

## ***BCSJ Award Article***

---

# **A New Photoisomerization Process of the 4-Cyanobutyl Group in a Cobaloxime Complex Crystal Observed by Neutron Diffraction**

**Takaaki Hosoya,<sup>1</sup> Hidehiro Uekusa,<sup>1</sup> Yuji Ohashi,<sup>\*1</sup> Takashi Ohhara,<sup>2</sup> and Ryota Kuroki<sup>2</sup>**

<sup>1</sup>Department of Chemistry and Materials Science, Tokyo Institute of Technology, 2-12-1 Ookayama, Meguro-ku, Tokyo 152-8551

<sup>2</sup>Neutron Science Research Center, Japan Atomic Energy Research Institute, 2-4 Shirane Shirakata, Tokai, Naka-gun, Ibaraki 319-1195

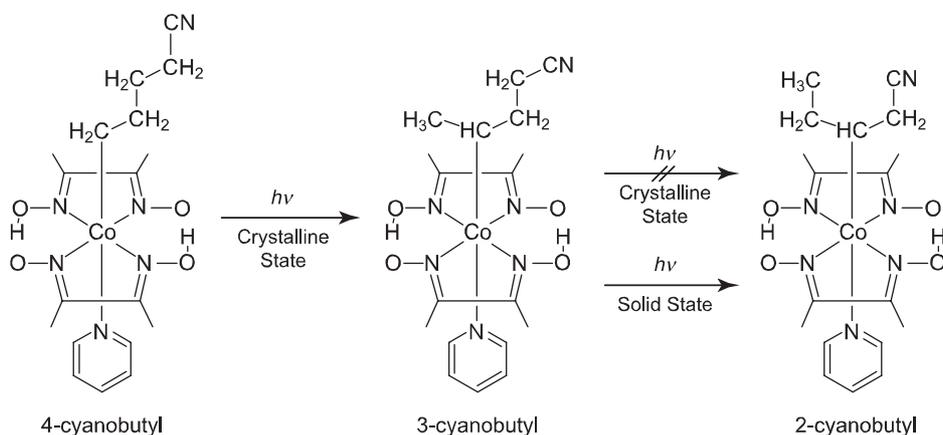
Received July 14, 2005; E-mail: thosoya@chem.titech.ac.jp

The 4-cyanobutyl group of (4-cyanobutyl)[3,4-lutidine](dimethylglyoximate)[*O*-(diphenylboryl)dimethylglyoximate]cobalt(III) was isomerized to the 1-cyanobutyl group with retention of the single-crystal form, although the corresponding cobaloxime complex without diphenylboryl in the equatorial ligands did not show such a photoisomerization. The *trans*–*cis*–*cis* conformation of the 4-cyanobutyl group caused by the steric repulsion from the diphenylboryl group is favorable to the crystalline-state reaction. In order to elucidate the detailed isomerization mechanism, two hydrogen atoms of the 4-cyanobutyl group were replaced with the deuterium atoms such as –CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CD<sub>2</sub>CN. After the photoisomerization, the crystal structure with deuterated 4-cyanobutyl group was analyzed by neutron diffraction. Only one of the two deuterium atoms of the 4-cyanobutyl group was transferred to the C<sup>1</sup> atom such as –CD(CN)CH<sub>2</sub>CH<sub>2</sub>CDH<sub>2</sub>. This result made clear that the photo-produced cyanobutyl radical turned upside down after homolytic cleavage of the Co–C bond, and then the Co(II) atom and the radical made a bond to form the 1-cyanobutyl group.

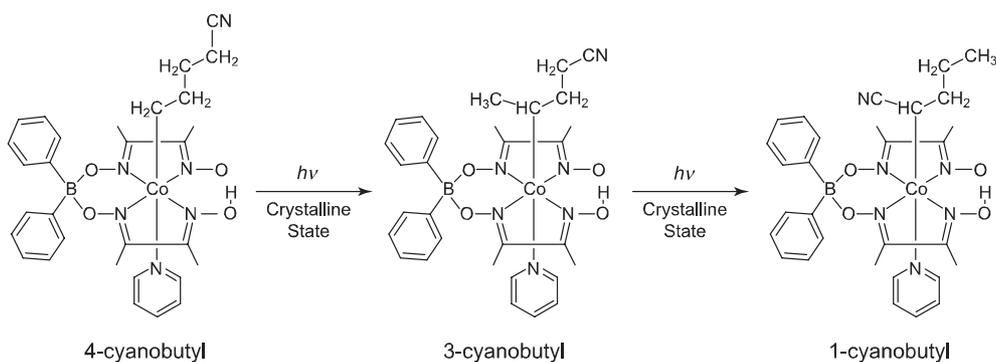
Recently, it has been elucidated that single-crystal X-ray diffraction analysis of the crystalline-state reaction is one of the most powerful methods for investigating the reaction mechanism in detail because the 3-dimensional motion of atoms can be directly observed during the reaction.<sup>1</sup> However, it is impossible to analyze the mechanism only from the structure analysis of the crystalline-state reaction when one of two hydrogen atoms bonded to a carbon atom is abstracted and transferred to the other carbon atom in the process of the reaction. The reaction accompanying hydrogen-atom transfer is one of the most elemental phenomena and is often observed in many organic, inorganic, enzymatic, and catalytic reactions. For the analysis of the mechanism, the deuterium atom is replaced with the target hydrogen atom, which is assumed to be transferred during the reaction. Although the transferred position of the deuterium atom can be estimated from the NMR and IR spectra in solution, the analysis of the spectra is difficult in the crystalline-state. Since it is possible to perform in-situ observation of the reaction process in the crystalline-state by X-ray analysis, it seems necessary to observe the transfer of the deuterium atom directly in the crystalline-state.

The replacement of the target hydrogen atom with the deuterium atom in the crystalline-state, on the other hand, can be used for the neutron diffraction technique, since neutron diffraction can clearly distinguish a deuterium atom from a hydrogen atom. Since the neutron scattering length for the deute-

rium atom is positive, whereas that of the hydrogen atom is negative, the deuterium and hydrogen positions can be shown as positive and negative peaks, respectively, in the nucleus density map. Therefore, the deuterium-atom transfer in the crystalline-state reaction can be directly observed by neutron diffraction analysis since the peak heights of the replaced deuterium and hydrogen atoms are gradually changed in the process of the isomerization. However, there are some serious problems to be overcome in neutron diffraction analysis of the crystalline-state reaction. Because of the weak intensity of the neutron beam as compared with that of X-rays, it is necessary to (1) use a large crystal more than 5 mm<sup>3</sup> to take the intensity data, although it is not easy to make large crystals for organic compounds, (2) penetrate light into the large crystal, although the photoreaction proceeds from the surface of the single crystal and the disordered product molecules in the surface block the light penetrating into the crystal, and (3) keep the produced crystal more than one or two weeks to take all the intensity data. Only a few examples of crystalline-state reactions in cobaloxime complexes have been reported by neutron diffraction.<sup>2–7</sup> Recently, a direct observation of deuterium transfer in chiral  $\beta$ -thiolactam formation in the crystalline state was reported, in which the absolute configuration of a chiral R–C\*HD–R' methylene in the crystal after photoirradiation indicated that the deuterium transfer occurred via an intramolecular path.<sup>8,9</sup>



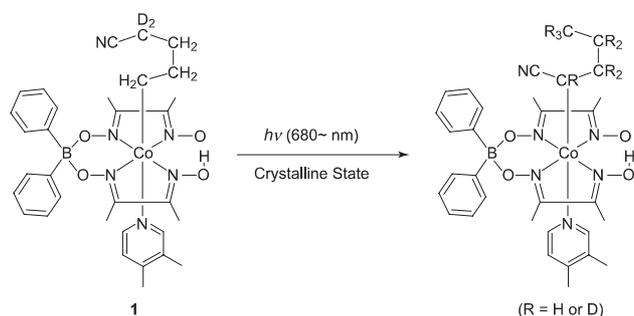
Scheme 1. 4-3-(2) Photoisomerization of 4-CB-Co<sup>III</sup>(dmgH)<sub>2</sub>-Py in the crystalline state (partially solid state). The practical names of 3-cyanobutyl ( $\gamma$ ) and 2-cyanobutyl ( $\beta$ ) are used instead of the formal ones of 4-cyanobutan-2-yl and 1-cyanobutan-2-yl, respectively.



Scheme 2. 4-3-1 Photoisomerization of 4-CB-Co<sup>III</sup>(dmgH)(dmgBPh<sub>2</sub>)-Py in the crystalline state.

In the case of a cobaloxime complex with a 4-cyanobutyl group, (4-cyanobutyl)[pyridine]bis(dimethylglyoximate)cobalt(III), 4-CB-Co(dmg)(dmgH)-Py, only a 4-3 isomerization was recently observed in the crystalline state,<sup>10</sup> as shown in Scheme 1. X-ray diffraction analysis of the crystal after irradiation showed 78.6(7)% of the reactant 4-cyanobutyl group and 21.4(7)% of the product 3-cyanobutyl group. The 2-cyanobutyl group was observed by 6% in the irradiated crystal with the <sup>1</sup>H NMR measurement. The reason why the isomerization did not proceed to the 2- or 1-cyanobutyl group in the crystalline state may be due to the size and the shape of the reaction cavity around the initial 4-cyanobutyl group. The reaction cavity was too small to accept the isomerized 2- or 1-cyanobutyl group.

Recently, an unusual result was observed in the crystalline-state photoisomerization of a cobaloxime complex, which has a diphenylboron group in the equatorial ligands. If the axial ligand of the complex is pyridine, the 4-cyanobutyl group is isomerized to a 1-cyanobutyl group via 3-cyanobutyl and 2-cyanobutyl groups as shown in the Scheme 2. For the complex with 3,4-lutidine instead of pyridine, however, the intermediate 3- and 2-cyanobutyl complexes were observed neither by X-ray diffraction nor by FT-IR measurement. In order to elucidate the mechanism, deuterium atoms were introduced in the 4-cyanobutyl group and the structure after photoreaction was analyzed by neutron diffraction as shown in Scheme 3.



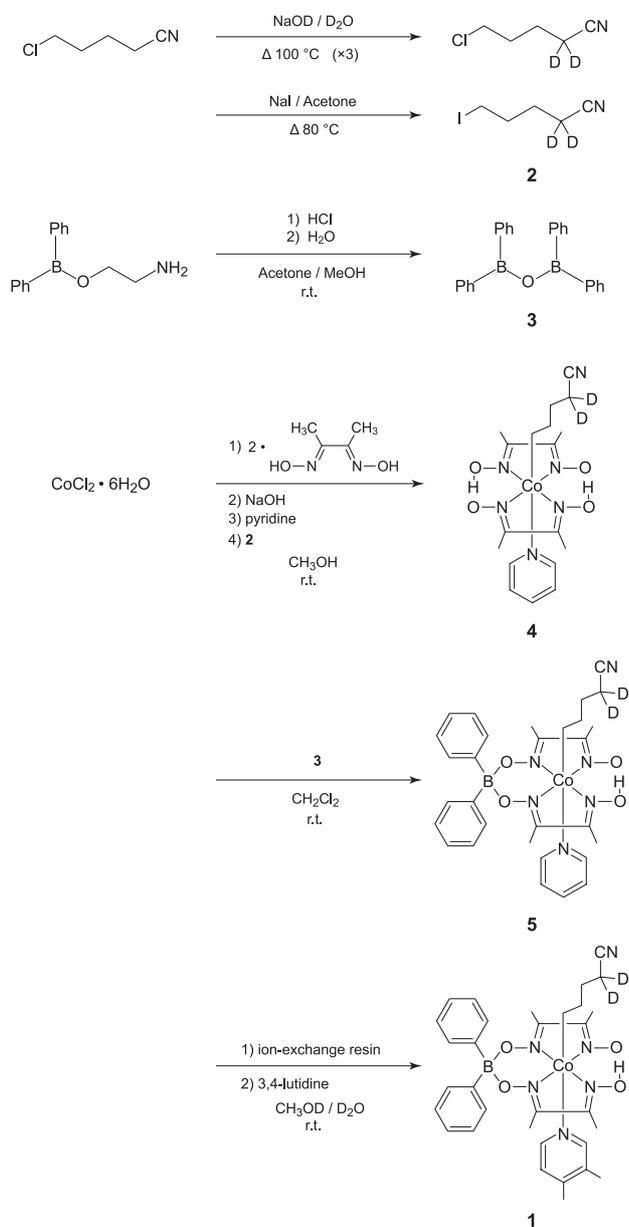
Scheme 3. Crystalline-state isomerization of **1**.

The present paper reports the result of the neutron diffraction analysis and discusses a new mechanism for the photoisomerization.

## Experimental

**Preparation.** (4-Cyanobutyl- $\alpha,\alpha$ -*d*<sub>2</sub>)[3,4-lutidine](dimethylglyoximate)[*O*-(diphenylboron)dimethylglyoximate]cobalt(III), cobaloxime complex (**1**), shown in Scheme 4, was synthesized from 5-iodovaleronitrile-2,2-*d*<sub>2</sub> (**2**), dimethylglyoxime, diphenylboronic anhydride (**3**), 3,4-lutidine, and cobalt(II) chloride hexahydrate as shown in Scheme 4.

**Synthesis of 5-Iodovaleronitrile-2,2-*d*<sub>2</sub> (**2**).** Compound **2** was prepared according to the reported method.<sup>5</sup> 5-Chlorovaleronitrile

Scheme 4. Synthesis procedure of **1**.

(25 g, 220 mmol), containing 100 mL of deuterium oxide ( $D_2O$ ) and sodium deuteroxide (2.5 mL of  $D_2O$  solution, 40 wt %) placed in a two necked flask, was refluxed at  $100^\circ C$  for 2 h under a  $N_2$  atmosphere. After cooling, the organic layer was extracted with dichloromethane, dried over anhydrous sodium sulfate ( $Na_2SO_4$ ), and then the solvent was evaporated. The above procedure was repeated twice. About 98% deuterated 5-chlorovaleronitrile-2,2- $d_2$  was obtained. Sodium iodide powder (32.978 g, 220 mmol) suspended in 100 mL of acetone was cooled in an ice bath and 5-chlorovaleronitrile-2,2- $d_2$  was added. The mixture was refluxed at  $80^\circ C$  for 2 days. After cooling, acetone was evaporated. Dichloromethane and distilled water were added and the organic layer was separated, washed with a saturated solution of sodium chloride, extracted with dichloromethane, dried over anhydrous  $Na_2SO_4$ , and then the solvent was evaporated. 5-Iodovaleronitrile-2,2- $d_2$  (**2**) was distilled at  $105^\circ C$  under 20 mmHg.

**Synthesis of Diphenylborinic Anhydride (3).** Compound **3** was prepared according to the reported method.<sup>11</sup> Diphenylborinic

acid 2-aminoethanol ester (10 g, 44 mmol) dissolved in acetone (100 mL) and methanol (100 mL) was placed in a 300-mL round bottom flask (brown color), and concentrated hydrochloric acid was added dropwise until the pH of the solution was 1–2. Water was added to finish the reaction after 1 h of stirring at room temperature, and diphenylborinic anhydride (**3**) was extracted with diethyl ether, and dried over anhydrous  $Na_2SO_4$ . Then, the solvent was evaporated thoroughly until the oily product became solid.

**(4-Cyanobutyl- $\alpha,\alpha$ - $d_2$ )[pyridine]bis(dimethylglyoximate)cobalt(III) (4).** Compound **4** was prepared using a method similar to the reported ones.<sup>12</sup> Cobalt(II) chloride hexahydrate (4.768 g, 20 mmol) dissolved in 100 mL of methanol was placed in a 300-mL two-necked round bottom flask, and dimethylglyoxime (4.644 g, 40 mmol) was added. Under a  $N_2$  atmosphere, a 10 mL aqueous solution of sodium hydroxide (1.61 g, 40 mmol) and pyridine (1.60 mL, 20 mmol) were added successively, and the color of the mixture varied from bluish purple to bistere. After sealing the flask with a rubber septum, sodium tetrahydroborate dissolved in 10 mL of distilled water and the pre-synthesized 5-iodovaleronitrile-2,2- $d_2$  (4.22 g, 20 mmol) were slowly added with a microsyringe attached to a needle through the septum in sequence, and then a brownish precipitate was observed. Distilled water was added and the mixture was stirred for 20 min. The precipitate was collected by suction filtration and washed with water three times. The crude of (4-cyanobutyl- $\alpha,\alpha$ - $d_2$ )[pyridine]bis(dimethylglyoximate)cobalt(III), 4-CB-Co(dmgH)<sub>2</sub>-Py (**4**), was recrystallized from an aqueous methanol solution. Dark-red crystals were obtained (yield: 5.615 g, 12.81 mmol).

#### Introduction of Diphenylboryl to the Cobaloxime Complex.

This process was carried out according to the reported method.<sup>13</sup> Crystals of **4** (4.38 g, 10 mmol) and diphenylborinic anhydride (**3**) (2.42 g, 7 mmol) were placed in a 200-mL two-necked round bottom flask. One of the openings was sealed with a rubber septum, the air of the flask was evacuated, and the flask was filled with nitrogen gas. 100 mL of dichloromethane was bubbled with nitrogen gas, and added to the flask with a microsyringe. The mixture was stirred for 2 days under light shielding at room temperature. After removing the solvent, the orange-color residue was washed with methanol and the monosubstituted complex was separated by silica-gel column chromatography (developing solvent: dichloromethane/ethyl acetate = 4/1), and recrystallized from a dichloromethane solution. Dark-red crystals of (4-cyanobutyl- $\alpha,\alpha$ - $d_2$ )[pyridine](dimethylglyoximate)[*O*-(diphenylboryl)dimethylglyoximate]cobalt(III), 4-CB-Co(dmgH)(dmgBPh<sub>2</sub>)-Py (**5**), were obtained (yield: 2.071 g, 3.649 mmol).

**Exchange of Axis Base Ligand.** This process was carried out using a method similar to the reported one.<sup>12</sup> The crystals of **5** (2.071 g, 3.649 mmol) were placed in a 200-mL round-bottom flask and dissolved in 30 mL of methanol-*d* and 5 mL of  $D_2O$ . To the solution 6 g of ion-exchange resins (DOWEX 50 W-X8) were added and stirred for two days at room temperature. The mixture was filtrated and 3,4-lutidine (0.391 g, 3.649 mmol) was added dropwise. After 1 h of stirring at room temperature, the solvent was removed with a rotary evaporator and the resulting orange solid was recrystallized by the vapor diffusion method from an acetonitrile–hexane solution at  $10^\circ C$  for 1 week. Crystals of **1** with dimensions appropriate for neutron diffraction (3–4 mm<sup>3</sup>) were obtained. The introduction of two deuterium atoms of **1** was confirmed by <sup>1</sup>H NMR measurement.

**Photoirradiation.** It is very important that the photoreaction should occur within a crystal, since the surface of the crystal is easily isomerized. However, a crystal large enough for neutron

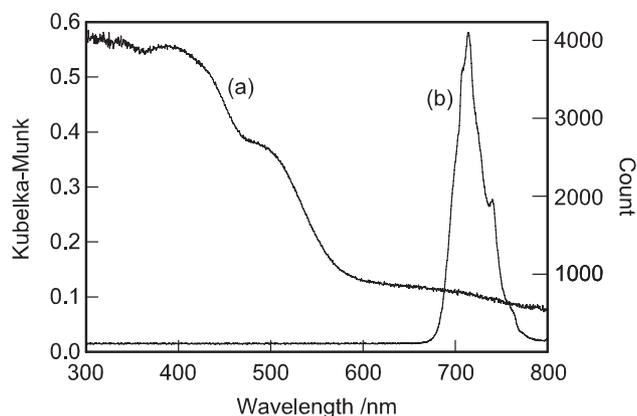


Fig. 1. (a) UV-vis reflectance spectrum of **I**. Vertical axis is converted from reflectance (%R) into Kubelka-Munk. (b) The light wavelength distribution of the Xe lamp through R-68 filter.

diffraction is very difficult to isomerize inside the crystal. If only the surface of the crystal is isomerized, the light cannot penetrate into the crystal because of the broken crystallinity of the surface and the total population of the photoproduct will be very low. The selection of the wavelengths is very important in the photoreaction of the single crystal. The ultraviolet-visible reflectance spectra of the powdered crystal were recorded on a spectrophotometer (JASCO V-560) in order to optimize the irradiation condition. As shown in Fig. 1, three peaks around the wavelengths of 400, 500, and 700 nm were observed, which were assigned to the ligand-to-metal charge transfer, the singlet, and triplet d-d transitions of the cobalt atom, respectively.<sup>14</sup> In order to keep the crystallinity during the photoreaction, the longer wavelengths around 700 nm due to the triplet d-d transition were selected for photoisomerization. A xenon lamp (SAN-EI SUPER BLIGHT 152S with USHIO xenon short-arc lamp UXL-151DO) was placed at a distance of 5 cm from the crystals of **1** as the light source and two filters were inserted between the lamp and the crystals: an R-68 filter (TOSHIBA) cutting off the light shorter than 680 nm and a heat absorbing water filter. A large crystal of **1**, crystal **III**, which has the dimensions of  $4.5 \times 1.5 \times 1.4 \text{ mm}^3$ , was selected. Both sides of **III** were irradiated under the above conditions for 2 days at 0 °C on a cool plate (NISSIN Cool Plate NCP-2215).

**FT-IR Spectroscopy.** The photoreaction was monitored using an FT-IR spectrometer (BIO-RAD FTS3000 IR spectrometer). KBr pellets about 1 mm thick were mounted in a pellet holder and were irradiated with light under the above conditions at room temperature. At appropriate intervals, successive FT-IR measurements of each pellet were carried out one by one.

**Single Crystal X-ray Diffraction Measurement and Structure Analysis.** Single-crystal diffraction measurements were carried out for a crystal of **1** before the photoirradiation. A crystal of **1** ( $0.30 \times 0.20 \times 0.10 \text{ mm}^3$ , crystal **I**) was mounted on a Bruker SMART CCD X-ray diffractometer. Diffraction data were collected at 297, 173, and 93 K, using *SAINTE* software.<sup>15</sup> Systematic error corrections, including absorption correction, were applied using the *SADABS* program.<sup>16</sup> The structure was solved by the direct method with the *SIR-2002* program.<sup>17</sup> The structure refinement on  $F^2$  was carried out with the full-matrix least-squares method using the *SHELXL-97* program.<sup>18</sup> The coordinated 3,4-lutidine moiety is disordered and the site occupancy factor (SOF) is constant with the temperature. This means that the 3,4-lutidine moiety is disor-

dered not dynamically, but statically. The non-hydrogen atoms including the disordered ones were refined anisotropically. The hydrogen atoms were refined isotropically except for the hydrogen atoms in the disordered 3,4-lutidine moiety, for which the positional parameters were calculated by the riding model and the isotropic displacement parameters were constrained by 1.2 times of those of the bonded atoms for the hydrogen atoms of the phenyl group or 1.5 times for the hydrogen atoms of the methyl group.

A small crystal ( $0.30 \times 0.10 \times 0.10 \text{ mm}^3$ , crystal **II**) was cut from crystal **III** after the photoirradiation described above. X-ray diffraction measurement of **II** was carried out by a SMART CCD diffractometer in the same ways as that of **I**. The structure was analyzed using the positional parameters of **I** as an initial model. Some extra peaks appeared on the difference electron density map around the 4-cyanobutyl group. The peaks were assigned to the produced 1-cyanobutyl group. The structure including the SOFs of the disordered 4- and 1-cyanobutyl groups were refined with *SHELXL-97*. The SOF of the disordered 3,4-lutidine was also refined. All non-hydrogen atoms were refined anisotropically. Positional and isotropic temperature parameters of the hydrogen atoms of the diphenylboryl group were refined. The other hydrogen atoms were calculated using riding models. The crystal data and experimental details of **I** and **II** are summarized in Table 1.

**Single-Crystal Neutron Diffraction Measurement.** The photoirradiated crystal of **III** was fixed on an aluminum pin and mounted on the BIX-III diffractometer,<sup>19,20</sup> equipped with a neutron imaging plate,<sup>21,22</sup> set up at the JRR-3M reactor of the Japan Atomic Energy Research Institute (JAERI). The neutron diffraction data were collected by the  $\omega$  scan method (oscillation range  $\Delta\omega = 1.0^\circ$ ) at 293 K using perfect-silicon-crystal-monochromated neutron radiation ( $\lambda = 1.51000 \text{ \AA}$ ). Since BIX-III is a single-axis cylindrical diffractometer, there is a large blind region around the rotation axis. To reduce the blind region, data were collected by changing the angle values of the aluminum pin (about 180, 135, and  $90^\circ$ ) instead of changing the  $\chi$  circle position for the ordinary X-ray diffractometer. Reflections were integrated with the *Denzo* program<sup>23</sup> and the data corrections without absorption correction were carried out with the *Scalepack* program.<sup>23</sup> Numerical absorption correction was done using the face indices determined by the SMART CCD diffractometer with the *ABSG* program<sup>24</sup> in *PLATON*.<sup>25</sup>

**Structure Refinement Using the Neutron Diffraction Data.** The positional parameters of non-hydrogen atoms were constrained using the coordinates of **II** as an initial model. The refinement was on  $F^2$  against all reflections by full-matrix least-squares using *SHELXL-97*. Hydrogen and deuterium atoms were observed in difference Fourier maps (neutron-scattering-length density maps) as negative and positive peaks.

**For Atoms except 1-Cyanobutyl Group:** After confirmation of the significant peaks, the hydrogen atoms except for the 1-cyanobutyl group were located at the ideal positions calculated by riding models in order to reduce the refinement parameters. The atomic displacement parameters of all the non-hydrogen atoms of 3,4-lutidine were refined isotropically because the two disordered groups were too close to refine anisotropically, and those of the other non-hydrogen atoms were treated anisotropically.

**For 1-Cyanobutyl Group:** Positional and isotropic-atomic-displacement parameters of non-hydrogen atoms were refined. In the difference Fourier map, the strong positive peak and some negative peaks were found, which correspond to a transferred deuterium atom bonded to the methine carbon and methylene hydrogen atoms of the 1-cyanobutyl groups, respectively. However, the

Table 1. Crystal Data and Experimental Details

	(I)	(II)	(III)
	X-ray: <b>1</b> initial	X-ray: <b>1</b> irradiated	Neutron: <b>1</b> irradiated
[Crystal data]			
Empirical Formula	C <sub>32</sub> H <sub>38</sub> BCoD <sub>2</sub> N <sub>6</sub> O <sub>4</sub>	C <sub>32</sub> H <sub>38</sub> BCoD <sub>2</sub> N <sub>6</sub> O <sub>4</sub>	C <sub>32</sub> H <sub>38</sub> BCoD <sub>2</sub> N <sub>6</sub> O <sub>4</sub>
Formula weight	644.44	644.44	644.44
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>
<i>a</i> /Å	11.2506(5)	11.5135(5)	11.4714(5)
<i>b</i> /Å	14.4396(6)	14.5963(6)	14.567(1)
<i>c</i> /Å	19.8097(9)	19.8069(8)	19.8202(9)
$\beta$ /°	93.349(1)	92.540(1)	92.839(3)
<i>V</i> /Å <sup>3</sup>	3212.7(2)	3325.4(2)	3308.1(3)
<i>Z</i>	4	4	4
<i>D<sub>x</sub></i> /Mg m <sup>-3</sup>	1.328	1.283	1.238
Radiation type	Mo K $\alpha$	Mo K $\alpha$	Thermal neutron
Wavelength/Å	0.71073	0.71073	1.51000
$\theta$ range/°	1.75–27.48	1.73–26.37	3.69–48.86
$\mu$ /mm <sup>-1</sup>	0.58	0.56	0.47
Temperature/K	173(2)	293(2)	293(2)
Crystal form, color	Block, dark red	Block, dark red	Block, dark red
Crystal size/mm	0.30 × 0.20 × 0.10	0.30 × 0.10 × 0.10	2.0 × 1.8 × 0.8
[Data collection]			
Diffractometer	Bruker SMART CCD	Bruker SMART CCD	BIX-III
Data collection method	$\omega$ scan	$\omega$ scan	$\omega$ scan
Absorption correction	Multi-scan	Multi-scan	Numerical (Gaussian)
<i>T</i> <sub>max</sub> , <i>T</i> <sub>min</sub>	1.000, 0.671	1.000, 0.691	0.662, 0.542
No. of measured, independent, observed ( <i>I</i> > 2 $\sigma$ ( <i>I</i> )) reflections	22611, 7365, 6179	30904, 6798, 4654	5666, 2425, 2424
<i>R</i> <sub>int</sub>	0.0315	0.0384	0.0503
$\theta$ <sub>max</sub> /°	27.48	26.37	48.86
Range of <i>h, k, l</i>	-14 ≤ <i>h</i> ≤ 14 -18 ≤ <i>k</i> ≤ 15 -21 ≤ <i>l</i> ≤ 25	-14 ≤ <i>h</i> ≤ 13 -18 ≤ <i>k</i> ≤ 18 -24 ≤ <i>l</i> ≤ 24	-11 ≤ <i>h</i> ≤ 11 -14 ≤ <i>k</i> ≤ 13 -19 ≤ <i>l</i> ≤ 18
[Refinement]			
Refinement on	<i>F</i> <sup>2</sup>	<i>F</i> <sup>2</sup>	<i>F</i> <sup>2</sup>
No. of reflections	7424	6798	2425
No. of parameters	598	578	438
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.018	1.059	1.255
<i>R</i> <sub>1</sub> ( <i>F</i> <sup>2</sup> > 2 $\sigma$ ( <i>F</i> <sup>2</sup> )), <i>wR</i> <sub>2</sub>	0.0335, 0.0913	0.0456, 0.1275	0.1591, 0.3283
( $\Delta$ / $\sigma$ ) <sub>max</sub>	0.002	0.001	0.003
$\Delta\rho$ <sub>max</sub> , $\Delta\rho$ <sub>min</sub> /e Å <sup>-3</sup>	0.30, -0.51	0.19, -0.40	0.13, -0.12

coordinates of hydrogen or deuterium atoms were calculated and only the atomic displacement parameters were refined. In the early stages of the refinement, all hydrogen atoms of the 1-cyanobutyl group were assumed to be disordered with deuterium atoms, i.e., Co–C(H<sub>a</sub>/D<sub>a</sub>)(CN)–C(H<sub>b</sub>/D<sub>b</sub>)(H<sub>c</sub>/D<sub>c</sub>)–C(H<sub>d</sub>/D<sub>d</sub>)(H<sub>e</sub>/D<sub>e</sub>)–C(H<sub>f</sub>/D<sub>f</sub>)<sub>3</sub>, where the subscript a–f means the site occupancy factors, which were refined with restraints such as SOF(H<sub>a</sub>) + SOF(D<sub>a</sub>) = SOF(2). Equivalent positional and isotropic-atomic-displacement parameters were used for H<sub>a</sub> and D<sub>a</sub>, etc. The structure was finally refined using the most favored model, Co–CD(CN)–CH<sub>2</sub>–CH<sub>2</sub>–C(H<sub>2/3</sub>D<sub>1/3</sub>)<sub>3</sub>, where the SOF of hydrogen and deuterium atoms were fixed with 2/3 and 1/3, respectively.

While the site occupancy factor of the disordered 4- and 1-cyanobutyl groups was refined, that of the 3,4-lutidine group was fixed with the value determined by X-rays. The crystal data

and experimental details were also summarized in Table 1.

The crystallographic data have been deposited with Cambridge Crystallographic Data Centre: Deposition numbers CCDC 295996–296000 for crystal **I** at 293, 173, and 93 K, crystal **II**, and crystal **III**, respectively. Copies of the data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html> (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1123 336033; e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)).

## Results and Discussion

**Structure Description before and after Irradiation Based on X-ray Diffraction Analysis.** The molecular and crystal structures of **I** are shown in Figs. 2 and 3, respectively. The 3,4-lutidine ligand is disordered statically about 50:50. One

of the phenyl rings of the diphenylboryl moiety is perpendicular to the dimethylglyoxime plane and looks like a wall in the neighborhood of the 4-cyanobutyl group. Such a conformation of the diphenylboryl is called the “up” form, which is also found in the related complex crystals.<sup>13,26</sup> This perpendicular phenyl ring has a great influence on the size and the shape of the reaction cavity for the reactive 4-cyanobutyl group.

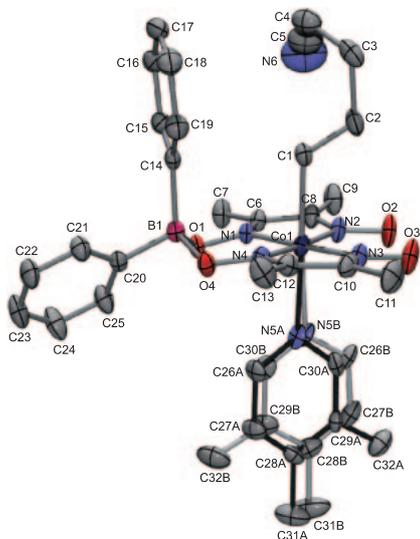


Fig. 2. Molecular structure of **I**. Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for clarity. The disordered 3,4-lutidine groups are illustrated with black (0.482(5)) and white (0.518(5)) bond colors.

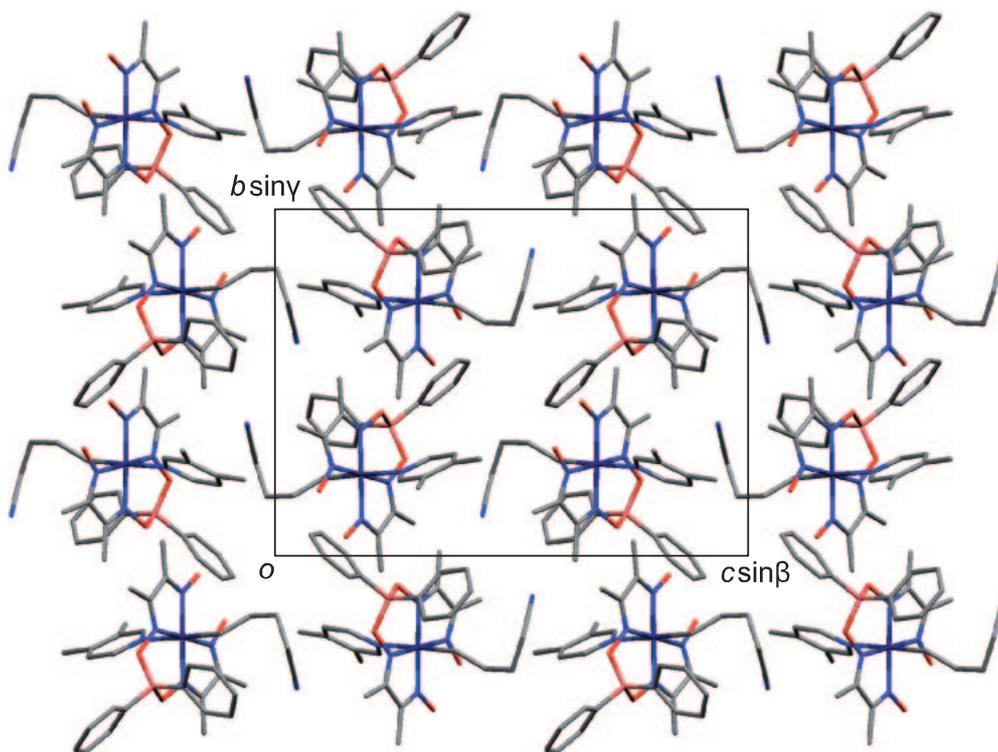


Fig. 3. Crystal structure of **I** viewed along the *a*-axis. Hydrogen atoms and one of the disordered 3,4-lutidine moieties are omitted for clarity.

The torsion angles of the 4-cyanobutyl group, Co1–C1–C2–C3, C1–C2–C3–C4, and C2–C3–C4–C5 are 179.9, –56.4, and –48.4°, respectively. This conformation of *trans-gauche-gauche* is different from those of the other 4-cyanobutyl cobaloxime complexes, which have all *trans* conformations.<sup>10</sup>

The molecular and crystal structures of **II** are shown in Figs. 4 and 5, respectively. The occupancy factor of the photo-produced 1-cyanobutyl group is 0.472(6). This means that

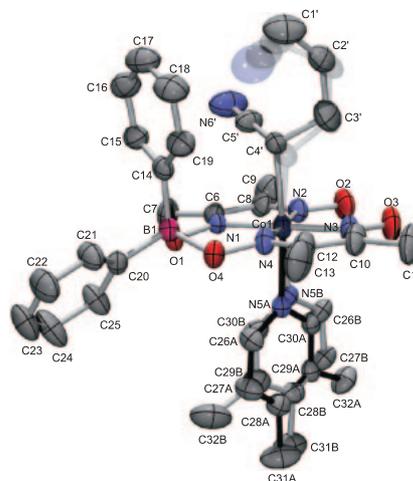


Fig. 4. Molecular structure of **II**. Thermal ellipsoids are drawn at 30% probability level. Hydrogen atoms are omitted for clarity. Transparent group indicates the unreacted 4-cyanobutyl group. The site occupancy factors of the 4- and 1-cyanobutyl groups are 0.528(6) and 0.472(6), respectively.

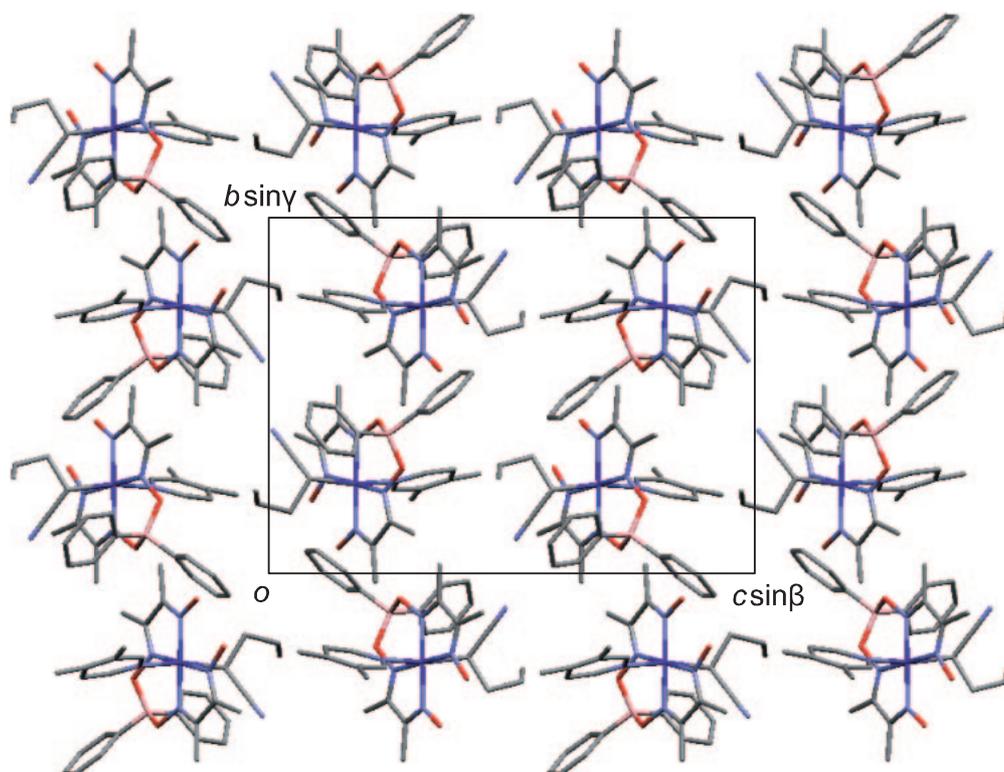


Fig. 5. Crystal structure of **II** viewed along the  $a$ -axis. Hydrogen atoms, one of the disordered 3,4-lutidine moieties, and 4-cyano-butyl groups are omitted for clarity.

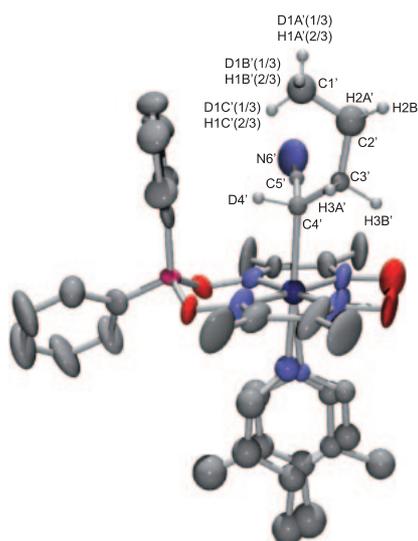


Fig. 6. Molecular structure of **III**. Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for clarity except those of the 1-cyanobutyl group.

about half of the 4-cyanobutyl group was isomerized to the 1-cyanobutyl group. Although the cyano group moves to a large extent in the isomerization, the methylene chain of the butyl group, C1–C2–C3–C4, takes nearly the same position during the photoreaction.

**Structure after Irradiation Based on Neutron Diffraction Analysis.** The photo-produced 1-cyanobutyl group should have two deuterium atoms. In the model described above, Co–C(H<sub>a</sub>/D<sub>a</sub>)(CN)–C(H<sub>b</sub>/D<sub>b</sub>)(H<sub>c</sub>/D<sub>c</sub>)–C(H<sub>d</sub>/D<sub>d</sub>)(H<sub>e</sub>/D<sub>e</sub>)–

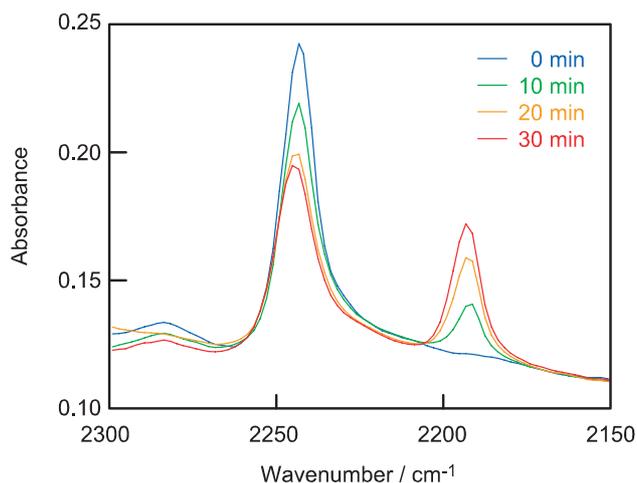
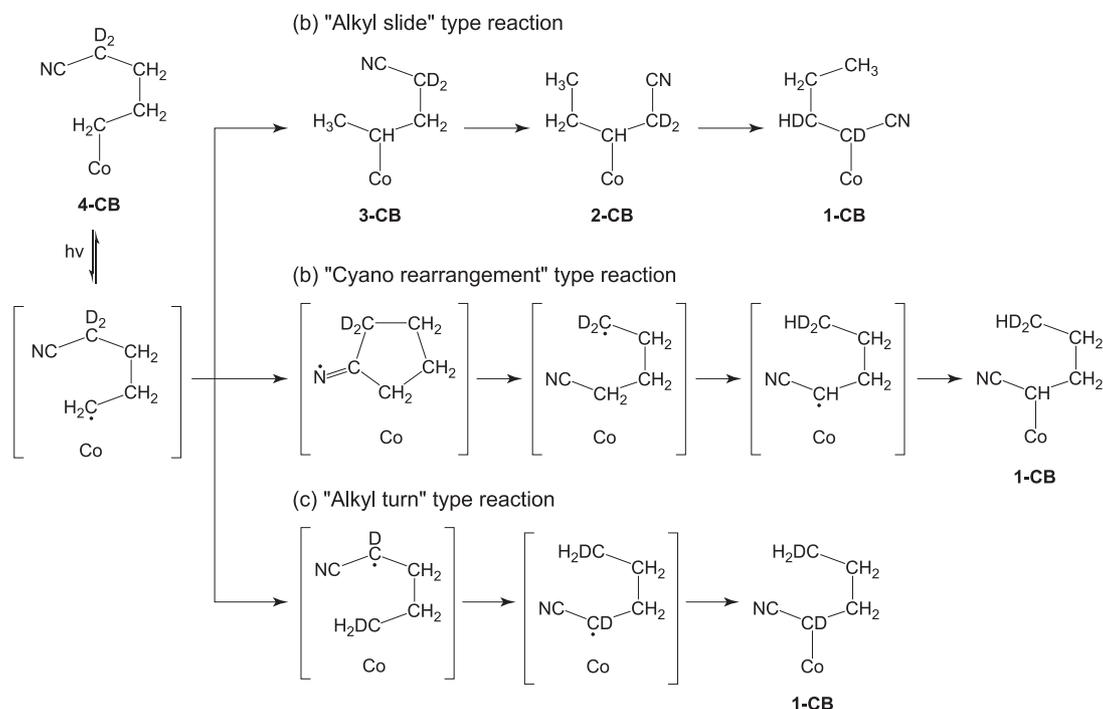


Fig. 7. Change of FT-IR spectra after 0, 10, 20, and 30 min irradiation.

C(H<sub>f</sub>/D<sub>f</sub>)<sub>3</sub>, the resulting SOF of D<sub>a</sub> is 0.453(8), that is 97.2% of SOF(2). On the other hand, the SOFs of D<sub>b</sub>, D<sub>c</sub>, D<sub>d</sub>, and D<sub>e</sub> are approximately 0. Furthermore, there were no significant peaks around the terminal methyl carbon. These results indicate the one deuterium atom, D4', is bound to the C<sup>1</sup> atom (C4') and another is distributed in the terminal methyl hydrogens, D1A', D1B', and D1C', in which the SOF of deuterium atoms was fixed at 1/3 of SOF(2). Figure 6 shows the major part of the molecular structure with the 1-cyanobutyl group.

**FT-IR Spectroscopy.** The IR spectra during the photoreaction are shown in Fig. 7. Only a band located at 2244 cm<sup>-1</sup>

Scheme 5. Three possible mechanism of the 4–1 photoisomerization of a single crystal of **1**.

before irradiation corresponds to the stretching vibration mode of the C≡N bond in the 4-cyanobutyl group. As the intensity decreases, the new band corresponding to the 1-cyanobutyl group appears at 2193 cm<sup>-1</sup> and the intensity increases. No other peaks can be found. This seems to indicate that the 4-cyanobutyl group in the cobaloxime complex **1** is directly isomerized to the 1-cyanobutyl group.

**Reaction Mechanism.** Three reaction processes from the 4-cyanobutyl group to the 1-cyanobutyl group may be possible as shown in Schemes 5a–5c. The first one, 5a, is called “alkyl slide” isomerization. This successive isomerization from the 4-cyanobutyl to 1-cyanobutyl group through the 3- and 2-cyanobutyl groups was observed in the previous isomerization reactions of the cyanoalkyl cobaloxime complexes. Although the 3- and 2-cyanobutyl groups were not observed in the X-ray and IR analyses, the intermediate 3- and 2-cyanobutyl groups may be too unstable to be observed in the measurements. However, if the reaction proceeds by this route, the two deuterium atoms in the 1-cyanobutyl group should be located at the C<sup>1</sup> and C<sup>2</sup> atoms, which are different from the structure obtained by the neutron diffraction.

The second one, 5b, is called “cyano rearrangement” isomerization. This is a direct rearrangement of a cyano group from C<sup>4</sup> to C<sup>1</sup> via a 5-membered ring, which is observed in organic reactions.<sup>27</sup> The photo-produced 4-cyanobutyl radical changes to a 5-membered ring to form a new C–C bond between the C<sup>1</sup> atom and the carbon atom of the cyano group, C<sup>CN</sup>. Then, the C<sup>4</sup> radical produced by the cleavage of the C<sup>4</sup>–C<sup>CN</sup> bond abstracts a hydrogen atom bound to the C<sup>1</sup> atom. Finally, a bond formation of the cobalt atom and C<sup>1</sup> atom follows. This 4–1 isomerization involves no intermediate 3- or 2-cyanobutyl cobaloximes, which is in agreement with the analyses of X-ray diffraction and FT-IR. The distance between the C<sup>1</sup> bound to the cobalt atom and the carbon atom of the cyano

group, 3.41 Å, is slightly longer than the sum of the van der Waals radii. However, the two deuterium atoms in the structure of the 1-cyanobutyl group should be located at the terminal methyl group, the C<sup>4</sup> atom. This is different from the result of the neutron diffraction.

The third one, 5c, is called “alkyl turn” isomerization. This process also involves no intermediate 3- or 2-cyanobutyl groups. The C<sup>1</sup> atom of the photo-produced 4-cyanobutyl radical abstracts one of the deuterium atoms bound to C<sup>4</sup>, then the 4-cyanobutyl radical is turned upside down. Finally, the bond between the cobalt atom and C<sup>1</sup> atom is formed. The distance between the C<sup>1</sup> atom and the deuterium atom is 2.66 Å, which is shorter than the sum of the van der Waals radii. This means that the two deuterium atoms in the structure of the 1-cyanobutyl group should be located at the C<sup>1</sup> and C<sup>4</sup> atoms, which is in good agreement with the observed neutron structure. Since the deuterium atom bonded to the C<sup>1</sup> atom showed 100% occupancy factor, the process of the alkyl turn should be irreversible. These results clearly indicate that the reaction proceeds in “alkyl turn”-type isomerization.

**Reaction Cavity.** The “alkyl turn” isomerization is very favorable in the crystalline-state reaction. In order to discuss the reactivity of the 4-cyanobutyl cobaloxime from the view point of steric repulsion, the reaction cavity for the 4-cyanobutyl group was calculated.<sup>28</sup> Its shape and size are important for the reactivity and selectivity of reaction in the crystalline state.<sup>1,29</sup> The reaction cavity for the 4-cyanobutyl group in the crystal structure before irradiation is shown in Fig. 8. The reaction cavity after irradiation, which includes both of the 4-cyanobutyl and 1-cyanobutyl groups, is shown in Fig. 9. The two cavities are very similar to each other since the reaction proceeds without degradation of the crystallinity. Since the surrounding atoms that make the reaction cavity of the 4-cyanobutyl group are stationary parts of the complex, the reaction

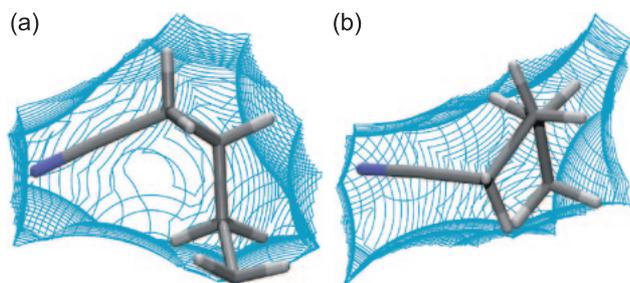


Fig. 8. Reaction cavity for the 4-cyanobutyl group before irradiation, (a) top view and (b) side view.

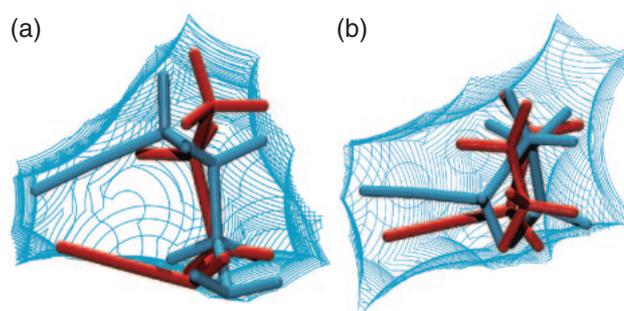


Fig. 9. Reaction cavity for the 4- and 1-cyanobutyl groups after irradiation, (a) top view and (b) side view. Blue and red pipe mean 4- and 1-cyanobutyl groups, respectively.

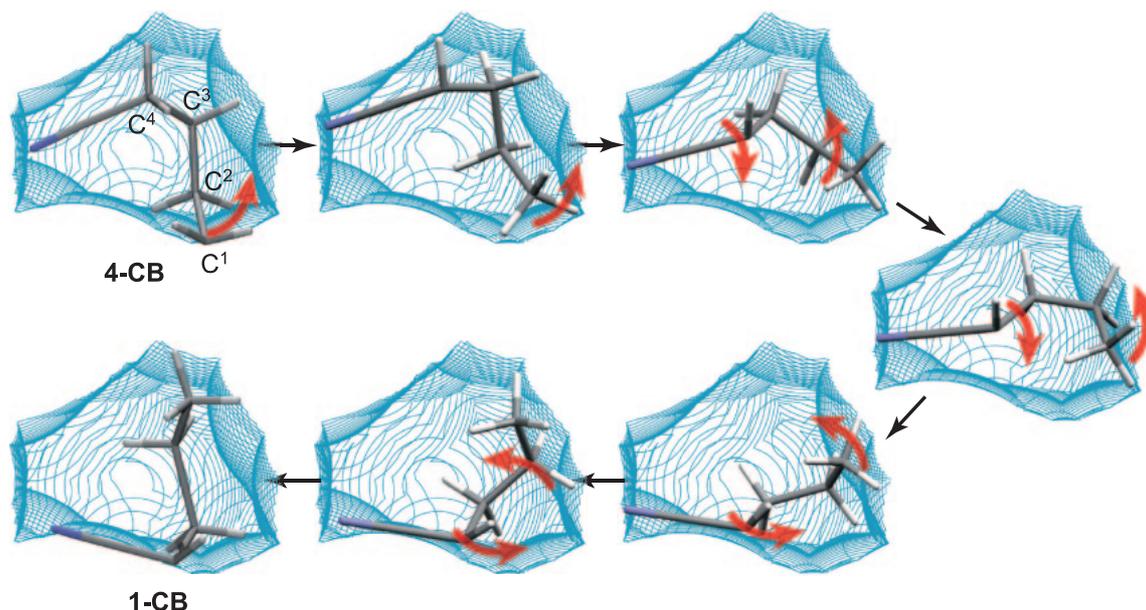


Fig. 10. Plausible motion of the 4-cyanobutyl radical in the original reaction cavity for the 4-cyanobutyl group during the “alkyl turn”-type reaction.

cavity does not change its shape or size during this crystalline-state reaction.

For the “alkyl turn” isomerization, the movement of the intermediate radicals in the reaction cavity of the 4-cyanobutyl group in the original crystal is estimated as shown in Fig. 10. Although the radical carbon at  $C^4$  keeps the  $sp^3$  conformation in the simulation, it does not make any difference in the simulation even if the radical carbon forms a planar conformation. Since the reaction cavity is large in the lateral direction, the long  $-CH_2-C\equiv N$  part of the photo-produced radical can use this space so as to rotate around the  $C^4-C^3$  bond like the pedal motion of a bicycle. Therefore, this reaction can proceed without destruction of the single-crystal form.

For the other two processes, the intermediate radicals suffer from strong steric repulsion in the cavity. This is the reason why the “alkyl-turn” isomerization proceeds in the cobaloxime complexes with 3,4-lutidine as an axial base ligand. Recently, the 4-cyanobutyl cobaloxime complexes with pyridine, 4-isopropylpyridine, and 4-ethylpyridine as axial base ligands were prepared. The preliminary experiments showed that the pyridine complex can be isomerized to the 1-cyanobutyl

group. However, the other two were not isomerized to the 1-cyanobutyl group. These results may be caused by the size and shape of the reaction cavity for the 4-cyanobutyl group in the original crystals.

### Conclusion

From the single-crystal X-ray analysis and FT-IR spectroscopy, the 4-cyanobutyl group of the 4-CB-Co(dmgh)-(dmgBPh<sub>2</sub>)-3,4-Lu was found to be isomerized to the 1-cyanobutyl group with retention of the single-crystal form and three processes of photoisomerization were assumed. Replacing the hydrogen atoms of the 4-cyanobutyl group with deuterium atoms in the complex crystal, the structure analysis of the photo-irradiated crystal by neutron diffraction revealed that the isomerization from the 4- to 1-cyanobutyl group proceeded in the “alkyl turn” route. The size and shape of the reaction cavity for the cyanobutyl group clearly suggest that the route is favorable with retention of the single-crystal form.

One of authors (T. H.) was supported by a Grant-in-Aid for JSPS (Japan Society for the Promotion of Science) Fellows.

## References

- 1 Y. Ohashi, *Acc. Chem. Res.* **1988**, *21*, 268.
- 2 Y. Ohgo, Y. Ohashi, W. T. Klooster, T. F. Koetzle, *Chem. Lett.* **1996**, 445.
- 3 Y. Ohgo, Y. Ohashi, W. T. Klooster, T. F. Koetzle, *Chem. Lett.* **1996**, 579.
- 4 Y. Ohgo, Y. Ohashi, W. T. Klooster, T. F. Koetzle, *Enantiomer* **1997**, *2*, 241.
- 5 T. Ohhara, J. Harada, Y. Ohashi, I. Tanaka, S. Kumazawa, N. Niimura, *Acta Crystallogr., Sect. B* **2000**, *56*, 245.
- 6 T. Ohhara, H. Uekusa, Y. Ohashi, I. Tanaka, S. Kumazawa, N. Niimura, *Acta Crystallogr., Sect. B* **2001**, *57*, 551.
- 7 T. Ohhara, S. Ikeda, H. Imura, H. Uekusa, Y. Ohashi, I. Tanaka, N. Niimura, *J. Am. Chem. Soc.* **2002**, *124*, 14736.
- 8 T. Hosoya, H. Uekusa, Y. Ohashi, T. Ohhara, H. Kimura, Y. Noda, *Chem. Lett.* **2003**, *32*, 742.
- 9 T. Hosoya, H. Uekusa, Y. Ohashi, T. Ohhara, I. Tanaka, N. Niimura, *Acta Crystallogr., Sect. B* **2006**, *62*, 153.
- 10 C. Vithana, H. Uekusa, Y. Ohashi, *Bull. Chem. Soc. Jpn.* **2001**, *74*, 287.
- 11 R. L. Letsinger, I. Skoog, *J. Am. Chem. Soc.* **1955**, *77*, 2491.
- 12 Y. Ohgo, S. Takeuchi, *J. Chem. Soc., Chem. Commun.* **1985**, 21.
- 13 R. Dreos, G. Tauzher, S. Vuano, F. Asaro, G. Pellizer, G. Nardin, L. Randaccio, S. Geremia, *J. Organomet. Chem.* **1995**, *505*, 135.
- 14 K. Ikeda, W. Liu, Y. R. Shen, H. Uekusa, Y. Ohashi, S. Koshihara, *J. Chem. Phys.* **2005**, *122*, 141103.
- 15 Burker, *SMART and SAINT: Software Reference Manual*, Burker AXS Inc., Madison, Wisconsin, U.S.A., **2000**.
- 16 M. G. Sheldrick, *SADABS Ver. 2, Systematic Error Correction Program*, University of Göttingen, Germany, **2001**.
- 17 M. C. Burla, M. Camalli, B. Carrozzini, G. L. Cascarano, C. Giacovazzo, G. Polidori, R. Spagna, *J. Appl. Crystallogr.* **2003**, *36*, 1103.
- 18 M. G. Sheldrick, *SHELXL-97, Program for the Refinement of Crystal Structures*, University of Göttingen, Germany, **1997**.
- 19 I. Tanaka, K. Kurihara, T. Chatake, N. Niimura, *J. Phys. Soc. Jpn., Suppl. A* **2001**, *70*, 459.
- 20 I. Tanaka, K. Kurihara, T. Chatake, N. Niimura, *J. Appl. Crystallogr.* **2002**, *35*, 34.
- 21 N. Niimura, Y. Karasawa, I. Tanaka, J. Miyahara, K. Takahashi, H. Saito, S. Koizumi, M. Hidaka, *Nucl. Instrum. Methods Phys. Res., Sect. A* **1994**, *349*, 521.
- 22 Y. Haga, S. Kumazawa, N. Niimura, *J. Appl. Crystallogr.* **1999**, *32*, 878.
- 23 Z. Otwinowski, W. Minor, Processing of X-ray Diffraction Data Collected in Oscillation Mode, *Methods in Enzymology*, ed. by C. W. Carter, Jr., R. M. Sweet, Academic Press, **1997**, Vol. 276, Part A, pp. 307–326.
- 24 P. Coppens, Absorption Correction Based on Face Indexing and Integration on a Gaussian Grid, *Crystallographic Computing*, **1970**, p. 255.
- 25 A. L. Spek, *J. Appl. Crystallogr.* **2003**, *36*, 7.
- 26 F. Asaro, R. Dreos, S. Geremia, G. Nardin, G. Pellizer, L. Randaccio, G. Tauzher, S. Vuano, *J. Organomet. Chem.* **1997**, *548*, 211.
- 27 A. Bury, P. Bougeard, S. J. Corker, M. D. Johnson, M. Perlmann, *J. Chem. Soc., Perkin Trans. 2* **1982**, 1367.
- 28 Y. Ohashi, K. Yanagi, T. Kurihara, Y. Sasada, Y. Ohgo, *J. Am. Chem. Soc.* **1981**, *103*, 5805.
- 29 T. Nemoto, Y. Ohashi, *Bull. Chem. Soc. Jpn.* **1999**, *72*, 1971.