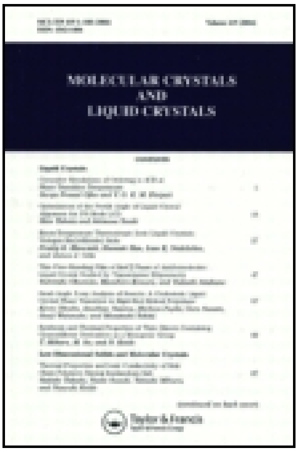

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Generation of Chirality in Crystalline-State Isomerization of Cobaloxme Complexes

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GENERATION OF CHIRALITY IN CRYSTALLINE-STATE ISOMERIZATION OF COBALOXIME COMPLEXES

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Abstract The chiral compounds were obtained from the racemic compounds and from achiral compounds in chiral crystal environment in the process of photoisomerization with retention of the single crystal form. The mechanism why and how the chirality was genarated was clearly elucidated by X-ray analyses.

INTRODUCTION

There are two cases for the generation of chirality in crystals. The first case is that chiral compounds are produced from racemic ones in chiral crystal environment. The second one is that chiral compounds are produced from achiral ones in chiral crystal environment. The latter case is usually called as the absolute asymmetric reaction. If the reaction proceeds in a crystal with retention of the single crystal form, which is called as a crystalline-state reaction, we can easily observe the mechanism how the chirality is generated in the crystal. In this paper, the above two cases are reported using the examples of the cobalt complexes.

RACEMIC-TO-CHIRAL TRANSFORMATION BY PHOTOIRRADIATION

It was found that the chiral cyanoethyl group bonded to the cobalt atom in some bis(dimethylglyoximato)cobalt(III), cobaloxime, complexes was racemized by X-ray or visible light exposure without degradation of the single crystal form as shown in Figure 1.[1] The rate of the racemization was so slow that several intermediate structures were obtained by X-ray analyses.[2] The similar crystalline-state racemizations have been observed for many cobaloxime complex crystals with different axial base ligands.[3] The reaction rates and the crystal structures for the crystals were compared with each other. And a quantitative relationship between the reaction rate and the crystal structure has been obtained. For the complex with piperidine as an axial base ligand, on the other hand, we found a very strange result that the racemic crystals showed optical activity when the crystal was only irradiated with visible light.[4]

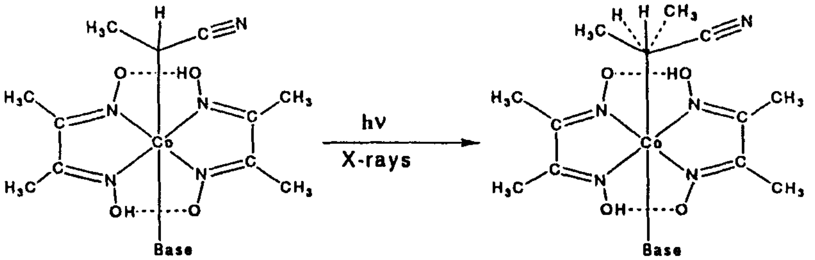


FIGURE 1. Racemization of cobaloxime complexes.

Figure 2 shows the crystal structure of the racemic piperidine complex viewed along the a axis. The space group is $P2_12_12_1$ as shown in Table 1 and there are two crystallographically independent molecules, A and B, in an asymmetric unit. The two molecules are not related by any pseudo symmetry. The A molecule has R cyanoethyl group whereas B has S cyanoethyl group. Therefore, the crystal is racemic but chiral. This means that the enantiomorphic crystal has S cyanoethyl group in the A molecule and the R group in B. One of the enantiomeric pair can be easily obtained by seeding in crystallization.

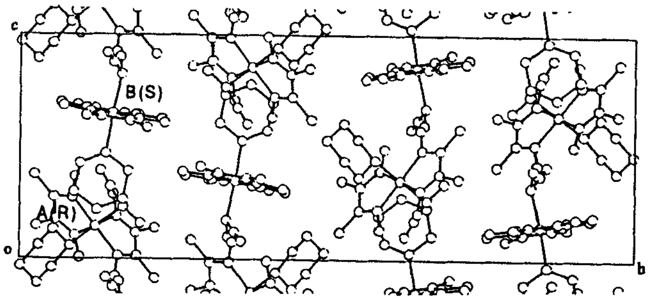


FIGURE 2. Crystal structure of racemic piperidine complex viewed along the a axis

When the crystal was exposed to a xenon lamp, the cell dimensions was gradually changed. After about 40 hours exposure, the change became insignificantly small. Table 1 also shows the crystal data after irradiation. The crystal structure after irradiation is shown in Figure 3. Although the A molecule was not changed and the cyanoethyl group has R configuration after irradiation, the cyanoethyl group of the B molecule changed from S configuration to the disordered racemates. Figure 4 shows the molecular structure of B after irradiation.

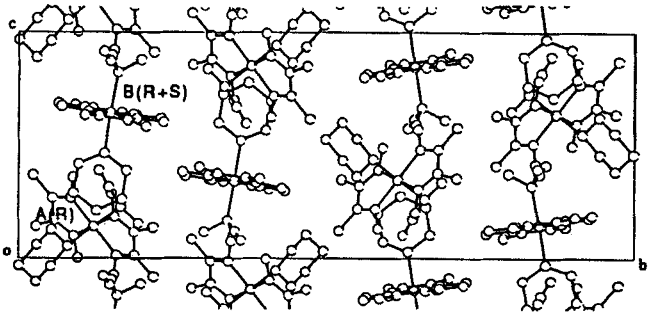


FIGURE 3. Crystal structure after irradiation.

TABLE 1. Crystal data before and after irradiation.

	before irradiation	after irradiation
Space Group:	$P2_12_12_1$	$P2_12_12_1$
Z:	8	8
a / Å :	11.688(5)	11.7215(7)
b / Å :	30.708(5)	30.761(3)
c / Å :	11.418(4)	11.384(1)
V / Å^3:	4098(2)	4105(1)

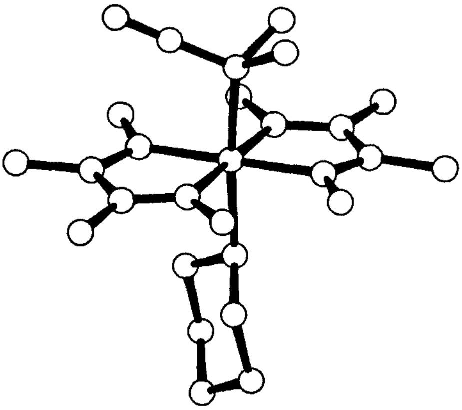


FIGURE 4. Disordered molecular structure of B after irradiation.

The racemization of only B molecule brings about the strange result. Before irradiation, the R:S ratio in the crystal is 50:50 and the crystal is racemic. However, the R:S ratio became about 75:25 after irradiation, since only B cyanoethyl group became racemic. The optical enrichment occurred in the racemic crystal only by photoirradiation. The crystal after irradiation was dissolved in a chloroform solution, of which the specific rotatory power, $[\alpha]_D$, showed about 30°.

The R:S ratio of the B cyanoethyl group after irradiation for a long time did not converged to 50:50 but to 40:60. This is because the environment of the B cyanoethyl group in the crystal is not symmetric. The reaction cavity for the B cyanoethyl group was drawn in the crystal before irradiation. The cavity size is large enough to accommodate the inverted group. In order to define the asymmetry of the reaction cavity, the cavity was divided into two parts by the plane composed of Co-C-C-N bonds. Before the irradiation the ratio of the left and right halves are 45:55 as shown in Figure 5. The ratio of left and right halves became approximately 50:50 after sufficient irradiation, although the ratio of R to S configurations became 40:60 after irradiation, This indicates that the R to S ratio after complete irradiation is not determined by the entropy term but by the enthalpy term, that is, steric repulsion with the surrounding atoms in the crystal. The details of the reaction process are described in the previous paper.[5]

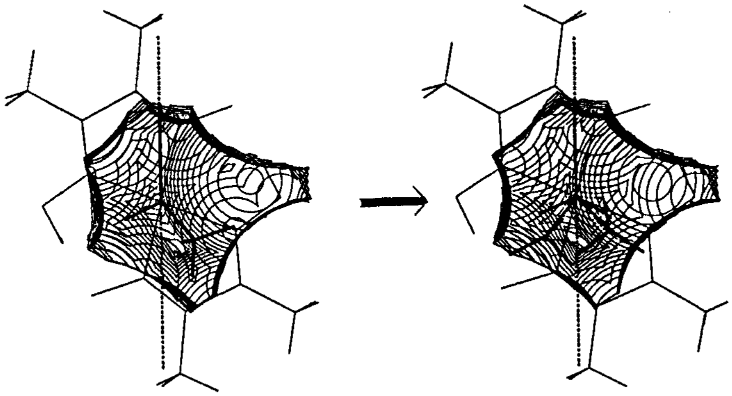


FIGURE 5. Change of the cavity shape.

ACHIRAL-TO-CHIRAL TRANSFORMATION BY PHOTOIRRADIATION

Recently it was found that the β-cyanoethyl group bonded to the cobalt atom in some cobaloxime complexes was isomerized to the α-cyanoethyl group on exposure to visible light as shown in Figure 6. This β-α photo-isomerization proceeds only in the solid state and the reverse reaction has not been observed.[6] In the isomerization the achiral β-cyanoethyl group is transformed to a chiral α-cyanoethyl group. This may indicate that if the environment of the β-cyanoethyl group in the reactant crystal is asymmetric, the chirality should effect on the asymmetry of the produced α-cyanoethyl group.

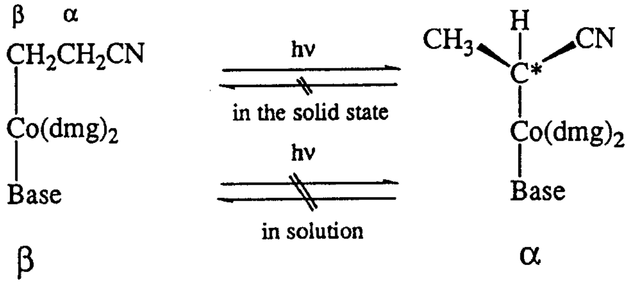


Figure 6. Reaction scheme of photoisomerization

Preliminary work showed that optical rotation was observed when the powdered sample was irradiated with a xenon lamp and its chloroform solution was measured by polarimeter.[7] In order to examine the mechanism how the chirality is produced, we intended to observe the β-α isomerization in the crystalline-state. After many trials, two cobaloxime complex crystals with 3-methylpyridine and 4-methylpyridine as axial base ligands showed the isomerization with retention of the single crystal form.

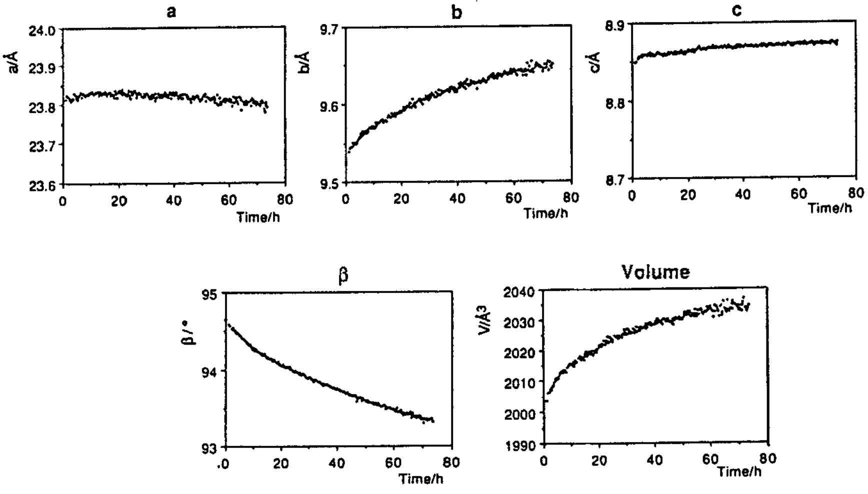


FIGURE 7. Change of cell dimensions.

Isomerization of the 3-Methylpyridine Complex

It was found that the β-cyanoethyl complex with 3-methylpyridine as an axial base ligand makes mixed crystal with the α-cyanoethyl complex in any composition.[8] This may indicate that the crystal with β-cyanoethyl group will be isomerized to the α-cyanoethyl group without degradation of the single crystal form. After many trials we found that the cell dimensions were gradually changed, using a new type of xenon lamp with high flux and a glassfiber tube which brought the light to the crystal mounted on a diffractometer.[9] Figure 7 shows the change of cell dimensions. After 74 hours exposure the change became insignificantly small. Figure 8(a) shows the crystal structure before irradiation. The space group is $P2_1/a$ and there is one molecule in an asymmetric unit. Figure 8(b) shows the crystal structure after irradiation. The new peaks appeared around the β-cyanoethyl group, which were assigned to the α-cyanoethyl group. The ratio of the β- and α-cyanoethyl groups became 45:55.

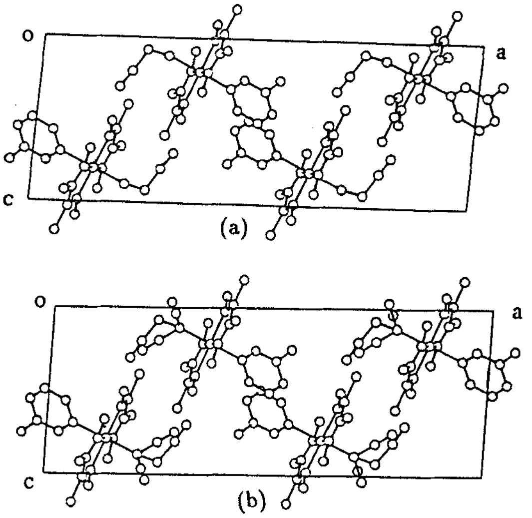


FIGURE 8. Crystal structures (a) before and (b) after irradiation

Figure 9 shows the molecular structure of the produced 3-methyl-pyridine complex. The produced α-cyanoethyl group has a disordered structure. But the R to S ratio is not 50:50 but is 20 to 35. It is clear that the chirality was generated in the crystal. Of course, the racemic product should be produced in a whole crystal, since this crystal has a center of symmetry.

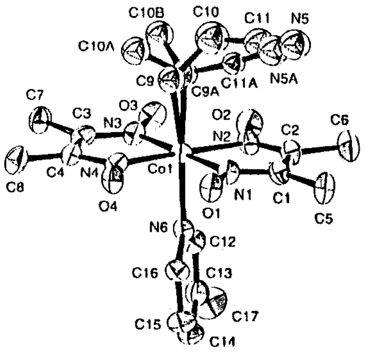


FIGURE 9. Molecular structure after irradiation

Isomerization of the 4-Methylpyridine Complex

Another β-cyanoethyl complex with 4-methylpyridine as an axial base ligand was also examined. This crystal exhibited a reversible phase transition with retention of the crystallinity at 343 K.[10] In the low temperature phase, the crystal has two crystallographically independent molecules in a unit cell. After the phase transition the length of the c axis is reduced to one-half of its initial value and only one molecule is in an asymmetric unit cell. The space group, $P2_1/a$, was conserved. The structure of high temperature phase is similar to that of 3-methylpyridine complex. Therefore, the 4-methylpyridine crystal was warmed to 346 K and exposed to the xenon lamp. The β-cyanoethyl group was gradually changed to α-cyanoethyl group with almost retention of the crystallinity.[9]

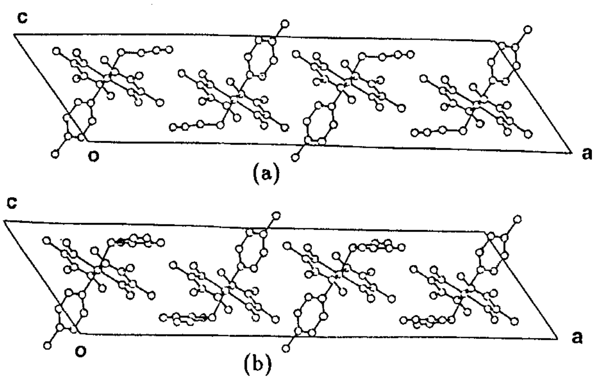


FIGURE 10. Crystal structure (a) before and (b) after the irradiation.

The crystal structures before and after the irradiation are compared in Figure 10. The α-cyanoethyl group appeared around the β-cyanoethyl group. The molecular structure after the irradiation is shown in Figure 11. The produced α-cyanoethyl group has an ordered structure and its configuration is R. No peaks assigned to the α-cyanoethyl group with S configuration were observed. The molecular structures before and after the irradiation are not significantly different to each other except the produced α-cyanoethyl group. The population of the produced α-cyanoethyl and the original β-cyanoethyl complexes are 0.30 and 0.70, respectively.

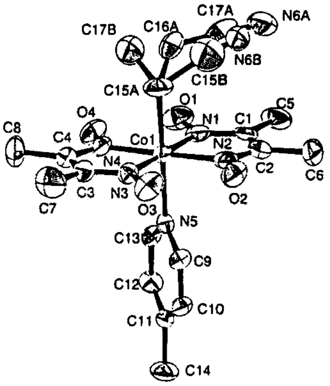
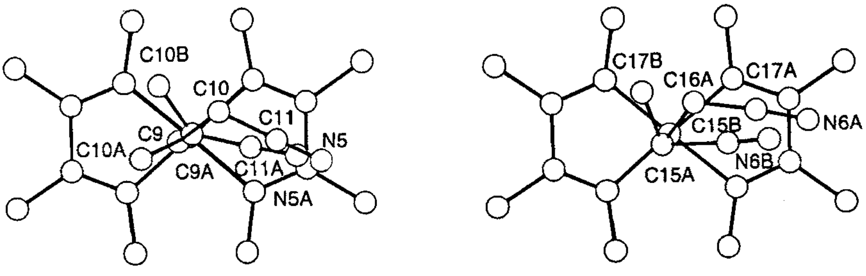


FIGURE 11. Disordered molecular structure after irradiation.

Generation of Asymmetry in the Photoisomerization

Figure 12 shows the molecular structures viewed along the normal to the cobaloxime plane after the irradiation for 3- and 4-methylpyridine crystals. Although the conformations of the initial β-cyanoethyl groups of both crystals are similar to each other, the configuration of the produced α-cyanoethyl groups are different; S configuration is dominant for 3-methylpiridine crystal whereas only R is produced for 4-methylpyridine crystal.



(a) (b)

FIGURE 12. Molecular structures viewed along the normal to the cobaloxime plane after irradiation. (a) 3-methypyridine complex and (b) 4-methylpyridine complex.

In the process of the isomerization, the β-cyanoethyl radical formed by the homolytic cleavage of the Co-C bond may be transformed to the α-cyanoethyl radical and then the recombination of the cobalt and the α-cyanoethyl radical would produce the α-cyanoethyl group. If the produced α-cyanoethyl group does not match the surrounding atoms, it would be easily restored to the α-cyanoethyl radical. Finally the ratio of the R and S configurations should depend on the repulsion with the surrounding atoms in the crystal structure.

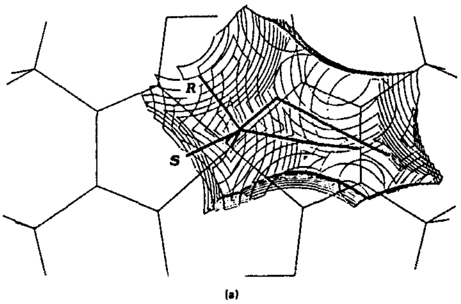


FIGURE 13. Reaction cavity for the β-cyanoethyl group of 3-methylpyridine complex

We defined the reaction cavity for the reactive group in the crystalline-state racemization, in order to estimate the repulsion with surrounding atoms quantitatively. The reaction cavity for the β-cyanoethyl group in the 3-methylpiridine crystal before the irradiation is shown in Figure 13, in which the produced α-cyanoethyl groups as well as the initial β-cyanoethyl group are also shown. The space in the cavity at the position of R methyl group is very thin and the methyl group protrudes from the cavity. On the other hand, a large part of the S methyl group is included in the cavity, since the cavity around the S-methyl group is thicker than that around the R-methyl group. The R-α-cyanoethyl group should have higher repulsion with the neighboring atoms than the S-α-cyanoethyl group. This may cause the unequal ratio of the R and S configurations of the produced α-cyanoethyl groups in the 3-methylpiridine crystal.

Figure 14 shows the reaction cavity for the β-cyanoethyl group of 4-methylpiridine crystal before irradiation viewed along the normal to the cobaloxime plane. The methyl group of the R-α-cyanoethyl group occupies the very wide space in the cavity whereas the S-methyl group has no space. This well explains the reason why only the R-α-cyanoethyl group is produced in the 4-methylpiridine crystal.

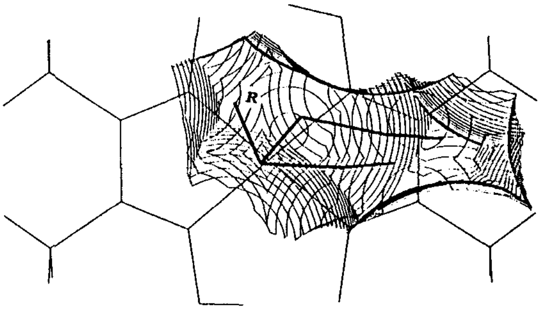


FIGURE 14. Reaction cavity for the β-cyanoethyl group of 4-methylpyridine complex

These facts clearly indicate that the asymmetry can be generated from the achiral molecule in a chiral crystal environment. Unfortunately both of the crystals have a centrosymmetric space group. The α-cyanoethyl groups with the opposite ratio of R and S configurations are produced at the inverted site. The optical rotation cannot be observed for these crystals. Recently the β-cyanoethyl crystal with a chiral space group was prepared. The β-cyanoethyl group was surrounded by the chiral environment. Although the crystal was decomposed in the process of photoisomerization, more than 90 % optical yield was obtained for this crystal.

The mechanism why and how the chirality is generated in a chiral crystal environment has been clarified for the cobaloxime crystals. The size and shape of the reaction cavity well explains the reaction mechanism. The idea of the reaction cavity may be a good guide to examine the process of the solid-state reaction.

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