

Neutron Diffraction Analysis of Photoisomerization of δ -Cyanobutyl Cobaloxime

Takaaki Hosoya^a, Hidehiro Uekusa^a, Yuji Ohashi^a, Takashi Ohhara^b, Ryota Kuroki^b, ^a*Department of Chemistry and Materials Science, Tokyo Institute of Technology.* ^b*Neutron Science Research Center, Japan Atomic Energy Research Institute.* E-mail: thosoya@chem.titech.ac.jp

δ -Cyanobutyl groups in cobaloxime complexes were known to be isomerized to γ -, β -, α -cyanobutyl groups successively on exposure to visible light with retention of single crystal form. However, in case of the photoisomerization of δ -cyanobutyl cobaloxime with bulky diphenylborone in the neighborhood of alkyl group, Ph₂B-cobaloxime, only α -form was observed by X-rays as photoproduct and FT-IR experiments showed that β -form was produced with decreasing α -form and gradually increased, *i.e.*, $\delta \rightarrow \alpha \rightarrow \beta$ reaction path not the "slide type" reaction $\delta \rightarrow \gamma \rightarrow \beta \rightarrow \alpha$ previously observed. This study was carried out to elucidate the detailed reaction mechanism by tracking the transfer of replaced two deuterium atoms. We prepared a large single crystal of δ -cyanobutyl-2,2-*d*₂ Ph₂B-cobaloxime complex and carried out a single crystal neutron diffraction measurement after 2 days irradiation with BIX-3 diffractometer. The final R factor was 16.36 %. The result showed that a half of the δ -form was isomerized to α -form and one of the two deuterium atoms bonded to α position of δ -cyanobutyl group was transferred to δ position, *i.e.*, from Co-CH₂CH₂CH₂CD₂CN to Co-CD(CN)CH₂CH₂CH₂D. This result indicated the cyanobutyl group turned upside down after homolytic cleavage of Co-C bond and directly isomerized from δ -form to α -form.

Keywords: neutron diffraction, hydrogen transfer, crystalline state reactions