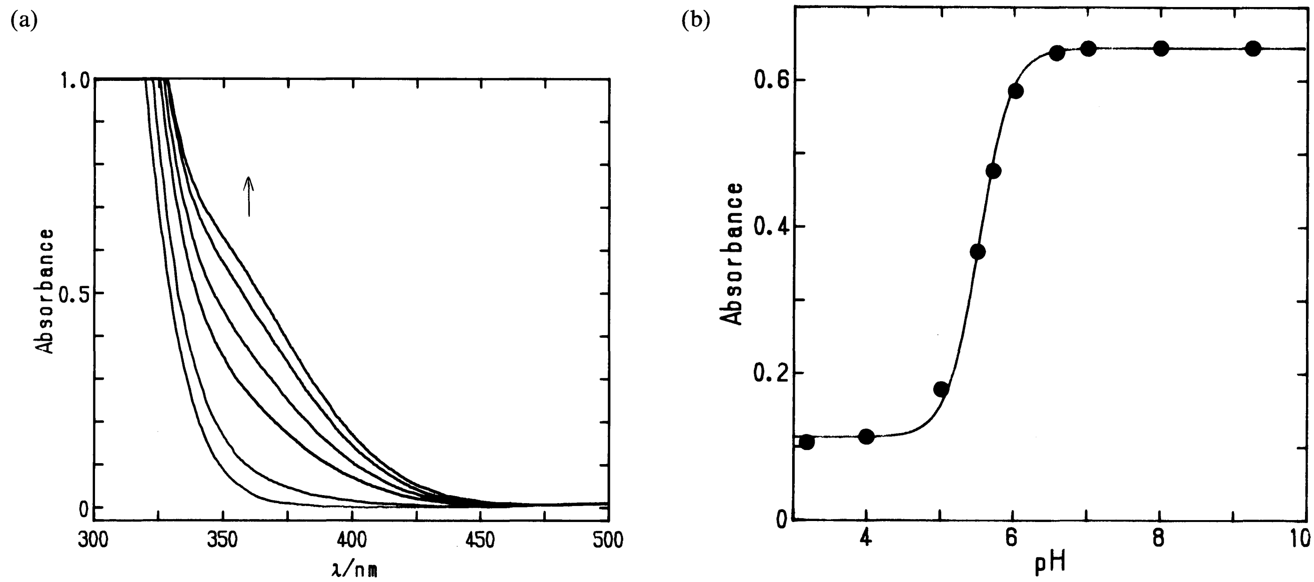

Fig. 6. Electronic absorption spectral changes for the 2:1 Cu(II)–AC_5O system: (a) absorption spectra (25.0 °C, $[Cu(ClO_4)_2]$=5.04 mM, I=0.50 ($NaClO_4$); the spectra changed along the direction of arrow with increasing pH being varied 3 to 10); (b) Plots of absorptions at 350 nm in (a) against pH (darked circle, experimental; solid line, calculated with the parameter values listed in Table 2).

has a relatively large $|D|$ value of about 0.1 cm^{-1}, this complex is of such a bridged type as that shown in Fig. 4.[6f)]

Under the condition of no microwave power saturation, the EPR spectral intensity, I_j is regarded as being proportional to the paramagnetic susceptibility of the dinuclear complex, and is expressed by

$$I_j = C/T[3+\exp(-2J/kT)]^{-1}, \qquad (10)$$

where C is a proportionality constant and J is the isotropic spin exchange interaction energy. The J value is therefore determined from the temperature variation of the relative EPR intensities.[7,14,34)] Since the EPR linewidths were constant over the entire temperature range, the relative peak heights of the first derivative $\Delta M_s=2$ spectra can be used as a substitute for I_j. The temperature dependence of the signal intensities, thus obtained, for the 21-2 species of the AC_3O system and for the 21-1 species of the AC_4O system are shown in Fig. 10. The solid lines are the relative intensity changes calculated by using Eq. 8 with $2J=-50$ cm^{-1} for the AC_3O system and $2J=-100$ cm^{-1} for the AC_4O system, respectively; the calculated ones by the use of these J values show good fits with the experimental data. Theoretical and experimental studies show that the copper–copper distances (r) and the Cu–O–Cu bridging angle (θ) are key factors in determining the magnitude of the exchange interactions.[5)] Hatfield and Hodgson have shown that the J value of doubly-bridged copper complexes varies steadily with the θ value, and that a singlet ground state occurs at $\theta>97.5°$, while at $\theta<97.5°$ a triplet ground state occurs.[27)] On the other hand, Charlot has shown that $|D|$ decreases with an increase in r for the case $\theta>90°$.[30a)] They summarized the J and D values for various di-μ-hydroxo or μ-alkoxo-bridged dinuclear copper(II) complexes with known bridging structures. According to them, the r and θ values of the 21-2 for the AC_3O system were estimated to be ca. 3 Å and ca. 100°, respectively.

The experimentally obtained zero-field splitting parameter ($|D|$) consists of two components: The magnetic dipole interaction between the two copper ions (D_{dd}) and spin-orbit coupling contribution (D_{so}).[5e,15)] For the 21-2 species of the AC_3O system, D_{dd} was calulated, based on the copper–copper distance estimated above, to be about 0.05 cm^{-1}, which corresponds to 10% of the observed $|D|$. D_{so} contains a term for the two-electron exchange integral, j, in the excited electronic configuration; the variation of D_{so} depends mostly on j.[5e,30a)] A theoretical calculation for a model complex shows that j has a maximum for θ close to 95°.[30a)] The fact that the 21-2 species of the AC_3O system has a relatively large D_{so} seems reasonable in view of the proposed complex structure. Since the 21-2 species of the AC_5O and AC_4O systems are estimated to have large zero-field splitting constant and small J values from the fact that they are EPR silent and from their μ_{eff} values (Table 2), respectively, the proposed structures also seem to be quite reasonable.

On the other hand, for the mono-μ-alkoxo-bridged complexes, the steric restriction on the structure is less than that for the double-bridged ones, and the bridged angle may be greater than that of double-bridged ones.

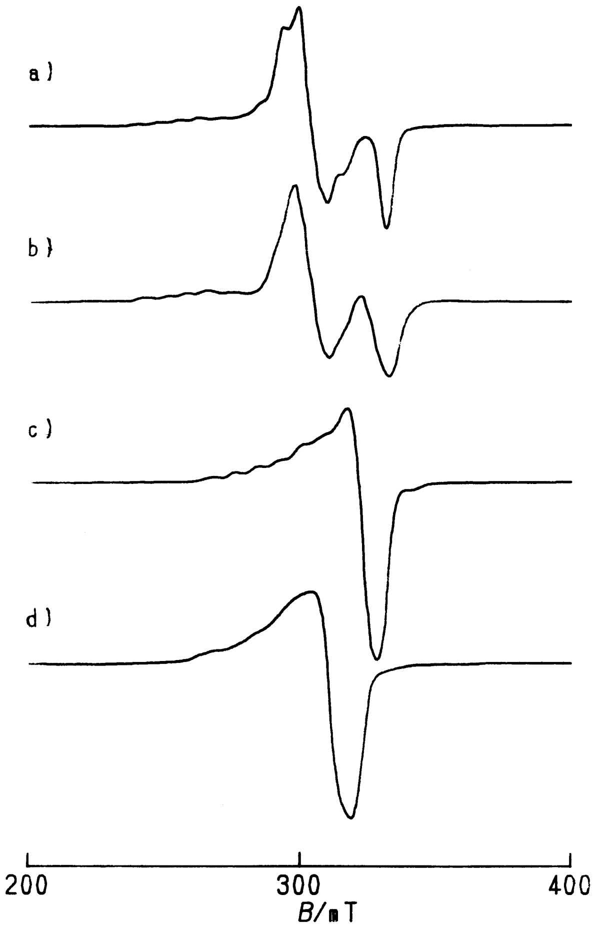

Fig. 7. Frozen solution EPR spectra ($\Delta M_s=1$) of 210 species at 77 K ($\nu=9.150$ GHz, pH=5.0, $[\mathrm{Cu(ClO_4)_2}]=5.04$ mM, $I=0.50$ ($\mathrm{NaClO_4}$)): (a), 2:1 Cu(II)-$\mathrm{AC_3O}$ system; (b) Dimer spectrum simulated with the following parameter values: $r=4.9$ Å, $\xi=5°$, $g_{/\!/}=2.29$, $g_{\perp}=2.05$, $|A_{/\!/}|=0.009\ \mathrm{cm^{-1}}$, $|A_{\perp}|=0.001\ \mathrm{cm^{-1}}$, $\Delta H_1=0.03$ T, $\Delta H_2=0.02$ T (ΔH_1 and ΔH_2 represent the line widths of $\Delta M_s=$ and $\Delta M_s=2$ spectra, respectively, see Fig. 8); (c), 2:1 Cu(II)-$\mathrm{AC_4O}$ system; (d), 2:1 Cu(II)-$\mathrm{AC_5O}$ system.

It seems reasonable to consider that the correlations of J and $|D|$ shown for di-μ-hydroxo or di-μ-alkoxo-bridged complexes also hold true for mono-μ-alkoxo-bridged complexes, since the magnitude of J and j are related to the overlap densities between the magnetic orbitals of the two copper centers and depend on θ. It is, therefore, expected that the 21-1 species of $\mathrm{AC_4O}$, which was estimated to have a large θ, has both a larger J value and a smaller $|D|$ values than do the 21-2 species. This expectation is consistent with the experimental observation that the 21-1 species has an appreciable antiferromagnetic interaction and a small $|D|$. This also strongly supports the estimated complex structure. As was shown above, J and $|D|$ are useful for estimating the coordination geometry of alkoxo ions in such μ-alkoxo-bridged dinuclear copper(II) complexes in solution.

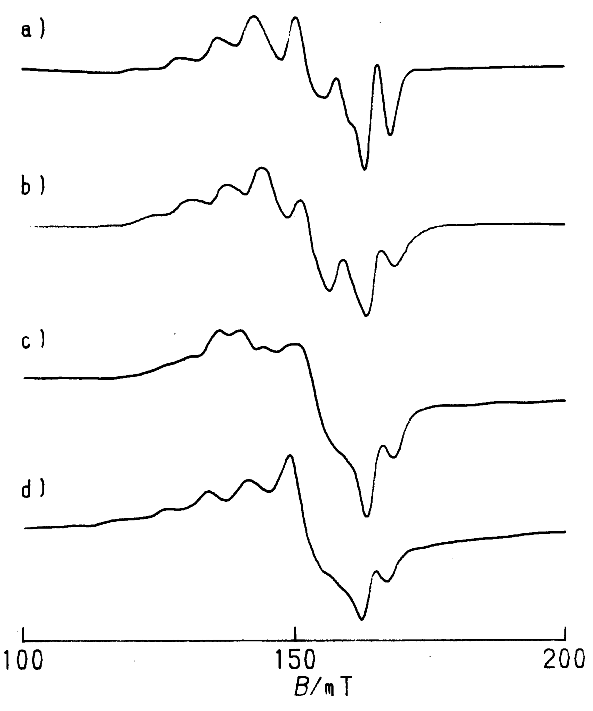

Fig. 8. Frozen solution EPR spectra ($\Delta M_s=2$) of 210 species at 77 K: (a), 2:1 Cu(II)-$\mathrm{AC_3O}$ system; (b), simulated spectrum; (c), 2:1 Cu(II)-$\mathrm{AC_4O}$ system; (d), 2:1 Cu(II)-$\mathrm{AC_5O}$ system. Measuring conditions and parameter values are the same as those listed in Fig. 7.

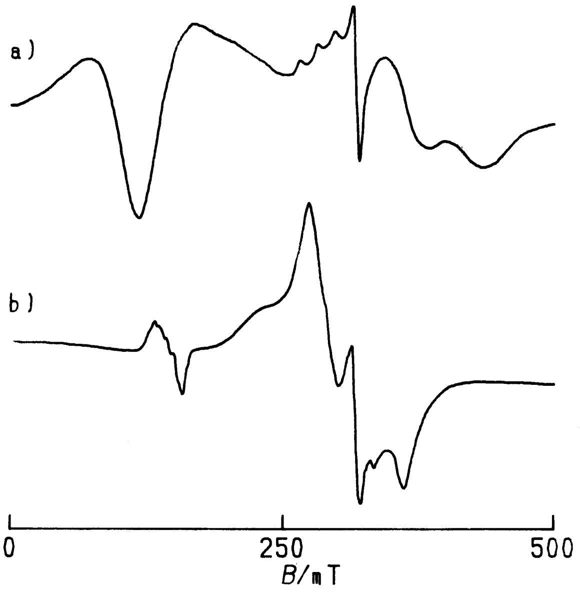

Fig. 9. Frozen solution EPR spectra of (a) 21-2 species of 2:1 Cu(II)-$\mathrm{AC_3O}$ system ($\nu=9.050$ GHz, pH=9.80, $[\mathrm{Cu(ClO_4)_2}]=20$ mM, $I=2.5$ ($\mathrm{NaClO_4}$)), (b) 21-1 species of 2:1 Cu(II)-$\mathrm{AC_4O}$ system ($\nu=9.050$ GHz, pH=7.50, $[\mathrm{Cu(ClO_4)_2}]=20$ mM, $I=2.5$ ($\mathrm{NaClO_4}$)).

Investigations of the crystal structures and details concerning the magnetism of the complexes are now in progress; correlations between the structures in solutions

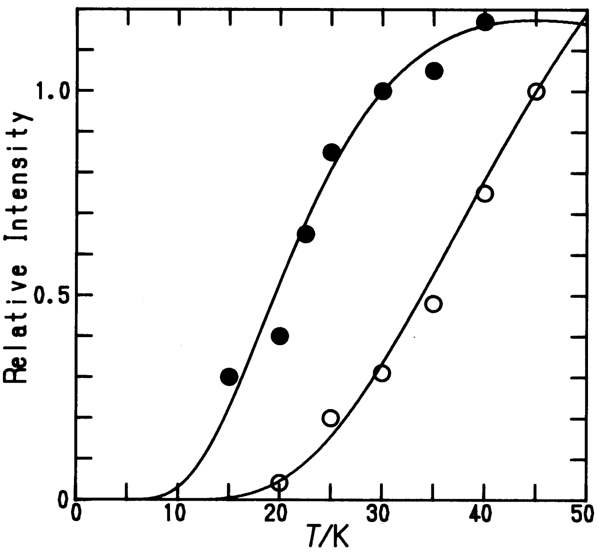

Fig. 10. Temperature dependence of the relative intensities of the low field transitions for the 21-1 species of 2:1 Cu(II)-AC$_4$O system (○) and for the 21-2 species of 2:1 Cu(II)-AC$_3$O system (●). Solid lines are calculated with $2J=-100\ \mathrm{cm}^{-2}$ (AC$_4$O system) and $2J=-50\ \mathrm{cm}^{-1}$ (AC$_3$O system), respectively.

and those in crystals are also under investigation.

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