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AN ESR STUDY OF COPPER(II) COMPLEXES WITH β-ALANINE

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A single crystal of bis(β-alaninato)copper(II) hexahydrate ($Cu(\beta\text{-ala})_2.6H_2O$) was prepared and measured by ESR. As the dehydration of $Cu(\beta\text{-ala})_2.6H_2O$ from the surface of the crystal is well known, the behaviour of the dehydration by three different drying methods was studied by ESR and it was found that the change from the $d_{x^2-y^2}$ ground-state to the d_{z^2} ground-state takes place.

An ESR study is a very useful method to investigate crystal structures, and to determine the ground-state. That is, $g_{\parallel} > g_{\perp}$ for the case of the $d_{x^2-y^2}$ ground-state, and the reverse is true for the case of d_{z^2} ground-state. In the previous paper[1], it was reported that the cis-complex gives an axial ESR spectrum and trans-complex a non-axial (rhombic by K,Q-band ESR spectrometer[2),3)]). The crystal structure of $Cu(\beta\text{-ala})_2.6H_2O$ was reported by Tomita[4]; β-alanine ligands combined to copper atom in a trans, square-planar arrangement and two apical H_2O molecules were coordinated and the water was dehydrated from the surface of the crystal. As to the powdered ESR spectrum of $Cu(\beta\text{-ala})_2.H_2O$, the spectrum of the $d_{x^2-y^2}$ ground-state[2] and that of the d_{z^2} ground-state[5] were reported separately, but the dehydration concerned was not reported any more for each case. Therefore, in this work, a single crystal of $Cu(\beta\text{-ala})_2.6H_2O$ was prepared and the g-values were obtained. Then the behaviour of the dehydration was studied by three different drying methods.

Experimental

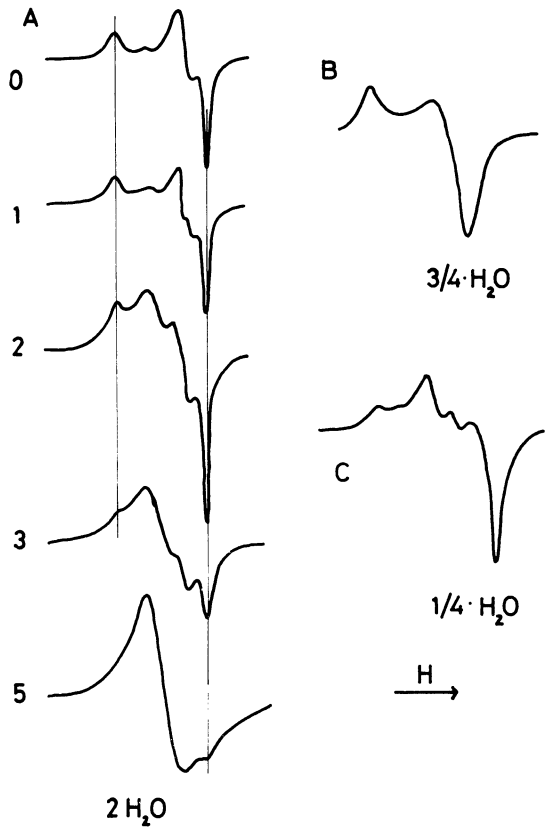
$Cu(\beta\text{-ala})_2.6H_2O$ was prepared by the method of Tomita[4]. The following methods of dehydration were used. (1) A single crystal was taken out from the solution, washed by alcohol, wiped with filter paper, dried in air for ten minutes and powdered. This sample was dried at room temperature (20 ~ 25°C). (Sample A) (2) A single crystal was dried at 70°C for an hour. (Sample B) (3) Sample A was dried in desiccator for one week. (Sample C)

The analytical results are shown in Table 1.

The ESR spectra were measured at room temperature with a JEOL X-band ESR spectrometer, model JES-ME-3X, equipped with 100 KHz field modulation unit.

Table 1 Analytical data of the complexes

complex	C% Found	C% Calcd.	H% Found	H% Calcd.	N% Found	N% Calcd.
$Cu(\beta\text{-ala})_2 \cdot 2H_2O$ (A_{10})	26.43	26.13	5.71	5.85	10.36	10.16
	26.00		6.06		10.12	
$Cu(\beta\text{-ala})_2 \cdot \frac{3}{4}H_2O$ (B)	28.43	28.50	5.38	5.21	10.98	11.06
	28.64		5.37		11.07	
$Cu(\beta\text{-ala})_2 \cdot \frac{1}{4}H_2O$ (C)	29.53	29.51	5.05	5.16	11.55	11.47
	29.51		5.18		11.47	



The crystal was attached with grease to horizontal and vertical faces of a quartz rod. The measurements of spectra were made at every 15° from 0° to 180°. In three experiments, a crystal was so mounted in order that rotation was made about each of three arbitrary orthogonal axes. DPPH(1,1-diphenyl-2-picrylhydrazyl) was used for the calibration of magnetic field.

Results and Discussion

The single crystal ESR spectrum of $Cu(\beta\text{-ala})_2 \cdot 6H_2O$ was analysed by using Hathaway's method[6] and $g_1 = 2.071$, $g_2 = 2.105$ and $g_3 = 2.238$ were obtained. These values agree with the g-values of the powdered ESR spectrum (Fig. $1A_o$). This shows the $d_{x^2-y^2}$ ground-state and a rhombic spectrum (refer to Fig. $1A_o$). In the previous paper[1], the trans-coordination was assumed and it coincided with the result of the crystal structure[4].

Fig. 1. Variation of the powdered ESR spectrum upon dehydration
A : Sample A, The number indicates the day after experiment. (The g-value of the line is 2.24(left) and 2.07(right).) B : Sample B, (The g-value of the two peak is 2.24(left) and 2.05(right).) C : Sample C

The variation of the powdered ESR spectra of copper(II) complexes with β-alanine is shown in Fig. 1. It shows that the spectrum of sample A varies upon dehydration. Here, the approximate g-values obtained by the Hathaway's method[7] were assumed to be equal to the principal g-values.

A_o shows the $d_{x^2-y^2}$ ground-state, while A_5 shows the d_{z^2} ground-state. As A_o is a hexahydrate and A_5 is a dihydrate, the variation of the structure is supposed to be responsible for the change by dehydration. The reflectance spectrum of A_5-sample shows only a broad band at ca. 14kK. Therefore, it is rather difficult to estimate the structure.

The ESR spectra of Samples B and C didn't change upon dehydration. As B is assumed mono-hydrate complex and the powdered ESR spectrum (Fig. 1B) non-axial, trans-coordination was estimated in the previous paper[1]. C is anhydrous complex and the powdered ESR spectrum (Fig. 1C) shows to be rhombic clearly. In spite of the contamination by the mono-hydrate species, this agrees with the result of the spectrum reported by Poznyak et al.[2]. Poznyak et al.'s sample is also believed to be anhydrous.

In the case of a rhombic spectrum like A_o and C_1, the $g_\perp$ component splits into two components and the wave function of the ground-state was given by the following form[8]:

$$\Psi = a|x^2 - y^2\rangle - b|3z^2 - r^2\rangle$$

where b is a mixing coefficient of the d_{z^2} state with the $d_{x^2-y^2}$ ground-state. The comparision of b-values is given in Table 2. The b-value of $Cu(\beta\text{-ala})_2.6H_2O$ is 0.058 and is smaller than that of the other copper(II) complexes with alanine. The fact that the b-value of $Cu(\beta\text{-ala})_2.H_2O$ is bigger than that of hexahydrate complex, is supposed to be caused by the change of the structure owing to the dehydration.

Table 2 b-values of complexes

complex	b	Ref.
$Cu(\beta\text{-ala})_2.6H_2O$	0.058	This work
$Cu(\beta\text{-ala})_2.H_2O$	0.075	(2)
$Cu(L\text{-ala})_2$	0.080	(3)

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