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Successive Crystalline-State Photoisomerization of the 4-Cyanobutyl Group in a Cobaloxime Complex

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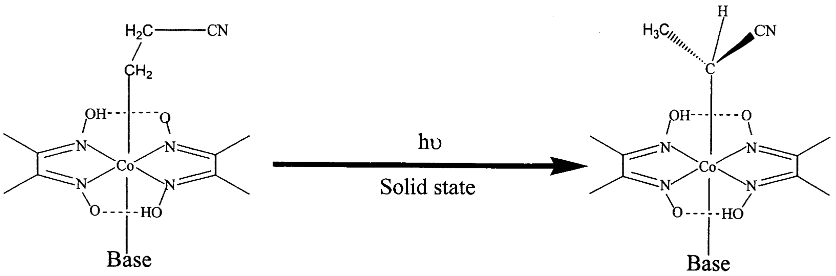
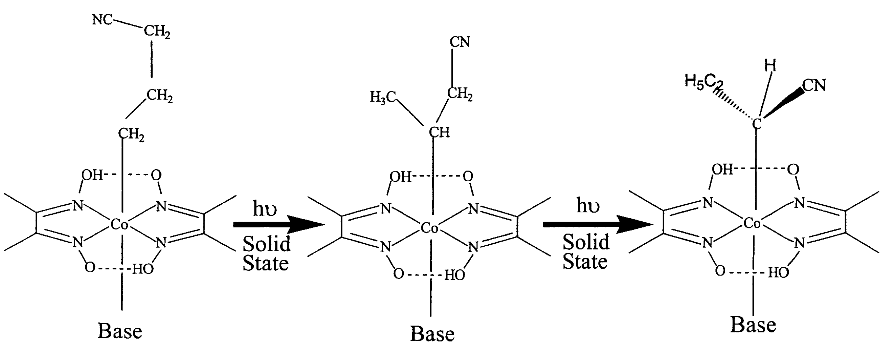
The 4-cyanobutyl group bonded to the cobalt atom in a cobaloxime complex crystal was isomerized to the 2-cyanobutyl group through the 3-cyanobutyl group on exposure to a xenon lamp with retention of the single crystal form. The X-ray crystal structure analysis of the initial crystal, (**I**), and the crystal after 66 hours exposure, (**II**), revealed that the produced 3-cyanobutyl group at one site in (**II**) is not disordered racemates but one enantiomer. The occupancy factors of the 4-cyanobutyl and the produced 3-cyanobutyl group were 0.786(7) and 0.214(7), respectively in (**II**). Although the structure of the produced 2-cyanobutyl group was not located on the difference electron density map, the NMR measurement clearly indicated that a small amount of the 2-cyanobutyl complex (ca. 6%) was produced.

It was found that the 2-cyanoethyl group bonded to the cobalt atom in some bis(dimethylglyoximato)cobalt(III), cobaloxime, complexes isomerizes to the 1-cyanoethyl group as shown in Scheme 1 when the powdered sample of the complex is irradiated with visible light.[1] If 3-methylpyridine or 4-methylpyridine is used as an axial base ligand, the isomerization proceeds with retention of the single crystal form.[2] The produced 1-cyanoethyl group has a chiral carbon atom bonded to the cobalt atom. The structures analyzed by X-rays after irradiation are not racemic at one site. For the 3-methylpyridine complex, the *R*:*S* ratio was 4:7 at one site, whereas only the *R* configuration could be observed at one site for the 4-methylpyridine complex. The shape of the reaction cavity for the original 2-cyanoethyl group well explains the chirality of the produced 1-cyanoethyl group.

Recently, it was reported that the 3-cyanopropyl group bonded to the cobalt atom in some cobaloxime complexes also isomerizes to the 1-cyanopropyl group, through the 2-cyanopropyl group in the solid state as shown in Scheme 2.[3] Since the produced 1-cyanopropyl group has a chiral carbon atom



Scheme 1.



Scheme 2.

bonded to the cobalt atom, it was assumed that the asymmetric induction may be possible when the chiral amine was used as an axial base ligand. When (*R*)-phenylethylamine was used, the isomerization proceeded without degradation of the crystallinity. The crystal structure analyzed by X-rays after irradiation indicated that the 3-cyanopropyl group was completely transformed to the 1-cyanopropyl group and that the $R:S$ ratio of the produced 1-cyanopropyl group was 0.07 : 0.93. The shape of the reaction cavity for the original 3-cyanopropyl group well explains the asymmetric induction.[4]

In the above 3-to-1 photoisomerization, it was impossible to observe the intermediate 2-cyanopropyl group. The two hydrogen atoms bonded to the C1 carbon atom of the 3-cyanopropyl group were replaced with the deuterium atoms and the complex crystal was irradiated with a xenon lamp. The crystal structure analyzed by neutron diffraction after irradiation clearly indicated that the reaction proceeded through the 2-cyanopropyl group.[5]

Recently, the cobaloxime complex with the 4-cyanobutyl group was prepared and the crystal was irradiated with the xenon lamp. The NMR and XRD measurements indicated the isomerization of the 4-cyanobutyl group. This paper reports the crystal structure after irradiation and the mechanism of the isomerization.

Experimental

Preparation. (4-cyanobutyl)bis(dimethylglyoximato)(pyridine)-cobalt(III) was prepared in a way similar to that reported previously.[6] The crystals were obtained from an aqueous methanol solution.

Crystal Structure Analysis. The crystal structures before, (**I**), and after, (**II**), irradiation were determined by X-ray crystallography. For the crystal of (**I**), the diffraction data were measured on a four-circle diffractometer, RIGAKU AFC-7R. The diffractometer was covered with a black sheet during the measurement to avoid room light. The absorption corrections with Ψ scan were applied ($T_{\min}$ and $T_{\max}$ were 0.5858 and 0.9193). The crystal data are given in Table 1. The crystal structure of (**I**) was analyzed by the direct method with SIR-92.[7] Non-hydrogen atoms were refined anisotropically by the full-matrix least-squares method using the program SHELXL-97.[8] The hydrogen atoms were included using the riding model. The details of the refinement are listed in Table 1.

Table 1. Crystal Data and Experimental Details for the Crystals (**I**) and (**II**)

	(**I**) Before irradiation	(**II**) After irradiation.
Chemical Formula	$Co_1N_6O_4C_{18}H_{27}$	$Co_1N_6O_4C_{18}H_{27}$
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$
a/Å	8.217 (3)	8.2923 (3)
b/Å	21.265 (2)	21.7512 (8)
c/Å	12.010 (2)	11.7830 (3)
β/°	93.15 (2)	92.887 (1)
V/Å^3	2095.4 (8)	2122.57 (12)
Z	4	4
Crystal description	Needle	Needle
Crystal size/mm	0.7 × 0.1 × 0.1	0.3 × 0.1 × 0.1
Crystal colour	Brown	Red
Diffractometer	AFC7R	SMART CCD system.
Data collection method	ω-2θ scan	ω scan
Wave length/Å	0.71069	0.71069
2θ for data collection/°	55.00	49.84
Temperature/K	296	295
Absorption coefficient/mm^{-1}	0.855	0.845
Reflections collected	5151	10044
Unique	4826 [R(int) = 0.0451]	3679 [R(int) = 0.0457]
F(000)	944	944
Range of h, k, l	$-10 \leq h \leq 0$	$-9 \leq h \leq 9$
	$0 \leq k \leq 27$	$-25 \leq k \leq 25$
	$-15 \leq l \leq 15$	$-13 \leq l \leq 13$
Refinement method	Full matrix least-squares	Full matrix least-squares
R_1, R_W [$I > 2\sigma(I)$]	0.0502, 0.1404	0.0762, 0.1782
S	1.055	1.080
Data, Parameters, Restraints	4826, 262, 0	3679, 278, 20
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.1P)^2 + P]$ where $P = (\mathrm{Max}(F_o^2, 0) + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.088P)^2 + 3.99P]$ where $P = (\mathrm{Max}(F_o^2, 0) + 2F_c^2)/3$
$\Delta\rho_{\max}, \Delta\rho_{\min}$/(eÅ^{-3})	0.543, −0.534	0.565, −0.482

The crystal was irradiated for 66 hours with a xenon lamp, SAN-EI Super Bright 150, through an optical fiber. The cell dimensions were significantly changed and the crystallinity was slightly decomposed. The intensity data were collected on a Siemens SMART CCD diffractometer. The data frames were integrated using program SAINT.[9] The absorption corrections by program SADABS[10] were applied ($T_{\min}$ and $T_{\max}$ were 0.7973 and 1.0000). The crystal 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. Such peaks were assigned to the newly produced 3-cyanobutyl group. The structure including the occupancy factor of the disordered 4- and 3-cyanobutyl groups was refined using the SHELXL-97. The non-hydrogen atoms except those of the newly appeared atoms were refined anisotropically. The positional parameters of the newly appeared atoms of 3-cyanobutyl group were refined but their thermal parameters were fixed. In this refinement model, C9 atom was common to 4- and 3-cyanobutyl groups and was refined anisotropically. The distances among disordered 4- and 3-cyanobutyl groups were restrained to the values observed in (**I**) and the 2-cyanoethyl complexes.[2] The hydrogen atoms were included using the riding model. The cell dimensions and the details of the refinement are also given in Table 1. Atomic scattering factors were taken from International Tables for Crystallography, volume C.[11] The CIF data of (**I**) and (**II**) are deposited as Document No. 74011 at the Office of the Editor of Bull. Chem. Soc. Jpn. Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition numbers 151710-151711.

NMR Measurement. ^{1}H NMR spectra before and after 66 hours irradiation were recorded on a JEOL 270EX spectrophotometer at 270 MHz, using $CDCl_3$ as the solvent. The chemical shifts are relative to the Me_4Si peak.

Results and Discussion

Figure 1 shows the crystal structure of (**I**) viewed along the *a* axis. There are no short contacts between the molecules. The molecular structure of (**I**) is shown in Fig. 2. The 4-cyanobutyl group takes an extended form to the cobaloxime plane; the torsion angles of Co–C9–C10–C11, C9–C10–C11–C12, and C10–C11–C12–C13 are −173.48(3), 162.77(2), and −170.46(2), respectively. Selected bond distances and angles are given in Table 2. The distances of Co–C9 and Co–N6, 2.026(3) and 2.073(2) Å, respectively, are nearly the same as those observed in the related complexes. The distances of C9–C10 and C11–C12, 1.470(5) and 1.484(6) Å, respectively, are slightly shorter than the usual Csp^3–Csp^3 distance, whereas the central C10–C11 bond has a usual distance, 1.529(5) Å. Other distances and angles are not significantly different from the analogous values in the related complexes determined so far.[2,4]

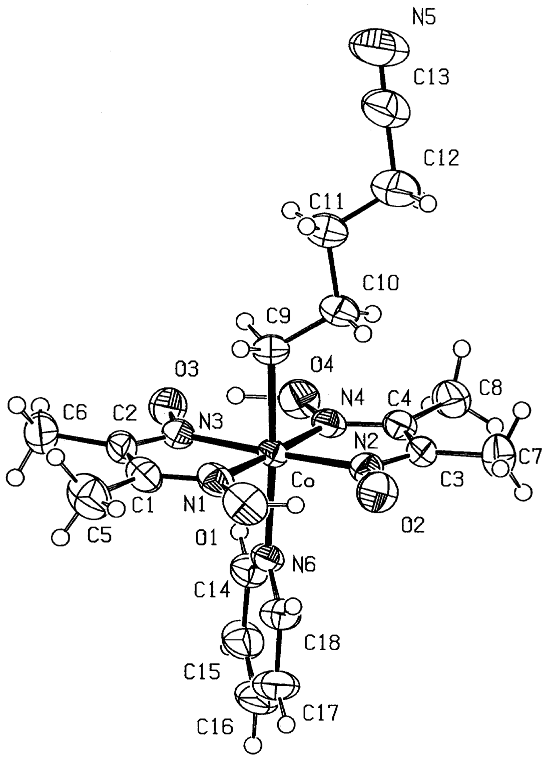


Fig. 2. Molecular structure of (**I**). Thermal ellipsoids were drawn at 30% probability level.

Figure 3 shows the crystal structure of (**II**) viewed along the *a* axis and the molecular structure is shown in Fig. 4. As shown in Table 1, the cell dimensions of *a* and *b* increased although

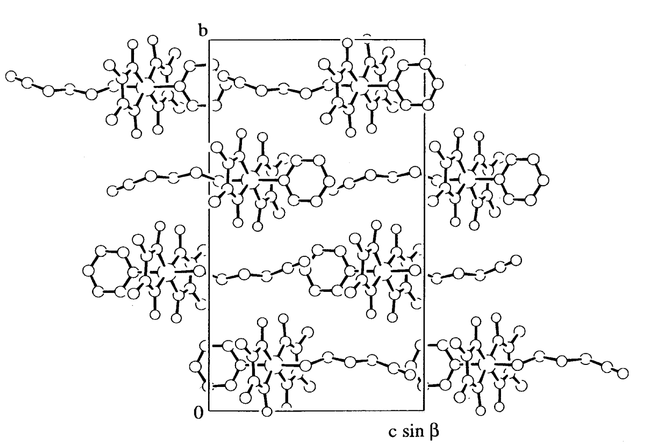


Fig. 1. Crystal structure of (**I**) viewed along the *a* axis. Hydrogen atoms were omitted for clarity.

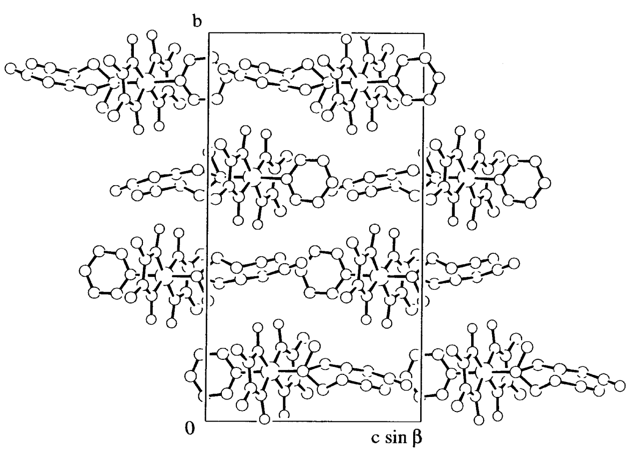


Fig. 3. Crystal structure of (**II**) viewed along the *a* axis. Hydrogen atoms were omitted for clarity.

Table 2. Selected Bond Lengths and Angles for (**I**) and (**II**)

	(**I**)	(**II**)
Bond lengths/Å		
Co–N(1)	1.879(3)	1.876(5)
Co–N(2)	1.873(3)	1.872(5)
Co–N(3)	1.883(3)	1.875(5)
Co–N(4)	1.875(3)	1.881(5)
Co–N(6)	2.073(2)	2.071(4)
Co–C(9)	2.025(3)	2.006(5)
N(6)–C(18)	1.332(4)	1.316(7)
N(6)–C(14)	1.331(4)	1.323(6)
N(5)–C(13)	1.101(5)	1.091(7)
C(9)–C(10)	1.470(5)	1.409(7)
C(10)–C(11)	1.528(5)	1.530(7)
C(11)–C(12)	1.484(6)	1.446(8)
C(12)–C(13)	1.461(6)	1.460(7)
C(9)–C(10B)		1.558(8)
C(9)–C(11B)		1.537(9)
C(11B)–C(12B)		1.492(10)
C(12B)–C(13B)		1.461(9)
C(13B)–N(5B)		1.109(9)
Bond angles/°		
N(1)–Co–N(2)	98.70(13)	98.8(2)
N(1)–Co–N(4)	178.05(11)	178.51(18)
N(1)–Co–C(9)	88.91(14)	88.2(2)
N(1)–Co–N(3)	81.60(13)	81.9(2)
N(3)–Co–C(9)	86.04(13)	86.2(2)
N(2)–Co–N(3)	177.34(11)	177.88(19)
N(2)–Co–N(4)	81.52(12)	81.4(2)
N(2)–Co–C(9)	89.19(13)	91.8(2)
N(4)–Co–C(9)	91.32(13)	90.3(2)
N(4)–Co–N(3)	98.09(12)	97.8(2)
N(6)–Co–C(9)	176.39(12)	176.6(2)
C(10)–C(9)–Co	121.5(2)	123.4(5)
C(11)–C(10)–C(9)	113.0(3)	113.7(6)
C(10)–C(11)–C(12)	110.8(4)	110.0(6)
C(11)–C(12)–C(13)	113.7(4)	114.8(7)
N(5)–C(13)–C(12)	178.2(6)	175.9(12)
C(10B)–C(9)–Co		117.3(6)
N(5B)–C(13B)–C(12B)		168(3)
C(10B)–C(9)–C(11B)		107.0(7)
C(11B)–C(12B)–C(13B)		113.8(11)
C(12B)–C(11B)–C(9)		110.2(9)

the *c* length decreased. The molecular structure is substantially the same as that for (**I**), except the 3-cyanobutyl group produced by photoisomerization. The produced 3-cyanobutyl group has a chiral carbon atom bonded to the cobalt atom. The chiral carbon of the produced 3-cyanobutyl group has one enantiomer at one site in a crystal, that is, the methyl carbon C10B takes an ordered structure. The occupancy factor of the produced 3-cyanobutyl group is 0.214(7). Selected bond distances and angles are also given in Table 2.

In order to examine the reason why only one enantiomer was produced at one site in a crystal, the reaction cavity for the 4-cyanobutyl group of (**I**) was calculated as shown in Fig. 5(a). After the isomerization, the C10 atom makes a bond with the cobalt atom and the C9 atom extracts one hydrogen atom from C10 to become a methyl group, C10B. The produced C10B oc-

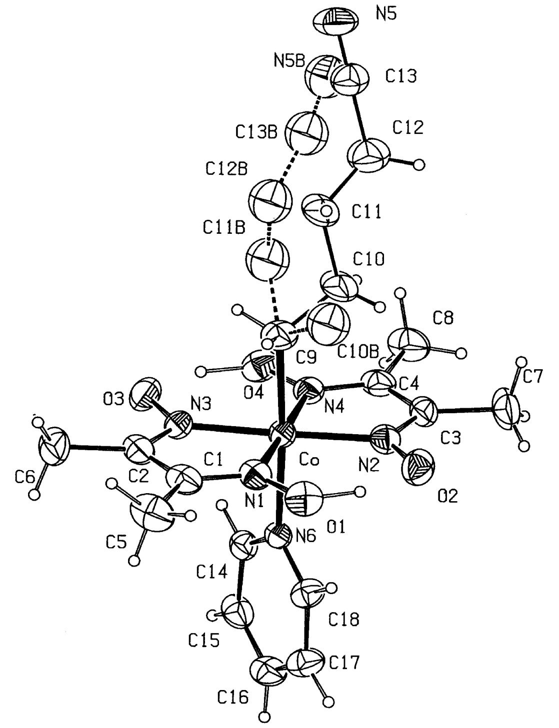
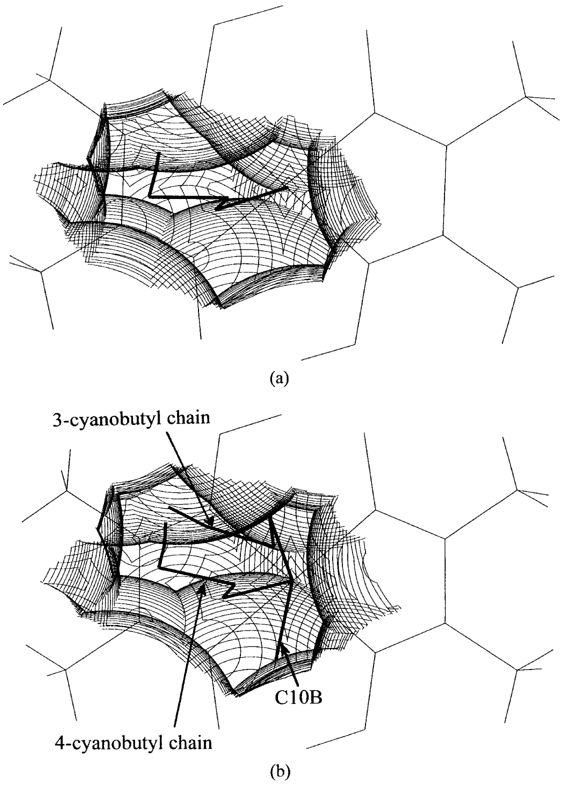


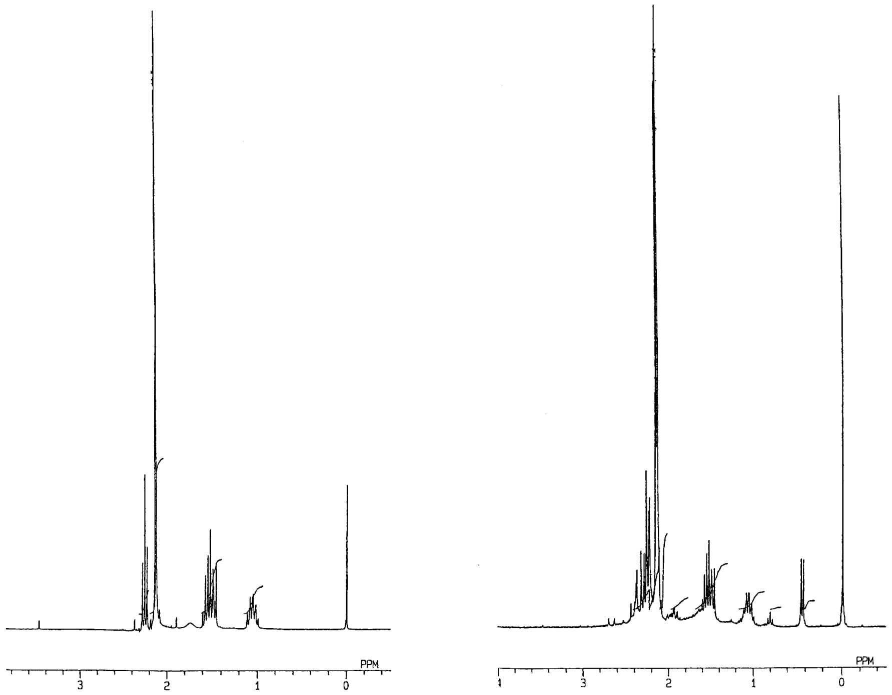
Fig. 4. Molecular structure of (**II**). Thermal ellipsoids were drawn at 30% probability level. Dotted bonds indicate the 3-cyanobutyl group. The occupancy factors of 4- and 3-cyanobutyl groups are 0.786(7) and 0.214(7), respectively.



(a)

(b)

Fig. 5. Reaction cavity diagrams for the 4-cyanobutyl group viewed normal to the cobaloxime plane, (a) for (**I**) and (b) for (**II**).



(a) (b)

Fig. 6. ^{1}H NMR spectra (a) before (**I**) and (b) after irradiation (**II**).

cupies the position neighboring to the C9 atom. Figure 5(b) displays the reaction cavity for the original 4-cyanobutyl and produced 3-cyanobutyl groups of (**II**), viewed normal to the cobaloxime plane in the same scale as that in Fig. 5(a). The produced 3-cyanobutyl group is well accommodated in the cavity. The 3-cyanobutyl group with the opposite configuration would suffer from heavy steric repulsion in the cavity. More quantitative energy calculations are now under investigation. Since the crystal has a center of symmetry, another enantiomeric 3-cyanobutyl group should be produced at the inverted site. Therefore, the product in a whole crystal is racemic.

The irradiated crystal was dissolved in a $CDCl_3$ solution and the NMR measurement was performed to examine whether or not the other photoproducts were made. Figure 6 shows the NMR spectra before and after irradiation, corresponding to the crystal of (**I**) and (**II**), respectively. The signals at δ 0.4286 and 0.4555 ppm were assigned to the methyl protons of the produced 3-cyanobutyl group and the signal at δ 0.8035 ppm was assigned to the methyl protons of the produced 2-cyanobutyl group. The amounts of the produced ones were estimated to be 27% for the 3-cyanobutyl group and 6% for the 2-cyanobutyl group. The observed occupancy factor of the produced 3-cyanobutyl group, 0.214(7), is smaller than that of the NMR measurement. Some parts of the photoproducts may not have lattice structure. There is no clear indication for the isomerization to the 1-cyanobutyl group at this stage. Although the NMR spectra obtained after the prolonged irradiation indicated a variety of by-products and the assignment of all the by-products was very difficult, the isomerization of the 2-cyanobutyl group to the 1-cyanobutyl group probably occurred, since the 2-cyanoethyl and 2-cyanopropyl groups were isomerized to 1-cyanoethyl and 1-cyanopropyl groups, respectively, with retention of the single crystal form.[2,5] The irradiation time in the above experiment was too short to observe the isomerization of the 2- to 1-cyanobutyl groups. After the cobaloxime complex crystals with the 2-cyanobutyl group have been prepared, the isomerization will be confirmed from the NMR spectra. The study is now in progress.

If the alkyl group has no electron-withdrawing group, such an isomerization has not been reported yet. This indicates that the alkyl radical produced by the Co–C bond cleavage in the process of the photoreaction should be stabilized if the radical was transferred to the neighboring carbon closer to the electron-withdrawing group. This may indicate that some hyperconjugation may be possible in the 4-cyanobutyl group. The short bond distances in the 4-cyanobutyl group, C9–C10 and C11–C12, may indicate the conjugation. Further study is in progress.

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