Direct Observation of Hydrogen-Deuterium Exchange Reaction in Cobaloxime Crystal by Neutron Diffraction

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After a crystal of [(R)-1-cyanoethyl-d$^{\alpha}$][(S)-1-phenylethylamine]bis(dimethylglyoximato)cobalt(III) was exposed to a xenon lamp for two weeks, its structure was analyzed by neutron diffraction. The deuterium atom was exchanged partially with one of the three methyl hydrogenes of the cyanoethyl group. The exchanged one is located closest to the deuterium atom.

It has been found that the chiral cyanoethyl group bonded to the cobalt atom in some cobaloxime complex crystals is racemized by X-ray or visible light exposure with retention of the single crystal form.[1] The mechanism of the inversion process has been assumed to involve homolytic cleavage of the Co-C bond by X-ray or visible light exposure and rotation of the resultant cyanoethyl radical around the C-C-N bond. The recombination of the Co (II) and the rotated cyanoethyl radical would produce the inverted cyanoethyl group.[2]

Although this mechanism appeared to be adequate, recently a serious weakness became apparent in the inversion process for bulky groups. When the chiral cyanoethyl group was replaced with the bis(ethoxycarbonyl)ethyl group, almost the same racemization with retention of the single crystal form was observed.[3] The mechanism outlined above would imply that the bis(ethoxycarbonyl)ethyl radical produced by the Co-C cleavage should rotate in the crystalline lattice. However, it is unreasonable for such a large radical to rotate with retention of the single crystal form. This result strongly suggests that a different mechanism should be invoked for such large chiral groups.

In order to examine the mechanism, we attempted to prepare the complex which has the α-deuterium bonded to the chiral carbon. Since very large crystals of the title complex recently were obtained successfully, we proceeded to analyze its structure after irradiation, by neutron diffraction. The structure analysis, to our surprise, showed no racemization but revealed that the deuterium atom is exchanged with a hydrogen atom of the neighboring methyl group.

The title complex was prepared using acrylonitrile-d$^{\alpha}$[4] in the manner reported previously[5] with slight modification.[6] A crystal with dimensions 2.7 x 2.8 x 0.7 mm was irradiated with a xenon lamp (San-ei SUPERBRIGHT-1500) from a distance of approximately 10 cm for two weeks. A part of the crystal was cut and the cell dimensions were measured to check the racemization. The cell dimensions showed a singificant change.

The crystal was mounted along the b axis on an aluminum pin with halocarbon grease and sealed inside an aluminum canister under helium atmosphere. The data were collected on the four-circle diffractometer at port H6S of the Brookhaven High Flux Beam Reactor. The neutron beam, monochromated by Ge, had a wavelength of 1.1640(1) Å. The measurement was carried out at room temperature (295 K), since the crystal was easily broken when it was cooled. The crystallinity probably deteriorated somewhat after the photoirradiation. A total of 2978 independent reflections, of which 1878 had $I > 2\sigma(I)$, were obtained.[7] The initial parameters were taken from those obtained by X-ray analysis and then were refined with the program SHELXL-93.[8] The final R ($Fo > 4\sigma(Fo)$) and $wR(Fo^2)$ are 0.08 and 0.20, respectively.

The crystal structure is essentially the same as that obtained by X-ray analysis.[9] Figure 1 shows the molecular structure,[10] which is also the same except that the parameters of the hydrogen atoms are obtained more precisely.[11] Bond distances and angles are essentially the same as the corresponding X-ray values.

Since the neutron scattering length for hydrogen is negative whereas that for deuterium is positive, H/D exchange is readily apparent from inspection of neutron Fourier map peaks. The H/D ratios obtained here are as follows: D9, 0.20:0.80(3); H10B, 0.83:0.17(3); H10A, 0.97:0.03(3) and H10C, 1.00:0.00. This result clearly indicates that the C9-D9 and C10-H10B bonds are easily cleaved, and that D9 and H10B are exchanged with one another.

The interatomic distances, Co...D9, Co... H10B, Co...H10A and Co...H10C are 2.49(3), 3.16(5), 3.29(6) and 3.96(5) Å, respectively. As the Co...H distance becomes shorter, the degree of exchange increases. This suggests that the D9 and H10B atoms have significant interactions with the cobalt atom. These interactions should accelerate the bond cleavage of C9-D9 and C10-H10B.

It is very interesting that the deuterium and hydrogen atoms in the neighborhood of the chiral carbon atom are cleaved easily and migrate around the carbon atom. If the D9 atom were to be extracted by the cobalt atom on exposure to the xenon lamp, the chiral C9 atom would take sp^2 hybridization. If the H10B atom cleaved from C10 were to attack C9 from the opposite side of D9 and D9 formed a bond to C10, then the chirality of the C9 atom would be inverted. This is very advantageous for retaining the crystalline lattice, since only hydrogen atoms bonded to C9 and C10 have large movements, while the other atoms move only slightly. Therefore, even if the chiral group is bulky, the movement of the atoms in the crystalline lattice is not significantly more pronounced than for a small group. It must be emphasized that not only the Co-C bond but also C-H bonds are easily cleaved by photoirradiation, if the transition metal comes close to the C-H bonds. Further experiments are in progress.

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6 [(*R*)-1-cyanoethyl-d$^{\alpha}$] [(*S*)-1-phenylethlamine]bis(dimethylglyoximato)-cobalt(III)
Cobalt acetate tetrahydrate (12.45 g, 0.05 mol) and dimethylglyoxime (11.61 g, 0.10 mol) were added to aqueous methanol (150 cm^3: methanol 140 cm^3 + water 10 cm^3) under Ar atmosphere with stirring. After stirring 10 min., acrylonitrile-d$^{\alpha}$ (3.78 g, 0.07 mol) and (*S*)-1-phenylethylamine (6.37cm^3, 0.05mol) 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 atomosphere. After the absorption of hydrogen was terminated, an aqueous solution of sodium hydroxide (200 cm^3) containing 4.0 g (0.10 mol) 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 diastereomeric crystals. The optical resolution was performed by the method of fractional crystallization from an aqueous methanol solution. The title compound was recrystallized several times from methanol solution to give 5.24 g (0.011 mol, 22.5 % yield) of crystals; $[\alpha]^{589}{}_{23}$ +58.5°(c 0.11, chloroform). The NMR measurement of the chlorofolm solution of the compound before irradiation showed that the deuterium atom was substituted completely and only to the H9 position.

7 The lattice parameters were determined by a least-squares fit of sin2θ values for 32 reflections within the range $51° < 2\theta < 62°$. Intensity data within the range of $0 \le h \le 11$; $-18 \le k \le 0$; $-12 \le l \le 12$ were measured by θ:2θ step scans using scan width $\Delta 2\theta = 3.2°$ for $2\theta \le 60°$ and $\Delta 2\theta = (1.64+4.03\tan\theta)°$ for $2\theta > 60°$. The intensities of two reflections [3 -5 5;7 0 -2] monitored at regular intervals showed no systematic variations. Integrated itensities I_o and variances $\sigma^2(I_o)$ were derived from the scan profiles. Absorption corrections were applied using $\mu_n = 2.263$ cm^{-1}, based on μ / ρ values given in *International Tables for X-ray Crystallography.* Minimum and maximum transmission factors were 1.170 and 1.936 respectively. Averaging F_o values of 183 symmetry-related pairs of reflections resulted in an internal agreement factor of 0.030. These averaged reflections were grouped with an additional 2795 reflections, which were measured only once, to yield 2978 independent observations. For the refinement model, starting nuclear parameters of all atoms were taken from the X-ray analysis. Coherent neutron scattering lengths (fm) for D(6.674), C(6.648), N(9.36), H(-3.741), O(5.803) and Co(2.78) were taken from the tabulation by Koester.[12] Refinement of the completed model of 59 independent atoms was carried out by full-matrix least squares methods using the program SHELXL-93. The weighting scheme was $w = [\sigma(F_o{}^2)^2+(0.0713P)^2]^{-1}$ where $P = (F_o{}^2+2F_c{}^2)/3$. The refinement converged with fit indices $R(F_o) = 0.150$ for 1878 unique reflections after merging; $wR(F_o{}^2) = 0.203$; $R(F_o) = 0.080$ for $F_o > 4\sigma(F_o)$ and $S = 1.15$ for all data.

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11The authors have deposited atomic coordinates at the CambridgeCrystallographic Data Center. The coordinates can be obtained on the request from The Director, Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK.

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