An ESR Study of the Copper(II) Complexes of DL-α-Alanine and L-α-Alanine

Hiroshi YOKOI and Taro ISOBE

Chemical Research Institute of Non-aqueous Solutions, Tohoku University, Katahira-cho, Sendai

(Received May 6, 1969)

The copper(II) complexes of α-amino acids contain almost planar chelate rings; therefore, no stereospecificity is expected.[1,2] An investigation of the properties of the copper(II) complexes of α-alanines, both in solution and in the solid state, has shown that there are almost no differences in properties between the copper(II) complexes of racemic- and *laevo*-α-alanines, except in some specific points.[1]

The purpose of this communication is to report the ESR results for the copper(II) complexes of racemic- and *laevo*-α-alanines, both in solution and in the solid state. Figure 1 shows the K-band ESR spectra of the powdered samples at room temperature. This figure indicates that the water of crystallization of [Cu(DL-α-alanine)$_2$]·H_2O, I, plays the very important role in determining the properties of the complex in a crystal, and that there is a clear difference in the absorption line shape between [Cu(DL-α-alanine)$_2$], II, and [Cu(L-α-alanine)$_2$], III, the former bing prepared by the elimination of the water of crystallization of I at 165°C *in vacuo.*

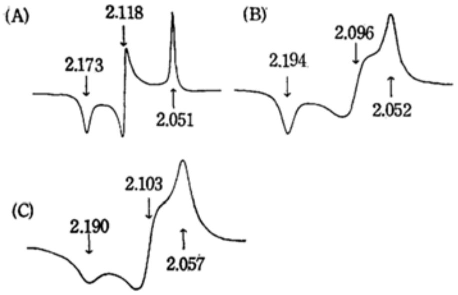

Fig. 1. The powder ESR spectra (K-band, 22°C). The numbers in this figure indicate g values.
(A) [Cu(DL-α-alanine)$_2$]·H_2O
(B) [Cu(DL-α-alanine)$_2$]
(C) [Cu(L-α-alanine)$_2$]

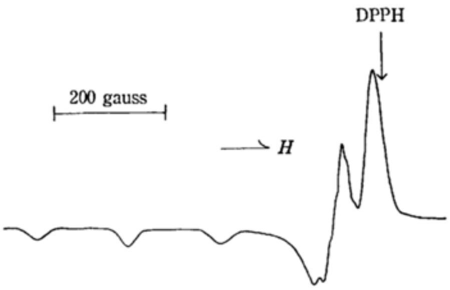

Fig. 2. The X-band ESR spectrum of [Cu(DL-α-alanine)$_2$] in aqueous-methanolic solution at 77°K.

Figure 2 shows the X-band ESR spectrum of I in an equivolume mixture of water and methanol at the temperture of liquid nitrogen. The results determined for the complexes in the solution are as follows:

I: $g_{//}=2.264$, $A_{//}=178\times10^{-4}\mathrm{cm}^{-1}$,
$A_{\mathrm{N}}^{\perp}=11.7\times10^{-4}\ \mathrm{cm}^{-1}$

III: $g_{//}=2.264$, $A_{//}=175\times10^{-4}\mathrm{cm}^{-1}$
$A_{\mathrm{N}}^{\perp}=11.1\times10^{-4}\ \mathrm{cm}^{-1}$

$A_{\mathrm{N}}^{\perp}$ was determined from the super-hyperfine structure observed on the $g_{\perp}$ component by the second-derivative X-band ESR measurements. These results show that there is a significant difference in the values of $A_{//}$ and $A_{\mathrm{N}}^{\perp}$ between I and III in solution.

In conclusion, all the ESR results obtained here indicate that there is some stereospecific difference in electronic structure between the copper(II) complexes of racemic- and *laevo*-α-alanines, both in solution and in the solid state. The details will be published elsewhere.

---

[1] R. D. Gillard, H. M. Irving, R. Parkins, N. C. Payne and L. D. Pettit, *Chem. Commun. (London)*, **1965**, 81.

[2] E. J. Corey and J. C. Bailar, *J. Am. Chem. Soc.*, **81**, 2620 (1959); W. E. Bennet, *ibid.*, **81**, 246 (1959).