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Direct observation of deuterium migration in crystalline-state reaction by single-crystal neutron diffraction. III. Photoracemization of 1-cyanoethyl cobaloxime complexes

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The H atoms bonded to the chiral C atoms (stereogenic center) of the 1-cyanoethyl groups in two cobalt complexes, [(*R*)-1-cyanoethyl]bis(dimethylglyoximato)(pyridine)cobalt(III) (2) and [(*R*,*S*)-1-cyanoethyl]bis(dimethylglyoximato)(piperidine)-cobalt(III) (3), were replaced with D atoms, such as Co—C*D(CH_3)CN. The crystals of the two cobalt complexes were irradiated with a xenon lamp for 72 h and 27 d, respectively. The unit-cell dimensions were gradually changed with retention of the single-crystal form. The crystal structures after irradiation were determined by neutron diffraction. In each crystal the chiral 1-cyanoethyl group of one of the two crystallographically independent molecules was partly inverted to the opposite configuration, whereas that of the other molecule kept the original configuration. The C*—D bond in the inverted group was completely conserved in the process of the inversion of the chiral alkyl group. This suggests that the inversion of the chiral 1-cyanoethyl group proceeds with the rotation of the cyanoethyl radical after the Co—C bond cleavage by photo-irradiation so that the opposite side of the radical faces the Co atom. This is followed by recombination of the Co—C bond to form the inverted 1-cyanoethyl group.

1. Introduction

The bis(dimethylglyoximato)cobalt(III), cobaloxime, complexes are of interest as model compounds of vitamin B_{12}. The B_{12}-dependent enzymes are known to catalyze various intramolecular rearrangements of methyl, hydroxyl, amino and carboxyl groups, which are accompanied by the migration of H atoms. The hydrogen migration mechanism has generated interest in chemistry and biochemistry (Dolphin, 1982; Garr *et al.*, 1996; Walker *et al.*, 1998; Dong *et al.*, 1999). Since the photoracemization of a cobaloxime complex with the chiral 1-cyanoethyl group 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), 2-cyanoethyl (Sekine *et al.*, 1997) and 3-cyanopropyl (Sekine *et al.*, 1998) groups bonded to the Co atoms in some cobaloxime complexes have been found to be racemized or isomerized on exposure to visible light without destroying the single-crystal form. Many investigations by single-crystal X-ray diffraction have shown that the reaction rate and chiral discrimination are controlled by the volume and shape of reaction cavity (Nemoto & Ohashi, 1999).

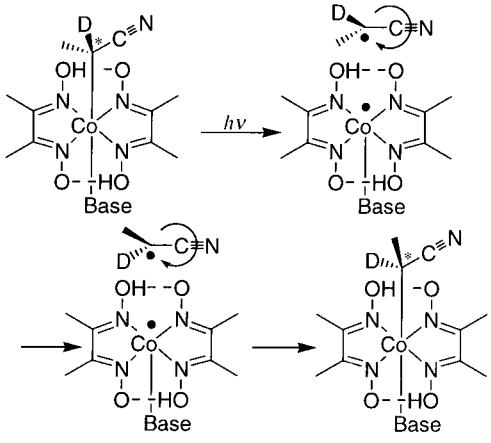
However, the mechanism of the reactions remains unsolved because there is little knowledge on the migration of H atoms in the process. To clarify this issue we proposed the direct observation of the structural change in the processes of crystalline-state reaction by single-crystal neutron diffraction. Single-crystal neutron diffraction is the most powerful method to determine the position and anisotropic displacement parameters (ADP) of H atoms accurately (Wilson, 2000) and it has been adopted to locate the precise hydrogen positions in hydrogen bonds (Brammer *et al.*, 1991; Wozniak *et al.*, 1996; Crabtree *et al.*, 1996; Wilson *et al.*, 1996; Jeffrey, 1997; Allen *et al.*, 1997; Frampton *et al.*, 1997; Mallinson *et al.*, 1999; Wilson, 2000) and metal hydride complexes (Lutz *et al.*, 1996; Bau *et al.*, 1997; Murphy *et al.*, 1998; Tanaka *et al.*, 1999; Basch *et al.*, 1999; Wilson, 2000), and for the temperature dependence of ADPs of H atoms (Wilson, 1997, 2000). In addition, single-crystal neutron diffraction analysis can distinguish H atoms from D atoms, 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 atoms in the process of crystalline-state reactions, the migration of the D atom, *i.e.* the hydrogen-transfer process, can easily be observed by neutron-diffraction analysis.

In a previous paper, the reaction mechanism of the crystalline-state 3–1 photoisomerization of the 3-cyanopropyl cobaloxime complex was proposed on the basis of a single-crystal neutron diffraction study (Ohhara *et al.*, 2000). The mechanism of the photo-inversion of 1-cyanoethyl cobaloxime complexes was proposed from ESR (electron spin resonance) spectra and molecular mechanics calculations as follows:

(i) the Co—C bond is cleaved homolytically by visible light to form Co^{II} and the cyanoethyl radical;

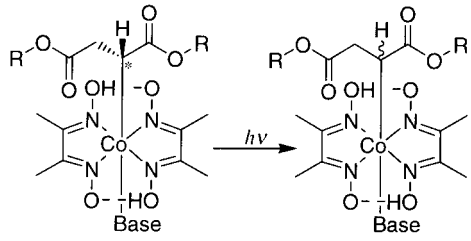
(ii) the organic radical rotates so that its opposite side faces the Co atom;

(iii) there is recombination between the radical and the Co atom to form the 1-cyanoethyl group with the opposite configuration [see (I); Uchida & Dunitz, 1990].



(I)

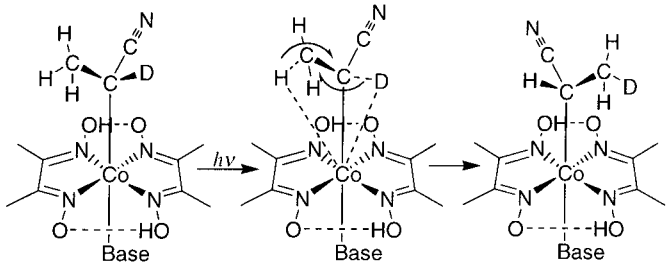
Recently, bulkier chiral groups than the 1-cyanoethyl group, such as the bis(methoxycarbonyl)ethyl (Ohashi *et al.*, 1995), bis(ethoxycarbonyl)ethyl and bis(allyloxycarbonyl)ethyl (Sato & Ohashi, 1999) groups, were found to be racemized on exposure to visible light without degradation of the crystallinity (II). These bulky reactive groups seem difficult to rotate



R: -CH_3, -CH_2CH_3, -CH=CH_2

(II)

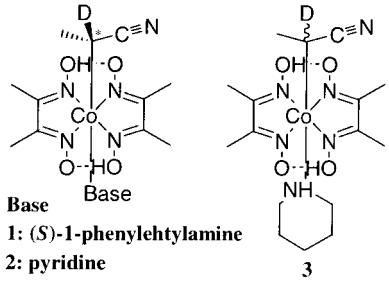
in such a restricted environment as a crystal lattice. Furthermore, the first single-crystal neutron diffraction study of the photoracemization of [(*R*)-1-cyanoethyl-d^{α}][(*S*)-phenylethylamine]cobaloxime (1), in which the H atom bonded to the chiral carbon (stereogenic center of the 1-cyanoethyl group) was replaced with a D atom, showed that the D atom was exchanged with the H atom of the neighboring methyl group on exposure to a Xe lamp (Fig. 1; Ohgo *et al.*, 1997). This result means that the C—H bond is easily cleaved on exposure to visible light and it was proposed that the inversion of the 1-cyanoethyl group would proceed without cleavage of the



(III)

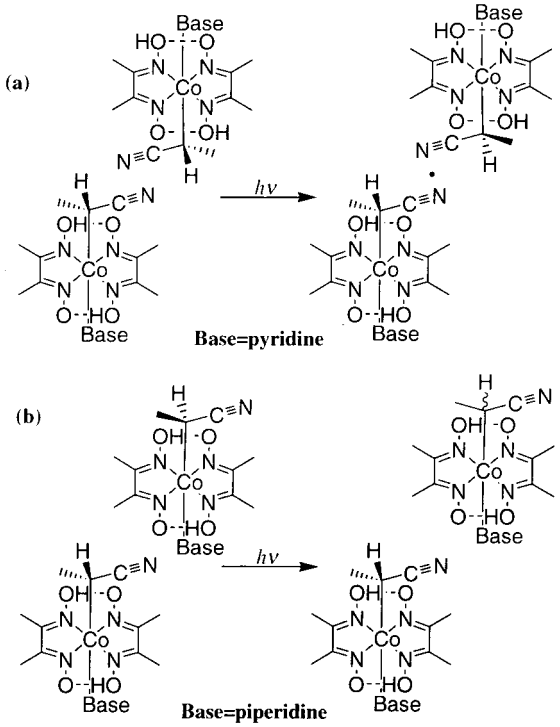
Co—C bond, as shown in (III). This mechanism seemed appropriate for a lattice-restricted reaction because the movement of the reactive group was smaller than the scheme shown in (I). However, the racemization was not observed because the crystal was so large that light was unable to penetrate into the crystal. Therefore, it was necessary to observe directly the hydrogen-transfer process in the photoracemization of the 1-cyanoethyl group by neutron diffraction.

In the present paper crystals of [(*R*)-1-cyanoethyl-d^{a}]-(pyridine)cobaloxime (2) and [(*R,S*)-1-cyanoethyl-d^{a}](piperidine)cobaloxime (3) were prepared [see (IV)] and analyzed



(IV)

by single-crystal neutron diffraction after photoirradiation. Both (2) and (3) have two crystallographically independent molecules in the asymmetric unit, and the 1-cyanoethyl group in only one of them is inverted to the opposite configuration by photoirradiation [see (V) (Ohashi *et al.*, 1982; Osano *et al.*,



(V)

1991). Therefore, it was appropriate to see the relationship between photo-inversion and D–H exchange by comparing the deuterium migration in two independent molecules. Single-crystal neutron diffraction analysis of crystalline-state reaction has two difficulties; a very large single crystal (~5 mm^3) is required and the visible light must penetrate into the crystal, and the photoreaction must occur inside the crystal without deteriorating the crystallinity. After many trials, such difficulties were overcome and the photo-inversion mechanism of the 1-cyanoethyl-d^α group has been analyzed.

2. Experimental

2.1. Preparation

2.1.1. [(*R*)-1-Cyanoethyl-d^α][(*S*)-1-phenylethylamine]cobaloxime (1). Cobalt acetate tetrahydrate (12.45 g, 5.0 mmol) and dimethylglyoxime (11.61 g, 10.0 mmol) were added to aqueous methanol (150 ml: methanol 140 ml + water 10 ml) under Ar atmosphere with stirring. After stirring for 10 min, acrylonitrile-d^α [(4): 5.4 g, 10.5 mmol] and (*S*)-1-phenylethylamine (6.37 ml, 5.0 mmol) were added. The reaction vessel was then connected to a hydrogen-gas burette and purged with hydrogen. The reaction mixture was stirred under a hydrogen atmosphere. After the absorption of hydrogen was terminated, 4.0 g of sodium hydroxide (10 mmol) dissolved in water (200 ml) was added, and then the solution was filtrated and left standing overnight at room temperature. Dark red crystals deposited and were collected by filtration. The crystals were a mixture of the diastereomeric crystals. The optical resolution was performed by fractional crystallization from an aqueous methanol solution. Compound (1) was recrystallized several times from methanol solution to give 5.24 g (11 mmol, 22.5% yield) of crystals; $[\alpha]_{589}^{23}$ + 58.5°(*c* 0.11, chloroform).

2.1.2. [(*R*)-1-Cyanoethyl-d^α](pyridine)cobaloxime (2). Compound (1) (5.0 g) was dissolved in 30 ml of MeOD and the mixture was stirred with 15 g of Dowex 50-80X (50–100 mesh, H form) and 5 ml of D_2O overnight. To the filtrate, an equimolar amount of pyridine was added and the mixture was evaporated to afford (2) as a powder.

2.1.3. [(*R,S*)-1-Cyanoethyl-d^α](piperidine)cobaloxime (3). Cobalt acetate tetrahydrate (12.45 g, 5.0 mmol) and dimethylglyoxime (11.61 g, 10.0 mmol) were added to aqueous methanol (150 ml: methanol 140 ml + water 10 ml) under an Ar atmosphere with stirring. After stirring for 10 min, acrylonitrile-d^α [(4): 5.4 g, 10.5 mmol] and aniline (4.53 ml, 5.0 mmol) were added. The reaction vessel was then connected to a hydrogen-gas burette and purged with hydrogen. The reaction mixture was stirred under a hydrogen atmosphere. After the absorption of hydrogen was terminated, an aqueous solution of sodium hydroxide (200 ml) containing 4.0 g (10 mmol) of sodium hydroxide was added and then the solution was left standing overnight at room temperature. Dark red crystals deposited and were collected by filtration. The crystals were a mixture of the enantiomeric crystals. 5.0 g of this powder were dissolved in 30 ml of MeOD and the mixture was stirred with 15 g of Dowex 50-80X (50–100 mesh, H form) and 5 ml of D_2O overnight. To the filtrate

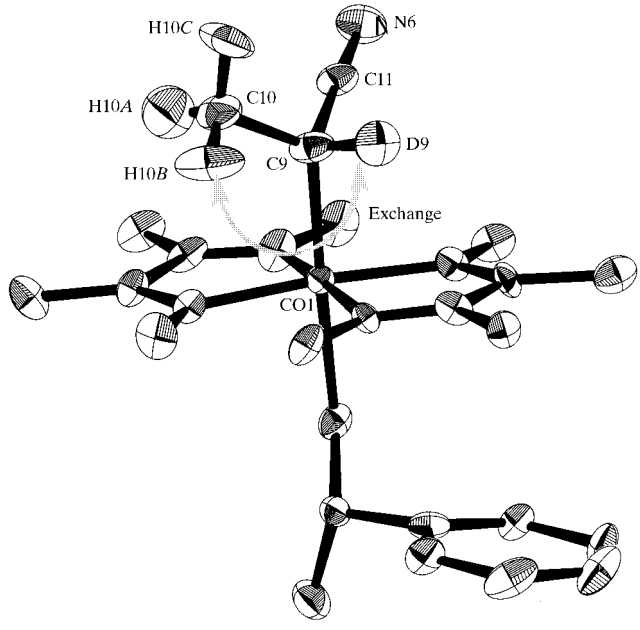


Figure 1
Hydrogen–deuterium exchange reaction in (1) observed by single-crystal neutron diffraction. Approximately 10% of the D atom bonded to the α-C atom of the 1-cyanoethyl-d^α group (D9) was exchanged with the H atom of the neighboring methyl group (H10*B*).

Table 1
Experimental details.

	(2) initial	(2) irradiated	(2) neutron
Crystal data			
Chemical formula	$C_{16}H_{23}CoN_6O_4$	$C_{16}H_{23}CoN_6O_4$	$C_{16}H_{22}CoDN_6O_4$
Chemical formula weight	422.33	422.33	423.33
Cell setting, space group	Monoclinic, $P2_1$	Monoclinic, $P2_1$	Monoclinic, $P2_1$
a, b, c (Å)	16.0665 (15), 12.5929 (11), 9.6440 (11)	16.023 (5), 12.6272 (18), 9.628 (2)	16.023 (5), 12.627 (2), 9.628 (2)
β (°)	94.626 (9)	94.23 (2)	94.23 (2)
V (Å^3)	1944.9 (3)	1942.6 (7)	1942.6 (7)
Z	4	4	4
D_x (Mg m^{-3})	1.442	1.444	0.752
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Neutron
Wavelength (Å)	0.71073	0.71073	1.06000
No. of reflections for cell parameters	25	25	From X-ray parameters
θ range (°)	14−15	14−15	–
μ (mm^{-1})	0.916	0.918	0.208
Temperature (K)	293 (2)	293 (2)	293 (2)
Crystal form, color	Plate, red	Plate, red	Plate, red
Crystal size (mm)	0.3 × 0.3 × 0.2	0.2 × 0.2 × 0.1	3.0 × 3.0 × 0.6
Data collection			
Diffractometer	Rigaku AFC-7*R*	Rigaku AFC-7*R*	BIX-I
Data collection method	2θ-ω scans	2θ-ω scans	0.2°ω step scans
Absorption correction	ψ scans (North *et al.*, 1968)	ψ scans (North *et al.*, 1968)	None
T_{min}	0.637	0.731	–
T_{max}	0.832	0.832	–
No. of measured, independent and observed parameters	4690, 4542, 3294	8931, 8580, 4898	1954, 1424, 1418
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
R_{int}	0.0302	0.0638	0.0763
θ_{max} (°)	27.52	37.49	41.95
Range of h, k, l	$-20 \rightarrow h \rightarrow 0$ $-16 \rightarrow k \rightarrow 0$ $-12 \rightarrow l \rightarrow 12$	$-21 \rightarrow h \rightarrow 21$ $0 \rightarrow k \rightarrow 16$ $-13 \rightarrow l \rightarrow 0$	$-17 \rightarrow h \rightarrow 19$ $-13 \rightarrow k \rightarrow 2$ $-11 \rightarrow l \rightarrow 8$
No. and frequency of standard reflections	3 every 100 reflections	3 every 100 reflections	–
Intensity decay (%)	0.86	1.04	–
Refinement			
Refinement on	F^2	F^2	F^2
$R[F^2>2\sigma(F^2)]$, $wR(F^2)$, S	0.0522, 0.1733, 1.019	0.0438, 0.155, 1.02	0.132, 0.3276, 3.311
No. of reflections and parameters used in refinement	4542, 498	8580, 587	1424, 464
H-atom treatment	Mixed	Mixed	Refine
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.1241P)^2 + 0.0000P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0888P)^2 + 0.0590P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.1000P)^2 + 0.0000P]$, where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$	0.000	0.012	0
$(\Delta/\sigma)_{max}$	0	0	−0.136
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.76, −1.129	1.017, −0.529	0.157, −0.099

	(3) initial	(3) irradiated	(3) neutron
Crystal data			
Chemical formula	$C_{16}H_{29}CoN_6O_4$	$C_{16}H_{29}CoN_6O_4$	$C_{16}H_{28}CoDN_6O_4$
Chemical formula weight	428.38	428.38	429.38
Cell setting, space group	Orthorhombic, $P2_12_12_1$	Orthorhombic, $P2_12_12_1$	Orthorhombic, $P2_12_12_1$
a, b, c (Å)	11.4309 (12), 11.6591 (6), 30.701 (3)	11.4039 (2), 11.7354 (2), 30.7446 (1)	11.4039 (2), 11.7354 (1), 30.7446 (2)
V (Å^3)	4091.6 (6)	4114.53 (10)	4114.53 (8)
Z	8	8	8
D_x (Mg m^{-3})	1.391	1.383	0.730
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Neutron
Wavelength (Å)	0.71073	0.71073	1.06000
No. of reflections for cell parameters	512	512	From X-ray parameters
θ range (°)	1.33–27.54	1.86–35.0	–
μ (mm^{-1})	0.872	0.867	0.244
Temperature (K)	293 (2)	293 (2)	293 (2)
Crystal form, color	Plate, dark red	Plate, dark red	Plate, dark red
Crystal size (mm)	0.3 × 0.3 × 0.1	0.3 × 0.3 × 0.2	3.0 × 3.0 × 1.0

Table 1 (continued)

	(3) initial	(3) irradiated	(3) neutron
Data collection			
Diffractometer	Bluker SMART CCD	Bluker SMART CCD	BIX–I
Data collection method	ω scans	ω scans	0.2° ω step scans
Absorption correction	Empirical (*SADABS*; Sheldrick, 1996)	Empirical (*SADABS*; Sheldrick, 1996)	None
T_{min}	0.632	0.627	–
T_{max}	0.781	0.743	–
No. of measured, independent and observed parameters	15 591, 8265, 7379	70 341, 18 013, 12 035	2928, 2137, 2124
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
R_{int}	0.1135	0.0476	0.0631
θ_{max} (°)	27.54	35.00	43.58
Range of h, k, l	$-14 \rightarrow h \rightarrow 11$ $-11 \rightarrow k \rightarrow 13$ $-38 \rightarrow l \rightarrow 39$	$-18 \rightarrow h \rightarrow 15$ $-17 \rightarrow k \rightarrow 18$ $-49 \rightarrow l \rightarrow 42$	$-12 \rightarrow h \rightarrow 11$ $-3 \rightarrow k \rightarrow 12$ $-28 \rightarrow l \rightarrow 32$
Refinement			
Refinement on	F^2	F^2	F^2
$R[F^2>2\sigma(F^2)]$, $wR(F^2)$, S	0.0837, 0.2523, 1.766	0.0454, 0.0966, 1.011	0.1036, 0.268, 1.158
No. of reflections and parameters used in refinement	8265, 491	18013, 629	2137, 805
H-atom treatment	Mixed	Mixed	Mixed
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.1000P)^2 + 0.0000P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0397P)^2 + 0.4994P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.2309P)^2 + 0.6072P]$, where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$	0.002	0.004	0.056
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.797, −1.338	0.479, −0.635	0.106, −0.084

Computer programs used: *TEXSAN*, *SIR*92 (Altomare *et al.*, 1994), *SHELXL*97 (Sheldrick, 1997), local program, initial structure was determined by X-ray, *SHELXL*93 (Sheldrick, 1993), *SMART* (Siemens, 1996), *SAINT* (Siemens, 1996).

was added equimolar piperidine and the mixture was evaporated to afford (3) as a powder.

2.1.4. Acrylonitrile-d^α (4). Compound (4) was prepared according to the reported method (Mathias & Colletti, 1988). The α-H atom of acrylonitrile was exchanged with a D atom using D_2O and 1,4-diazabicyclo[2,2,2]octane (DABCO) catalysts for three cycles. For each cycle the amounts of D_2O and DABCO were adjusted, depending on the amount of acrylonitrile used in the cycle. For the first cycle, acrylonitrile (19.95 g, 380 mmol) and DABCO (4.2 g, 40 mmol) were added to 100 ml of deuterium oxide under an Ar atmosphere and stirred overnight. The acrylonitrile was extracted by diethyl ether (30 ml × 3) and dried over anhydrous magnesium sulfate. The yield after three cycles was 8.5 g of 99 atom %D acrylonitrile-d^α.

2.2. Crystallization and photoirradiation

Compound (2) (1.4 g) was dissolved in a mixed solution of MeOH (19 ml) and H_2O (30 ml) and left for 4 d at room temperature. Crystals large enough (∼3.0 × 3.0 × 0.6 mm) for single-crystal neutron diffraction were obtained. Several crystals with similar size were irradiated with a 20 W fluorescent lamp for 36 h. One of the crystals was used for the single-crystal neutron diffraction study and another one was used for X-ray analysis.

Compound (3) (1.4 g) was dissolved in a mixed solution of MeOH (19 ml) and H_2O (30 ml) and left for 1 month at room temperature. Large crystals (∼3.0 × 3.0 × 1.0 mm) were obtained. A crystal was analyzed by X-rays and then irradiated with a Xe lamp (USHIO SUPER BRIGHT 152S) for 28 d. During photoirradiation, the crystal was rotated using a motor with a velocity of 0.2 r.p.m. to exposure the light uniformly. After irradiation, this crystal was analyzed by neutron diffraction. Another large crystal irradiated under the same condition was cut to a small piece (0.3 × 0.3 × 0.2 mm) and the structure was analyzed by X-rays.

2.3. Single-crystal X-ray diffraction

Single-crystal X-ray diffraction was carried out for the crystals of (2) and (3) before irradiation to confirm whether the crystals had the same structure as those of the reported ones (Ohashi *et al.*, 1982; Nemoto & Ohashi, 1999) and after irradiation to confirm the progress of the photo-inversion and to determine the positions of non-H/D atoms. Crystals of (2) and (3) before and after irradiation were each mounted on a Rigaku AFC-7*R* four-circle diffractometer for (2) (both before and after irradiation) and on a Siemens Smart CCD diffractometer for (3) (before and after irradiation), respectively, and the three-dimensional intensity data were collected using monochromated Mo $K\alpha$ radiation in all four measurements. The four structures were solved by direct methods using *SIR*92 (Cascarano *et al.*, 1994) and the structure refinements were carried out with *SHELXL*97 (Sheldrick, 1997). The 1-cyanoethyl groups of (2) and (3) after irradiation are disordered and the occupancy factor of each group was refined. The bond lengths of the disordered 1-cyanoethyl groups were restricted to have ideal values. All non-H atoms were refined with the anisotropic temperature factors except the disordered 1-cyanoethyl-d^α groups. The crystal data and experimental details are summarized in Table 1.

2.4. Single-crystal neutron-diffraction measurements

One of the irradiated crystals of (2), 3.0 × 3.0 × 0.6 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 (Niimura, Tanaka, Minezaki *et al.*, 1995) set up at the JRR-3M reactor of the Japan Atomic Energy Research Institute (JAERI). The neutron beam, monochromated by a bent Si perfect crystal (Niimura, Tanaka, Karasawa *et al.*, 1995), has a wavelength of 1.06 Å. The intensity data were collected at 18 area-detector positions by an 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 using some intense reflections [$I > 10\sigma(I)$]. The reflection peaks were identified with a threshold of $I > 5\sigma(I)$ by *PKSK* (local program for BIX-I) and were integrated using *INTX* (a local program). The Lorentz correction was carried out and then the data were modified to the *SHELXL*-type format.

One of the irradiated crystals of (3), 3.0 × 3.0 × 1.0 mm, was mounted on a BIX-I diffractometer. The intensity data were collected at 16 area-detector positions by an ω step-scan method. The maximum and minimum d-spacing values were 15.77 and 0.77 Å, respectively. A total of 2137 independent reflections were observed. The other experimental conditions were the same as those for crystal (2).

2.5. Structure refinement by neutron-diffraction data

Refinement of the structure was carried out using *SHELXL*93 (Sheldrick, 1993) for (2) and *SHELXL*97 (Sheldrick, 1997) for (3). The cell parameters and the positional parameters of non-H/D atoms were fixed to the values obtained by X-ray analysis (after irradiation). The displacement parameters of all the atoms were refined anisotropically, except those of the H atoms of (2), and the cobalt and the disordered atoms of (2) and (3), which were refined isotropically. The occupancy factors of the disordered 1-cyanoethyl groups were also refined to have the same temperature factors between the corresponding atoms. The details of the refinement are given in Table 1.[1]

3. Results and discussion

X-ray diffraction measurements of (2) and (3) before irradiation confirmed that the crystal structures of (2) and (3) are the same as those reported previously (Ohashi *et al.*, 1982; Nemoto & Ohashi, 1999). Figs. 2 and 3 show the crystal structure of (2) and (3) before irradiation, respectively. Both crystals have two crystallographically independent molecules, *A* and *B*. After irradiation, the 1-cyanoethyl group of only the *B* molecule in each crystal is inverted to the opposite configuration by photoirradiation (Ohashi *et al.*, 1982; Nemoto & Ohashi, 1999). Fig. 4 shows the molecular structures of molecules *A* and *B* of (2) after irradiation, which were determined by single-crystal neutron diffraction. The molecular structure of *A* is not significantly different from that before irradiation determined by X-rays. On the other hand, the (*R*)-1-cyanoethyl group of the *B* molecule is partly inverted to the opposite configuration. The occupancy factor of the inverted (*S*)-1-cyanoethyl group is 0.303 (9), which is in good agreement with that obtained by X-ray analysis, 0.293 (2). In the 1-cyanoethyl group of *A*, the occupancy factor of the D atoms bonded to the chiral C atom is almost 100%. The occupancy factors of the D atoms in the disordered 1-cyanoethyl group of the *B* molecule are the same as those of the other non-H atoms. These results indicate that exchange

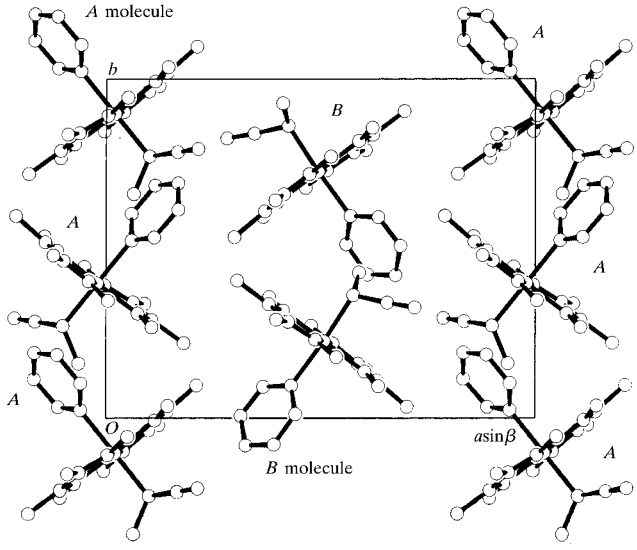


Figure 2
Crystal structure of (2) viewed along the *c* axis before photoirradiation. There are two crystallographically independent molecules, *A* and *B*.

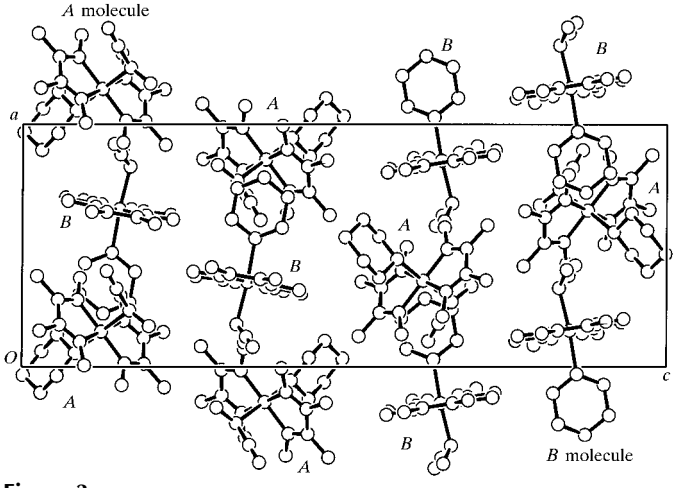


Figure 3
Crystal structure of (3) viewed along the *b* axis before irradiation. There are two crystallographically independent molecules, *A* and *B*.

[1] Supplementary data for this paper are available from the IUCr electronic archives (Reference: BS0016). Services for accessing these data are described at the back of the journal.

with the H atoms of the neighboring methyl group does not occur, not only in *A* but also in *B*. The D atom is also bonded to the chiral C atom after inversion.

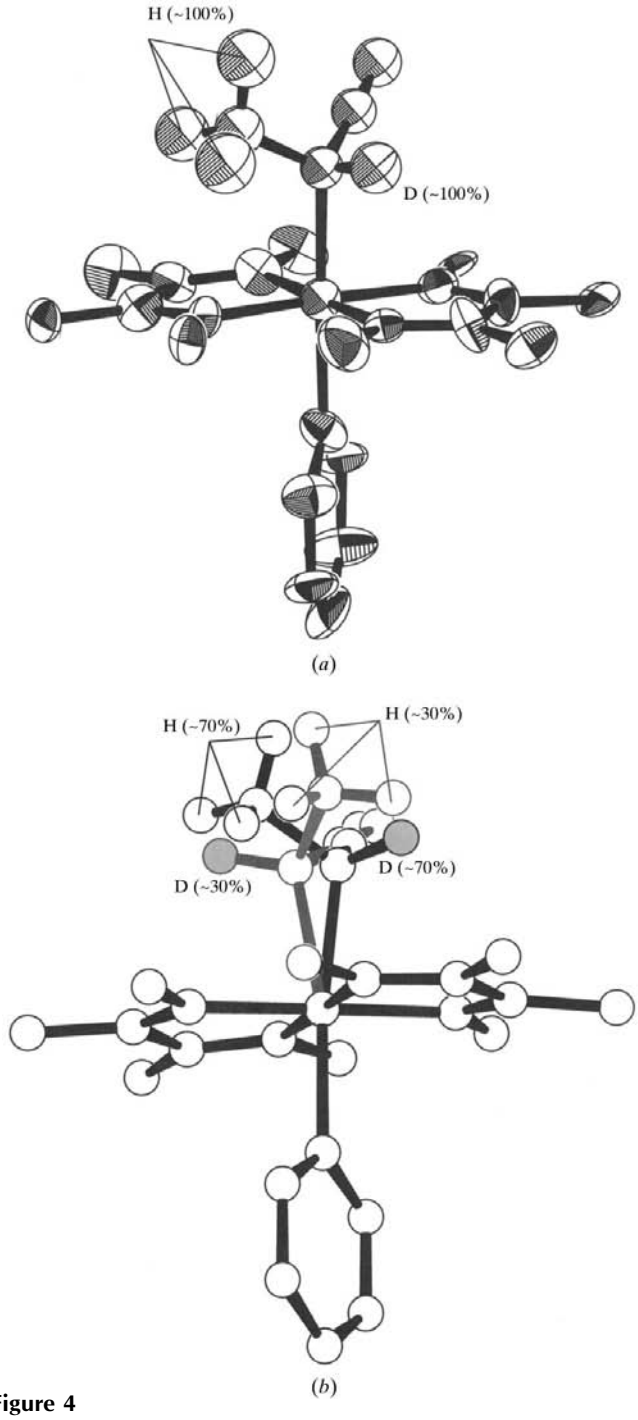


Figure 4
(*a*) Structure of molecule *A* of (2). H atoms of the dimethylglyoximato and pyridine ligands are omitted for clarity. The thermal ellipsoids are drawn at the 30% probability level. The occupancy factors of the D and H atoms of the (*R*)-1-cyanoethyl-d^{α} group are 100%. (*b*) Structure of molecule *B* of (2). The 1-cyanoethyl group is disordered. The black area (70%) shows the initial (*R*)-1-cyanoethyl group and the gray area (30%) shows the (*S*)-1-cyanoethyl group produced by irradiation. The shaded circles represent the D atoms. The occupancy factors of the D and H atoms in the disordered 1-cyanoethyl group are the same as those of the non-H/D atoms.

Fig. 5 shows the molecular structures of *A* and *B* of (3) after irradiation. Molecule *A* retained the same structure more-or-less as that before irradiation, except the D atom in the 1-

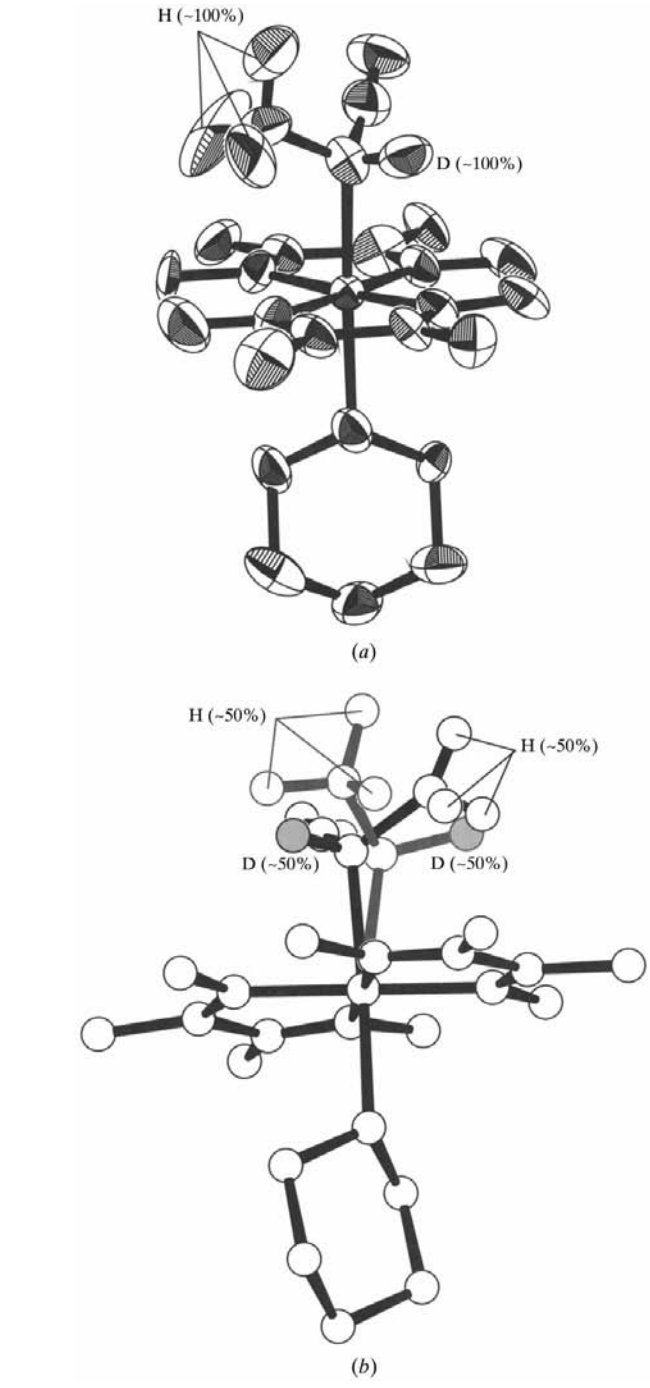


Figure 5
(*a*) Structure of molecule *A* of (3). H atoms of the dimethylglyoximato and pyridine ligands are omitted for clarity. The thermal ellipsoids are drawn at the 30% probability level. The occupancy factors of the D and H atoms of the (*R*)-1-cyanoethyl-d^{α} group are 100%. (*b*) Structure of molecule *B* of (3). The 1-cyanoethyl group is disordered. The black area (50%) shows the initial (*S*)-1-cyanoethyl group and the gray area (50%) shows the (*R*)-1-cyanoethyl group produced by irradiation. The shaded circles represent the D atoms. The occupancy factors of the D and H atoms in the disordered 1-cyanoethyl group are the same as those of the non-H/D atoms.

cyanoethyl group. The occupancy factor of the D atom is ~100%. In the *B* molecule, on the other hand, the 1-cyanoethyl group is partly inverted to form the opposite configuration and takes a disordered structure. The occupancy factor of the inverted structure is 0.503 (3). This value is slightly different from that obtained by X-ray analysis, 0.412 (5). The D atom is completely bonded to the chiral C atom in either case, whether the 1-cyanoethyl group is inverted or not, that is, the hydrogen migration was not observed. These results clearly suggest that the inversion of the 1-cyanoethyl group proceeds *via* rotation of the cyanoethyl radical after Co—C bond cleavage, as shown in (I), and the deuterium–hydrogen exchange, as shown in (III), does not occur in the process of racemization.

The photoirradiations of (2) and (3) were also carried out under different conditions to examine the effect of irradiation time and light source. A crystal of (2) was irradiated for 36 h by a fluorescent lamp and (3) was treated for 28 d by a Xe lamp. The deuterium–hydrogen exchange was not observed in either case. In a previous study, the neutron diffraction analysis of (1) after 2 weeks of irradiation with a Xe lamp showed the D–H exchange reaction in the 1-cyanoethyl group (Ohgo *et al.*, 1997). In order to reproduce the D–H exchange in (1), the H atom bonded to the chiral carbon was also replaced with D and the crystal was irradiated with the same conditions as those reported (light source: Xe lamp; irradiation time: 2 weeks; crystal size: 2.5 × 2.5 × 0.7 mm). The irradiated crystal was dissolved in chloroform-*d* and the ^{1}H NMR spectrum was measured using a 270 MHz ^{1}H NMR spectrometer (Jeol EX-270). No definitive evidence of the D–H exchange was observed. Thus, the D–H exchange may proceed under some unknown conditions in the 1-cyanoethyl cobaloxime complex in the previous experiment. Further investigation seems necessary because our recent experiment clearly showed that, by photoirradiation, the crystalline-state D–H exchange occurred in the bulkier chiral group, $-C^*D(CO_2C_2H_5)CH_2CO_2C_2H_5$, bonded to the Co atom of the [(*R*)-bis(ethoxycarbonyl)ethyl](pyridine)cobaloxime complex.

4. Summary

The single-crystal neutron diffraction analysis of (2) and (3) clearly showed that the crystalline-state photoinversion of the 1-cyanoethyl-d^α group proceeded without exchange between the D atom bonded to the chiral carbon and the H atoms of neighboring methyl group. This result indicates that the inversion mechanism should occur as follows: the cyanoethyl-d^α radical after the Co—C bond cleavage by photoirradiation rotates so that the opposite side of the radical faces the Co atom and recombines with the Co atom as shown in (I). Since hydrogen migration is very common in organic and organometallic reactions, we believe that single-crystal neutron diffraction will play a more important role in these fields in the near future.

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