

Direct observation of deuterium migration in crystalline-state reaction by single-crystal neutron diffraction. II. 3–1 Photoisomerization of a cobaloxime complex

Takashi Ohhara,^a Jun Harada,^{a,b}
Yuji Ohashi,^{a*} Ichiro Tanaka,^c
Shintaro Kumazawa^c and Nobuo
Niimura^c

^aDepartment of Chemistry and Materials Science, Tokyo Institute of Technology, Okayama, Meguro-ku, Tokyo 152-8551, Japan, ^bCREST Fellow, Japan Science and Technology Corporation, Kawaguchi, Saitama 332-0012, Japan, and ^cAdvanced Science Research Center, Japan Atomic Energy Research Institute (JAERI), Tokai, Ibaraki 319-1195, Japan

Correspondence e-mail:
yohashi@chem.titech.ac.jp

Received 25 June 1999
Accepted 17 September 1999

Single crystal neutron diffraction analysis of photo-exposed (3-cyanopropyl- $d_2^{\alpha,\alpha}$)-[(*R*)-1-phenylethylamine- d_{11}]bis(dimethylglyoximate- d_{14})cobalt(III) was carried out in order to clarify the mechanism of the crystalline-state photoisomerization of the 3-cyanopropyl group bonded to the Co atom in some cobaloxime complexes. Before irradiation the two H atoms bonded to the C¹ atom of the 3-cyanopropyl group were exchanged with the D atoms such as $-\text{CH}_2\text{CH}_2\text{CD}_2\text{CN}$. On exposure to a xenon lamp, the cell dimensions of the crystal were gradually changed. After 7 d exposure the change became insignificantly small. The structure was analyzed by neutron diffraction. The 3-cyanopropyl group was transformed to the 1-cyanopropyl group such as $-\text{CD}(\text{CN})\text{C}(\text{H}_{1/2}, \text{D}_{1/2})_2\text{CH}_3$ with retention of the single-crystal form. This indicates that one of the D atoms bonded to C¹ migrates to either position bonded to C². The other atoms of the complex remained unchanged. These results indicate that photoisomerization proceeded in two steps: the 3-cyanopropyl group was isomerized to the 2-cyanopropyl group in the first place and then the 2-cyanopropyl group was transformed to the 1-cyanopropyl group. Moreover, it was made clear that the second-step isomerization was irreversible, since one of the D atoms was retained. The disordered structure at C² is estimated to be caused by the interconversion between the 1-cyanopropyl group produced and its dehydrogenated olefin after the photoisomerization.

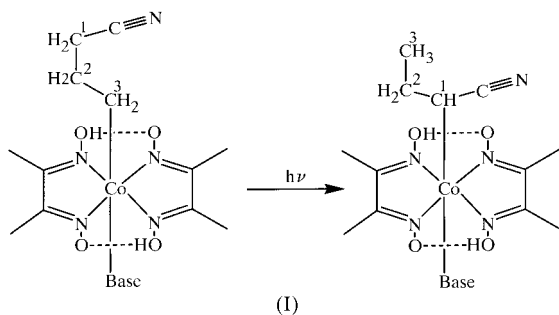
1. Introduction

Since the photoracemization of a cobaloxime complex was found to proceed with retention of the single crystal form (Ohashi & Sasada, 1977), such crystalline-state reactions have been highly regarded because their reaction processes at the initial, intermediate and final stages have been analyzed by single-crystal X-ray diffraction. Several reactive groups such as 1-cyanoethyl (Ohashi, 1988), 1-methoxycarbonyl ethyl (Sekine, Saitoh *et al.*, 1998), 1,2-bis(methoxycarbonyl)ethyl (Ohashi *et al.*, 1995) and 1,2-bis(ethoxycarbonyl)ethyl (Sato & Ohashi, 1999) bonded to the Co atoms in some cobaloxime complexes have been found to be racemized on exposure to a xenon lamp without destroying the single-crystal form. Moreover, the 2-cyanoethyl group bonded to the Co atom in some cobaloxime complex crystals was found to be isomerized to the 1-cyanoethyl group with retention of the single-crystal form by irradiation with the xenon lamp (Sekine *et al.*, 1997*a,b*). The rate and selectivity of the reactions have been explained on the basis of the crystal structure, *i.e.* the reaction cavity (Ohashi *et al.*, 1981). However, the reaction mechanisms of Co–C bond cleavage by photo-irradiation, the rotation or

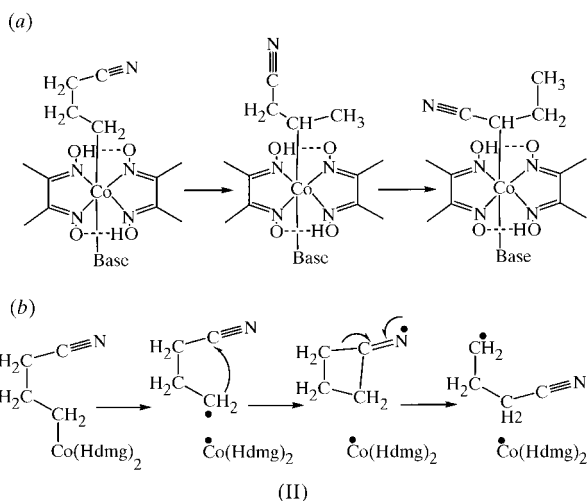
translation of the alkyl radical produced and the recombination of the Co—C bond in the process of racemization or isomerization have been obscure.

The single-crystal neutron diffraction analysis, on the other hand, can distinguish the H atom from the D atom, because the H atom has negative neutron scattering length, while the D atom has a positive one (Koester, 1977). This suggests that if the H atoms in specific positions of the reactive group are exchanged with the D atom and the crystallinity was kept in the reaction, the reaction process will be made clear since the migration of the D atom, *i.e.* the hydrogen-transfer process, is easily observed by neutron diffraction analysis. In the previous paper the racemization process of the 1-cyanoethyl group was analyzed by neutron diffraction and successfully elucidated (Ohgo *et al.*, 1997, part I of this series; Ohhara *et al.*, 1998).

Recently, a novel solid-state reaction, 3–1 photoisomerization, of the 3-cyanopropyl group bonded to the Co atom in



some cobaloxime complex crystals was found by Ohgo and co-workers [Kurashima *et al.*, 1995; (I)]. When (*R*)-1-phenylethylamine was used as an axial base ligand (1*a*), the isomerization proceeded with retention of the single-crystal form (Sekine, Yoshiike *et al.*, 1998). The structures which were analyzed by X-rays before and after irradiation (Fig. 1) suggest two possible mechanisms. One is the two-step



isomerization as shown in (II*a*). This scheme may require a large amount of atomic motion of the 3-cyanopropyl group in the crystal lattice and it seemed difficult to retain the single-crystal form. Another mechanism is the direct translation of the cyano group (Bury *et al.*, 1982), as shown in (II*b*). It is

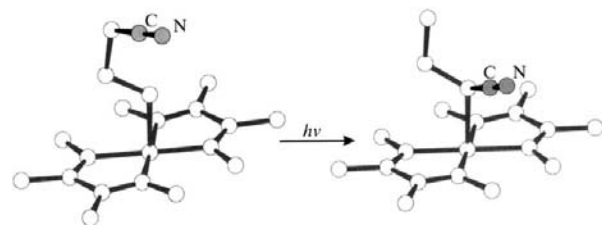


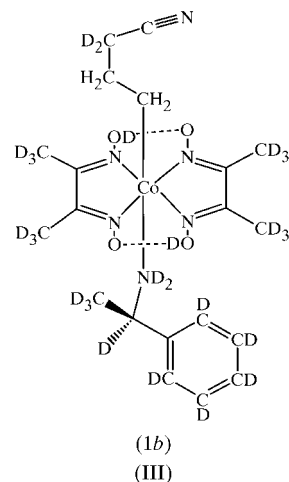
Figure 1

Structural change in the 3-cyanopropyl group on exposure to a xenon lamp.

impossible to distinguish the two mechanisms only by the X-ray crystal structure analyses before and after the reaction.

In order to clarify the mechanism, we intended to analyze the structures before and after reaction by neutron diffraction in addition to X-ray diffraction, since the hydrogen migrates to the neighboring C atoms during the process of the reaction. Although the single-crystal neutron diffraction technique is a powerful method to analyze the mechanism of hydrogen migration, several difficulties should be overcome. In the first place, a considerably large ($\sim 8 \text{ mm}^3$) single crystal is necessary for neutron diffraction. Next, the visible light should penetrate into such a large crystal and the photoreaction should occur inside the crystal without deteriorating the crystallinity. More than 20 complexes were prepared changing the axial base ligand and the crystals were exposed to the xenon lamp. It was found after many trials that the crystals of the complex with (*R*)-1-phenylethylamine as an axial base ligand were large enough for neutron diffraction and that the photoisomerization proceeded $\sim 90\%$ without deteriorating the crystallinity in a large enough crystal for neutron diffraction.

In order to obtain the precise intensity data by neutron diffraction, however, the number of H atoms should be decreased since the H-atom incoherent scattering increases the background of the Bragg reflection. For the analysis of the disordered structure, data collection with precise intensity measurements is essential. All the H atoms of the equatorial ligands, bis(dimethylglyoximate) moiety, and the axial base ligand, (*R*)-1-phenylethylamine, were replaced with D atoms (III). For the 3-cyanopropyl group, two H atoms bonded to the

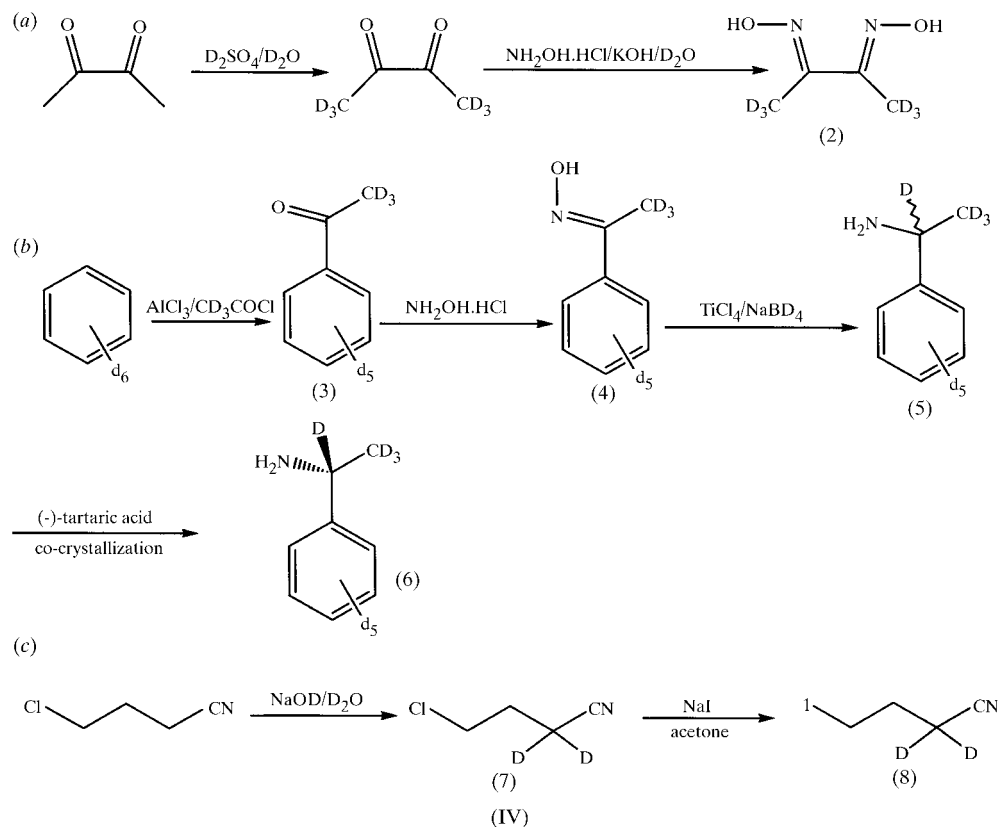


C^1 atom neighboring the cyano group were replaced with D atoms. At least one of the D atoms should migrate to the other C atoms, since the C^1 atom of the 3-cyanopropyl group bonds with the Co atom after irradiation. This paper reports the structural change during photoisomerization and proposes the mechanism of the isomerization.

2. Experimental

2.1. Preparation of complexes

2.1.1. (3-Cyanopropyl- $d_2^{\alpha,\alpha}$)[(R)-1-phenylethylamine- d_{11}]cobaloxime- d_{14} (1b). Compound (1b) was prepared from $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, dimethylglyoxime- d_6 (2), (R)-1-phenylethylamine- d_{11} (3) and 3-iodobutyronitrile- $d_2^{\alpha,\alpha}$ (4) using a method similar to that reported by Ohgo & Takeuchi (1985). To the mixture of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (3.57 g, 15 mmol) and (2) (3.66 g, 30 mmol) dissolved in 30 ml of methanol was added NaOH (1.2 g, 15 mmol) dissolved in 5 ml of water under an Ar atmosphere with stirring. Pyridine (1.21 ml, 15 mmol), (4) (2.95 g, 15 mmol) and 0.57 g of NaBH_4 dissolved in 5 ml of water were then added successively, and the mixture was stirred for 20 min. The addition of 100 ml of water and filtration afforded 3.15 g of (3-cyanopropyl- $d_2^{\alpha,\alpha}$)(pyridine)cobaloxime- d_{14} . This cobaloxime complex was then dissolved in 30 ml of MeOD and the mixture was stirred with 10 g of Dowex 50-80X (50–100 mesh, H form) and 5 ml of D_2O overnight. To the filtrate was added equimolar (3) and the mixture was evaporated to afford powder of (1b) (3.34 g, yield 95.0%). The starting materials, (2), (3) and (4), were prepared as shown in (IV). The details are given below.



2.1.2. Dimethylglyoxime- d_7 (2). Compound (2) was prepared according to the reported method (Arduengo III *et al.*, 1994; Zav'yalov & Ezhova, 1984), as shown in (IVa). The methyl H atoms of butane-2,3-dione were exchanged with deuterium using D_2O and D_2SO_4 catalysts 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 368 K for 12 h. The butane-2,3-dione was isolated by distillation under atmospheric pressure at 351–353 K 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 butane-2,3-dione- d_6 produced 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 butane-2,3-dione- d_6 (17.67 g) prepared was refluxed with $\text{HCl} \cdot \text{H}_2\text{NOH}$ (142.1 g), KOH (85% pure, 93.7 g) and D_2O (400 ml) at 368–373 K for 90 min. The white precipitate of (2) was filtered and washed with $\text{NaHCO}_3(\text{aq.})$ and water. The yield was 18.4 g of 98.5 atom %D.

2.1.3. Acetophenone- d_8 (3). Compound (3) was prepared according to the usual Friedel–Crafts reaction (Mross & Zundel, 1968) between benzene- d_6 (Aldrich, 99.6 atom %D) and acetyl chloride- d_3 (Aldrich, >99 atom %D).

2.1.4. Acetophenone oxime- d_8 (4). To a solution of hydroxylamine hydrochloride (39.66 g, 0.57 mol) and potassium hydroxide (25.7 g, 0.46 mol) in D_2O (190 ml) was added acetophenone- d_8 (14.13 g, 0.11 mol). The mixture was heated at 363–373 K for 3.5 h and then cooled to room temperature.

The aqueous solution was extracted with dichloromethane. The organic layer was washed with aqueous sodium bicarbonate and then with water. The organic layer was then dried over Na_2SO_4 and the solvent was removed to yield acetophenone oxime- d_8 as a white solid (14.92 g, 95%).

2.1.5. 1-Phenylethylamine- d_9 (5). Compound (5) was prepared according to the method reported (Kano *et al.*, 1980), under an Ar atmosphere. To an ice-cooled stirred mixture of titanium(IV) chloride (13 ml, 0.12 mol), sodium borodeuteride (9.90 g, 0.24 mol; Aldrich, 98 atom %D) and anhydrous 1,2-dimethoxyethane (220 ml) was added dropwise a solution of acetophenone oxime- d_8 (8.00 g, 0.05586 mol) in anhydrous 1,2-dimethoxyethane (50 ml). The mixture was stirred for 14 h at room temperature

Table 1

Experimental details.

	X-ray: initial structure	X-ray: irradiated structure	Neutron: irradiated structure
Crystal data			
Chemical formula	[Co(C ₄ D ₇ N ₂ O ₂) ₂ - (C ₄ H ₄ D ₂ N)(C ₈ D ₁₁ N)]	[Co(C ₄ D ₇ N ₂ O ₂) ₂ - (C ₄ H ₄ D ₂ N)(C ₈ D ₁₁ N)]	[Co(C ₄ D ₇ N ₂ O ₂) ₂ - (C ₄ H ₄ D ₂ N)(C ₈ D ₁₁ N)]
Chemical formula weight	504	504	504
Cell setting	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁	<i>P</i> 2 ₁	<i>P</i> 2 ₁
<i>a</i> (Å)	9.6772 (1)	9.1579 (1)	9.1579 (1)
<i>b</i> (Å)	13.8988 (2)	13.9694 (2)	13.9694 (2)
<i>c</i> (Å)	8.9432 (1)	9.2757 (1)	9.2757 (1)
β (°)	96.322 (1)	99.954 (1)	99.954 (1)
<i>V</i> (Å ³)	1195.56 (3)	1168.78 (2)	1168.78 (2)
<i>Z</i>	2	2	2
<i>D_x</i> (Mg m ⁻³)	1.329	1.359	1.359
Radiation type	Mo <i>K</i> α	Mo <i>K</i> α	Neutron
Wavelength (Å)	0.71073	0.71073	1.060
No. of reflections for cell parameters	512	512	—
θ range (°)	3–30	2–30	—
μ (mm ⁻¹)	0.754	0.771	0.132
<i>F</i> (000)	504	504	504
Temperature (K)	293 (2)	293 (2)	293 (2)
Crystal form	Plate	Plate	Plate
Crystal size (mm)	0.4 × 0.3 × 0.15	0.5 × 0.3 × 0.1	3.5 × 3.5 × 0.7
Crystal color	Red	Red	Red
Data collection			
Diffractometer	Siemens SMART CCD	Siemens SMART CCD	BIX-I
Data collection method	ω scan	ω scan	ω scan
Absorption correction	Empirical (<i>SADABS</i> ; (Sheldrick, 1996)	Empirical (<i>SADABS</i> ; (Sheldrick, 1996)	None
<i>T</i> _{min}	0.696	0.461	—
<i>T</i> _{max}	0.801	0.753	—
No. of measured reflections	14 136	10 177	2540
No. of independent reflections	7077	6655	1509
No. of observed reflections	6573	5273	1497
Criterion for observed reflections	<i>I</i> > 2 σ (<i>I</i>)	<i>I</i> > 2 σ (<i>I</i>)	<i>I</i> > 2 σ (<i>I</i>)
<i>R</i> _{int}	0.0146	0.0407	0.0676
θ _{max}	30.52	30.75	43.37
Range of <i>h</i> , <i>k</i> , <i>l</i>	–13 → <i>h</i> → 13 –19 → <i>k</i> → 19 –12 → <i>l</i> → 12	–12 → <i>h</i> → 13 –19 → <i>k</i> → 18 –13 → <i>l</i> → 7	–11 → <i>h</i> → 9 –14 → <i>k</i> → 1 –11 → <i>l</i> → 10
Refinement			
Refinement on	<i>F</i> ²	<i>F</i> ²	<i>F</i> ²
<i>R</i> (<i>F</i>) [<i>F</i> ² > 2 σ (<i>F</i> ²)]	0.0262	0.0471	0.1065
<i>wR</i> (<i>F</i> ²) [all reflections]	0.0701	0.1177	0.2853
<i>S</i>	1.007	1.072	1.107
No. of reflections used in refinement	7077	6655	1509
No. of parameters used	341	281	422
H-atom treatment	Mixture of independent and constrained refinement	Mixture of independent and riding model	All H- and D-atom parameters refined
Weighting scheme	$w = 1/[\sigma^2(F_o^2 + (0.0505P)^2)]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2 + (0.0501P)^2)]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2 + (0.2366P)^2 + 0.144P)]$, where $P = (F_o^2 + 2F_c^2)/3$
(Δ/σ) _{max}	0.001	–0.004	–0.024
$\Delta\rho$ _{max} (e Å ⁻³)	0.273	0.842	0.146
$\Delta\rho$ _{min} (e Å ⁻³)	–0.240	–1.189	–0.109
Extinction method	None	None	None
Source of atomic scattering factors	<i>International Tables for Crystallography</i> (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)	<i>International Tables for Crystallography</i> (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)	<i>International Tables for Crystallography</i> (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
Computer programs			
Data collection	<i>SMART</i> (Siemens, 1995)	<i>SMART</i> (Siemens, 1995)	Local program
Cell refinement	<i>SMART</i> (Siemens, 1995)	<i>SMART</i> (Siemens, 1995)	Local program
Data reduction	<i>SAINT</i> (Siemens, 1995)	<i>SAINT</i> (Siemens, 1995)	Local program
Structure solution	<i>SIR97</i> (Altomare <i>et al.</i> , 1999)	<i>SIR97</i> (Altomare <i>et al.</i> , 1999)	Initial structure determined by X-rays
Structure refinement	<i>SHELXL97</i> (Sheldrick, 1997)	<i>SHELXL97</i> (Sheldrick, 1997)	<i>SHELXL93</i> (Sheldrick, 1993)

and then the reaction was quenched by the addition of water with ice-cooling. After basification with 28% aqueous ammonia, the reaction mixture was filtered through Celite with suction and washed with ether. After removal of the organic solvent from the filtrate, dichloromethane was added to the residue. The organic layer was separated and the water layer was extracted with dichloromethane. The combined extract was washed with saturated aqueous sodium chloride and dried over Na_2SO_4 . Removal of the solvent yielded 1-phenylethylamine- d_9 as a colorless liquid (6.32 g, 87%).

2.1.6. (*R*)-1-Phenylethylamine- d_9 (6). Optical resolution of the 1-phenylethylamine- d_9 was carried out according to the published procedure (Theilacker & Winkler, 1954).

2.1.7. 4-Chlorobutyronitrile-2,2- d_2 (7). To a mixture of 4-chlorobutyronitrile (20.14 g, 0.19 mol) and D_2O (120 ml; Aldrich, 99.9 atom %D) was added a D_2O solution of NaOD (40 wt %, 2.0 ml; Aldrich, 99.9 atom %D). The mixture was vigorously stirred under reflux for 2 h and then cooled to room temperature. The aqueous mixture was extracted with dichloromethane. The extract was concentrated and to the residue was added D_2O (120 ml) and a D_2O solution of NaOD (40 wt %, 2.0 ml). The mixture was vigorously stirred under reflux for 2 h and then cooled to room temperature. The aqueous mixture was extracted with dichloromethane. Removal of the solvent yielded 4-chlorobutyronitrile-2,2- d_2 (>99 atom %D) as a yellow liquid (13.39 g, 65%).

2.1.8. 4-Iodobutyronitrile- $d_2^{\alpha,\alpha}$ (8). Compound (8) was prepared according to the reported method (Edwards III & Glenn, 1976). To a powder of sodium iodide (38.0 g, 0.25 mol) was added acetone (115 ml) at 273–278 K with stirring. To the mixture was added 4-chlorobutyronitrile- $d_2^{\alpha,\alpha}$ (13.39 g, 0.13 mol) at room temperature. The mixture was heated under reflux for 48 h and then cooled to room temperature. After removal of the solvent, dichloromethane and water were added to the residue. The organic layer was separated and the water layer was extracted with dichloromethane. The combined organic layer was dried over MgSO_4 and the solvent was removed. The residue was distilled under reduced pres-

sure (354 K, 5 mmHg) to yield 4-iodobutyronitrile- $d_2^{\alpha,\alpha}$ as a pale yellow liquid (18.96 g, 76%).

2.2. Recrystallization of (1b) and exposure to visible light

Compound (1b) (1.4 g) was solved in a mixed solution of MeOD (19 ml) and D_2O (30 ml) and left for 2 weeks at room temperature. Then large crystals ($\sim 3.5 \times 3.5 \times 0.7$ mm), large enough for single-crystal neutron diffraction, were obtained. Some of the large crystals with analogous size and morphology were irradiated with a Xe lamp (USHIO SUPER BRIGHT 152S) for 7 d.

2.3. Determination of the crystal structure by X-rays before and after irradiation

A crystal of (1b) before irradiation was mounted on a Siemens Smart CCD diffractometer and the three-dimensional intensity data were collected using monochromated Mo $K\alpha$ radiation. A small size crystal cut from the irradiated large crystal was mounted on a Siemens Smart CCD diffractometer. The intensity measurement was carried out in the same way as that before irradiation. The crystal structures before and after irradiation were refined with the program *SHELXL97* (Sheldrick, 1997). The crystal data and measurement conditions are shown in Table 1.¹

2.4. Single-crystal neutron diffraction measurement

One of the irradiated crystals, $3.5 \times 3.5 \times 0.7$ mm, was fixed on an aluminium pin by halocarbon grease (MOLYKOTE HP-300 grease) and the pin was mounted on the BIX-I neutron diffractometer set up at the JRR-3M reactor at the Japanese Atomic Energy Research Institute (JAERI). The diffractometer has a three-axes goniometer and two conventional gas-filled proportional area detectors which are two-dimensionally movable (active area 25×25 cm; pixel size 2×2 mm; solid angle 24° in one side; Niimura, Tanaka, Minezaki *et al.*, 1995). The neutron beam, monochromated by a bent Si perfect crystal (Niimura, Tanaka, Karasawa & Minakawa, 1995), has a wavelength of 1.06 Å. The intensity data were collected at 16 area-detector positions by a ω step-scan method (0.2° per step) at room temperature. The maximum and minimum d -spacing values were 9.12 and 0.77 Å, respectively. A total of 1509 independent reflections were observed. Cell parameters were fixed to the values determined by X-rays and the U matrix was refined for each area-detector position by using some intense reflections [$I > 10\sigma(I)$]. The reflection peaks were picked up with the threshold $I > 5\sigma(I)$ by the *PKSK* program (local program for BIX-I) and were integrated by the *INTX* program (local program). The Lorentz correction was carried out and then the data were modified to *SHELXL* format.

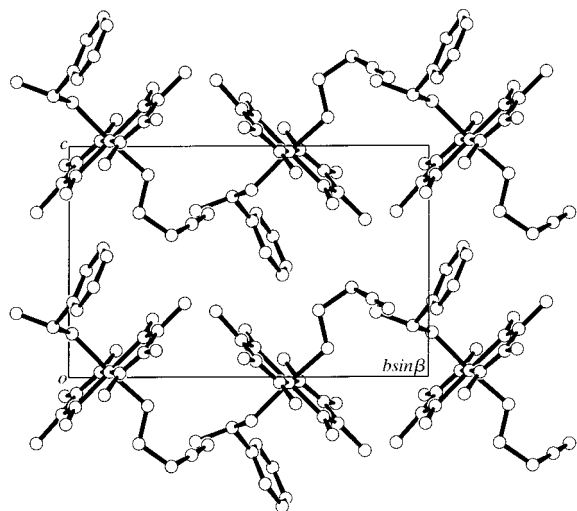


Figure 2
Crystal structure of (1b) before irradiation, viewed along the a axis.

¹Supplementary data for this paper are available from the IUCr electronic archives (Reference: SE0292). Services for accessing these data are described at the back of the journal.

2.5. Structure refinement by neutron diffraction data

Refinement of the structure was carried out with the program *SHELXL93* (Sheldrick, 1993). The positional parameters of non-H and non-D atoms, except those of the original 3-cyanopropyl and 1-cyanopropyl groups produced, were fixed to those obtained by X-ray analysis. The positional parameters of the H and D atoms of the 3-cyanopropyl and 1-cyanopropyl groups, the displacement parameters of all the atoms and the occupancy factors of the disordered groups were refined. The displacement parameters of the ordered atoms were refined anisotropically and those for the disordered atoms were performed isotropically. The D atoms between O...O in the cobaloxime plane were not assigned probably because the

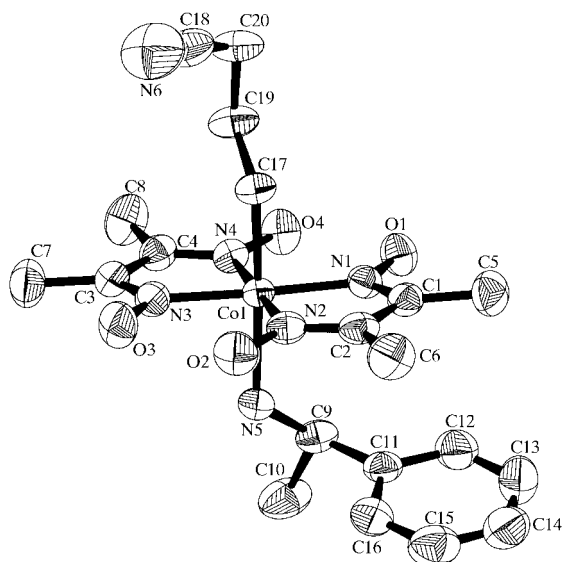


Figure 3
Molecular structure of (1b) before irradiation with atomic numbering. The thermal ellipsoids are drawn at the 50% probability level.

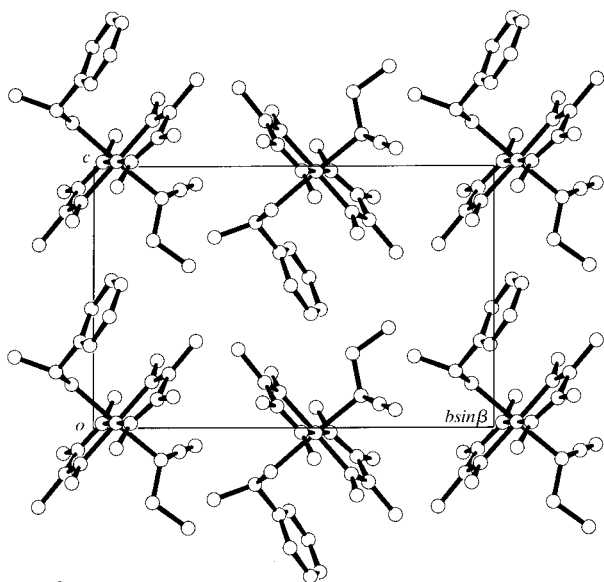


Figure 4
Crystal structure of (1b) after 7 d irradiation, viewed along the *a* axis. Only the (*S*)-1-cyanopropyl group among the disordered groups is shown for clarity.

imperfect H–D exchange cancelled the positive or negative peaks. The details of the refinement are given in Table 1.

3. Description of the structures

3.1. X-ray analyses before and after irradiation

Fig. 2 shows the crystal structure viewed along the *a* axis before irradiation, which is determined by X-rays. The molecules are arranged as a ribbon along the 2_1 axis (*b* axis). The molecular structure with the numbering of the atoms is shown in Fig. 3. The crystal was irradiated with the xenon lamp for 7 d. The cell dimensions changed with retention of the single-crystal form, as given in Table 1. The crystal structure determined by X-rays is shown in Fig. 4. Although the structures of the equatorial ligands and axial base ligand are approximately the same as those before irradiation, most of the 3-cyanopropyl groups were transformed to the (*S*)-1-cyanopropyl group. The other residual peaks were assigned to the (*R*)-1-cyanopropyl group and the original 3-cyanopropyl group. The occupancy factors of (*S*)- and (*R*)-1-cyanopropyl and 3-cyanopropyl groups are 0.83, 0.06, and 0.11, respectively. The molecular structure with the (*S*)-1-cyanopropyl group is shown in Fig. 5. The structures of the minor parts, (*R*)-1-cyanopropyl and 3-cyanopropyl groups, are shown in Figs. 6(*a*) and (*b*), respectively.

3.2. Structure after irradiation by neutron diffraction

Fig. 7 shows the major part of the molecule structure with the (*S*)-1-cyanopropyl group. The (*S*)-1-cyanopropyl group produced has a D atom bonded to the C¹ atom, D17, and another D atom bonded to the C² atom, D19A and D19B, disordered. The ratio of D/H at D17 is 100%, whereas the D/H ratios at D19A and D19B are 0.5. In addition, since the occupancy factors of all D atoms of the axial amine are almost

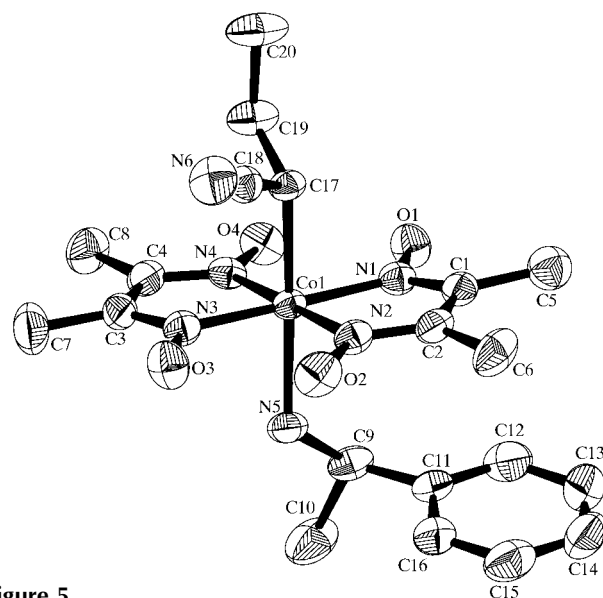
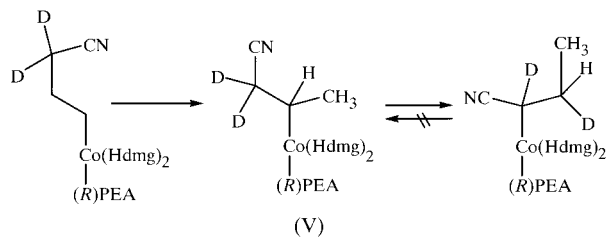


Figure 5
Molecular structure of the (*S*)-1-cyanopropyl group produced, with atom numbering. The thermal ellipsoids are drawn at the 50% probability level.

100%, there is no intermolecular H/D exchange between the 3-cyanopropyl group and the neighboring axial amine ligand. These results clearly indicate that the reaction proceeds in two



steps, 3–2 and 2–1, as shown in (V). Moreover, the second 2–1 step should be irreversible, because the D17 atom would be partly exchanged with the H atom, H19A or H19B if the second step were reversible. Since Ohgo *et al.* suggested from the NMR measurement that the first step is reversible (Kurashima *et al.*, 1995), the 1-cyanopropyl group is more stable than the 2-cyanopropyl and 3-cyanopropyl groups, *i.e.* 1-cyanopropyl \gg 2-cyanopropyl $>$ 3-cyanopropyl. Although the atomic motion of the cyanopropyl group seems to be considerably large, the crystallinity may be kept since the molecule

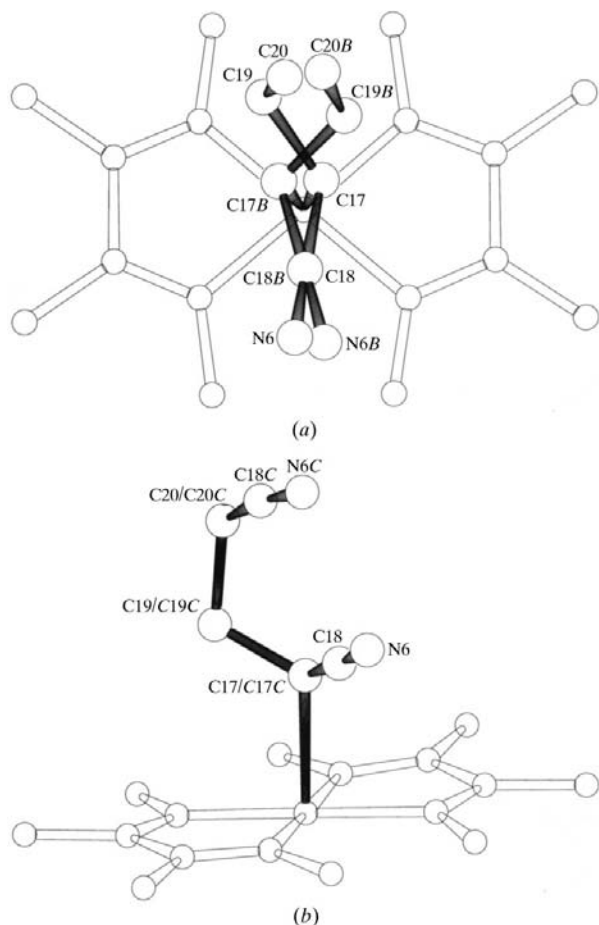


Figure 6
(a) The disordered structures of (*S*)- and (*R*)-1-cyanopropyl groups, with atom numbering. The atoms labeled *B* belong to the minor (*R*)-1-cyanopropyl group. (b) The disordered structure of (*S*)-1-cyanopropyl and 3-cyanopropyl groups, with atom numbering. The atoms labeled *C* belong to the original 3-cyanopropyl group.

after reaction occupies a space similar to that before the reaction. In the original 3-cyanopropyl group observed as a minor part, no exchange between H and D atoms was observed.

4. Discussion

4.1. Intermediate structure by molecular mechanics

Neutron diffraction revealed that the isomerization proceeds in two steps. It seems important to estimate the structure of the intermediate 2-cyanopropyl group, which has *S* and *R* configurations. Since the 2-cyanopropyl group is produced in the original crystalline lattice by photoirradiation, the 2-cyanopropyl group with a more stable configuration would be produced. In order to estimate the energy of the 2-cyanopropyl group produced in the original lattice, a mini crystal lattice model was applied (Zimmerman & Zhu, 1995; Zimmerman & Sebek, 1997). A mini crystal lattice composed of the 36 original 3-cyanopropyl complexes was computationally generated by referring to the known crystal structure of the 3-cyanopropyl complex. Then, a central complex was replaced with a (*R*)- or (*S*)-2-cyanopropyl complex. The energy-minimized calculation was performed with the *Cerius*² program (Molecular Simulations Inc., 1994). A universal force field (Rappe *et al.*, 1992; Castonguay & Rappe, 1992; Rappe & Colwell, 1993) was adopted. Although the positions of all the atoms belonging to the 2-cyanopropyl group of the central molecule and all the H atoms of the surrounding molecules were refined (Buttar *et al.*, 1998), the other atoms were fixed. The calculated energy for the (*R*)-2-cyanopropyl complex is $4509.10 \times 10^3 \text{ kJ mol}^{-1}$, whereas that for the (*S*)-2-cyanopropyl complex is $4548.72 \times 10^3 \text{ kJ mol}^{-1}$. The (*R*)-2-cyanopropyl complex is more stable by $39.62 \times 10^3 \text{ kJ mol}^{-1}$ than

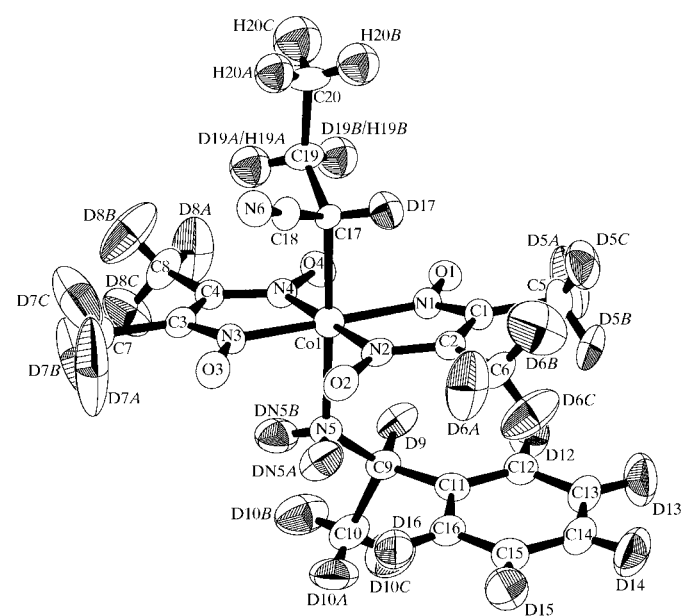
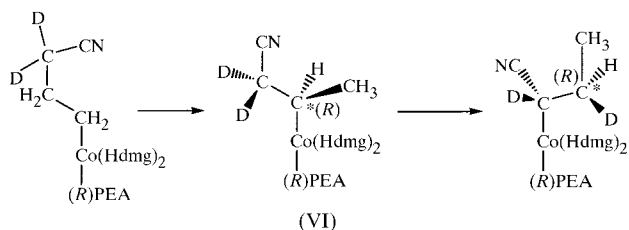
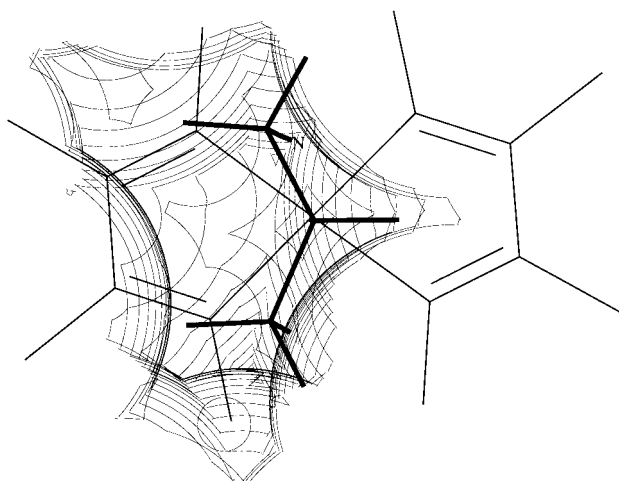


Figure 7
Molecular structure of (1b) analyzed by neutron diffraction. The thermal ellipsoids are drawn at the 30% probability level. The unshaded thermal ellipsoids are non-H or -D atoms.

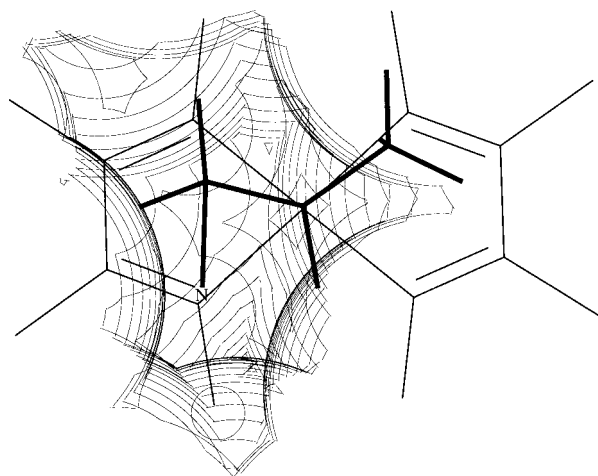
the (*S*)-2-cyanopropyl complex. As shown in (VI), the (*R*)-2-cyanopropyl complex is estimated to be produced in the intermediate step.



The above discussion is also supported by the cavity shape. Fig. 8 shows the reaction cavity for the 3-cyanopropyl group in the original crystal structure. The 2-cyanopropyl group produced with *R* or *S* configuration with minimum energy is drawn in the cavity. The 2-cyanopropyl group with *R* configuration is better accommodated in the cavity than its enantiomer.



(a)



(b)

Figure 8

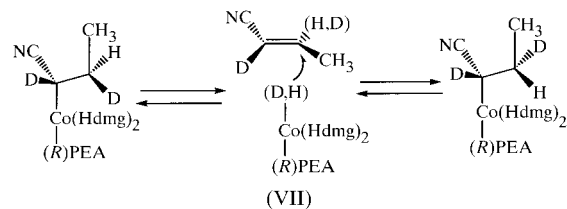
Reaction cavity for the 3-cyanopropyl group in the original crystal accommodating (a) the (*R*)-2-cyanopropyl group and (b) the (*S*)-2-cyanopropyl group. The *R* isomer fits the cavity better.

When the central molecule was replaced with the original 3-cyanopropyl complex or the complex product (*S*)-1-cyanopropyl, the calculated energies are smaller by 28.03 kJ mol⁻¹ and larger by 14.23 kJ mol⁻¹ for the 3-cyanopropyl and (*S*)-1-cyanopropyl complexes, respectively, than that for the (*R*)-2-cyanopropyl complex. Since the 1-cyanopropyl group is more stable electronically than the 2-cyanopropyl group, as described in §3.2, this may explain the reason why the intermediate 2-cyanopropyl group is undetectable during the reaction.

4.2. Olefin formation

It seems adequate to assume that the absolute configuration of the C² atom of the (*S*)-1-cyanopropyl complex produced is *R*, as shown in (VI), since the Co atom would be replaced with the D atom. However, the configuration of the C² atom of the analyzed structure by neutron diffraction is racemic.

This may be explained by the mechanism of olefin formation. As shown in (VII), the Co–C bond would be cleaved by continuous exposure to the xenon lamp and the olefin and cobalt hydride, {CD(CN) = CHCH₃} + Co–D or {CD(CN) = CDCH₃} + Co–H, would be produced. Then the olefin and cobalt hydride may return to the 1-cyanopropyl cobalt. In these equilibrium steps, the H and D atoms are easily exchanged with each other. It is proposed that the disordered structure at the C2 atom is caused by the equilibrium steps, as shown in (VII), after the 1-cyanopropyl group was produced.



4.3. Asymmetric induction

In the 2–1 isomerization, most of the 2-cyanopropyl groups were transformed to the (*S*)-1-cyanopropyl group. Fig. 9 shows the reaction cavity for the 3-cyanopropyl group in the original crystal. The 1-cyanopropyl groups produced with *S* and *R* configurations, which are the same as those in Fig. 6(a), are also shown. The *S* configuration is better accommodated than the *R* configuration. Fig. 10 shows the cavity for the 1-cyanopropyl group in the crystal after irradiation. The shape of the cavity is very similar to that before irradiation and the 1-cyanopropyl group with *S* configuration is suited to this cavity. Fig. 10 explains why the crystallinity is kept in the isomerization and why the *S* configuration is preferably produced.

5. Summary

From the single-crystal neutron diffraction analysis of the photoirradiated crystal of (1b), the following mechanism has been established:

- (i) the photoisomerization of the 3-cyanopropyl group occurs in the two-step, 3–2 and 2–1 isomerization,
- (ii) the 2–1 isomerization is irreversible,

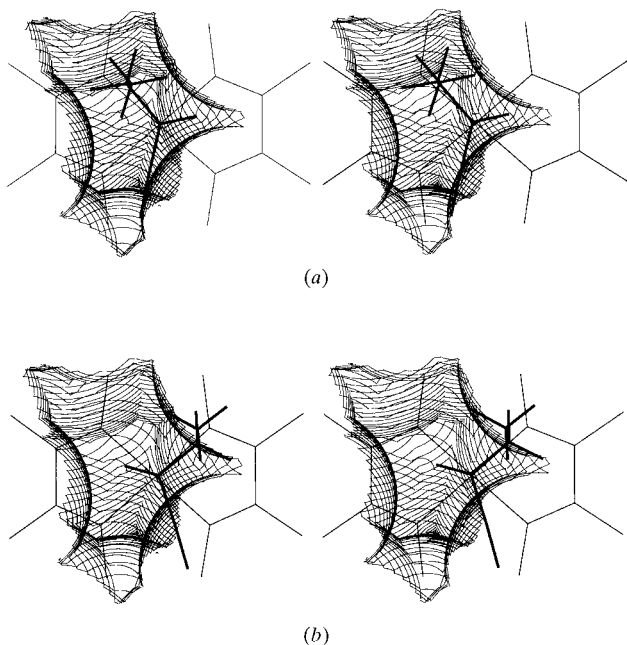


Figure 9
Stereoviews of the reaction cavity for the 3-cyanopropyl group in the original crystal accommodating (a) the (*S*)-1-cyanopropyl group produced and (b) the (*R*)-1-cyanopropyl group.

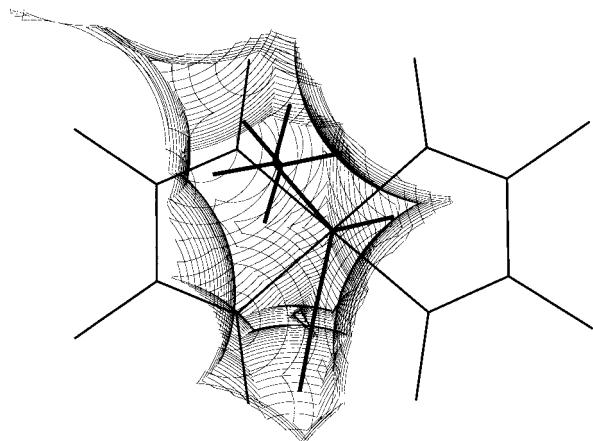


Figure 10
Reaction cavity for the 1-cyanopropyl group after irradiation accommodating the (*S*)-1-cyanopropyl group.

(iii) the equilibrium between the 1-cyanopropyl cobalt and the propionitrile + cobalt hydride causes the disordered structure at the C2 atom after the 1-cyanopropyl group is produced, and

(iv) the chirality of the 1-cyanopropyl group depends on the asymmetric environment surrounding the cyanopropyl group before irradiation.

The single-crystal neutron diffraction provides important information on the reaction mechanism. We believe that this method will play an important role in the field of crystal chemistry.

This work was partly supported by CREST from Japan Science and Technology Corporation (JST).

References

- Altomare, A., Burla, M. C., Camalli, M., Cascarano, G. L., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115–119.
- Arduengo III, A. J., Dias, H. V. R., Dixon, D. A., Harlow, R. L., Klooster, W. T. & Koetzle, T. F. (1994). *J. Am. Chem. Soc.* **116**, 6812–6822.
- Bury, A., Bougeard, P., Corker, S. J., Johnson, M. D. & Perlmann, M. (1982). *J. Chem. Soc. Perkin Trans. 2*, pp. 1367–1372.
- Buttar, D., Charlton, M. H., Docherty, R. & Starbuck, J. (1998). *J. Chem. Soc. Perkin Trans. 2*, pp. 763–772.
- Castonguay, L. A. & Rappe, A. K. (1992). *J. Am. Chem. Soc.* **114**, 5832–5842.
- Edwards III, W. B. & Glenn, D. F. (1976). *J. Label. Compd. Radiopharm.* **12**, 145–151.
- Kano, S., Tanaka, Y., Sugino, E. & Hibino, S. (1980). *Synthesis*, pp. 695–697.
- Koester, L. (1977). *Springer Tracts in Modern Physics*, Vol. 80, Neutron Physics. New York: Springer-Verlag.
- Kurashima, F., Takatsu, N., Ishida, I., Arai, Y., Takeuchi, S. & Ohgo, Y. (1995). Annual Meeting of the Chemical Society of Japan, Kyoto, Abstract II, p. 290.
- Molecular Simulations Inc. (1994). *Cerius²*. Release 1.6. Burlington, Massachusetts.
- Mross, W. D. & Zundel, G. (1968). *Chem. Ber.* **101**, 2865–2869.
- Niimura, N., Tanaka, I., Karasawa, Y. & Minakawa, N. (1995). *Physica B*, **213**, 929–928.
- Niimura, N., Tanaka, I., Minezaki, Y., Karasawa, Y., Tanaka, I., Miki, K., Sato, M., Hidaka, M., Minakawa, N. & Morii, Y. (1995). *Physica B*, **213**, 786–789.
- Ohashi, Y. (1988). *Acc. Chem. Res.* **21**, 268–274.
- Ohashi, Y., Sakai, Y., Sekine, A., Arai, Y., Ohgo, Y., Kamiya, N. & Iwasaki, H. (1995). *Bull. Chem. Soc. Jpn.* **68**, 2517–2525.
- Ohashi, Y. & Sasada, Y. (1977). *Nature*, **267**, 142–144.
- Ohashi, Y., Yanagi, K., Kurihara, T., Sasada, Y. & Ohgo, Y. (1981). *J. Am. Chem. Soc.* **103**, 5805–5821.
- Ohgo, Y., Ohashi, Y., Klooster, W. T. & Koetzle, T. F. (1997). *Enantiomer*, **2**, 241–248.
- Ohgo, Y. & Takeuchi, S. (1985). *J. Chem. Soc. Chem. Commun.* pp. 21–22.
- Ohhara, T., Uekusa, H., Ohashi, Y., Tanaka, I., Kumazawa, S. & Niimura, N. (1998). *Chem. Lett.* pp. 365–366.
- Rappe, A. K., Casewit, C. J., Colwell, K. S., Goddard-III, W. A. & Skiff, W. M. (1992). *J. Am. Chem. Soc.* **114**, 10024–10035.
- Rappe, A. K. & Colwell, K. S. (1993). *Inorg. Chem.* **32**, 3438–3450.
- Sato, H. & Ohashi, Y. (1999). *Bull. Chem. Soc. Jpn.* **72**, 367–375.
- Sekine, A., Saitoh, M., Hashizume, D., Uekusa, H., Ohashi, Y., Arai, Y. & Ohgo, Y. (1998). *Enantiomer*, **3**, 159–168.
- Sekine, A., Tatsuki, H. & Ohashi, Y. (1997a). *J. Organomet. Chem.* pp. 536–537.
- Sekine, A., Tatsuki, H. & Ohashi, Y. (1997b). *J. Organomet. Chem.* pp. 389–398.
- Sekine, A., Yoshiike, M., Ohashi, Y., Ishida, K., Arai, Y. & Ohgo, Y. (1998). *Mol. Cryst. Liq. Cryst.* **313**, 321–326.
- Sheldrick, G. M. (1993). *SHELXL93*. University of Göttingen, Germany.
- Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
- Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
- Siemens (1995). *SMART and SAINT*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Theilacker, W. & Winkler, H. G. (1954). *Chem. Ber.* **87**, 690–691.
- Zav'yalov, S. I. & Ezhova, G. I. (1984). *Bull. Acad. Sci. USSR Div. Chem. Sci.* p. 142.
- Zimmerman, H. E. & Sebek, P. (1997). *J. Am. Chem. Soc.* **119**, 3677–3690.
- Zimmerman, H. E. & Zhu, Z. (1995). *J. Am. Chem. Soc.* **117**, 5245–5262.