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Direct Observation of Deuterium Migration in Crystalline-State Reaction by Single Crystal Neutron Diffraction IV. “Hula-Twist” Rotation of a Long Alkyl Radical Produced by Photoirradiation

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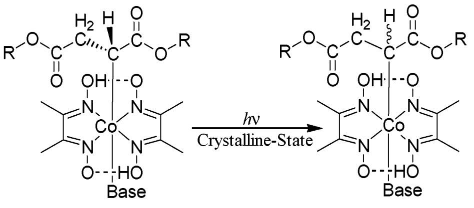
Received July 26, 2002

Abstract: When the crystal of [(*R*)-1,2-bis(ethoxycarbonyl)ethyl](pyridine)bis(dimethylglyoximato)cobalt(III) was exposed to a xenon lamp, the chiral 1,2-bis(ethoxycarbonyl)ethyl group was partly inverted to the opposite configuration and finally the racemic group was produced with retention of the single crystal form. To make clear the mechanism, the hydrogen atom bonded to the chiral carbon of the chiral group was exchanged with the deuterium atom and the crystal was exposed to the xenon lamp for 3 days. The crystal after irradiation was analyzed by neutron diffraction. About 33% of the (*R*)-isomers were inverted to the (*S*) isomers in a crystal. The deuterium atom in the (*S*)-isomer was bonded to the same chiral carbon atom. This result clearly indicates that the inversion proceeds in the three steps; (i) the Co−C bond was homolytically cleaved by photoirradiation and the 1,2-bis(ethoxycarbonyl)ethyl radical and Co(II) were produced, (ii) the radical rotated by 180° directing the C−D bond to the cobalt atom and the opposite plane of the radical faced to the cobalt atom, and (iii) the radical made a bond with Co(II). Because the peripheral atoms of the long radical occupy approximately the same positions in the process of the radical rotation, the crystal was not decomposed. The above rotation is a good example of hula-twist rotation in the process of photoisomerization of polyenes such as rhodopsin.

Introduction

Scheme 1. Crystalline-state Photoracemization of Bulky Alkyl Groups in Cobaloxime Complexes



-R = $-CH_3$, $-CH_2CH_3$, $-CH_2CH{=}CH_2$

Cobaloxime complexes, model compounds of vitamin B_{12}, have been of interest because the alkyl groups bonded to the cobalt atom in the complexes are isomerized on exposure to visible light with retention of the single crystal form. In serial studies of such crystalline-state reactions of cobaloxime complexes, a variety of racemizations of the chiral alkyl groups such as 1-cyanoethyl group,[1,2] 1-methoxycarbonylethyl group,[3−5] and 1,2-bis(methoxycarbonyl)ethyl group[6−8] have been reported. Recently, bulkier 1,2-bis(ethoxycarbonyl)ethyl and 1,2-bis(allyloxycarbonyl)ethyl groups were also found to be racemized with retention of the single crystal form by photoirradiation (Scheme 1).[9] These findings brought us a question how such bulky alkyl groups are racemized in the restricted crystalline lattice. We proposed from X-ray and ESR measurements that the photoracemization of smaller groups such as the 1-cyanoethyl group proceed in the three steps; (1) the Co−C bond was cleaved homolytically by photoirradiation, (2) the rotation of

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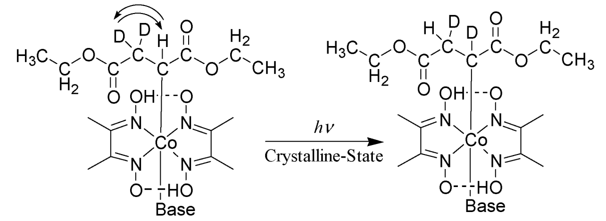
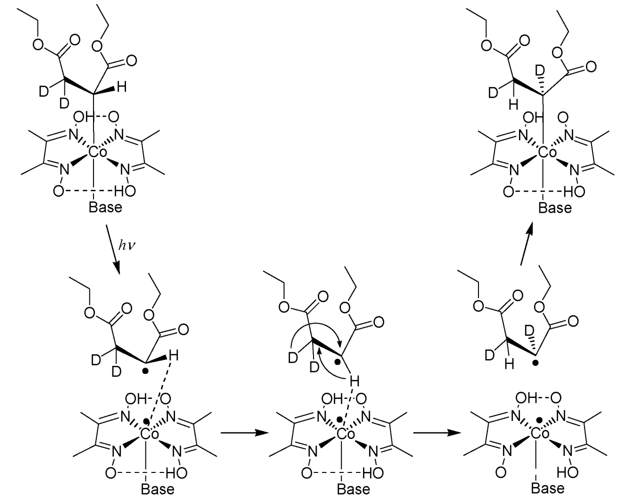
10.1021/ja027872g CCC: $22.00 © 2002 American Chemical Society

Scheme 2. H−D Exchange Reaction Observed by ^{1}H-nmr



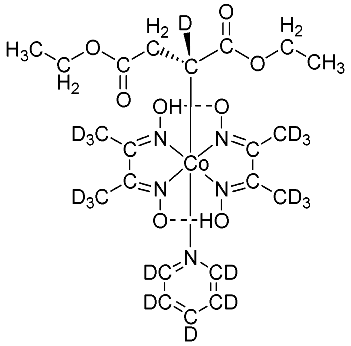
Scheme 3. H−D Exchange Mechanism. Broken Lines Denote Intramolecular Interactions.



the produced radical to face the opposite side to the cobalt atom, and then (3) the recombination between the radical and the Co atom.[10] However, the 1,2-bis(alkoxycarbonyl)ethyl group seems too bulky to be racemized with the same mechanism. The photoinversion process of such bulky groups in crystalline-lattice is very interesting as it would be a model of enzymatic activities or catalytic reactions under restricted environment.

Recently, Arai and Ohgo reported the solid-state hydrogen migration by photoirradiation in the complex of [(*R*)-1,2-bis-(ethoxycarbonyl)ethyl-$d_2^{\beta,\beta}$](pyridine) cobaloxime (Scheme 2).[11] In this experiment, powdered crystals were exposed to visible light and then the hydrogen migration was detected by ^{1}H NMR measurement. From the result, a 1,2-hydrogen migration mechanism as shown in Scheme 3 was proposed, that is, after the Co−C bond cleavage by photoirradiation, hydrogen atom bonded to the chiral α-carbon atom interacts with the cobalt-(II) atom and the C−H bond is weakened, then a deuterium atom bonded to the neighboring methylene group attacks to the α-carbon atom from the opposite side of the hydrogen atom and the hydrogen atom is transferred to the methylene group, and finally the deuterium atom makes a bond to the α-carbon atom and the bulky alkyl group inverts to the opposite configuration. This causes the photoinversion of the bulky alkyl group in crystalline-lattice. This mechanism is more probable than that proposed for the 1-cyanoethyl group from the topochemical point of view because the movement of the non-hydrogen atoms of the bulky alkyl group is smaller than that for the 1-cyanoethyl group. In addition, the structure of [(*R*)-1,2-bis(ethoxycarbonyl)ethyl](pyridine) cobaloxime after irradiation indicated that the two ethoxycarbonyl groups after photoinversion occupy nearly the same positions as those before irradiation.[9]

Scheme 4. Compound 1



To analyze the mechanism of hydrogen migration, we proposed to apply the single-crystal neutron diffraction technique.[12,13] The single-crystal neutron diffraction can distinguish hydrogen atoms from deuterium atoms because the hydrogen atom has negative neutron scattering length, whereas the deuterium atom has positive one.[14] This suggests that if the hydrogen atoms in specific positions of the reactive group are replaced with the deuterium atom, the migration of the deuterium atom in the process of crystalline-state reactions is easily observed by neutron-diffraction analysis.

In the present paper, we carried out a single-crystal neutron diffraction measurement of a photoexposed [(*R*)-1,2-bis(ethoxycarbonyl)ethyl-d_1^{α}](pyridine-d_5)bis(dimethylglyoximato-d_6)cobalt-(III) (**1**; Scheme 4) to clarify the mechanism of the photoinversion of the bulky 1,2-bis(ethoxycarbonyl)ethyl group in crystalline-lattice. The hydrogen atom bonded to the chiral α-carbon atom is replaced with a deuterium atom as a marker such as $-C^*D(CO_2C_2H_5)CH_2CO_2C_2H_5$, and hydrogen atoms bonded to the pyridine and dimethylglyoximato ligands were also replaced with deuterium atoms in order to reduce the background intensity caused by incoherent scattering.

Results and Discussions

Figures 1 and 2 show the molecular and crystal structure of photoexposed **1** determined by X-rays. About 48% of (*R*)-1,2-bis(ethoxycarbonyl)ethyl groups were inverted to the opposite configuration by photoirradiation for 3 days. In comparison with the structure of the corresponding nondeuterated compound, there is no significant structural difference caused by the deuteration. Figure 3 shows the structure of **1** before and after the inversion determined by neutron diffraction. About 33% of (*R*)-1,2-bis(ethoxycarbonyl)ethyl groups were inverted to the opposite configuration by photoexposure. Because the surface part was cut off from a photoexposed large crystal and was used for X-ray diffraction measurement, the difference in inversion ratio of the alkyl group between X-ray and neutron analyses is probably due to partial penetration of light into the inner part of the large crystal used for neutron experiment. In the inverted (*S*) group, a deuterium atom is completely bonded to the chiral α-carbon atom as well as that of the (*R*) group. In addition,

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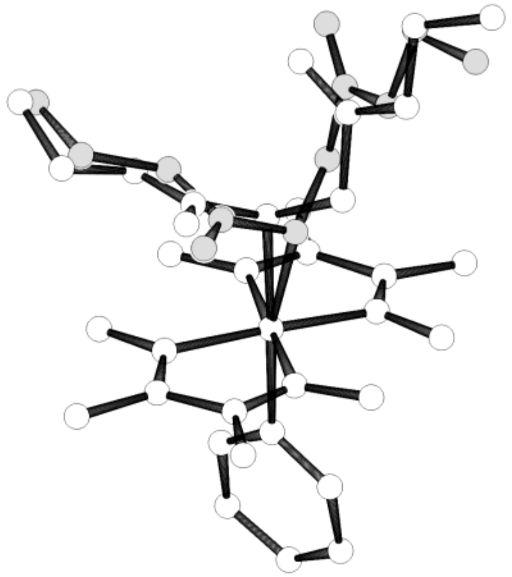


Figure 1. Molecular structure of the photoexposed **1** determined by X-rays. The gray circles denote the (*S*)-1,2-bis(ethoxycarbonyl)ethyl group produced by photoirradiation.

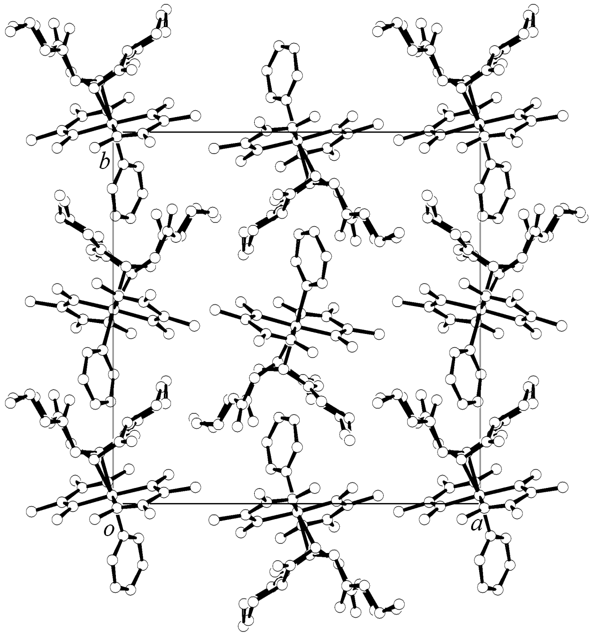


Figure 2. Crystal structure of the photoexposed **1** determined by X-rays viewed along the *a* axis.

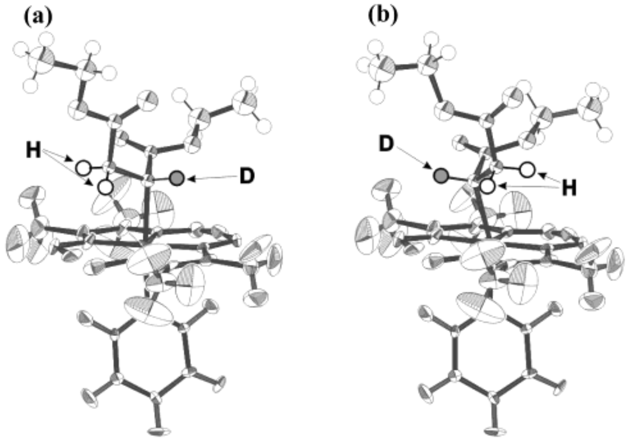


Figure 3. Ortep diagrams of Molecular structures of photoexposed **1** determined by neutron diffraction. The thermal ellipsoids of the dimethylglyoximato and pyridine ligands are drawn at the 30% probability levels. The structure was disordered into two parts, (a) (*R*)-1,2-bis(ethoxycarbonyl)ethyl group, before inversion, with 0.67 of occupancy factor and (b) (*S*)-1,2-bis(ethoxycarbonyl)ethyl group, after inversion, with 0.33 of occupancy factor.

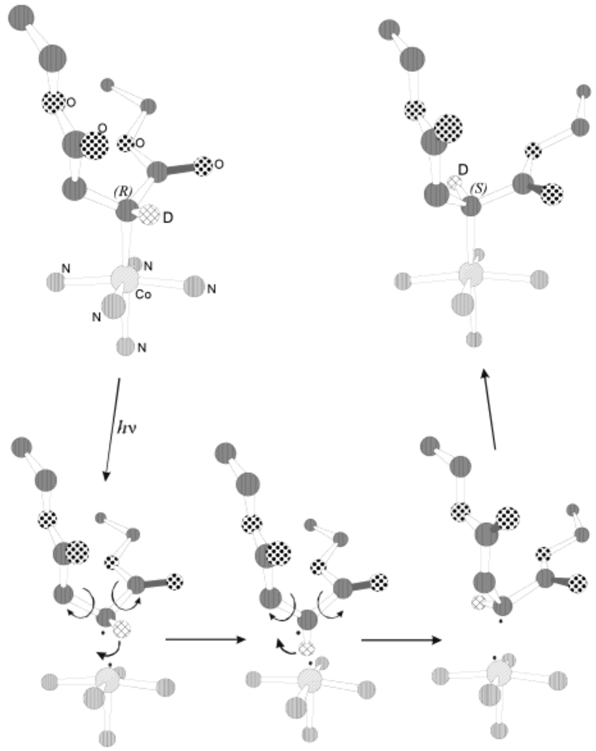


Figure 4. "Hula-Twist motion" of the reactive part in the photoisomerization; (a) at first the alkyl group is *R* configuration, (b) after the generation of the alkyl radical by cleavage of Co−C bond, the C•D−CH_2 bond and C•D−CO bond rotate, (c) the deuterium atom passes through between the chiral carbon atom and the cobalt atom, (d) then the deuterium atom goes to the opposite side of the chiral carbon atom, (e) and finally the chiral carbon atom and cobalt atom are recombined to form the opposite configuration of alkyl group.

two hydrogen atoms are completely bonded to the neighboring methylene group in the (*S*) group. These results suggest that, against expectation from NMR measurement, the photoinversion of the bulky alkyl group does not proceed with the proposed mechanism as shown in Scheme 3. The C*−D bond in the inverted alkyl group was completely kept in the process of inversion of the bulky chiral alkyl group. These indicate a new mechanism of photoinversion of the bulky alkyl group in crystalline-lattice as shown in Figure 4. Before photo-irradiation the alkyl group has (*R*) configuration. On exposure to visible light the Co−C bond is cleaved and the 1,2-bis(ethoxycarbonyl)-ethyl radical and Co(II) are produced. The two bonds of C−CH_2 and C−CO_2 of the produced radical rotate in the sense indicated by arrows. The deuterium atom passes between the chiral carbon atom and the cobalt atom and then the deuterium atom moves to the opposite side of the chiral carbon atom. Finally the chiral carbon atom and cobalt atom are recombined to form the opposite configuration of the alkyl group. In this mechanism, the 1,2-hydrogen migration is not required and the amount of the atomic movement in the process of inversion becomes very small. Figure 4 seems to be the most suitable mechanism for the photoracemization of the bulky alkyl group of the

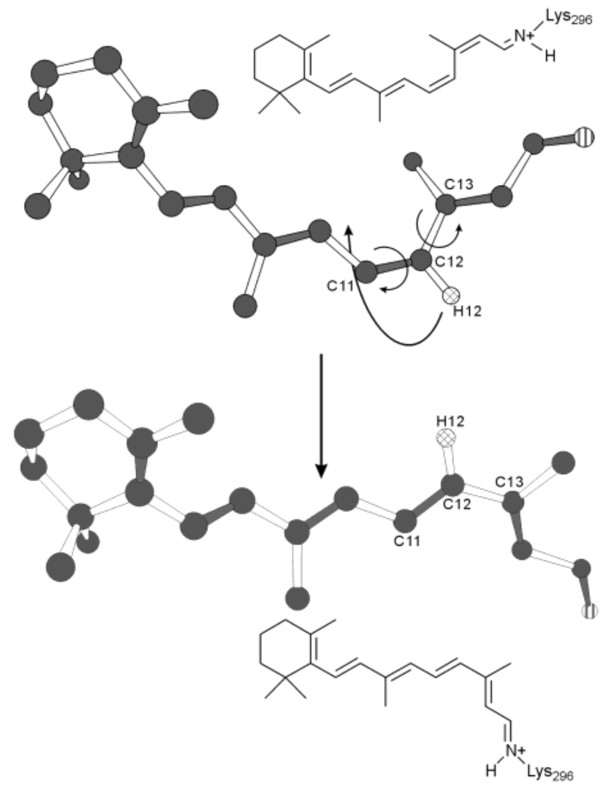


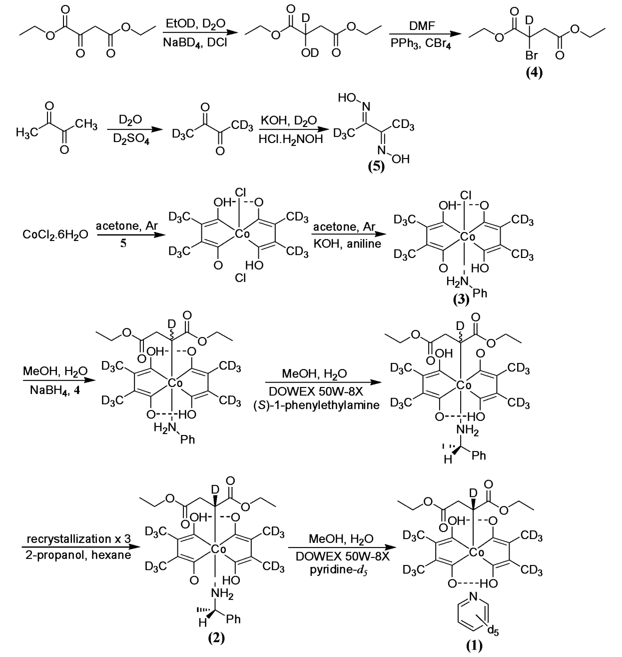
Figure 5. "Hula-Twist" model of the cis–trans isomerization of retinylidene chromophore in rhodopsin. The C11–C12 double bond and the C12–C13 single bond rotate simultaneously and the H14 migrates to the opposite side of the alkyl chain.

cobaloxime complexes in a restrained environment. This motion is very similar to the "hula-twist motion", a model motion of the cis-trans isomerization of retinylidene chromophore in rhodopsin (Figure 5).[15–18] Such a motion has been believed to be very suitable for isomerizations in highly restricted environment, for example, environments of enzymatic reactions or catalytic reactions. The present inversion process seems to be the first direct observation of hula-twist motion in a restricted enviroment, crystalline lattice, although the sp^2 carbon of the double bond is replaced with that of the sp^2 radical carbon.

Our very recent single-crystal X-ray and ^{1}H NMR studies suggested that the 1,2-deuterium–hydrogen exchange reaction as shown in Scheme 2 also occurred by photoirradiation for a long time, although the exchange occurred independently from the inversion of the alkyl group. Such a 1,2-deuterium–hydrogen exchange reaction was also observed in the cobaloxime complex with the 1-cyanoethyl group.[19]

In this work, we showed that the neutron diffraction is a strong tool for verifying the accepted mechanism often based on weak experimental evidence even though not easily applicable in all situations. Because the hydrogen migration is very popular in organic and organometallic reactions, we believe that the single-crystal neutron-diffraction will play more important role in near future.

Scheme 5. Synthetic Scheme of Compound 1



Experimental Section

Preparation. The compounds in this work were prepared in the way shown in Scheme 5, which is similar to that reported in ref 11.

[(R)-1,2-bis(ethoxycarbonyl)ethyl-$d_1{}^{\alpha}$](pyridine-d_5)bis(dimethylglyoximato-d_6)-cobalt-(III) (1). [(*R*)-1,2-bis(ethoxycarbonyl)ethyl-$d_1{}^{\alpha}$][(*S*)-1-phenylethylamine] bis(dimethylglyoximato-d_6)cobalt(III) (**2**) (0.5 g; 0.84 mmol) was suspended in a mixture of methanol (45 mL) and water (5 mL). To the mixture was added anion-exchange resin (DOWEX 50W-8 × 50mesh; 0.56 g) and stirred for 6 h. The mixture was filtered to remove ion-exchange resin. To the solution was added pyridine-d_5 (0.07 mL; 0.84 mmol). The reaction mixture was stirred for 6 h and the solution was concentrated in vacuo to give crystals of **1**. The formation of 1 was confirmed by ^{1}H NMR.

[(R)-1,2-bis(ethoxycarbonyl)ethyl-$d_1{}^{\alpha}$][(S)-1-phenylethylamine]-bis(dimethylglyoximato-d_6)cobalt(III) (2). (Aniline)(chloro)bis(dimethylglyoximato-d_6)cobalt(III) (**3**) (5.02 g; 11.68 mmol) was suspended in methanol (600 mL) and cooled with an ice bath under Ar atmosphere. To the solution was added a solution of sodium borohydride (1.06 g; 27.99 mmol) in water (10 mL), and the mixture was stirred for 15 min. To the mixture was added acetone (2 mL), and the mixture was stirred for 10 min. Diethyl 2-bromo-2-deuteriobutanedioate (**4**) (4.01 g; 15.78 mmol) was added to the mixture. After 2 h stirring, the product was extracted by dichloromethane and washed with water. Dichloromethane solution was dried over anhydrous sodium sulfate and concentrated in vacuo to give dark red crystals of [(*R*,*S*)-1,2-bis(ethoxycarbonyl)ethyl-$d_1{}^{\alpha}$](aniline)bis(dimethylglyoximato-d_6)cobalt(III) (1.67 g; 3.00 mmol). To the mixture of this dark red crystals (1.67 g; 3.00 mmol) and methanol (45 mL) was added ion-exchange resin (DOWEX 50W–X8 50mesh, 2.02 g) and water (10 mL). The reaction mixture was stirred for 6 h and was filtered to remove ion-exchange resin. To the solution was added (*S*)-1-phenylethylamine (0.38 mL; 2.988 mmol). The reaction mixture was stirred for 6 h, and the solution was concentrated in vacuo to give crystals of [(*R*,*S*)-1,2-bis(ethoxycarbonyl)ethyl-$d_1{}^{\alpha}$] [(*S*)-1-phenylethylamine]bis(dimethylglyoximato-d_6)cobalt(III). The crystals of the diastereomixture were separated by three times recrystallization from a mixture of 2-propanol–hexane and crystals of **2** were given. The optical purity of **2** was confirmed by HPLC with chiral column (DAISEL CHEM. Inc., CHIRALPAK AD). The optical purity was higher than 98%*ee*.

(Aniline)(chloro)bis(dimethylglyoximato-d_6)cobalt(III) (3). To the mixture of cobalt(II) chloride hexahydrate (11.55 g, 48.54 mmol) and

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acetone (200 mL) was added dimethylglyoxime-d_7 (**5**) (10.55 g, 86.35 mmol) and the reaction mixture was stirred overnight. The precipitate was filtered and dried to give *trans*-[Co(dimethylglyoximato-d_6)$_2$Cl$_2$] (14.83 g, 39.74 mmol). To the solution of KOH (2.68 g, 39.7 mmol) was added *trans*-[Co(dimethylglyoximato-d_6)$_2$Cl$_2$] (14.83 g, 39.74 mmol), and the mixture was stirred for 2 min. To the reaction mixture was added aniline (3.6 mL, 39.7 mmol) and stirred 1 h. The precipitate was filtered and dried to give a brown powder of **3** (11.60 g, 26.98 mmol).

Diethyl 2-bromo-2-deuteriobutanedioate (4). A solution of diethyl oxalacetate sodium salt (53.0 g; 252.1 mmol) in water (600 mL) was neutralized by 6M HCl (39 mL) on cooling. Diethyl oxalacetate was extracted with dichloromethane. The organic layer was dried over anhydrous magnesium sulfate and concentrated in vacuo. The residue was dissolved in ethanol-d_1 (180 mL) and D_2O (90 mL) was added to the solution. To the solution was added a solution of sodium borodeuteride (3.0 g; 71.72 mmol) in D_2O (100 mL) while cooling. After 2 min of stirring, the solution was neutralized by DCl on cooling. Concentration in vacuo gave a crude of diethyl 2-deuterioxy-2-deuteriobutanedioate (27.06 g; 141.51 mmol). This crude was dissolved in *N*,*N*-dimethylformamide (DMF) (200 mL). To the solution were added a solution of triphenylphosphine (74.82 g; 285.18 mmol) in DMF (250 mL) and tetrabromomethane (40.09 g; 141.99 mmol) in DMF (90 mL) on cooling. The solution was stirred for 1 day and concentrated in vacuo. The residue was purified roughly by column chromatography on silica gel (ethyl acetate−hexane), and distilled in vacuo to give a liquid of **4** (20.78 g; 81.77 mmol). The formation of **4** was confirmed by ^{1}H NMR.

Dimethylglyoxime-d$_7$ (5). **5** was prepared according to the reported method.[20] The methyl hydrogen atoms of butane-2,3-dione were exchanged with deuterium using D_2O and D_2SO_4 catalyst for seven cycles. For each cycle, the amounts of D_2O and D_2SO_4 were adjusted depending on the amount of butanedione used in the cycle. For the first cycle, butane-2,3-dione (100 g), D_2O (200 mL), and D_2SO_4 (2 mL) were heated at 95 °C for 12 h. The butane-2,3-dione was isolated by distillation under atmospheric pressure at 78−80 °C and was separated from D_2O, which codistilled. The butane-2,3-dione thus isolated was used without further purification in the next cycle. After the final cycle, the produced butane-2,3-dione-d_6 was dried over anhydrous magnesium sulfate. The yield after seven cycles was 19.5 g of 99.1 atom %D butane-2,3-dione-d_6. The prepared butane-2,3-dione-d_6 (17.67 g) was refluxed with HCl·H_2NOH (142.1 g), KOH (85% pure, 93.7 g) and D_2O (400 mL) at 95−100 °C for 90 min. The white precipitate of **5** was filtered and washed with $NaHCO_3$(aq) and water. The yield was 18.4 g of 98.5 atom %D. The formation of **5** and the intermediate species were confirmed ^{1}H NMR.

Crystallization and Photoirradiation. 1.50 g of **1** was solved in acetone (20 mL) and left for one week in 50 mL flask at room temperature. And large crystals (∼1.5 × 1.0 × 0.4 mm), enough size for single-crystal neutron diffraction, were obtained. Some of large crystals with analogous size and morphology were exposed to red and infrared light longer than 690 nm, corresponding to the absorption edge[21] of the crystal of **1**, for 3 d. The photoexposure was carried out with a Xe lamp (USHIO SUPER BRIGHT 152S) and a short-cut filter (TOSHIBA R-69).

Single-Crystal X-ray Diffraction Study. A small piece of a red crystal of **1** cut from the photoexposed large crystal (0.2 × 0.1 × 0.1 mm) was mounted on the Rigaku AFC7R four-circle diffractometer with Mo*K*α radiation ($\lambda = 0.710\,73$ Å). The structure was solved by direct method with program SIR-97[22] and structural parameters were refined with program SHELXL-97.[23] $C_{21}H_{14}N_5O_8CoD_{18}$, MW=559.6, orthorhombic, space group $P2_12_12_1$, $T = 293$ K, $a = 9.121(7)$ Å, $b = 16.72(1)$ Å, $c = 16.949(8)$ Å, $V = 2593(3)$ Å^3, $Z = 4$. Anisotropic least-squares refinement (301 parameters) on 4289 independent merged reflections ($R_{\mathrm{int}} = 0.02$) converged at $wR_2(F^2) = 0.1133$ for all data; $R_1(F) = 0.0398$ for 3818 observed data ($I > 2\sigma(I)$), GOF = 1.048.

Single-Crystal Neutron Diffraction Study. One of the photoexposed crystals of **1**, 1.5 × 1.0 × 0.4 mm, was fixed on an aluminum pin by halocarbon grease (MOLYKOTE HP-300 grease) and mounted on the BIX-3 neutron diffractometer[24] equipped with a neutron imaging plate (NIP)[25] set up at the JRR-3M reactor at Japan Atomic Energy Research Institute (JAERI). Although the BIX-3 diffractometer was developed for biomacromolecular crystals with longer than 2 Å wavelength incident neutrons, crystals of small organic molecules such as **1** can be measured by using short wavelength incident neutrons. The neutron beam, monochromated by a bent Si perfect crystal,[26] has a wavelength of 1.23 Å. The intensity data were collected with oscillation method ($\Delta\omega = 1.0°$) at room temperature. The maximum and minimum *d*-spacing values were 11.7 and 0.87 Å, respectively. A total of 2300 independent reflections were observed. Cell parameters and the U matrix was refined for each NIP image with the program DENZO.[27] Each reflection was integrated by box sum method and the Lorentz correction was carried out simultaneously with the program DENZO.[27] Finally, the *hkl* data were modified to the SHELXL-type format.

Refinement of the structure was carried out with the program SHELXL-97.[23] The occupancy factors of the each atom of glyoximato ligands and axial pyridine were fixed to 1.0, the occupancy factors of (*R*)- and (*S*)-1,2-bis(ethoxycarbonyl)ethyl group (the reactive part), the positional parameters of the reactive parts and each atom of the glyoximato ligands and axial pyridine, anisotropic displacement parameters of each atom of the glyoximato ligands and pyridine and isotropic displacement parameters of each atom of the reactive parts were refined. The reactive parts were treated as rigid groups in the refinement of positional parameters. $C_{21}H_{14}N_5O_8CoD_{18}$, MW = 559.6, orthorhombic, space group $P2_12_12_1$, $T = 293$ K, $a = 9.133(1)$ Å, $b = 16.813(1)$ Å, $c = 16.911(1)$ Å, $V = 2596.7(4)$ Å^3, $Z = 4$. Least-squares refinement (423 parameters) on 2300 independent merged reflections ($R_{\mathrm{int}} = 0.068$) converged at $wR_2(F^2) = 0.3098$ for all data; $R_1(F) = 0.1256$ for 2213 observed data ($I > 2\sigma(I)$), GOF = 2.754.

Acknowledgment. This work was partially supported by the CREST fund from Japan Science and Technology Corporation, JST. One of the authors (T.O.) thanks to the Research Fellowship from the Japan Society for the Promotion of Science, JSPS.

JA027872G

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