is of a new type in the chemistry of polymer–metal complexes. Similar studies involving other heavy metal ions are now in progress. Many natural macromolecules contain a large number of OH groups. The above new interaction mode between cupric ions and PVA is suggestive of the binding of heavy metal ions in nature.

Acknowledgment. The authors express their deep gratitude of Prof. H. Sugiyama for his unfailing guidance throughout the course of this work.

Registry No. PVA, 9002-89-5; $Cu(OH)_2$, 20427-59-2; Cu^{2+}, 15158-11-9.

Interaction Modes between Heavy Metal Ions and Water-Soluble Polymers. 2. Spectroscopic and Magnetic Reexamination of the Aqueous Solutions of Cupric Ions and Poly(acrylic acid)

Hiroshi Yokoi,* Satoshi Kawata, and Masamoto Iwaizumi

Contribution from the Chemical Research Institute of Non-Aqueous Solutions, Tohoku University, Sendai 980, Japan. *Received September 16, 1985*

Abstract: The interaction between cupric ions and poly(acrylic acid) (PAA) in aqueous solutions has been reexamined by EPR, magnetic susceptibility, and optical absorption. Cupric ions exist in solutions at pH <3 as ordinary hydrated ions, and in the pH range 3–8, two mononuclear complexes with carboxyl groups of PAA are formed in equilibrium with other complex species; the two complexes have the same coordination structures as $Cu(OAc)^+$ and $Cu(OAc)_2$, where OAc^- denotes acetate anion. Around pH 4, two slightly different binuclear copper(II) complexes of the cupric acetate type are formed in high yields; at [PAA polymer residue]/[Cu^{2+}] $\lesssim 10$, about 90% of the cupric ions form such binuclear complexes. At pH >6, $Cu(OH)_2$ is gradually formed and complex species other than $Cu(OH)_2$ finally disappear at pH >9. $Cu(OH)_2$ does not deposit but remains in solution by hydrophobic interaction with PAA, as in the case with poly(vinyl alcohol).

Poly(acrylic acid) (PAA) is a familiar synthetic water-soluble polymer. In the preceding paper,[1] we found that there is a new interaction mode between cupric ions and poly(vinyl alcohol) (PVA). The difference between PAA and PVA in interaction with heavy metal ions is that PAA contains carboxyl groups as weak ligands for these ions. Various spectroscopic, equilibrium, and related studies of aqueous solutions of cupric ions and PAA have been reported.[2-10] Similar studies were carried out of aqueous Cu^{2+} solutions with PAA analogues, poly(methacrylic acid) and poly(L-glutamic acid).[5,6,10-14] However, the identification of copper(II) complexes formed in these solutions is still obscure, since aqueous Cu^{2+}–PAA solution systems involve interactions between cupric ions and PAA which cannot be fully clarified by these usual techniques. At present, the EPR method is considered the most useful technique for identification of unknown copper(II) complexes in solutions,[15] although this method is not applicable to apparently EPR-silent copper(II) complexes often formed in solutions. Therefore, in order to elucidate the intrinsic nature of complex formation in aqueous Cu^{2+}–PAA solutions, information on the quantitative contribution of cupric ions to every observed EPR spectrum is indispensable. Most EPR studies so far reported for aqueous Cu^{2+}–PAA[6] and Cu^{2+}–PVA[16] lack for these kinds of data.

The purpose of this paper is to reexamine aqueous Cu^{2+}–PAA solutions by EPR, magnetic susceptibility, and optical absorption techniques and to elucidate the interaction mode between cupric ions and PAA in detail.

Experimental Section

Spectroscopic and Magnetic Measurements. A JEOL Model JES-FE2XG EPR spectrometer was used to measure EPR spectra of aqueous sample solutions at room temperature and of the frozen solutions at 77 K. All the EPR sample solutions contained 2.50 mM cupric ions, 0.10 M $NaClO_4$, and 10.0–100 mM PAA (polymer residue concentration). Hereafter, the concentration of PAA is expressed as R = [PAA polymer residue]/[Cu^{2+}]. The real intensities of room temperature EPR spectra were obtained by double integration of the observed first-derivative spectra with a NEC PC-9801 computer. The room temperature EPR spectra were measured under a constant condition of the spectrometer by using the same sample tube in order to enable their EPR intensities to be compared exactly with each other. The pH adjustment was done throughout this work without any buffer. A JEOL Model JNM-FX90Q

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(1) For Part 1, see: Yokoi, H.; Kawata, S.; Iwaizumi, M. *J. Am. Chem. Soc.*, preceding paper in this issue.

(2) Wall, H. P.; Gill, S. J. *J. Phys. Chem.* **1954**, *58*, 1128.

(3) Gregor, H. P.; Luttinger, L. B.; Loebel, E. M. *J. Phys. Chem.* **1955**, *59*, 34.

(4) McLaren, J. V.; Watts, J. D.; Gilbert, A. *J. Polym. Sci.* **1967**, *C-16*, 1903.

(5) Kotliar, A. M.; Morawetz, H. *J. Am. Chem. Soc.* **1955**, *77*, 3692.

(6) Noji, S.; Yamaoka, K. *Macromolecules*, **1979**, *12*, 1110.

(7) Yamaoka, K.; Masujima, T. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 1819.

(8) Nishikawa, H.; Tsuchida, E. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 1545.

(9) Yamada, R.; Tamura, K.; Harada, S.; Yasunaga, T. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 3413.

(10) Marinsky, J. A. *Coord. Chem. Rev.* **1976**, *19*, 125.

(11) Katchalsky, A.; Spitnik, P. *J. Polym. Sci.* **1947**, *2*, 432.

(12) Leyte, J. C.; Zuiderweg, L. H.; van Reisen, M. *J. Phys. Chem.* **1968**, *72*, 1127. Marinsky, J. A.; Anspach, W. M. *J. Phys. Chem.* **1975**, *79*, 439.

(13) Yamaoka, K.; Masujima, T. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 1286. Masujima, T.; Yamaoka, K. *Biopolymers* **1980**, *19*, 477.

(14) Koide, M.; Tsuchida, E. *Makromol. Chem.* **1981**, *182*, 359.

(15) Peisach, J.; Blumberg, W. E. *Arch. Biochem. Biophys.* **1974**, *165*, 691. Yokoi, H.; Addison, A. W. *Inorg. Chem.* **1977**, *16*, 1341. Yokoi, H.; Hanaki, A. *Chem. Lett.* **1984**, 481.

(16) Sumita, O.; Fukuda, A.; Kuze, E. *J. Polym. Sci., Polym. Phys. Ed.* **1978**, *16*, 1801.

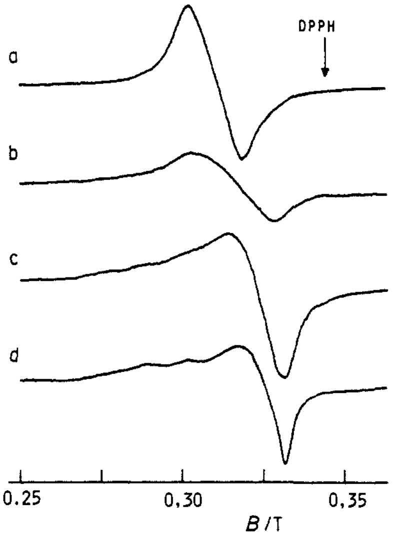

Figure 1. Room temperature EPR spectra (X-band) of aqueous Cu^{2+}–PAA solutions at R = 10 at different pH values: a, pH 3.1; b, pH 4.0; c, pH 6.1; d, pH 8.5.

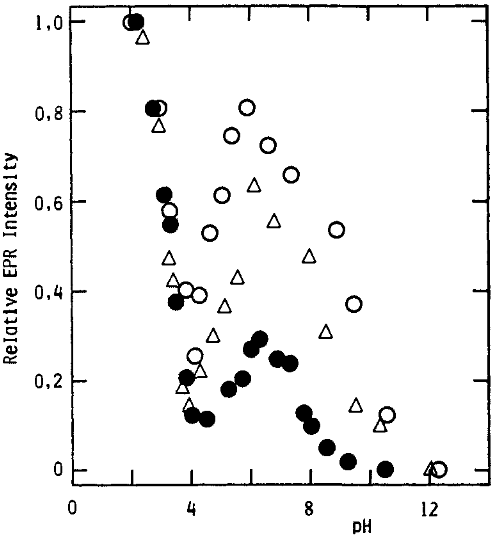

Figure 2. Plots of the intensities of room temperature EPR spectra against pH for aqueous Cu^{2+}–PAA solutions: ●, R = 4; △, R = 10; ○, R = 20.

FT NMR spectrometer was used to measure magnetic susceptibility at room temperature by the Evans method,[17] where the sample solutions contained 20.0 mM cupric ions, PAA at R = 10, and 2% *tert*-butyl alcohol as an indicator. Visible and UV spectra were recorded at room temperature on a Shimadzu UV-240 spectrophotometer, using quartz 10- and 1-mm cells.

Chemicals. An aqueous solution (25 wt. %) of PAA with the average molecular weight 90 000 was purchased from Aldrich Chemical Co. All the other reagents were of reagent grade or higher and were used without further purification.

Results and Discussion

Room Temperature EPR Spectra. Some room temperature EPR spectra of aqueous Cu^{2+}–PAA solutions at R = 10 at different pH values are shown in Figure 1. These room temperature spectra were remarkably pH and R dependent in both line shape and intensity. The EPR spectra at pH ≤3 are rather symmetric in line shape and resemble those of ordinary hydrated Cu^{2+}. The spectra become a little broader in line width at pH ~4 and show anisotropic line shapes at higher pH values, with indistinct hyperfine structures. Plots of the intensities of room temperature EPR spectra against pH at three different R values (Figure 2) indicate that the intensities change in a complicated way with pH.

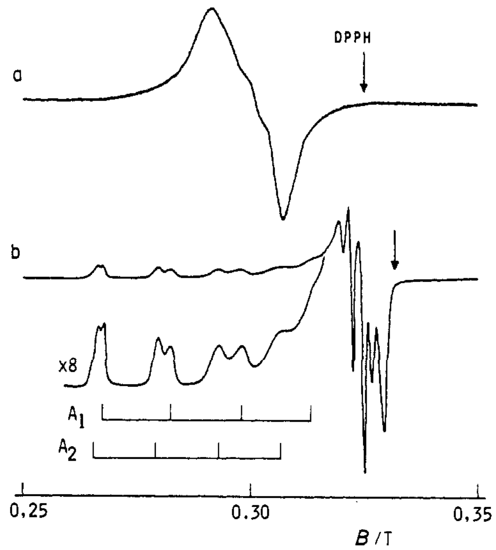

Figure 3. Room temperature EPR spectrum at pH 5.7 (a) and its frozen solution EPR spectrum at 77 K (b) for an aqueous Cu^{2+}–acetic acid solution with $[Cu^{2+}]$ = 2.50 mM, [acetic acid] = 100 mM, and $[NaClO_4]$ = 0.10 M.

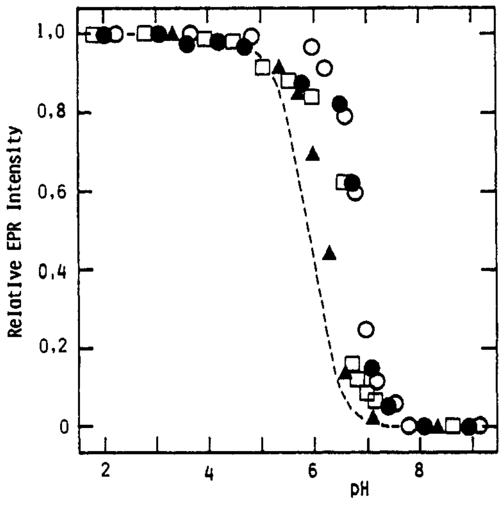

Figure 4. Plots of the intensities of room temperature EPR spectra against pH for aqueous Cu^{2+}–acetic acid and –PTCA solutions: ○, [acetic acid] = 100 mM and I = 0.50; ●, [acetic acid] = 50 mM and I = 0.50; □, [acetic acid] = 10 mM and I = 0.10; ▲, [PTCA] = 3.33 mM and I = 0.10; ---, [acetic acid] = [PTCA] = 0 and I = 0.10. PTCA denotes 1,3,5-pentanetricarboxylic acid.

It is important to compare PAA and low molecular weight carboxylic acids in their interactions with cupric ions. Figure 3 shows the room temperature EPR spectrum of an aqueous Cu^{2+}–acetic acid solution at pH 5.7 and its frozen solution spectrum at 77 K. Plots of the intensities of room temperature EPR spectra against pH for aqueous Cu^{2+}–acetic acid solutions at different R values are shown in Figure 4, together with those for aqueous Cu^{2+}–PTCA solutions, where PTCA denotes 1,3,5-pentanetricarboxylic acid. All plots in Figure 4 fall on smooth sigmoid curves, and the curves shift to higher pH ranges than the dashed curve observed for aqueous solution of cupric ions alone.[1] Figure 4 shows that EPR intensities in any case are reduced to zero at pH >7.5 owing to the formation of $Cu(OH)_2$.[1] The above shift of the curves merely means that the formation of $Cu(OH)_2$ is depressed by the competitive formation of weak copper(II) complexes with acetic acid and PTCA; this depressing effect in aqueous Cu^{2+}–acetic acid solutions becomes more profound with an increasing concentration of acetic acid, as shown in Figure 4.

The shapes of the plots in Figures 2 and 4 are quite different, indicating that PAA and low molecular weight carboxylic acids differ in their interactions with cupric ions. In Figure 2, all plots

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(17) Evans, D. E. *Proc. Chem. Soc.* **1958**, 115. Loliger, J.; Scheffold, R. *J. Chem. Educ.* **1972**, *49*, 646.

exhibit minima at pH ~4 and maxima at pH ~6. With $R \lesssim 10$, about 90% of cupric ions at the minima become apparently EPR silent at least in the magnetic field range 0.2–0.4 T. There is no possibility of a reduction of Cu(II) to Cu(I) in these solutions at pH ~4. Accordingly, it is concluded that the formation of some binuclear or poly-nuclear copper(II) complex with a fairly strong antiferromagnetic interaction by a specific binding of cupric ions with carboxyl groups of PAA at pH ~4 is responsible for the minima at this pH. On the other hand, EPR intensities again decrease beyond the maximum at pH 6 and drop to zero at high pH. Non-zero EPR intensities in Figure 2 remain at higher pH ranges than in Figure 4, indicating that the formation of $Cu(OH)_2$ is depressed in PAA solutions more than in low molecular weight carboxylic acid solutions. This is because the carboxyl groups of PAA form more stable complexes with cupric ions than low molecular-weight carboxylic acids probably owing to a polyelectrolyte effect [3,10] and the high concentration of carboxyl groups in the polymer domains, to which most cupric ions are confined. The $Cu(OH)_2$ species finally formed in these solutions does not deposit but is solubilized by PAA, as in the case of PVA.[1]

Frozen Solution EPR Spectra. Useful information on the structures and number of copper(II) complexes in solutions can be obtained by analyses of the frozen solution EPR spectra.[15] Most mononuclear copper(II) complexes in frozen solutions show EPR spectra of an axial or nearly axial type, from which at least the EPR parameters of $g_\parallel$ and $A_\parallel$ are easily determinable. In this study, a copper(II) complex is identified and represented by a set of $g_\parallel$ and $A_\parallel$, as is commonly done.[15] The frozen solution EPR spectra of aqueous Cu^{2+} solutions with acetic acid and PAA at pH <3 correspond to those of hydrated cupric ions with $g_\parallel = 2.420$ and $|A_\parallel| = 0.0138$ cm^{-1}, as reported previously.[1] A frozen solution EPR spectrum for aqueous Cu^{2+}–acetic acid solutions at pH 5.7 is shown in Figure 3, spectrum b. Inspection of this spectrum indicates that there exist only two different mononuclear copper(II) complex with $g_\parallel = 2.360$, $|A_\parallel| = 0.0158$ cm^{-1} (A_1) and $g_\parallel = 2.330$, $|A_\parallel| = 0.0180$ cm^{-1} (A_2); the A_1 species is preferentially formed at pH lower than 4.0. Studies of the formation constants of copper (II) acetate complexes show that in aqueous Cu^{2+}–acetic acid solutions only $Cu(OAc)^+$ and $Cu(OAc)_2$ are formed;[18] in these formulae coordinated water molecules are omitted. Accordingly, these two acetate complexes can be identified as the above A_1 and A_2 species, since the $g_\parallel$ values of Cu^{2+}, $Cu(OAc)^+$, and $Cu(OAc)_2$ decrease in this order, parallel to the ligand field strength in planar 4-coordination.[15]

Some frozen solution EPR spectra of aqueous Cu^{2+}–PAA solutions at $R = 4$ and 40 at different pH values are shown in Figures 5 and 6, respectively. Generally speaking, the EPR spectra of ordinary hydrated cupric ions are observed at pH $\lesssim 3$, whereas other types of spectra appear at higher pH ranges. At pH 4–7, however, a characteristic single broad signal is superimposed on EPR spectra with hyperfine structures at varying intensity ratios; the ratios are especially high for the solutions at lower R values, as exemplified in Figure 5, spectra b and c. This single broad EPR signal undoubtedly originates from dipolar broadening of the A_1 and A_2 spectra owing to the close proximity of these mononuclear species to each other. In addition, a closer proximity of these species to each other is further brought about by pH-dependent conformational changes of the Cu^{2+}–PAA complex molecules.[8] The PAA molecule is known to be contracted at low pH but expand at pH >5 owing to electrostatic repulsion between carboxylate anions.[19] Coordination of cupric ions to these carboxylates also contributes to the molecular contraction by the bridging linkage within PAA chains and by charge neutralization. The appearance of the above single broad EPR signal, therefore, is considered as an apparent measure of the molecular contraction of the Cu^{2+}–PAA complexes.

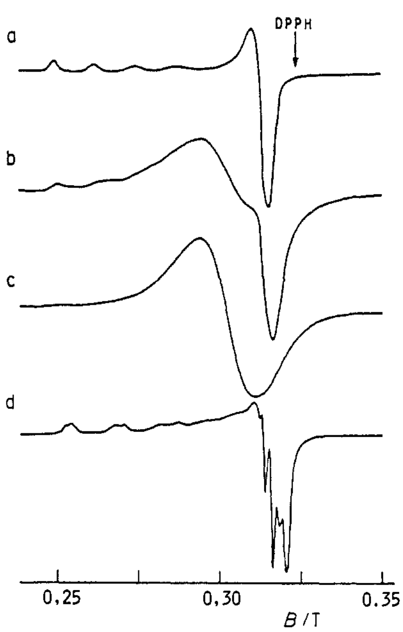

Figure 5. Frozen solution EPR spectra at 77 K for aqueous Cu^{2+}–PAA solutions at $R = 4$ at different pH values: a, pH 2.0; b, pH 4.0; c, pH 5.7; d, pH 9.6.

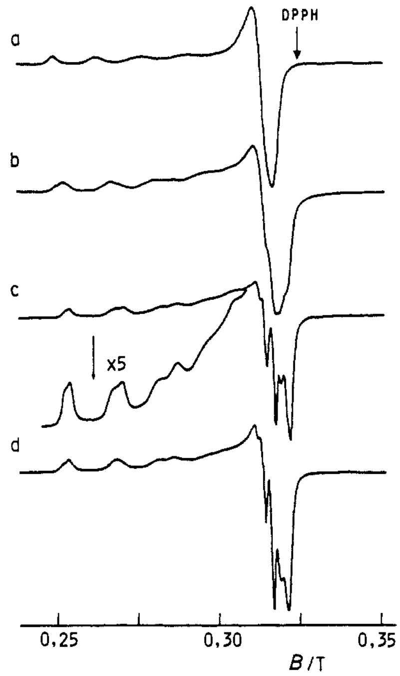

Figure 6. Frozen solution EPR spectra at 77 K for aqueous Cu^{2+}–PAA solutions at $R = 40$ at different pH values: a, pH 2.8; b, pH 4.1; c, pH 6.9; d, pH 10.0

Table I summarizes all the $g_\parallel$ and $A_\parallel$ values determined for mononuclear copper(II) complexes formed in aqueous Cu^{2+}–PAA solutions, together with those in aqueous Cu^{2+}–acetic acid solutions. This table clearly shows that two mononuclear copper(II) complexes with $g_\parallel = 2.360$, $|A_\parallel| = 0.0158$ cm^{-1} (P_1) and $g_\parallel = 2.330$,

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(18) Tanaka, N.; Kato, K. *Bull. Chem. Soc. Jpn.* **1960**, *33*, 417. In most studies of copper(II) acetate complexes in aqueous solutions, the complex formation has been interpreted in terms of K_1 and K_2 alone, but, in a few studies, in terms of K_3 or K_3 and K_4 besides, where K denotes consecutive formation constants in logarithmic units; generally, K_3 is smaller than K_1 and K_2, and K_4, negative (Sillén, L. G.; Martell, A. E. In *Stability Constants of Metal-Ion Complexes*; Spec. Publ.; Chem. Soc.: (a) 1964, No. 17; (b) 1971, No. 25). The formation of $Cu(OAc)_3^-$ and $Cu(OAc)_4^{2-}$ in sufficiently concentrated solutions of acetate was also suggested spectrophotometrically on rather superficial grounds (Pedersen, K. J. *K. Dan. Vidensk. Selsk. Mat.-Fys. Medd.* **1945**, *22*, 25. Klotz, I. M.; Faller, I. L.; Urquhart, J. M. *J. Phys. Chem.* **1950**, *54*, 18). In this study, however, these complexes could never be detected by the EPR technique, in spite of a high EPR sensitivity in detecting a new copper(II) complex which is remarkably different in EPR parameters from other coexisting complexes; $Cu(OAc)_3^-$ would be detectable by EPR, if it coexisted even at about 1% of the concentration of $Cu(OAc)_2$ or $Cu(OAc)^+$.

(19) Katchalsky, A.; Eisenberg, H. *J. Polym. Sci.* **1951**, *6*, 145. Tamaki, K.; Imai, K.; Nishino, J.; Sakaguchi, Y. *Kobunshi Kagaku* **1973**, *30*, 608.

Table I. EPR Parameters for Mononuclear Copper(II) Complexes Detected in Aqueous Cu^{2+}-PAA and -Acetic Acid Solutions

			first species		second species	
ligand	R	pH	$g_\parallel$	$\lvert A_\parallel \rvert$, cm^{-1}	$g_\parallel$	$\lvert A_\parallel \rvert$, cm^{-1}
PAA	40	2.00	2.420	0.0138		
		2.80[a]	2.408	0.0148		
		3.20	2.371	0.0154		
		3.70	2.369	0.0156		
		4.05	2.366	0.0157	2.331	0.0182
		4.50	2.362	0.0158	2.330	0.0181
		5.10	2.362	0.0158	2.330	0.0180
		6.20	2.362	0.0158	2.329	0.0180
		6.90	2.361	0.0158	2.330	0.0181
		7.80	2.361	0.0157	2.329	0.0181
		9.35	2.360	0.0158	2.330	0.0180
		10.00	2.360	0.0157	2.330	0.0180
	20	2.00	2.421	0.0139		
		2.90[a]	2.405	0.0152		
		3.30	2.374	0.0158		
		3.50	2.375	0.0158		
		4.33	2.365	0.0157		
		5.22	2.360	0.0157	2.330	0.0181
		6.60	2.360	0.0157	2.330	0.0182
		9.55	2.360	0.0157	2.330	0.0180
		9.90	2.360	0.0158	2.330	0.0182
	10	2.00	2.421	0.0139		
		3.25[a]	2.402	0.0153		
		9.40	2.362	0.0156	2.329	0.0180
	4	2.00	2.420	0.0139		
		3.25[a]	2.402	0.0153		
		9.60	2.364	0.0156		
HOAc	40	3.60	2.370	0.0154		
		5.50	2.360	0.0158	2.330	0.0180

[a] Parameter values are tentative, since second species coexists at a low concentration ratio.

$|A_\parallel| = 0.0180\ cm^{-1}$ (P_2) are formed in aqueous Cu^{2+}–PAA solutions. Interestingly, the P_1 and P_2 species coincide in the $g_\parallel$ and $A_\parallel$ values with the above A_1 and A_2 ones, respectively, indicating that the P_1 and P_2 species have the same coordination structures as the A_1 and A_2. These A_1 and A_2 species in solutions are strain-free in coordination structure. It is of importance for the chemistry of polymer–metal complexes that mononuclear copper(II) complexes formed in aqueous Cu^{2+}–PAA solutions are also strain-free in coordination structure.

The frozen solution EPR spectra recorded over the wide field range 0–0.5 T with high gains for 10 mM cupric ions and 20 mM PAA in the mixed solvents (v/v) of 55% water, 20% ethanol, and 25% dioxane and of 80% water and 20% methanol are shown in Figure 7, spectra a and b, respectively. These spectra show broad signals at 0.05 T and two signals at 0.40–0.45 T, except an intense signal with hyperfine structures at 0.25–0.33 T. The powder EPR spectrum of cupric acetate monohydrate at room temperature is also shown in Figure 7c for comparison. The spectra recorded with high gains in a and b of Figure 7 are basically similar to that in Figure 7c. The above two signals observed in the range 0.40–0.45 T varied in their intensity ratio with the composition of the solutions, indicating that there exist two slightly different binuclear copper(II) complexes of the cupric acetate type corresponding to these two signals, respectively. The powder EPR spectrum of cupric acetate monohydrate (Figure 7c) is of a triplet-state type with $D = 0.34\ cm^{-1}$,[20] whereas the above two triplet-state spectra are of the type with $D \sim 0.35$ and $0.38\ cm^{-1}$, respectively, on the assumption that the latter two have the same g value as the former, where D denotes the zero-field splitting parameter.

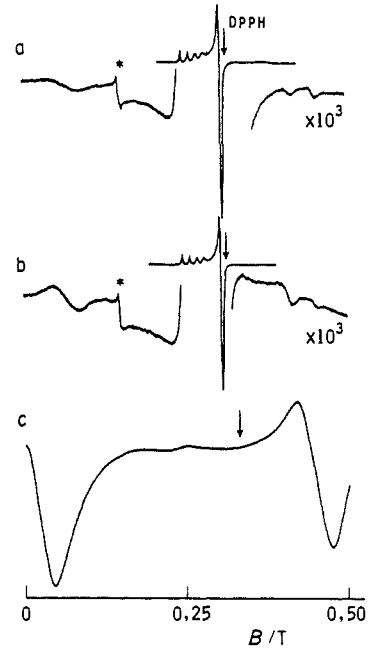

Figure 7. Triplet-state EPR spectra of binuclear copper(II) complexes: a, frozen solution (77 K) of 10 mM cupric ions and PAA at $R = 2$ in the mixed solvent (v/v) of 55% water, 20% ethanol, and 25% dioxane; b, frozen solution (77 K) of cupric ions and PAA at the same respective concentrations as in part a in the mixed solvent (v/v) of 80% water and 20% ethanol; c, powder EPR spectrum of cupric acetate monohydrate at room temperature. EPR signals with asterisks are due to paramagnetic impurities in the sample tubes and Dewar vessels.

Table II. Effective Magnetic Moments (μ_{eff}) for Aqueous Cu^{2+}-PAA Solutions at Room Temperature

pH	μ_{eff}, μ_B	pH	μ_{eff}, μ_B
2.78	1.83	6.24	1.61
4.24	1.34	6.54	1.55
4.94	1.44	8.14	1.44
5.94	1.65		

Magnetic Susceptibility. Magnetic susceptibilities of the aqueous Cu^{2+}–PAA solutions with 20 mM cupric ions and PAA at $R = 20$ at room temperature were measured by the Evans method. The μ_{eff} values derived from them are summarized in Table II. Inspection of this table shows that the μ_{eff} vs. pH relationship fluctuates in near parallel with the EPR intensity vs. pH one in Figure 2. $\mu_{eff} = 1.83\ \mu_B$ at pH 2.78 obviously corresponds to ordinary hydrated cupric ions, while $\mu_{eff} = 1.34\ \mu_B$ at pH 4.24 demonstrates that a binuclear or polynuclear copper(II) complex with a fairly strong antiferromagnetic interaction is formed at this pH. Since 20–25% of cupric ions forms mononuclear complexes in the solution at this pH, as estimated from Figure 2, the real μ_{eff} value of the antiferromagnetic complex is somewhat smaller than the observed value of 1.34 μ_B. Interestingly, cupric acetate monohydrate shows a well-known antiferromagnetism with $\mu_{eff} = 1.43\ \mu_B$, while cupric acetate mono-dioxane adduct has $\mu_{eff} = 1.30\ \mu_B$. Roughly speaking, these μ_{eff} values of cupric acetates are comparable to that of the above antiferromagnetic complexes formed in aqueous Cu^{2+}–PAA solutions. Table II also indicates that, at pH ~6, μ_{eff} reaches a maximum and then decreases gradually. At pH >6, the decrease of μ_{eff} is explainable as due to the formation of $Cu(OH)_2$.[1]

Visible and UV Spectra. The formation of binuclear copper(II) complexes of the cupric acetate type in aqueous Cu^{2+}–PMA and –PLG solutions has been predicted by the observation of weak absorptions at ~370 nm and additionally by magnetic susceptibility measurements for the former solutions,[12,14] where PMA and PLG denote poly(methacrylic acid) and poly(L-glutamic acid), respectively. Absorptions at ~370 nm for the Cu^{2+}–PLG solutions have been reported to appear more easily by addition of dioxane.

Some visible and UV spectra of aqueous Cu^{2+}–PAA solutions at different pH values at room temperature are shown in Figure

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(20) Catterick, J.; Thornton, P. *Adv. Inorg. Chem. Radiochem.* **1977**, *20*, 291.

(21) Kato, M.; Jonassen, H. B.; Fanning, J. C. *Chem. Rev.* **1964**, *64*, 99.

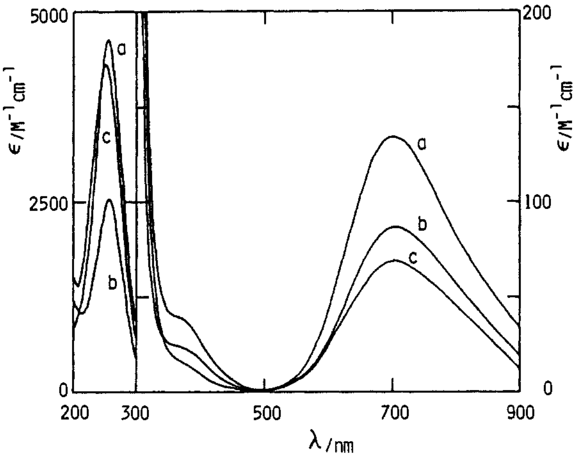

Figure 8. Visible and ultraviolet spectra of aqueous Cu^{2+}–PAA solutions at $R = 5$ at room temperature at different pH values: a, pH 4.0; b, pH 3.5; c, pH 6.3.

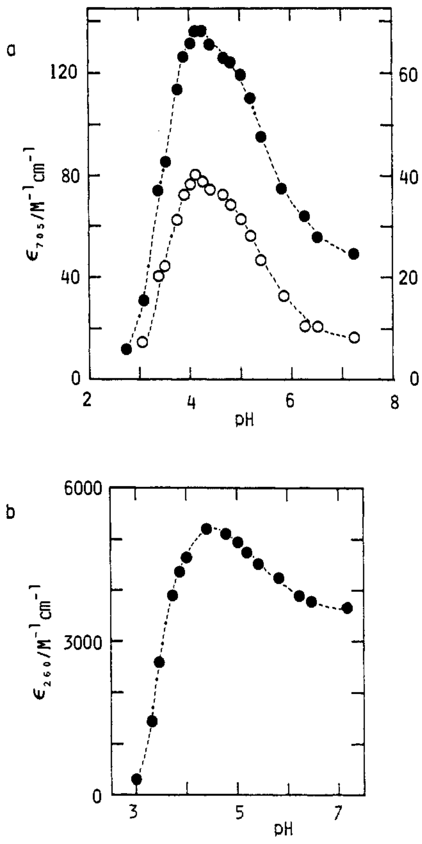

Figure 9. Plots of visible and ultraviolet spectral intensities at 705, 370, and 260 nm against pH for aqueous Cu^{2+}–PAA solutions.

8, where there are three absorption bands at ~700, ~370, and ~260 nm. Figure 9 shows plots of the molecular extinction coefficients at 705, 370, and 260 nm against pH. Both plots in Figure 9a reach maxima at pH 4.0, but the maximum in Figure 9b shifts to pH slightly higher than 4.0. The pH at these maxima is in accord with the pH at which formation of the above antiferromagnetic complexes is maximized, indicating that they contribute mainly to the absorptions at 705 and 370 nm and partly to the one at 260 nm. The appearance of these absorption bands was promoted by addition of dioxane. It is well-known that absorptions at ~370 nm are characteristic of binuclear copper(II) complexes of cupric acetate type.[20] These complexes also show a characteristic absorption at ~700 nm. These absorption spectral data lead also to the conclusion that some binuclear copper(II) complex of the cupric acetate type is formed in aqueous Cu^{2+}–PAA solutions around pH 4.0.

Concluding Remarks. In aqueous Cu^{2+}–PAA solutions, cupric ions exist at pH <3 as ordinary hydrated Cu^{2+}. In the pH range 3–8, mononuclear copper(II) complexes with one and two carboxyl groups of PAA always exist in equilibrium with other complex species. These two complexes have the same coordination structures as the low molecular weight acetate complexes $Cu(OAc)^+$ and $Cu(OAc)_2$, suggesting that coordination of cupric ions to carboxyl groups of PAA is strain-free. The 1:1 complex preferentially appears at pH <4. At $R \lesssim 10$, mononuclear complexes are in close proximity with each other, owing to the molecular contraction of the polyion chain. Around pH 4, furthermore, two slightly different binuclear copper(II) complexes of the cupric acetate type are formed in equilibrium with other complex species. At $R \lesssim 10$, about 90% of the cupric ions form binuclear complexes at pH 4. This fact demonstrates that specific hydrophobic domains are produced inside the Cu^{2+}–PAA complexes around this pH, since any binuclear complex of the cupric acetate type is never formed in aqueous solutions.[23] At pH >6, $Cu(OH)_2$ is gradually formed in equilibrium with the other complexes which finally disappear at pH >9. By comparison between PAA and low molecular weight carboxylic acids in these experiments, it is clearly shown that complexes with carboxyl groups of PAA are stabler than complexes with low molecular weight carboxylic acids, owing to so-called polymer effects of PAA (a high local concentration of carboxyl groups and a polyelectrolyte field effect). The $Cu(OH)_2$ species finally formed in aqueous Cu^{2+}–PAA solutions does not deposit but remains in solution by hydrophobic interaction with PAA, as in the case with PVA.[1]

Carboxyl groups are very familiar functional groups of natural macromolecules, just as alcoholic OH groups. The above interaction mode between cupric ions and PAA also gives an important clue to analyses of the interactions of heavy metal ions with various natural macromolecules.

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Registry No. PAA, 9003-01-4; Cu^{2+}, 15158-11-9; $Cu(OH)_2$, 20427-59-2.

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(22) Morawetz first reported the UV absorption maximum at 260 nm of a copper(II) complex of PMA, in relation to the UV spectra of copper(II) acetate complexes, but his interpretation of this absorption was undoubtedly wrong (Morawetz, H. *J. Polym. Sci.* **1955**, *17*, 442).

(23) Martin, R. L.; Whitley, A. *J. Chem. Soc.* **1958**, 1394.