Direct Observation of Correlation between Crystalline-State Deuterium Transfer and Racemization of 1-Cyanoethylcobaloxime Complex by Neutron Diffraction

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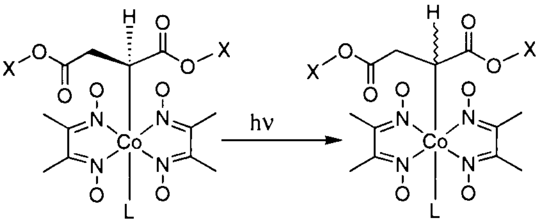
The [(R)-1-cyanoethyl-d$^{\alpha}$] group, which has a deuterium atom attached to the chiral carbon and is bonded to the cobalt atom, in a cobaloxime complex with pyridine as an axial base ligand is inverted to the opposite configuration on exposure to visible light with retention of the single crystal form. The C-D bond is not cleaved in the process of the inversion.

The chiral 1-cyanoethyl group bonded to the cobalt atom in some cobaloxime complex crystals was found to be racemized on exposure to visible light with retention of the single crystal form.[1] The racemization process was assumed from the esr spectra as follows; the Co-C bond was cleaved homolytically by visible light to form Co(II) and cyanoethyl radical, rotation of the produced radical to face the opposite side to the cobalt atom and recombination between the radical and the Co atom to form the 1-cyanoethyl group with the opposite configuration.[2] Recently the bulkier chiral groups than the cyanoethyl group, such as the bis(methoxycarbonyl)ethyl, bis(ethoxycarbonyl)ethyl and bis(allyloxycarbonyl)ethyl groups, were found to be racemized on exposure to visible light without degradation of the crystallinity.[3,4] (Scheme.1)



X=methyl, ethyl, allyl

Scheme 1. Racemization of bulky chiral groups in cobaloxime complexs.

In the previous paper,[5,6] it was reported that the crystal of [(*R*)-1-cyanoethyl-d$^{\alpha}$][(*S*)-phenylethylamine]cobaloxime (**1**), in which the hydrogen atom bonded to the chiral carbon was replaced with the deuterium atom, was analyzed by neutron diffraction technique after three weeks exposure. Surprisingly, the structure indicated that the deuterium atom was exchanged with the hydrogen atom of the neighboring methyl group. The racemization was not observed probably because the crystal was too large that light was unable to penetrate into the crystal. This means the C-H bond is easily cleaved by photoirradiation.

In order to make clear the racemization more precisely, another complex, [(*R*)-1-cyanoethyl](pyridine)cobaloxime (**2a**) was examined. The crystal, (**2a**), has two crystallographically independent molecules, A and B, and the chiral 1-cyanoethyl group of the B molecule is completely inverted to the opposite configuration whereas the chiral group of A is retained unchanged.[7] In the same way as that reported previously,[5] (**1**) was prepared and then the axial amine, (*S*)-phenylethyl amine, was replaced with pyridine to form (**2b**), [(*R*)-1-cyanoethyl-d$^{\alpha}$](pyridine)cobaloxime. The crystal adequate to the neutron work, 3.0 x 3.0 x 0.6mm, was obtained from an aqueous methanol solution by slow evaporation at room temperature.

The crystal, (**2b**), was irradiated with a 20w fluorescent lamp for 36 hours. The approximately the same size of the crystal was also irradiated with the lamp in the same conditions and the structure was determined by X-ray analysis. About 30% of the chiral 1-cyanoethyl group of B was inverted to the opposite configuration. The cell dimensions of the crystal for neutron work are insignificantly different from those determined by X-rays.

The crystal was fixed on an alminium pin by halocarbon

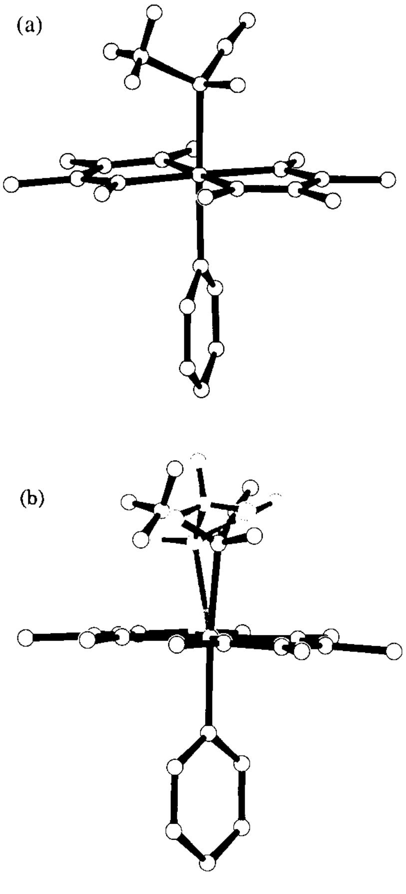


Figure 1. The ORTEP-II[11] drawing of molecular structure of (a)A and (b)B. The (*R*)-1-cyanoethyl group of only B molecule is partly inverted to the *S*(gray) configuration.

glease and the pin was mounted on the BIX-I neutron diffractometer set up at the JRR-3M reactor at Japan Atomic Energy Research Institute (JAERI). The BIX-I diffractometer with a two dimensional PSD[8] has been developed in order to analyze biomolecules. This analysis is the first one performed successfully with this diffractometer. The neutron beam, monochromated by a bent Si crystal,[9] has a wavelength of 1.06 Å The intensity data collection was carried out at room temperature. The minimum and maximum d values are 9.89Å and 0.79Å, respectively. A total of 1424 independent reflections were observed. Since the number of reflections is too small, only coordinates of hydrogen and deuterium atoms, the atomic coordinates and the occupancy factor of the inverted 1-cyanoethyl group, and the thermal parameters of all atoms were refined with the program SHELXL-93.[10] The coordinates of non-hydrogen atoms were taken from those obtained by X-ray analysis and were not refined. The final R value converged to 0.115. The hydrogen atoms of the methyl groups of dimethylglyoxime moieties are disordered, which was not observed in the X-ray analysis.

Figure 1 shows the molecular structures of A and B. The A molecule is not significantly different from the initial one analyzed by X-ray. The (*R*)-1-cyanoethyl group of the B molecule is partly inverted to the *S* configuration. The occupancy factor of the inverted group is 0.248(5). The deuterium atoms of the A and B molecules are not exchanged with the hydrogen atoms of the neighboring methyl groups. Moreover, the deuterium atom of the inverted 1-cyanoethyl group of the B molecule is not transferred to the methyl hydrogens. This results indicate that the inversion of the chiral 1-cyanoethyl group proceeds via rotation of the cyanoethyl radical after the Co-C bond cleavage. In the photoirradiation of the crystal of the *S*-phenylethylamine complex, the crystal was irradiated with a xenon lamp for three weeks. The different wavelength and irradiation period may be responsible to the different process of the racemization, which demands further investigation.

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References and Notes

1 Y. Ohashi, *Acc. Chem. Res.*, **21**, 268 (1988).
2 A. Uchida and Dunitz, , *Acta. Cryst.* **B46**, 45 (1990).
3 Y. Ohashi, Y. Sakai, A. Sekine, Y. Arai, Y. Ohgo, N. Kamiya, and H. Iwasaki, *Bull. Chem. Soc. Jpn.*, **68**, 2517 (1995).
4 H. Sato, Y. Sakai, Y. Ohashi, Y. Arai, and Y. Ohgo, *Acta. Cryst.*, **C52**, 1086 (1996).
5 Y. Ohgo, Y. Ohashi, W. T. Klooster, and T. F. Koetzle, *Chem. Lett.*, **1996**, 445.
6 Y. Ohgo, Y. Ohashi, W. T. Klooster, and T. F. Koetzle, *Enantiomer*, **2**, 241 (1997).
7 Y. Ohashi, K. Yanagi, T. Kurihara, Y. Sasada, and Y. Ohgo, *J. Am. Chem. Soc.*, **104**, 6353 (1982).
8 N. Niimura, I. Tanaka, Y. Minezaki, Y. Karasawa, I. Tanaka, K. Miki, M. Sato, M. Hidaka, N. Minakawa, and Y. Morii, *Physica B*, **213**, 786 (1995).
9 N. Niimura, I. Tanaka, Y. Karasawa, and N. Minakawa, *Physica B*, **213**, 929 (1995).
10 G. M. Sheldrick, SHELXL-93 (1993), Program for the Refinement of Crystal Structures, Univ. of Göttingen, Germany.
11 C. K. Johnson, ORTEP-II (1976), Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.