

Single Crystal Neutron Diffraction Study of the 3-2-1 Two-Step Photoisomerization of 3-Cyanopropyl Cobaloxime Complex

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The crystal of 3-cyanopropyl(aniline)cobaloxime complex shows 3-2-1 two step photoisomerization with retention of single crystal form. On exposure to near-infrared radiation (>780 nm), the composition of intermediate 2-cyanopropyl complex increased in the crystal and its structure was determined by X-rays. The produced 2-cyanopropyl group was not racemic but had one enantiomer. Then a large crystal was irradiated for 10 days and the single crystal neutron diffraction was carried out with the BIX-3 diffractometer at JRR-3M reactor (JAERI). The results shows that the chiral β -position carbon atom of the reactive group was racemized in the second step, and it indicates that the olefinic molecular and the cobalthydride may exist in the intermediate stage of the reaction.

KEYWORDS: crystalline-state reaction, neutron diffraction, cobaloxime complex, BIX-3

§1. Introduction

Research efforts have been focused to cobaloxime complexes since these are model compounds of the enzymatic activation of Vitamin B₁₂ and a chiral hydrogenate catalytic reaction, and are well known to show various types of crystalline-state photoreactions which proceed with retention of single crystal form.^{1–3)} Many investigations have shown that the reaction rate and chiral discrimination are controlled by the volume and shape of reaction cavity.⁴⁾ However, the mechanism of the reaction remains unsolved because there is only little knowledge about the migration of hydrogen atoms in the reaction processes. The detailed structural knowledge will afford important information for the enzymatic and catalytic reactions which occur in highly restricted environment like crystalline lattice.

In our previous work,⁵⁾ it was reported that the crystalline-state 3-1 photoisomerization of 3-cyanopropyl cobaloxime complex occurred in the 3-2-1 two steps (Fig. 1). Hydrogen atoms in specific positions of the reactive group were exchanged with deuterium atoms as markers, and then the migration of the deuterium atoms was analyzed by single crystal neutron diffraction. However, some ambiguities remained because the structure of the intermediate 2-cyanopropyl complex was not determined rigidly.

Recently, it was found that the occupancy of the intermediate 2-cyanopropyl complex increases by the exposure of near-infrared radiation (>780 nm) to a crystal of (3-cyanopropyl- $d_2^{\alpha,\alpha}$)(aniline)cobaloxime- d_{12} complex (**1**). This report shows the structures of intermediate 2-cyanopropyl complex determined by X-rays and the final 1-cyanopropyl complex determined by neutrons, and proposes a detailed mechanism of the 3-2-1 isomerization.

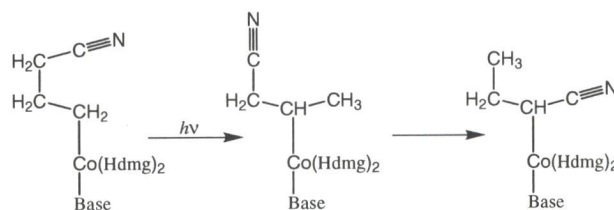


Fig. 1. Crystalline-state 3-2-1 stepwise photoisomerization of 3-cyanopropyl cobaloxime complex.

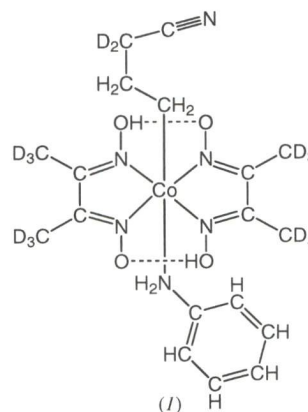


Fig. 2. Molecular structure of compound **1**.

§2. Experimental

Cobaloxime complex **1** (Fig. 2) was synthesized according to the reference,⁵⁾ and single crystals were obtained by slow evaporation from ethyl acetate solution with small portion of water. The hydrogen atoms of the dimethylglyoximate ligands were also re-

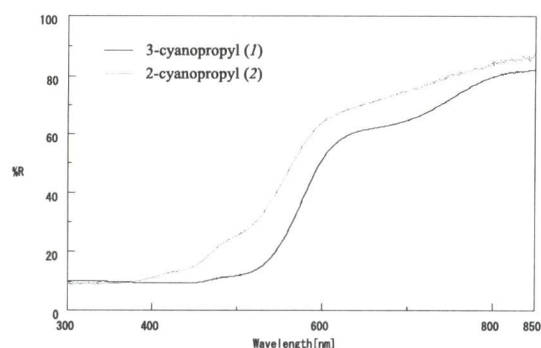


Fig. 3. Solid-state UV-VIS reflection spectrum of 3-cyanopropyl (solid-line) and 2-cyanopropyl(aniline)cobaloxime (broken line) complexes.

Table I. Crystal data of *1* after irradiation.

	4 days irradiation	10 days irradiation
$a/\text{\AA}$	20.5268	21.2158
$b/\text{\AA}$	8.4894	8.4871
$c/\text{\AA}$	25.6649	26.3612
$\beta/^\circ$	105.742	104.535
Space group	$C2/c$	$C2/c$
Radiation	X-ray	neutron
Wavelength/ \AA	0.71073	2.35
$2\theta_{\max}$	59.3	140.0
Unique reflections	6031	614
$R[F_o > 4\sigma(F_o)]$	0.0682	0.2904

placed with deuterium atoms in order to reduce the incoherent scattering of neutron by hydrogen atoms. The UV-VIS spectra (Fig. 3) of compounds *1* and 2-cyanopropyl(aniline)cobaloxime (*2*), synthesized separately, showed that *1* has broader absorption tail than *2* in near-infrared region, and it was expected that the occupancy of intermediate 2-cyanopropyl group would increase by near-infrared irradiation. After 4 days irradiation with near-infrared radiation (>780 nm) for crystals of *1*, the formation of the intermediate 2-cyanopropyl group was confirmed by IR spectroscopy. Single crystal X-ray diffraction was carried out by Siemens Smart-CCD diffractometer at 83K with $\text{MoK}\alpha$ radiation ($\lambda=0.71073$ Å) in the range $2\theta \leq 60^\circ$. The initial model structure was determined by direct method with the program SIR97,⁶⁾ and refined with the program SHELXL-97.⁷⁾ After 10 days irradiation with red light (>690 nm), single crystal neutron diffraction of *1* was also carried out by the neutron-IP used BIX-3 diffractometer at JRR-3M reactor (JAERI) at room temperature. The wavelength of incident neutron beam was 2.35 Å and the max value of 2θ was 140° . The measurement took 3 days. The initial model structure was determined by X-rays and refined with program SHELXL-97. Details of the experiment of diffraction are shown in Table I.

§3. Results and Discussions

X-ray diffraction data of *1* after 4 days irradiation shows that two initial 3-cyanopropyl, one final 1-cyanopropyl and two intermediate 2-cyanopropyl groups coexist statistically. Figure 4 shows the disordered struc-

ture of the intermediate 2-cyanopropyl complex determined by X-rays. Each occupancy factor of the 2-cyanopropyl group is 0.15. Both of the 2-cyanopropyl groups have *R* configuration. Possible reason why only the *R* configuration of the intermediate 2-cyanopropyl group was produced is explained by the fact that the (*R*)-2-cyanopropyl group is better accommodated in the cavity for the initial crystal than the *S*-isomer. On the other hand, only 3-cyanopropyl and the 1-cyanopropyl groups were observed by the neutron diffraction of *1* after 10 days irradiation. The occupancy factors of both groups were 0.4 and 0.6, respectively. Figure 5 shows the structure of the final 1-cyanopropyl complex determined by neutrons with hydrogen and deuterium atoms at the reactive part. The configuration of the observed 1-cyanopropyl group is *S*. One of the two deuterium atoms bonded to the α -carbon atom of the initial 3-cyanopropyl complex is also bonded to the α -carbon atom of the final 1-cyanopropyl complex, and the other is transferred to the β -carbon atom of the 1-cyanopropyl group. This figure also shows that the configuration of the chiral β -methylene carbon, $\text{R-C}^*\text{HD-R}'$, of the produced 1-cyanopropyl group is racemic. These results show that the 3-2-1 isomerization of *1* mainly proceeds

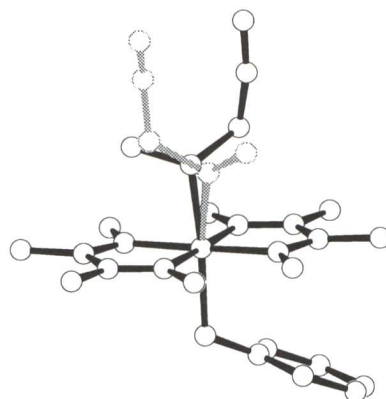


Fig. 4. Structure of the intermediate 2-cyanopropyl group. 3- and 1-cyanopropyl groups were omitted for simplification.

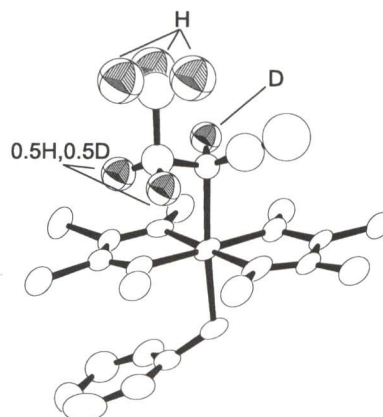


Fig. 5. Structure of the final stage of the 3-2-1 isomerization, 1-cyanopropyl group, determined by single crystal neutron diffraction. 3-cyanopropyl group was omitted for simplification.

from 3-cyanopropyl to (*R*)-2-cyanopropyl and finally to (*S*)-1-cyanopropyl complex, and the configuration of the β -carbon atom is racemized in the second step as shown in figure 6. In the process of racemization of the β -carbon atom, we propose the formation of olefin and cobalthydride species as shown in figure 7 after the final 1-cyanopropyl group is produced.

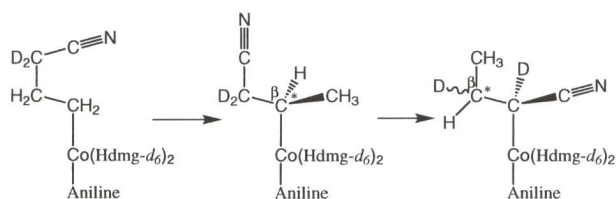


Fig. 6. Process of the 3-2-1 photoisomerization of compound 1.

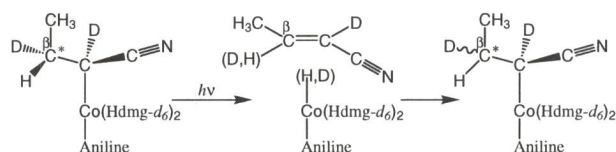


Fig. 7. Formation of the olefinic meta-stable species.

§4. Conclusion

The mechanism of the crystalline-state 3-2-1 photoisomerization of the 3-cyanopropyl cobaloxime complex was elucidated by the combination of single crystal X-ray and neutron diffraction measurements. Since the intensities of neutrons are still restricted due partly to the limited machine time, it was impossible to obtain the intermediate structure by the neutron diffraction. The structure of the 2-cyanopropyl complex was analyzed by X-rays. However, by evolution of the neutron source and diffractometer, it will become possible to determine the positions of hydrogen atoms bonded to meta-stable or transient species which are generated in processes of crystalline-state reactions.

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