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ESR Studies on the Dimer Formation Between Copper Ions in the Poly(Vinylimidazole) · Copper(II) Complex

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Summary

ESR studies were made on the poly(vinylimidazole)·copper(II) complex in a lower magnetic field near 1600 gauss. The absorption in this region was observed for the poly(vinylimidazole)·copper(II) complex system , while no absorption was present for the imidazole·copper(II) complex. The result was interpreted in terms of the dipolar interaction between copper(II) ions in the polymeric complex system, where the copper (II) ions were put together on the polymeric ligand in a highly condensed state.

Recently, dimeric (BOAS et al. 1969) and binuclear (LANE et al. 1978; COUGHLIN et al. 1979) copper(II) complexes have received much attention, since some of copper atoms in copper-containing proteins are known to be present in dimeric forms, which plays important roles in biological systems (FEE, 1975). For instance, the type III copper in multicopper oxidases exists in an ESR non-detectable form and is associated with two-electron accepting unit (FEE, 1975). Hemocyanine, in which two copper atoms exist also as an antiferromagnetically coupled dimeric form, provides a potential side for the molecular oxygen (HIMMELWRIGHT et al. 1979). On the coordination geometry and/or on the nature of donor atoms in the active centers, no information is hitherto available. However, in the case of bovine erythrocyte superoxide dismutase (BEEM et al. 1977) and cytochrome c oxidase (PALMER et al. 1976), a histidine bridge has been postulated to link copper(II) and zinc(II) centers, and high-spin iron(III) and copper(II) centers, respectively.

We investigated earlier the properties of copper (II) complex with poly(vinylimidazole) extensively so far, in comparison with those of the corresponding low-molecular-weight copper(II) complexes (SATO et al. 1977; SATO et al. 1978). From the results of

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ESR spectra observed in $g = 2$ region near 3200 gauss, we suggested that the coordination geometry of the polymeric copper(II) complex system is distorted from tetragonal symmetry or, the coordination bond lengthens, as compared with those of the low-molecular-weight copper(II) complex system (SATO et al. 1978).

In this communication, we wish to report the ESR spectral study on the poly(vinylimidazole)·copper(II) complex as well as the imidazole·copper(II) complex in $g = 4$ reion near 1600 gauss, in order to get further information on the nature of the polymeric copper(II) complex, because no such an investigation on the metal complexes of synthetic polymers seems to be done previously.

Fig.1 shows the ESR spectra in $g = 4$ region from 1200 to 1800 gauss for the several different concentrations of the polymeric ligand, the concentration of copper(II) being kept constant. A small, broad absorption was clearly observed near 1600 gauss, when the concentration ratio of copper(II) to imidazole group was 1 ; 10. The absorption in question tends to be much smaller or becomes not to be observable when the ratio was 1 : 1 or 1 : 40. In the case of the corresponding copper(II) complex with imidazole, such an absorption could not be seen over the ligand concentrations.

The absorptions similar to those shown in Fig.1 had been reported for the amino acid·copper(II) complexes, which were interpreted in terms of dimer formation of copper(II) ions in the complex (BOAS et al. 1969). The distance between two copper(II) ions and other factors have also been studied by ESR spectroscopy, comparing them to those simulated on a computer, with assumption that the copper(II) ions were coupled by dipolar interactions (UITERKAMP et al. 1974). Broad signals near $g = 2$ and the resolved signals near $g = 4$ could obviously be interpreted as being due to $\Delta M = 1$ and $\Delta M = 2$ transitions respectively, which might be held also for the copper(II) ions coupled by dipole-dipole interaction. Thus, there seems to exist an interaction between the copper(II) ions in the polymeric copper(II) complex system.

The poly(vinylimidazole)·copper(II) complex, which clearly dissolved in water, is in a rather specific homogeneous state, which differs greatly from that of the low-molecular-weight copper(II) complex. Since the copper(II) ions are bound to the pendant imidazolyl groups which are partially localized along the polymeric chain, the copper ions are put together on the site where the polymeric ligand exists. therefore, it is plausible that the dipolar interaction between copper(II) ions is present in the poly(vinylimi-

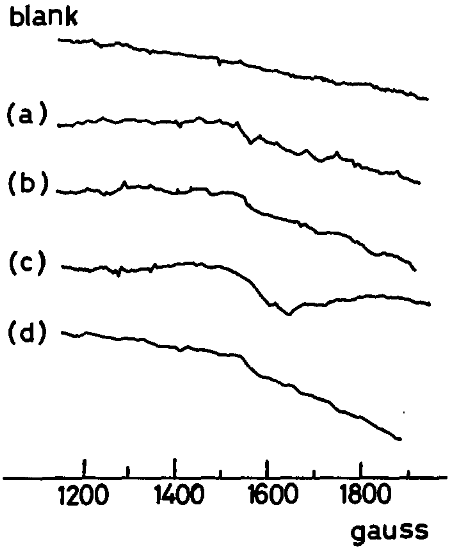

Fig.1. ESR spectra of poly(vinylimidazole)·copper(II) complex (ΔM = 2) in frozen aqueous solution (77°K) at pH = 4.7. Concentration ratio of copper(II) to imidazolyl group was: (a) 1:1, (b) 1:4, (c) 1:10, and (d) 1:40.

dazole)·copper(II) complex in which copper(II) ions are forced to put together on the polymeric chain in a highly condensed state, while it is not the case for the imidazole·copper(II) complex. In addition, such an interaction appears to become stronger, when the concentration ratio is about 1:10, resulting in the preferable position of the copper(II) ions for the interaction. The schematic representation of the dimeric complex is shown in Fig,2.

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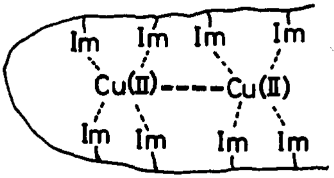

Fig.2. Schematic representation of the dimeric species in poly(vinylimidazole)·copper(II) complex

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