Acta Cryst. (1998). A**54**, 842–849

Real-Time *In Situ* Observation of Chemical Reactions

YUJI OHASHI

Department of Chemistry, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152-8551, Japan.
E-mail: yohashi@chem.titech.ac.jp

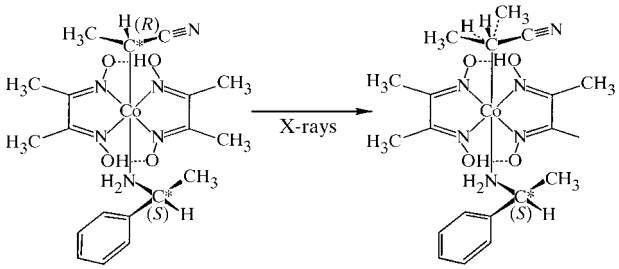
(*Received 11 May 1998; accepted 6 July 1998*)

Abstract

The process of chemical reaction in a crystal can be observed by stepwise crystal structure analysis if the single-crystal integrity is preserved during the reaction. Such a reaction is called a 'crystalline-state reaction' and the stepwise crystal structure analysis is termed 'real-time *in situ* observation'. Five examples of real-time *in situ* observation of crystalline-state reactions are briefly described. The first example is the optical enrichment of a racemic crystal by irradiation with visible light. The second example is *in situ* observation of hydrogen–deuterium exchange by neutron diffraction. The third example is the direct observation of the two-step inversion of a bulky chiral group on exposure to visible light. The fourth example is the real-time observation of two-step isomerization from a 3-cyanopropyl group to a 1-cyanopropyl group by irradiation with visible light. The fifth example is the insertion reaction of an oxygen molecule into an overcrowded distibene compound. In all the examples, the reaction mechanisms are clarified by the real-time *in situ* observation, which is a powerful method to analyze the mechanism of chemical reactions.

1. Introduction

A variety of solid-state organic reactions have been studied based on crystal structures before and after reactions during the past two decades (Desiraju, 1987; Pierrot, 1990; Ohashi, 1993, 1996). Although the energetic or kinetic aspect of the chemical reactions have been extensively studied by spectroscopy, thermal analysis, theoretical calculation and chemical kinetics, the processes of solid-state reactions, especially steric effects on the reactivity, have been proposed on the basis of crystal structures. Since the reactant crystal, in general, is decomposed in the process of the reaction, a crystal suitable for X-ray analysis after the reaction is obtained by recrystallization of the product, assuming the structure is maintained during crystallization. However, this assumption is sometimes incorrect. If the single-crystal integrity, on the other hand, is preserved during the reaction, the process of the reaction can be directly observed using only one crystal. About 20 years ago, we found that the chiral 1-cyanoethyl group bonded to the Co atom in a cobalt complex crystal was racemized on exposure to X-ray or visible light with retention of the single-crystal form



(Ohashi & Sasada, 1977). Moreover, the rate of the racemization, $1.10 \times 10^{-2}\ h^{-1}$, which was estimated from the change of cell dimensions assuming first-order kinetics, was so slow that the inversion process of the chiral group was clearly analyzed by the three-dimensional intensity data collected at several intermediate stages. Since such a reaction is very informative in analyzing the reaction mechanism, we called it a 'crystalline-state reaction' (Ohashi *et al.*, 1981). A variety of crystalline-state reactions have been reported (Ohashi, 1988). Although the 'single-crystal-to-single-crystal reaction' is often used in the same meaning as crystalline-state reaction, the former reactions include not only crystalline-state reactions but also reactions that show a sudden change of cell dimensions during the reaction, probably due to the phase transition following the reaction. When the crystal shows the gradual change of cell dimensions, it may sometimes be possible to observe the structures of the metastable intermediate stages. This paper focuses on the real-time *in situ* observation of five kinds of crystalline-state reactions. Recent development of time-resolved structure analyses

Yuji Ohashi received his BSc, MSc and DSc from the University of Tokyo. He joined the faculty of the Tokyo Institute of Technology in 1968 and in 1985 moved to Ochanomizu University. He moved back to the Tokyo Institute of Technology in 1989, where he is now Professor of the Department of Chemistry and Materials Science. His current research is focused on reaction mechanisms of organic crystals, especially crystal structure analysis at the excited or metastable state.

of inorganic materials and biological macromolecules are summarized in a text book (Helliwell & Rentzepis, 1997), in which the reviews of the Laue technique by synchrotron radiation are very informative (Larson & Tischler, 1997; Helliwell, 1997; Bradbrook *et al.*, 1997).

2. Optical enrichment of a racemic crystal by irradiation with visible light

The first example is the direct observation to clarify why optical rotation is observed when a racemic crystal is exposed to visible light (Osano, Uchida & Ohashi, 1991). The molecule is a bis(dimethylglyoximato)cobalt(III), cobaloxime, complex with a chiral 1-cyanoethyl group and piperidine as axial ligands as shown in Fig. 1. The racemic crystal belongs to a chiral space group $P2_12_12_1$ as shown in Fig. 2. There are two molecules with *R* and *S* configuration at *A* and *B* sites in the unit cell. The chiral crystal is isostructural and has two chiral molecules with the same *R* configuration at the two sites (Osano, Danno *et al.*, 1991). When the chiral crystals were dissolved in an aqueous methanol solution, the chiral complex was easily racemized, since the Co–C bond is cleaved by visible light. The rate constant of racemization is 2.0–3.0 h^{-1} in an aqueous methanol solution despite the difference on the axial base ligand of the complex (Baba *et al.*, 1987). The mechanism of the Co–C bond cleavage has been extensively studied, since the Co–C bond formation and cleavage play important roles in the function of vitamin B_{12} (Dolphin, 1982).

Several racemic crystals shown in Fig. 2 were exposed to a xenon lamp for 40 h and were dissolved in a chloroform solution. The optical rotation of the solution measured with the polarimeter showed the specific rotation $[\alpha]_D = 30°$. The racemic compound was transformed to chiral substances only by photo-irradiation. A single crystal of 0.4 × 0.3 × 0.3 mm was mounted on a four-circle diffractometer and was irradiated with a xenon lamp using a guide tube. The cell dimensions of the crystal were gradually changed. After 20 h exposure, the change became insignificantly small. The crystal structure analyzed is the same as that in Fig. 2 except that the chiral cyanoethyl group at the *B* site is partly inverted to the opposite configuration and takes a disordered structure. The occupancy factor indicated that 40% of the cyanoethyl group with the *S* configuration was converted to the *R* configuration. This means that the *R*:*S* ratio became 70:30 from 50:50. This is the reason why the optical rotation appeared after the irradiation.

The reason why only the chiral cyanoethyl group at the *B* site was partly inverted to the opposite configuration and the final *R*:*S* ratio at the *B* site became not 50:50 but 40:60 is explained by the reaction cavity for the cyanoethyl group, the definition of which was proposed by us in order to estimate the void space around the reactive group in the crystal structure (Ohashi *et al.*, 1981). The cavities for the cyanoethyl groups at *A* and *B* sites before irradiation are 7.0 and 14.2 $Å^3$. Unequal void space around the chiral groups between the two crystallographically independent molecules causes such an unusual optical enrichment. The cavity after 20 h exposure becomes symmetric if the *R*:*S* ratio is 40:60. Since the chiral space group is kept after the irradiation, the symmetric environment at the *B* site does not correspond to equal *R* and *S* configurations. The complex crystal, which has the 1-cyanoethyl group with *R*:*S* ratio 50:50 at the *B* site, was obtained from a solution containing the two enantiomeric complexes with *R*:*S* ratio of 3:1 and its structure was analyzed. The cavity for the 1-cyanoethyl group at the *B* site is not symmetric. This suggests that such an asymmetric environment at the *B* site is a driving force to invert the configuration of the chiral group and to make a symmetric environment. In other words, the chirality of the crystal causes the unequal *R*:*S* ratio in the crystal when the Co–C bond is cleaved and recombined on exposure to visible light.

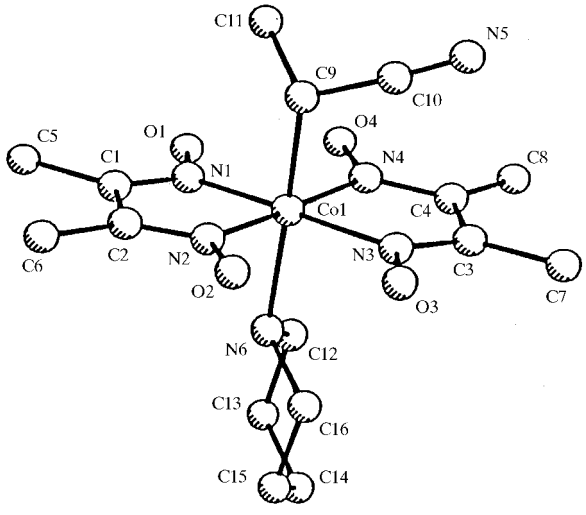


Fig. 1. The molecular structure of [(*R*)-1-cyanoethyl](piperidine)-cobaloxime.

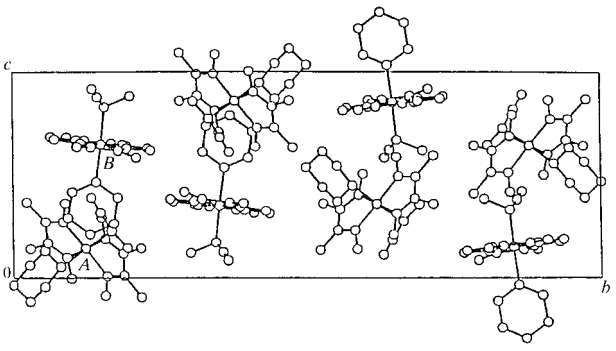


Fig. 2. The crystal structure of racemic [1-cyanoethyl](piperidine)-cobaloxime viewed along the *a* axis. The 1-cyanoethyl groups of *A* and *B* molecules have *R* and *S* configurations, respectively.

Similar results were obtained for the cobaloxime crystal with pyrrolidine as an axial base ligand (Nemoto, 1997).

3. *In situ* observation of hydrogen–deuterium exchange by neutron diffraction

When the chiral 1-cyanoethyl group is inverted to the opposite configuration, one of the four bonds around the chiral carbon atom should be cleaved by photo-irradiation. The ESR measurement suggested that the Co—C bond was cleaved homolytically since the cyanoethyl radical was observed (Ohashi *et al.*, 1981). However, it was recently found that the crystal with a bulkier chiral group was racemized with retention of the single-crystal form (Sato & Ohashi, 1998). This suggests that a process other than Co—C bond cleavage may exist in the racemization. The crystal of [(*R*)-1-cyanoethyl-d_α]-[(*S*)-1-phenylethylamine]cobaloxime, in which the H atom bonded to the chiral carbon was replaced with a D atom, was prepared. A crystal suitable for neutron diffraction, 2.7 × 2.8 × 0.7 mm, was exposed to a xenon lamp for two weeks. A small part of the crystal was cut off and the structure was analyzed by X-rays. The analyzed structure indicated that 17% of the (*R*)-1-cyanoethyl groups were inverted and the disordered racemic structure was observed.

The structure of the mother crystal was analyzed by neutron diffraction at Brookhaven National Laboratory (Ohgo *et al.*, 1997). The analyzed structure was not racemic but the original chiral one. Probably the light was unable to penetrate into the crystal since the crystal was too large. However, the structure indicated that the deuterium atom, D9, was exchanged with the H atom, H10*B*, of the neighboring methyl group as shown in Fig. 3(*a*). This means that the C—H or C—D bond should be cleaved on exposure to a xenon lamp. The short contacts between the H or D atom bonded to the chiral C atom and the Co atom and between the methyl H atom and the Co atom may be responsible for the H- or D-atom extraction from the C atoms. If the H or D atom attacks the chiral carbon from the opposite side after the hydrogen extraction, the configuration of the chiral C atom is inverted. Although visible light has insufficient energy to cleave the C—H bond, the Co atom that has close contacts with the H atoms may decrease the C—H bond energy.

Since the crystal was not racemized in the above experiment, it is necessary to observe H-atom exchange in the crystal after the racemization. The crystal of [(*R*)-1-cyanoethyl-d^α](pyridine)cobaloxime, in which the axial base ligand was replaced with pyridine, was prepared (Ohhara, Uekusa *et al.*, 1998). The pyridine complex crystal has two crystallographically independent molecules, *A* and *B*, and the chiral cyanoethyl group of the *B* molecule is completely inverted to the opposite configuration whereas the chiral group of *A* remains unchanged (Ohashi *et al.*, 1982). A crystal suitable for neutron diffraction, 3.0 × 3.0 × 0.6 mm, was irradiated with a fluorescent lamp for 36 h and the structure was analyzed by neutron diffraction at the Japan Atomic Energy Research Institute (JAERI).

Fig. 3(*b*) shows the molecular structure of *B* before and after the irradiation. The *A* molecule is not significantly different from the initial one analyzed by X-rays. The (*R*)-1-cyanoethyl group of *B* is partly inverted to the *S* configuration. The occupancy factor of the inverted group is 0.248 (5). The D atoms of the *A* and *B* molecules are not exchanged with the H atoms of the neighboring methyl groups nor with the other H atoms of the cobaloxime moiety or pyridine. These results indicate that the inversion of the chiral cyanoethyl group proceeds *via* rotation of the cyanoethyl radical after the Co—C bond cleavage and recombination with the Co atom. The different wavelength and irradiation period may be responsible for the different process of the racemization. Recently, the piperidine complex with the D atom bonded to the chiral C atom was prepared and the racemic crystal was obtained, the structure of which is shown in the previous section. The structure after 30 d irradiation with the xenon lamp was analyzed by neutron diffraction. The chiral 1-cyanoethyl group of *B* was almost racemized. The disordered structure of the 1-cyanoethyl group is approximately the same as that in Fig. 3(*b*) and the D atom was not exchanged with the

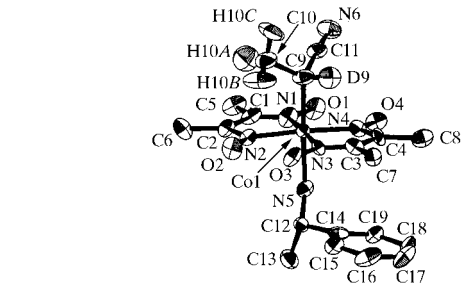


Fig. 3. (*a*) The molecular structure of the deuterated 1-phenylethylamine complex. After the irradiation, about 17% of the D9 and H10*B* were exchanged with each other. (*b*) The molecular structure of molecule *B* of the pyridine complex before and after irradiation. Only the inverted group is shown after irradiation, although the disordered structure of the original and inverted groups was observed.

other H atoms as observed in the pyridine complex (Ohhara, Harada *et al.*, 1998). These results suggest that two inversion processes should be taken into account.

4. A new IP diffractometer for rapid data collection and observation of metastable structure

Recently, a bulkier chiral group, the 1,2-bis(methoxycarbonyl)ethyl (bmce) group, $-C^*H(CO_2CH_3)CH_2CO_2CH_3$, was also found to be racemized by irradiation with visible light. The complex with diphenylmethylphosphine as an axial base ligand was racemized very rapidly (Ohashi *et al.*, 1995). Fig. 4 shows the change of cell dimensions on exposure to a xenon lamp. The change was too fast for the three-dimensional intensity data to be collected with a conventional four-circle diffractometer.

A new diffractometer for rapid data collection using an imaging plate (IP) as the two-dimensional detector (IPD-WAS) was developed (Kamiya & Iwasaki, 1995). Modified ones, R-Axis-IIcs and DIP3000, were also developed by Ohashi & Uekusa (1996) and Iwasaki *et al.* (1995), respectively. About 100 h are necessary for the three-dimensional intensity data collection using the usual four-circle diffractometer but all the data could be collected within 1 h using IPD-WAS. The quality of the data is approximately the same as that collected by a four-circle diffractometer.

The three-dimensional intensity data were collected at four stages I to IV, which are before irradiation and after 1.3, 7.0 and 10.0 h irradiation, respectively, which are indicated in Fig. 4. The space group is changed from noncentrosymmetric $P2_1$ to centrosymmetric $P2_1/a$.

The crystal structure viewed along the *c* axis at stage I is shown in Fig. 5(*a*). There are two crystallographically independent molecules, *A* and *B*, in the asymmetric unit.

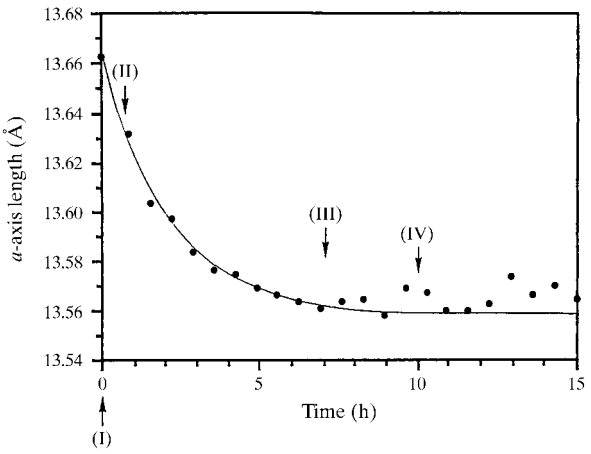


Fig. 4. The change of the *a*-axis length with exposure time. The curve is well explained by first-order kinetics. The three-dimensional intensity data were collected at four stages, I, II, III and IV. Each data collection was performed within 1 h.

The two molecules are closely related by a pseudo-inversion center except for the chiral groups. The molecular structure of *B* is shown in Fig. 6. The *A* molecule has nearly the same structure. One of the two methoxycarbonyl groups (C14, O8, O7 and C13) is almost perpendicular to the cobaloxime plane, whereas the other one (C11, O6, O5 and C10) is nearly parallel to the plane. The crystal structure viewed along the *c* axis at stage IV is shown in Fig. 5(*b*). The space group was changed to the centrosymmetric one and the pseudo-inversion center became a crystallographic one. This indicates that the chiral group of *B* is inverted to the opposite configuration whereas the chiral group of *A* remains unchanged. Although the bmce group of *B* is

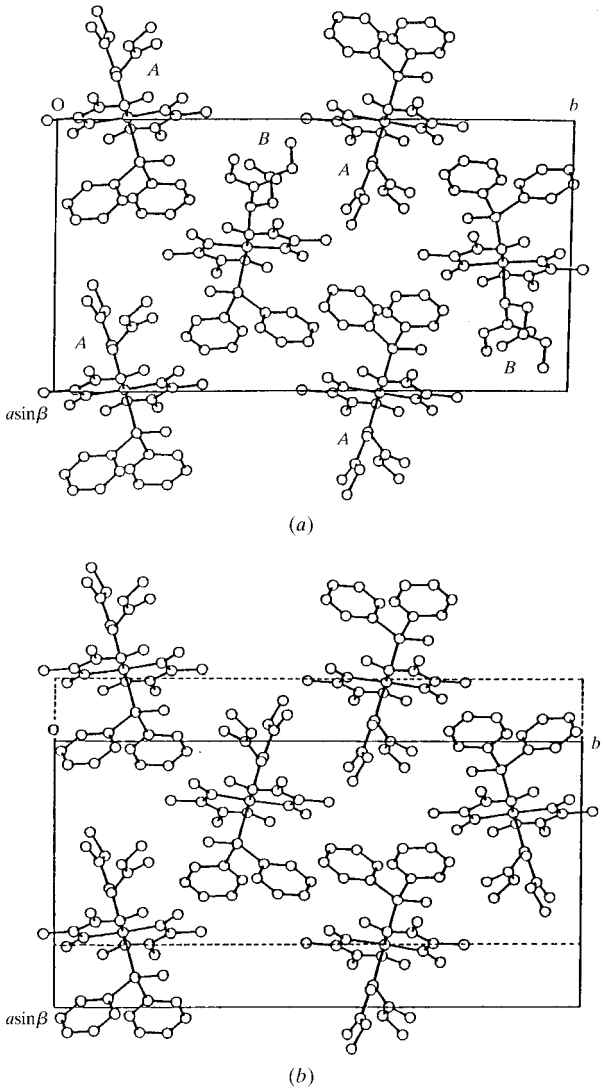


Fig. 5. The crystal structures of the bmce complex at stages (*a*) I and (*b*) IV. A minor part of the disordered bmce groups of molecule *B* at stage IV is omitted for clarity.

not completely inverted at stage IV, it should be completely inverted after infinite irradiation, which is assumed at stage V. The reason for only the chiral group of *B* being inverted is well explained by the cavity size for the chiral group. The volumes of the cavities are 47.4 and 55.0 Å^3 for the *A* and *B* bmce groups, respectively. The bmce group with the larger cavity is more easily inverted as observed in the cyanoethyl complexes.

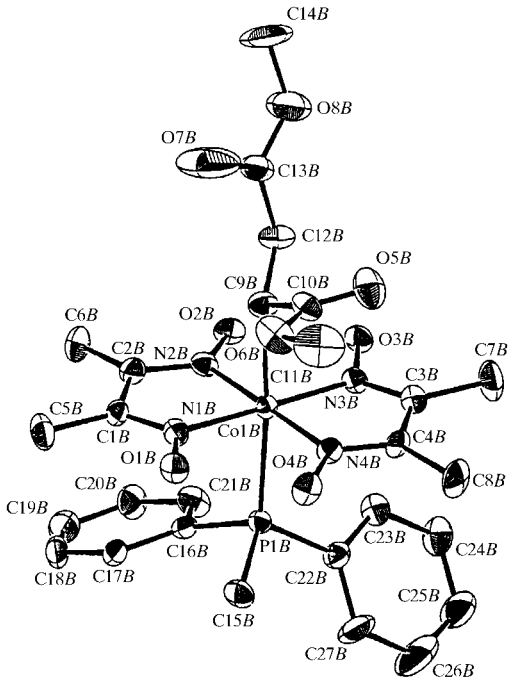


Fig. 6. The molecular structure of the bmce complex of *B*. The two methoxycarbonyl groups take perpendicular and parallel conformations to the cobaloxime plane, respectively.

At stages II and III, the bmce group of *B* takes disordered structures. The stepwise motion of the *B* bmce group is summarized in Fig. 7. At stage II, the perpendicular methoxycarbonyl group to the cobaloxime plane librates around the C(12)—C(13) bond. The torsion angle of C(9)—C(12)—C(13)—O(7) varies from −31 (1)° to the range −19 (2)–−67.2 (2)°. At stage III, the rotation around the C(12)—C(13) bond occurs and the torsion angle C(9)—C(12)—C(13)—O(7) is in the range −24 (2)–−31 (1)°. Moreover, the methoxycarbonyl group with the parallel conformation to the cobaloxime plane is partly inverted to the opposite configuration. The ratio of the original *R* configuration to the inverted *S* configuration became 40:60. The libration around the C(12)—C(13) bond may cause the motion of the bmce group in the neighboring *A* molecule although the *A* bmce group remains unaltered, and then the motion of the *A* molecule may trigger the inversion of the *B* bmce group since the *A* and *B* bmce groups are in contact with each other around the inversion center. It must be emphasized that, after most of the perpendicular methoxycarbonyl groups in the *B* bmce groups changed their conformation, inversion of the parallel methoxycarbonyl group occurred. At stage IV, the perpendicular methoxycarbonyl group takes an ordered structure and the inversion of the parallel methoxycarbonyl group proceeds. After infinite exposure, at stage V, the *B* bmce group has an ordered structure as a whole and the true crystallographic inversion center appears between the *A* and *B* bmce groups.

The disordered structures observed at stages II and III clearly indicate that the *B* bmce group changes its conformation of the perpendicular methoxycarbonyl group in the first step and then it is inverted to the opposite configuration. In other words, the *B* bmce

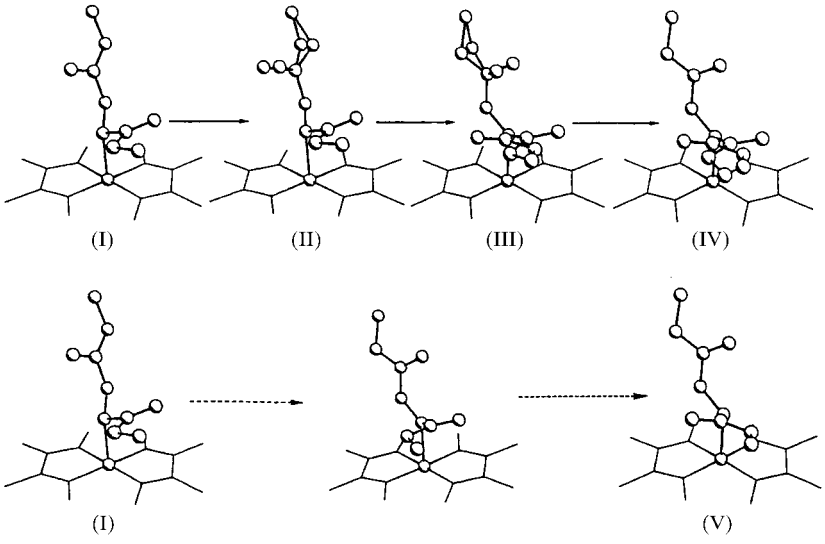
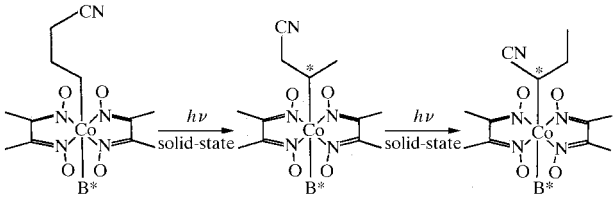


Fig. 7. Conformational and configurational change of the bmce group of molecule *B* in the process of the inversion. The lower figure indicates that the inversion occurs in two steps; rotation of the perpendicular methoxycarbonyl group and then inversion of the parallel methoxycarbonyl group.

group takes a metastable intermediate structure in the process of the inversion, as shown in the lower part of Fig. 7. Such a stepwise inversion may cause the racemization without degradation of the crystallinity.

5. Intermediate structure of a two-step photoisomerization

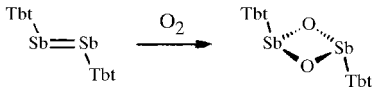
Recently, cobaloxime complexes with a 3-cyanopropyl group were found to be isomerized to the 1-cyanopropyl group



(Kurashima *et al.*, 1995). The rate constants of the 2–1 step isomerization are greater than those of the 3–2 step isomerization in most complexes. Among several 3-cyanopropyl complexes, the complex with aniline as an axial base ligand was isomerized to the 1-cyanopropyl complex with retention of the single-crystal form on exposure to visible light (Yoshiike, 1998). Fig. 8(*a*) shows the molecular structure before irradiation. The crystal was exposed to a xenon lamp for 334 h. The change of cell dimensions became insignificantly small. The molecular structure is shown in Fig. 8(*b*), in which the initial 3-cyanopropyl group (N5′, C12′, C11′, C10′ and C9′), the intermediate 2-cyanopropyl group (N5*B*, C12*B*, C11*B*, C9′ and C9*B*) and final 1-cyanopropyl group (N5*A*, C12*A*, C9′, C10′ and C11′) clearly coexist. The occupancy factors are 0.44 (9), 0.22 (10) and 0.34 (9) for 3-, 2- and 1-cyanopropyl groups. The other 3-cyanopropyl complexes with different axial base ligands, such as (*R*)-1-phenylethylamine and (*R*)-*p*-tolylethylamine, also showed the crystalline-state reaction. However, the reaction rates of these crystals are so large that the intermediate structure as shown in Fig. 8(*b*) have not been observed. Time-resolved structure analysis is now under survey.

6. Oxygen insertion to distibene compound

Recently, a distibene compound was synthesized from 1,3,5,2,4,6-triselenatristibene and the compound is very unstable to oxygen:



Tbt=2,4,6-tris[bis(trimethylsilyl)methyl]phenyl

(Tokitoh *et al.*, 1998). When the crystal was kept in the open air, the cell dimensions gradually changed. After 30 h exposure, the *b*-axis length and the unit-cell volume abruptly increased and the change became very slow after a further 10 h exposure. The three-dimensional intensity data were collected before and after the change with the R-Axis-IIcs diffractometer and the crystal structures were analyzed. The structures shown in Figs. 9(*a*) and (*b*) clearly indicate that the oxygen molecule is inserted in the Sb═Sb bond with retention of the single-crystal form. It may be possible to imagine that the extremely bulky substituent 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl group provides molecular oxygen

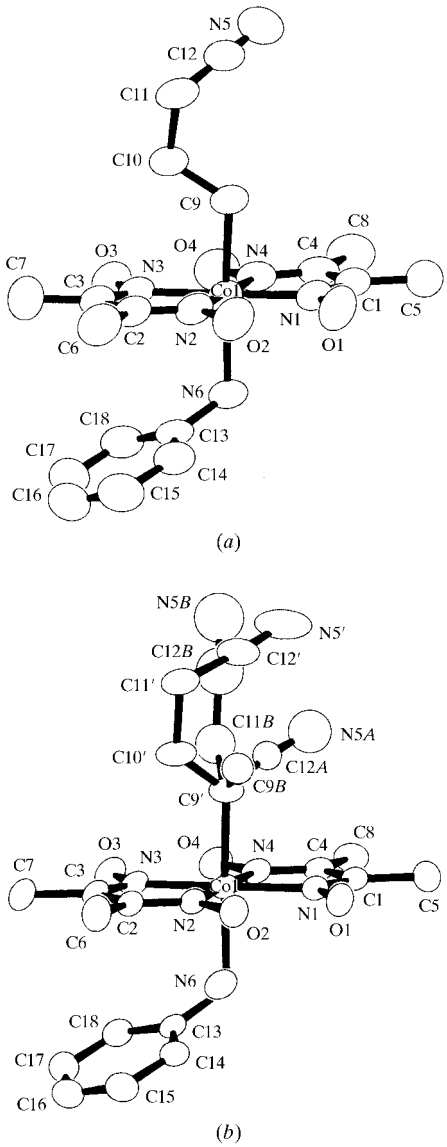


Fig. 8. The molecular structures of the aniline complex (*a*) before irradiation and (*b*) after 334 h irradiation with a xenon lamp. The original 3-cyanopropyl group has atoms of N5′, C12′, C11′, C10′ and C9′, the intermediate 2-cyanopropyl group has N5*B*, C12*B*, C11*B*, C9′ and C9*B*, and the final 1-cyanopropyl group has N5*A*, C12*A*, C9′, C10′ and C11′.

with enough space for the insertion retaining the crystalline lattice.

7. Time-resolved structure analysis

The above examples suggests that the more rapidly the intensity data are collected, the faster reactions can be observed. In order to obtain the three-dimensional data more rapidly, a new detector should be developed (Helliwell & Rentzepis, 1997). Recently, Tanimori *et al.* (1996) developed a new detector with a 10 cm square detective area, the multistrip gas chamber (MSGC), which is similar to the multiwire proportional chamber (MWPC), although the accuracy and linearity is better than those of MWPC. A fine-position resolution of $\sim$100 mm and a counting rate up to 2×10^7 counts s^{-1} were obtained. Moreover, the energy information of each X-ray photon is obtained, although the energy resolution is about 13%. This may be an advantage for the Laue method. Preliminary work to test the performance was satisfactory (Ochi, 1998). We are now designing and constructing a new diffractometer using MSGC as a detector. The three-dimensional intensity data will be collected within several μs using synchrotron radiation. Structure analysis of the photo-excited molecule will be possible using the new diffractometer in the near future.

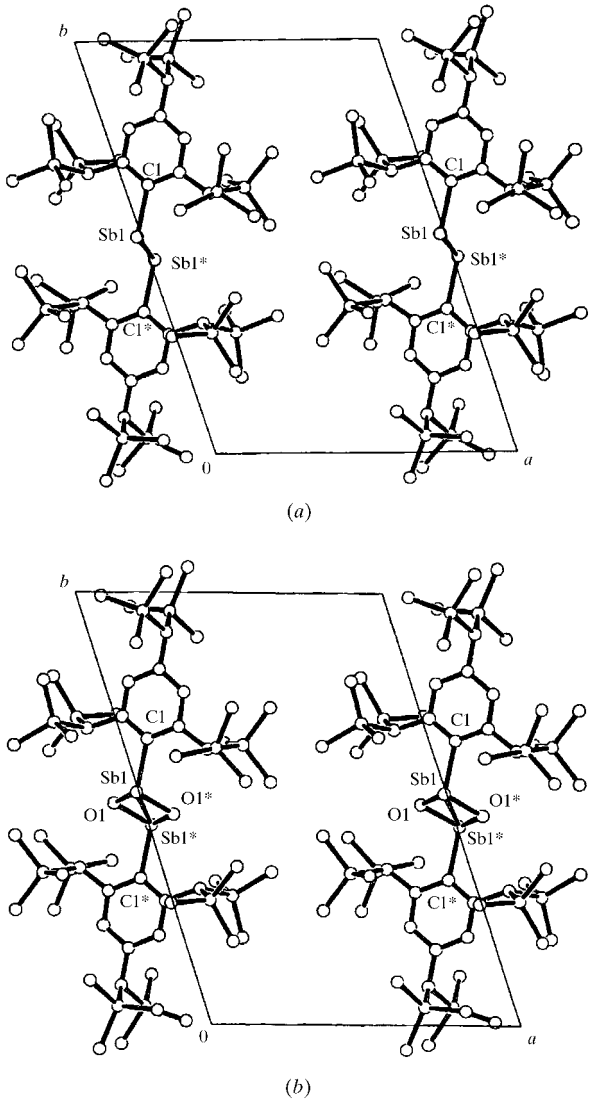


Fig. 9. The crystal structures of the distibene complex (*a*) before and (*b*) after the cell change. The molecular oxygen is inserted in the Sb═Sb bond.

The work reported here was partially supported by Grant-in-Aids for Scientific Research on Priority Area from the Ministry of Education, Science, Sports and Culture, and CREST from the Japan Science and Technology Corporation (JST). The author heartily thanks many collaborators with whom he enjoyed the studies presented here.

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