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Direct Observation of Steric Hindrance in the Process of Photoisomerization of Cobaloxime Complexes

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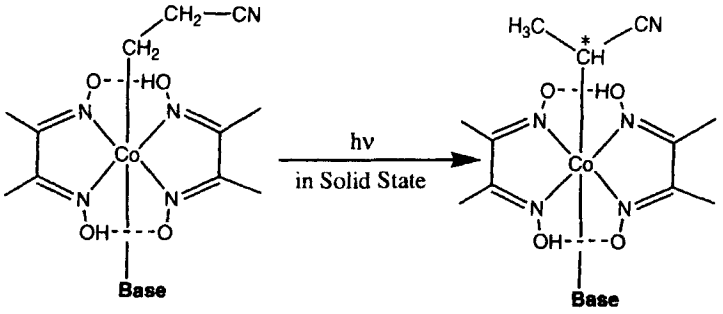
The cobaloxime complex crystals with the β-cyanoethyl group as an axial group and the biphenylboron group substituted to the equatorial ligand were prepared. When the crystals were irradiated with a xenon lamp, the β-cyanoethyl groups were changed to the α-cyanoethyl group with retention of the single crystal forms. The produced α-cyanoethyl groups were not racemic but chiral depending on the asymmetry around the β-cyanoethyl groups in the original crystals. It was made clear from the structure analyses before and after the reaction that the steric repulsion of the biphenylboron group with the produced α-cyanoethyl group is responsible to the generation of chirality.

Keywords: photoisomerization; cobaloxime complex; X-ray crystal structure analysis; asymmetric reaction; solid-state reaction

INTRODUCTION

It was found that the β-cyanoethyl group bonded to the cobalt atom in some cobaloxime complexes is isomerized to the α-cyanoethyl group when the powdered sample of the complex was irradiated with a xenon



β-cyanoethyl cobaloxime α-cyanoethyl cobaloxime

SCHEME 1

lamp. This reaction proceeds only in the solid state and the reverse reaction has notbeen observed.[1] The crystals were decomposed as the reaction proceeded.

We examined the relation between the reaction rate and the crystal structure changing the axial base ligand, and found that the reaction rate is controlled by the three factors; hydrogen bond, conformation of the β-cyanoethyl group and the size of the reaction cavity.[2]

Then we tried to search the solid state isomerization with retention of the single crystal form, changing the axial base ligand. After many trials, the crystal of the complex with N-(2-hydroxyethyl)isonicotinamide as an axial base ligand proceeded retaining the single crystal form. After the photoirradiation, the β-cyanoethyl group was transformed to the disordered structure composed of the produced α-cyanoethyl group and the original β-cyanoethyl group as shown in Figure 1. The ratio of the α- and β-cyanoethyl groups was 73:27. The produced α-cyanoethyl group, however, was not racemic but completely chiral (R or S) at one molecular site.[3]

Although the above example is very informative, it is very difficult to say which configuration is produced before we analyze the crystal structure, since it is imposible to predict the crystal structure. We must consider how to control the reaction pathway. The first method is the formation of host-guest complexes with a series of host molecules,

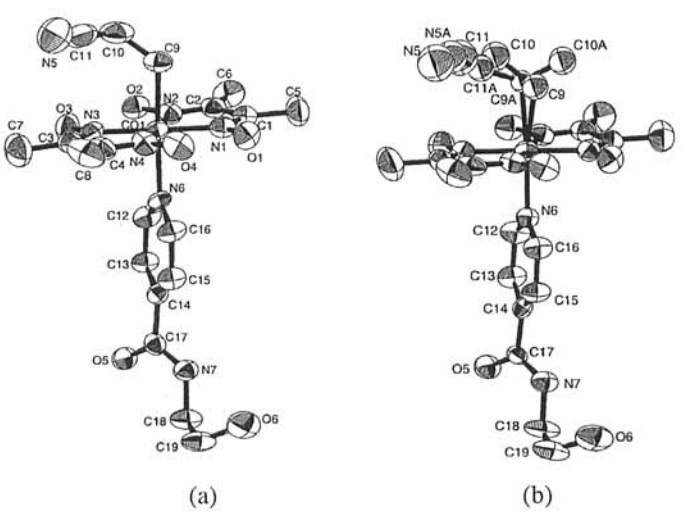


FIGURE 1 Structural change of the N-(2-hydroxyethyl)isonicotinamide complex (a) before and (b) after irradiation

which was already reported.[4] The second is the insertion of the bulky substituents in the vicinity of the reactive group. After many trials to introduce the bulky groups, we found that the biphenylboron group substituted to the equatorial ligand gave steric hindrance to the reactive group as shown in Figure 2.

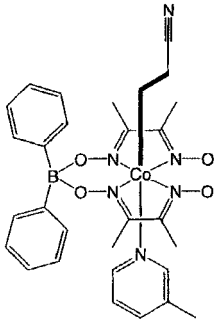


FIGURE 2 Cobaloxime complex with the biphenylboron group

More than 40 cobaloxime complexes with the biphenylboron group were prepared changing the axial amine. For only complexes with 3-methyl-pyridine (**1**) and *S*-nicotine (**2**) as axial amines, the crystals retained the single crystal forms on exposure to a xenon lamp. This paper reports how to control and design the reactivity in the solid state photoisomerization using the bulky substitutent in the vicinity of the reactive group.

MOLECULAR STRCUTRES

Figure 3 shows the molecular structures of (**1**) and (**2**). In both of the molecules the β-cyanoethyl groups take the conformation perpendicular to the cobaloxime plane, that is, the central C-C bond of the β-cyanoethyl group is *trans*. In the molecule of (**1**) the plane composed of C-C-C-N atoms of the β-cyanoethyl group is approximately perpendicular to the axial phenyl ring of the biphenylboron group, whereas the palne is nearly parallel to the phenyl ring in the molecule (**2**).

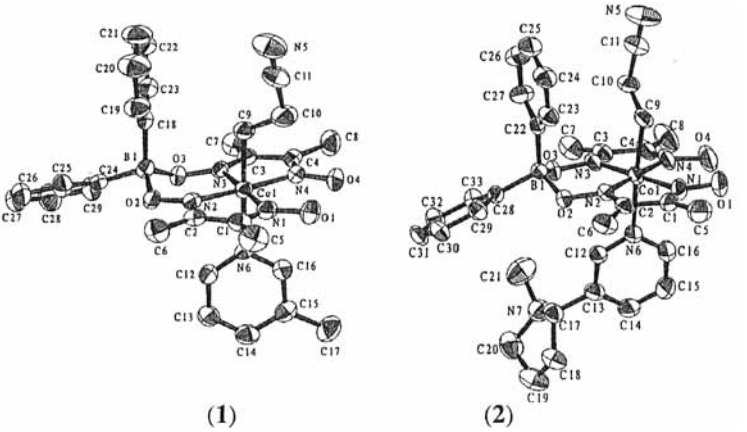


FIGURE 3 Molecular structures of (**1**) and (**2**)

In order to examine the stable conformation of the β-cyanoethyl group in the initial crystal structure, the molecular mechanics calcula-

tion was performed using the Cerius^2 program.[15] The minimum energies were calculated, rotating the β-cyanoethyl group around the Co-C bond. There are three local minima, 130, 220 and 310°, as shown in Figure 4. The angles correspond to the parallel, perpendicular and parallel confomations observed in the molecules of (**1**) and (**2**). This suggests that the conformations observed in the crystal structures may be preserved in solution.

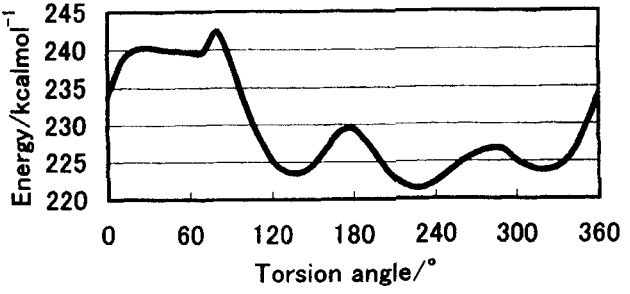
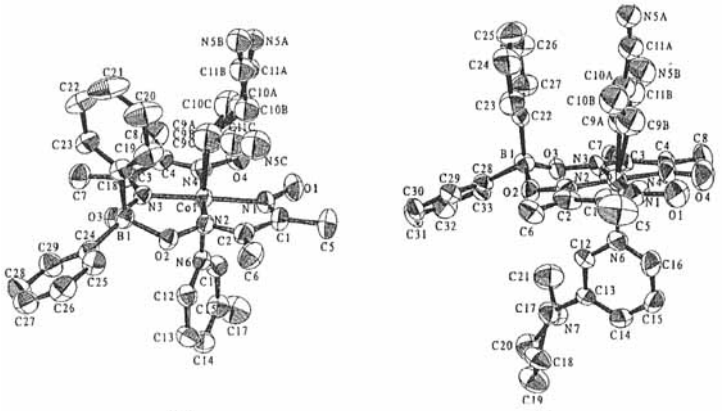


FIGURE 4 Calculated energy minima around the Co-C bond of the β-cyanoethyl group

PHOTOIRRADIATION

Each crystal was irradiated with a xenon lamp. The wavelength longer than 630nm was used. A crystal of (**1**) was exposed to the xenon lamp for 72 hours before the change of cell domensions was insignificantly small, whereas for the (**2**) crystal 48 hours exposure was necessary.

The cell dimensions of (**1**) after irradiation are similar to those before irradiation, but the unit cell volume increased significantly. There appeared extra peaks, which were assigned to the atoms of the produced α-cyanoethyl group, around the β-cyanoethyl group. The conversion was estimated to be 13% from the occupancy factors of the produced α-cyanoethyl group. Figure 5(a) shows the molecular structures of (**1**) after irradiation. The produced α-cyanoethyl group was not disordered but had only one enantiomer at a site.



(1) (2)

FIGURE 5 Molecuar structures of (**1**) and (**2**) after irradiation

The unit cell volume of (**2**) after the irradiation decreased. This is the reason why the conversion of (**2**) is greater than that of (**1**), although the exposure time is shorter than that of (**1**). Figure 5(b) shows the molecular structures of (**2**) after irradiation. Both of the two crystallographically independent molecules in an asymmetric unit show the ordered α-cyanoethyl group in addition to the original β-cyanoethyl group. The occupancy factors of the α-cyanoethyl group are about 30%. Since the two crystallo-graphically independent molecules of (**2**) have pseudo symmetry before irradiation, the produced α-cyanoethyl groups after irradiation have opposite configurations to each other.

REACTION PROCESS

Next, we must explain how the absolute configuration of the α-cyanoethyl group is produced. Figure 6 shows the structural change in the isomerization for the complexes (**1**) and (**2**). The minimum energy around the Co-C bond was calculated for the produced α-cyanoethyl group with *R* configuration, using the Cerius[2] program. The α-cyanoethyl group of the molecule (**1**) takes the conformation with the global minimum, whereas those of (**2**) have the conformations with the local minima, although the configurations are opposite to each other. This

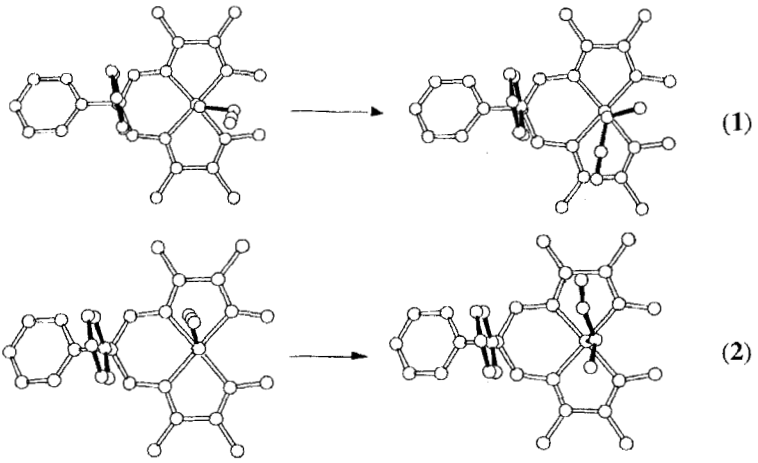


FIGURE 6 Structural changes of the cyanoethyl groups in (**1**) and (**2**)

means that the conformations of the α-cyanoethyl groups found in the two crystals may be produced even if the reaction occurred in solution.

There remains the final question why the produced α-cyanoethyl groups are different in the two crystals. The reaction cavities for the β-cyanoethyl groups in the original crystals are shown in Figure 7. The cavity for (**1**) was divided into two by the plane composed of the C-C-C-N bond. The two parts have the volumes of 9.3 Å^3 and 3.4 Å^3. If we

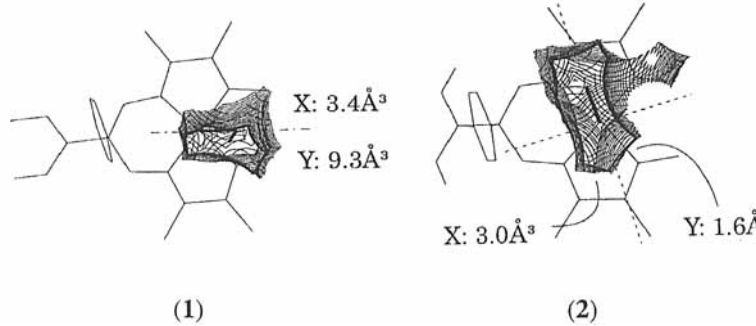


FIGURE 7 Reaction cavities for the β-cyanoethyl groups of (**1**) and (**2**)

assume that the cyano and methyl groups of the produced α-cyanoethyl group occupy the larger and smaller parts, respectively, the same structure as the observed α-cyanoethyl group will be obtained.

The cavity for (2) was divided into four by the plane composed of the C-C-C-N bond and its normal plane. The widest part is up and left. The second widest is down and left. It is clear that the cyano and methyl groups occupy the widest and second widest parts, respectively. The produced α-cyanoethyl group has a conformation with the second minimum energy and the configuration must have R, which is the same as the observed one.

SUMMARY

Structure analyses before, intermediate and after the reaction using one crystal give us much information on the reaction mechnism. It is possible to control the reaction pathway by introducing a bulky substituent neighboring to the active site. A few plausible structures of the product can be estimated from the molecular mechanics calculation. The real structure observed is well explained by the reaction cavity.

Acknowledgment

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