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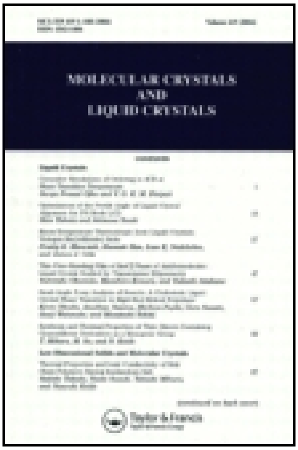

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X-ray Analysis of Successive Reaction in Crystalline State Photoisomerization of Cobaloxime Complexes

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X-ray Analysis of Successive Reaction in Crystalline State Photoisomerization of Cobaloxime Complexes

AKIKO SEKINE[a], MIZUHO YOSHIIKE[a], YUJI OHASHI[a], KANAKO ISHIDA[b], YOSHIFUSA ARAI[b] and YOSHIAKI OHGO[b]
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The γ-cyanopropyl group bonded to the cobalt atom in some cobaloxime complexes was isomerized to the α-cyanopropyl group through β-cyanopropyl group on exposure to visible light in the solid state. For the complex with 1-phenylethylamine as an axial base ligand almost chiral α-cyanopropyl group was produced with retention of the single crystal form. The mechanism is discussed on the basis of the structural change.

Keywords: crystalline-state reaction, photoisomerization, cobaloxime complexes, absolute synthesis

INTRODUCTION

It was found that the β-cyanoethyl group bonded to the cobalt atoms in some cobaloxime complexes was isomerized to the α-cyanoethyl group when the powdered sample of the complex was

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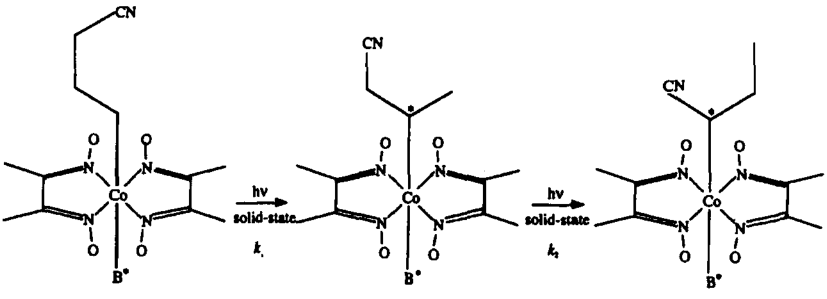
irradiated with visible light.[1] Recently the cobaloxime complexes with the γ-cyanopropyl group instead of the β-cyanoethyl group were prepared. When the powdered sample of the γ-cyanopropyl complex was irradiated with visible light, the γ-cyanopropyl group was isomerized to the α-cyanopropyl group through the β-cyanopropyl group. Since the final α-cyanopropyl group has a chiral carbon atom, the asymmetric induction may be possible when the chiral crystal environment is applied. Three chiral amines were introduced as axial base ligands, (R)-phenylethylamine (1), (S)-phenylalaninol(2), and (R)-2-aminobutanol (3). When the crystal of (1) was irradiated with visible light, the γ-cyanopropyl group was completely isomerized to the α-cyanoethyl group with retention of the single crystal form. This paper reports such a novel crystalline-state photoisomerization and discuss the mechanism.



Scheme γ – α photoisomerization of cobaloxime complex

RESULTS AND DISCUSSION

Crystal Structure Analysis

The crystal structures of the three complexes were analyzed by X-rays using the 4-circle diffractometer or IP diffractometer. Figure 1 shows crystal structures of 1, 2 and 3. Each crystal has one crystallographically independent molecule in its unit cell.

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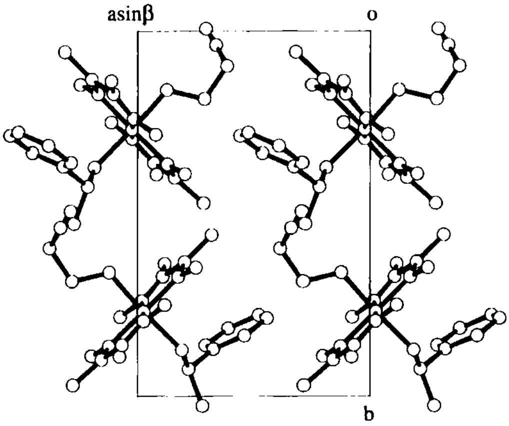
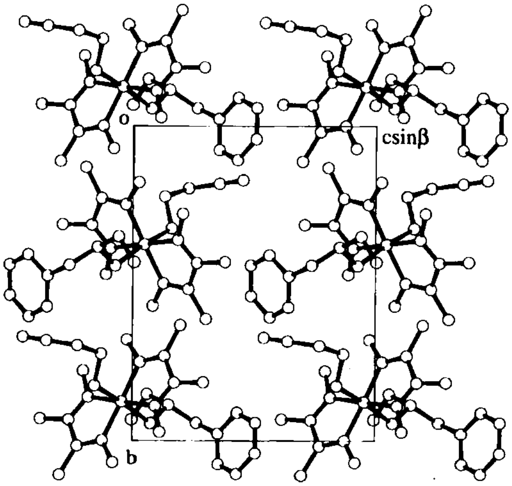


(a)



(b)

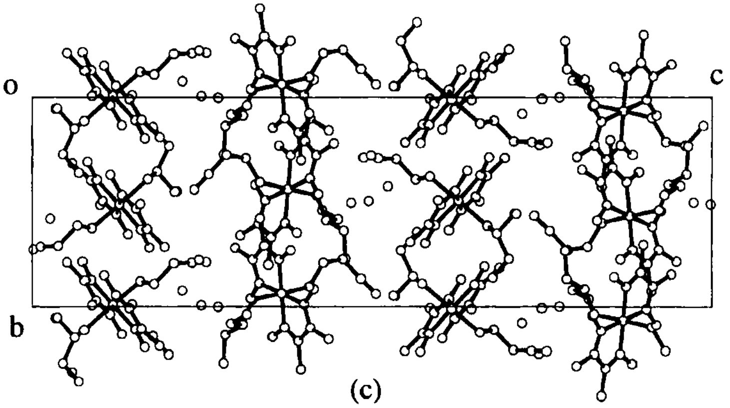


FIGURE 1 Crystal structures of (a) 1 , (b) 2, and (c) 3

Photoisomerization of powdered samples

The powdered sample of each complex was irradiated with a xenon lamp. The reaction rate of the isomerization from γ- to β-cyanopropyl group and β- to α-cyanopropyl group was measured by HPLC for each complex. Table I shows the reaction rates, reaction yields and enantiomer excess for the three complexes.

Table I Reaction rate, reaction yield and enantiomer excess

complex	1	2	3
k / s^{-1}	1.0×10^{-3}	4.2×10^{-5}	9.9×10^{-5}
yield	81.3	9.2	12.2
e.e./%	67.2	12.3	26.3

Photoisomerization in a crystal

Since the crystal 1 has much greater reaction rate than the other two, it is probable that the crystal 1 show the isomerization with retention of the single crystal, considering from the isomerization of β- to α-cyanoethyl group crystal.[2] One single crystal was mounted on a 4-circle diffractometer and irradiated with the xenon

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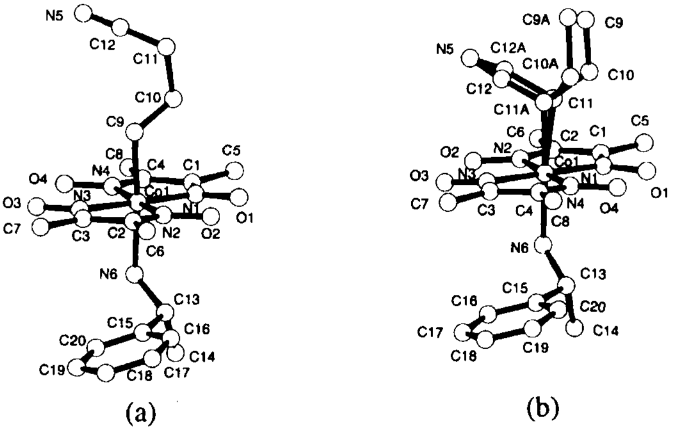
lamp. The cell dimensions were gradually changed. After two weeks exposure, the cell change was converged and then the three-dimensional intensity data were collected. The crystal structure after the irradiation was approximately the same as before the irradiation except for the γ-cyanopropyl group. The molecular structures before and after the irradiation is shown in Fig. 2. Surprisingly, the γ-cyanopropyl group was completely transformed to the α-cyanopropyl group and no β- and γ-cyanopropyl groups were observed. The produced α-cyanopropyl group is disordered with R- and S-configurations. The occupancy factors of R- and S-enantiomers were 0.07 and 0.93, respectively.



(a) (b)

FIGURE 2 Molecular structure of 1 (a) before and (b) after the irradiation.

Mechanism of the γ - α photoisomerization

The reaction cavity for the γ-cyanopropyl group in each crystal was calculated. The volumes of the cavities of 1, 2 and 3 are 29.2, 20.9 and 23.7Å^3, respectively. The isomerization rates of the three complexes given in Table II depend on the above volumes. The similar correlation between the reaction rate and the cavity size has been observed in the solid-state photoisomerization of the β-cyanoethyl complex[2] and the crystalline-state photoracemization[3].

Figure 4 shows the cavity for the γ-cyanopropyl group of 1. The shape of the cavity well explains why the α-cyanopropyl group is produced with retention of the single crystal from, since it is very similar to that of the produced α-cyanopropyl group. However, it seem very difficult the cavity includes the β-cyanopropyl group without destroying the crystallinity. This is a reason why the reaction rate of β to α is much greater than that of γ to β and the β-cyanopropyl was undetectable in the crystalline-state isomerization of 1. The shape of the cavity for the γ-cyanopropyl group also well explains why the produced α-cyanopropyl group has mainly S-configuration.

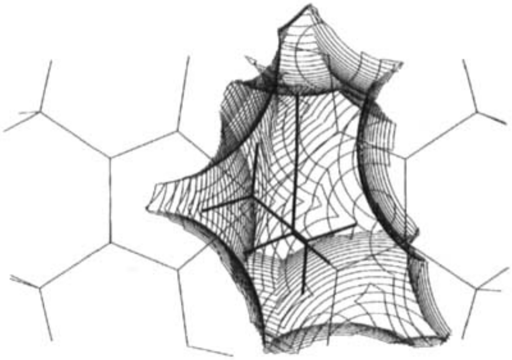


FIGURE 4 Cavity of 1 viewed along the normal to the cobaloxime plane

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