

Analysis of Crystalline-State Photo-Racemization of a Cobaloxime Complex Containing Bulky Substituents

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A single crystal structure determination of a photo-reacted crystal of [(*R*)-1,2-diethoxycarbonyl-1-*d*]-[pyridine-*d*₅]-bis[di(methyl-*d*₃)glyoximate]cobalt(III) was carried out using the BIX-3 diffractometer settled in the JRR-3M reactor at JAERI (Japan Atomic Energy Research Institute). It revealed that the compound was only racemized but was not isomerized in the crystalline state. It also revealed that the deuterium atom attached to the C atom directly bonded to the Co atom remains bonded to the identical C atom after the racemization, which proves that the racemization proceeds via a radical intermediate.

KEYWORDS: crystalline-state reaction, cobaloxime complex, photo-racemization, neutron diffraction, BIX-3

§1. Introduction

Observation of the crystalline-state photoracemization of simple ligands such as cyanoethyl groups on the Co atoms in their bisdimethylglyoximate complexes dates from late 1970's.¹⁾ Subsequent explorations revealed that more complicated and bulkier ligands, such as methoxycarbonyl-ethyl, ethoxycarbonyl-ethyl and diethoxycarbonyl-ethyl groups, also racemize upon photo-irradiation without degrading the crystallinity, in spite of their severe steric hindrances.^{2–7)} An example of photoracemization of a bulky ligand is illustrated in Fig. 1.

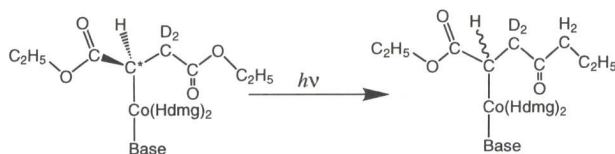


Fig. 1. Photoracemization of the diethoxycarbonyl-ethyl group of a cobaloxime complex.

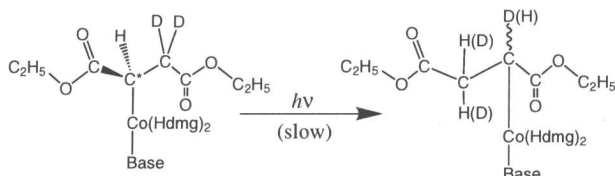


Fig. 2. Photoisomerization of the diethoxycarbonyl-ethyl group of a cobaloxime complex.

Recently, Arai *et al.*^{8–10)} reported the solid-state photo-reactions of deuterium-labeled diethoxycarbonyl-ethyl cobaloxime complexes. They found that the photo-irradiation leads not only to the racemization shown in Fig. 1 but, although to by far a lesser extent,

also to the isomerization associated with the rearrangement of the Co-C bonds shown in Fig. 2. They also concluded that the photo-racemizations proceed via radical intermediates. However, they used powdered samples for the photo-irradiation experiments and thus it still remains unsolved whether the racemization and isomerization reactions proceed also in the crystalline state where the surface reactions hardly occur.

In this study, we investigated the crystalline-state photoreaction of [(*R*)-1,2-diethoxycarbonyl-1-*d*]-[pyridine-*d*₅]-bis[di(methyl-*d*₃)glyoximate]cobalt(III) (**1**), the structure of which is illustrated in Fig. 3. An *in situ* observation of the reaction was made possible by the single crystal structure determination of the deuteriated sample using the neutron diffraction method. The reaction mechanism will be discussed in conjunction with the reaction cavity analysis.

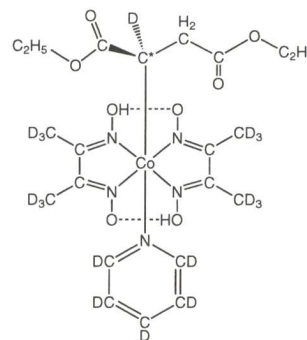


Fig. 3. Structure of **1**.

§2. Experimental

In order to investigate the reaction mechanism, the methyne hydrogen atom of the diethoxycarbonyl-ethyl ligand was labeled with deuterium. To reduce the

incoherent scattering of neutrons by hydrogen atoms, the dimethylglyoximate and pyridine ligands were also deuterated. Diethyl oxalacetate, which was obtained by neutralizing diethyl oxalacetate sodium salt with HCl in aqueous solution, was reduced by NaBD₄ in ethanol/water mixed solvent to give diethyl 2-hydroxybutane-2-*d*-dioate. It was then converted to diethyl 2-bromobutane-2-*d*-dioate by treating with triphenylphosphine and CBr₄ in *N,N*-dimethylformamide. Cobaloxime complex **1** was synthesized according to the reference¹¹⁾ with diethyl 2-bromobutane-2-*d*-dioate, di(methyl-*d*₃)glyoxime,¹²⁾ pyridine-*d*₅ and CoCl₃·6H₂O. Single crystals of **1** were obtained by slow evaporation from acetone.

In order to prevent the degradation of crystallinity, single crystals of **1** were sealed in vacuo and irradiated with near-infrared radiation (> 780 nm). As a full structure analysis using solely the neutron diffraction data is not practical due to the experimental limitations, the structure of the photo-irradiated crystal was first determined by the X-ray diffraction method. A crystal with the dimensions of 0.4×0.3×0.25 mm was mounted on a AFC7R four circle diffractometer and the diffraction data up to 2θ 55° were collected at room temperature. The structure was solved by the direct method with the program SIR97¹³⁾ and was refined by the full-matrix least-squares with the program SHELXL97.¹⁴⁾ The crystal data are summarized in Table I.

A single crystal neutron diffraction experiment was carried out for a crystal of **1** with the dimension of 2.5 × 1.6 × 0.8 mm after the photo-irradiation for 48 h. The BIX-3 diffractometer settled in the JRR-3M reactor at JAERI was used to obtain 180 frames of oscillation images (Δω = 1.0°), which were then processed by the program DENZO.¹⁵⁾ In order to obtain precise contents of the *R* and *S* isomers in this particular crystal, the identical crystal (2.5 × 1.6 × 0.8 mm) was analyzed again by the X-ray diffraction method after the neutron diffraction experiment. The occupancies of the *R* and *S* isomers turned out to be 0.609(7) and 0.391(7), respectively. Refinement of the neutron data was carried out with the program SHELXL97.¹⁴⁾ The fractional coordinates for the D or H atoms in the dimethylglyoximate and pyridine ligands and the isotropic displacement parameters were refined. Positions of the other D or H atoms were re-generated based on the geometrical considerations using the C-H distances of 1.059 Å for the methyl groups, 1.092 Å for the methylene groups, and 1.093 Å for the methyne group. The positional parameters for non-H atoms were fixed to those obtained by the X-ray analysis. The result of the refinement together with the crystal data are listed in Table I.

§3. Results and Discussions

Figure 4 shows the structure of **1** in a photo-irradiated crystal determined by the X-ray diffraction method. It is a disordered structure containing both the *R* and *S* diethoxycarbonyl ethyl groups with the occupancies of 0.524(6) and 0.476(6), respectively. The *R* configuration corresponds to the initial structure and the *S* corresponds

Table I. Crystal data of **1** after the photo-irradiation.

	X-ray	neutron
crystal size/mm	0.4 × 0.3 × 0.25	2.5 × 1.6 × 0.8
<i>a</i> /Å	16.772(10)	16.764(4)
<i>b</i> /Å	16.949(8)	16.921(5)
<i>c</i> /Å	9.121(7)	9.120(2)
Space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>P</i> 2 ₁ 2 ₁ 2 ₁
Wavelength/Å	0.71069	2.35
2θ _{max} /°	55.0	140.0
Unique reflections	4289	656
No. of restraints	8	94
No. of parameters	440	83
<i>R</i> [<i>F</i> _o > 4σ(<i>F</i> _o)]	0.0291	0.2163

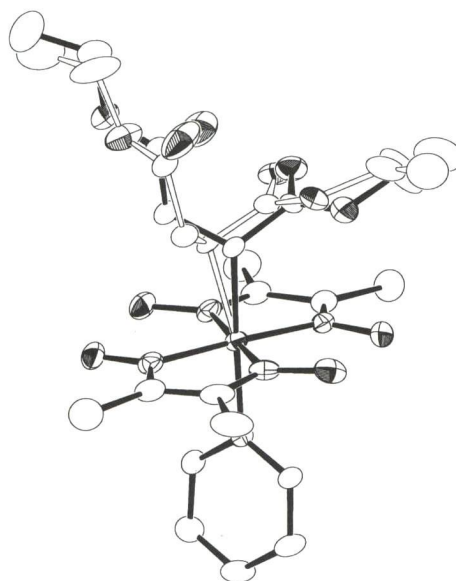


Fig. 4. ORTEP¹⁶⁾ drawing of **1** in a photo-irradiated crystal determined by the X-ray diffraction method. Ellipsoids are scaled to encompass the 20% probability levels. Hydrogen atoms are omitted for clarity. Co and O atoms are shown in octant-shaded ellipsoids and C atoms in open ellipsoids. Bonds in the initial *R* configuration are shown filled and those of the final *S* configuration are shown unfilled.

to the inverted one.

The neutron diffraction experiment revealed that the methyne hydrogen atom of the diethoxycarbonyl ethyl ligand in the photo-racemized product remained fully occupied by deuterium. Therefore, the mechanism of the photo-racemization should involve the homolytic cleavage of the Co-C bond and the generation of a radical intermediate.¹⁷⁾ To complete the chiral inversion, the radical C atom with the *sp*² configuration should rotate to bring the hydrogen atom to the opposite side. There are two possibilities for this rotation: the methyne hydrogen atom passing through the proximity of the Co atom (Type I) and the opposite side of the C atom (Type II). Figure 5(c) illustrates that, in the hypothetical reaction intermediate for the Type II mechanism, the carbonyl oxygen atoms of the diethoxycarbonyl ethyl group do not fit in the reaction cavity shown in Fig. 5(a). On the other hand, the cavity better accommodates the Type I intermediate shown in Fig. 5(b). Therefore, we conclude that

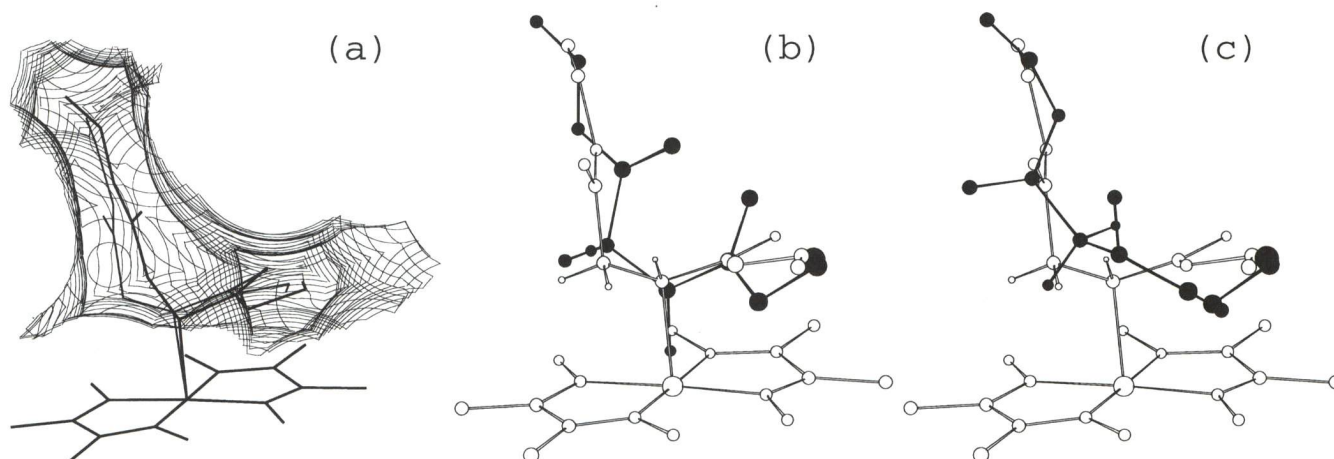


Fig. 5. (a) Reaction cavity of the diethoxycarbonylethyl ligand in **1** superimposed with the structure of the initial (shown in thick lines) and photo-inverted (shown in thin lines) structures. (b) A hypothetical Type I intermediate configuration of the diethoxycarbonylethyl ligand (shown in filled circles) superimposed with the photo-racemized product (shown in open circles). Hydrogen atoms except for those of the methyne and methylene groups in the diethoxycarbonylethyl ligand are omitted for clarity. (c) A hypothetical Type II intermediate configuration of the diethoxycarbonylethyl ligand (shown in filled circles) superimposed with the photo-racemized product.

the chiral inversion of the diethoxycarbonylethyl group proceed through the Type I mechanism.

In the crystal of **1**, the Co atom is located 3.07 Å from the methylene carbon atom and 3.05 Å from one of the methylene hydrogen atom of the diethoxycarbonylethyl ligand, which satisfies the criteria for the proceeding of the β - α isomerization reaction.¹⁸ It agrees with the observation of the isomerization reaction reported by Arai *et al.*^{8–10} However, we observed no evidence for the isomerization in the photo-irradiated crystal of **1**, probably because the shape of the reaction cavity cannot accommodate the isomerized diethoxycarbonylethyl ligand, as shown in Fig. 5(a). Therefore, the isomerization observed by Arai *et al.* may better be attributed to a surface reaction. This result well illustrates the difference between the solid-state reaction where both the bulk and surface reactions proceed at the same time and the crystalline-state reaction where only the bulk reaction proceeds.

§4. Conclusion

The single crystal neutron diffraction experiment of a photo-irradiated [(*R*)-1,2-diethoxycarbonylethyl-1-*d*]-[pyridine-*d*₅]-bis[di(methyl-*d*₃)glyoximate]cobalt(III) revealed that the deuterium atom attached to the C atom directly bonded to the Co atom remains bonded to the same C atom after the photo-racemization. This demonstrates that the photo-racemization in this compound proceeds via a radical intermediate generated by a homolytic cleavage of the Co–C bond. From the reaction cavity analysis, it was suggested that the generated radical rotates in the direction where the hydrogen atom travels the proximity of the Co atom. The reaction cavity analysis also demonstrated that the isomerization reaction of the diethoxycarbonylethyl group, which was

observed in the powdered sample, can only proceed at the surface of the crystals.

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