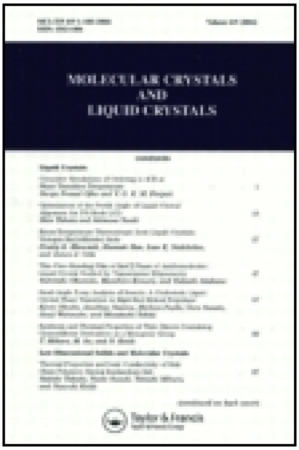


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

# Crystalline-State Photoisomerization and Photoinduced Phase Transition of a Cobaloxime Complex

Akiko Sekine [a] , Hiroaki Tatsuki [a] & Yuji Ohashi [a]

[a] Department of Chemistry, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo, 152, Japan

Version of record first published: 24 Sep 2006.

To cite this article: Akiko Sekine , Hiroaki Tatsuki & Yuji Ohashi (1994): Crystalline-State Photoisomerization and Photoinduced Phase Transition of a Cobaloxime Complex, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 242:1, 109-117

To link to this article: http://dx.doi.org/10.1080/10587259408037743

*Mol. Cryst. Liq. Cryst.* 1994, Vol. 242, pp. 109-117
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

# CRYSTALLINE-STATE PHOTOISOMERIZATION AND PHOTOINDUCED PHASE TRANSITION OF A COBALOXIME COMPLEX

AKIKO SEKINE, HIROAKI TATSUKI and YUJI OHASHI
Department of Chemistry, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152, Japan

Abstract The crystal of (β-cyanoethyl)bis(dimethylglyoximato)(4-methylpyridine)cobalt(III) exhibits a reversible single crystal-to-single crystal thermal phase transition at 343 K. The β-cyanoethyl group of the crystal was isomerized to α-cyanoethyl group retaining the single crystal form when the crystal was irradiated with a strong Xe lamp above 343 K, although the crystal was decomposed below the temperature. On the other hand, when the crystal was exposed to a weak Xe lamp at 340 K, the crystal showed the phase transition after 20 hours exposure keeping the single crystal form. The crystal after the phase transition also exhibited the β-α photoisomerization on exposure to the strong Xe lamp. The mechanism has clearly been elucidated on the basis of the analyzed structures before and after the photoisomerization or phase transition.

## INTRODUCTION

It has been found that the β-cyanoethyl (β-ce) group bonded to the cobalt atom is isomerized to α-cyanoethyl (α-ce) group in some cobaloxime complexes on exposure to visible light in the solid state, as shown in Fig. 1.[1] Several cobaloxime complexes with β-ce group have been prepared, and a linear relation between the isomerization rate and the reaction cavity

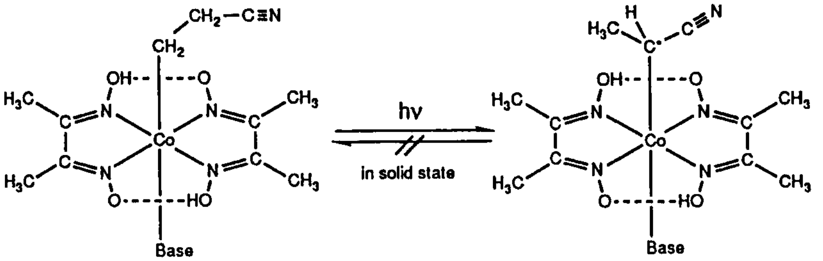


FIGURE 1 β–α photoisomerization of cobaloxime complexes

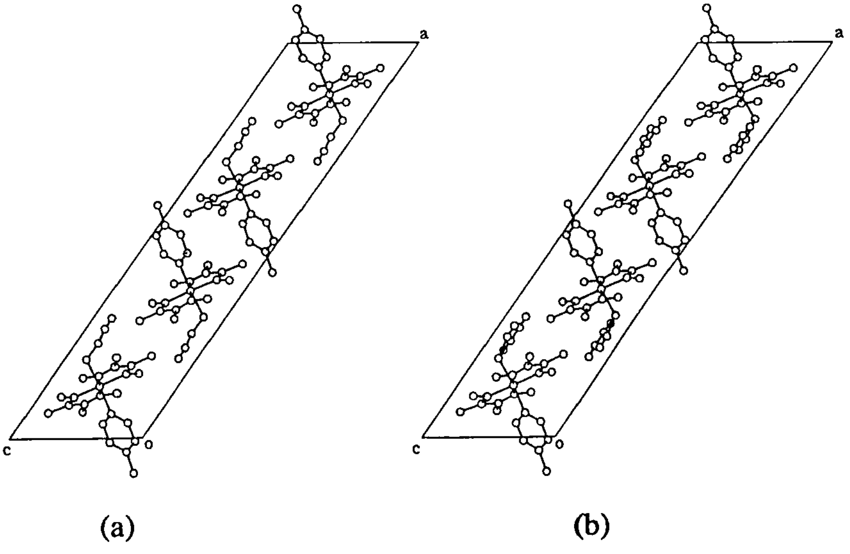
for the β-ce group in the reactant crystal has been obtained.[2-4] For the complex with 3-methylpyridine as an axial base ligand the mixed crystals with the β-ce and α-ce complexes were prepared and acceleration of reaction rate due to the product complex was observed for the mixed crystals.[5] Recently it was observed that the β-ce group in the 3-methylpyridine complex crystal was isomerized to the α-ce group on exposure to visible light retaining the single crystal form.[6]

The complex with 4-methylpyridine as an axial base ligand exhibits a reversible single crystal-to-single crystal thermal phase transition when the crystal was warmed up to 343 K.[7] The present work was undertaken to examine the reactivity above and below the phase transition temperature. Contrary to our expectation, two quite new results have been observed; one is that the β-ce group is isomerized without degradation of the crystallinity in the high temperature phase, the other is that the phase transition occurs below the transition temperature if the crystal was exposed to a weak Xe lamp. This paper reports the above two results.

## PHOTOISOMERIZATION RETAINING THE SINGLE CRYSTAL FORM

The crystal structure of the high temperature phase was determined at 346

K with hot-air-flow method. Then the crystal was exposed at the temperature to visible light which was brought to the crystal by a light guide from a Xe lamp. The cell dimensions were gradually changed and after about 50 hours exposure the change became significantly small. The irradiation was stopped and the structure was determined in the same condition before the irradiation. As shown in Fig. 2, only the β-ce group was changed from an ordered structure to a disordered one. The α-ce group with only R configuration appeared after the irradiation. The ratio of α-ce to β-ce groups is 0.43. Although the S configuration is produced at an inverted site because of the centrosymmetric crystal, this suggests that asymmetric induction may be possible in the present β−α photoisomerization if the crystal is chiral.



(a) (b)

FIGURE 2 Crystal Structures of (a) before and (b) after the irradiation in the high temperature phase

## PHOTOINDUCED PHASE TRANSITION

In order to examine whether the β-ce group in the low temperature phase is changed to the α-ce group retaining the single crystal form or not, the crystal was exposed to visible light at room temperature in the same conditions as those for the crystal of high temperature phase. But the crystal was gradually decomposed. Finally the crystal was warmed up to 340 K and the light was weakened by about one tenth. After about 20 hours exposure, the cell dimensions abruptly changed as shown in Fig. 3.

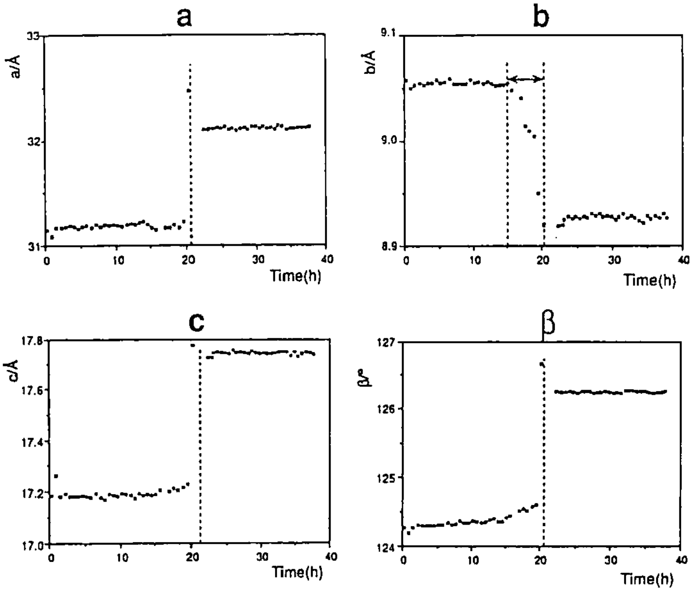
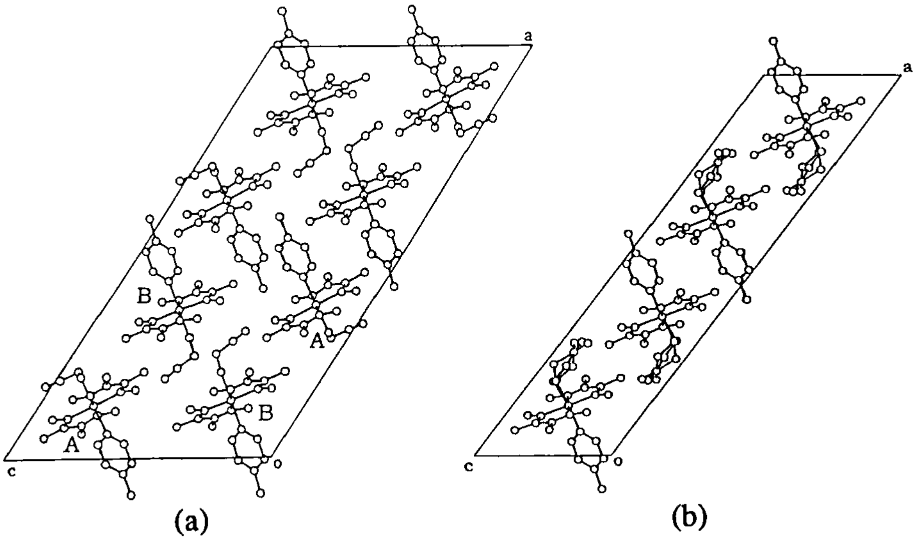


FIGURE 3 Change of lattice parameters on exposure to visible light

The length of the c axis became about a half, although the c values in Fig. 3 are doubled for comparison. The crystal data at 340 K before (I) and after (II) the change are as follows; (I) a = 31.18(2), b = 9.058(5), c = 17.16(1) Å, β = 124.21(4)°, V = 4007(5) Å$^3$, $P2_1/a$, Z = 8 and Dx = 1.45 g cm$^{-3}$; (II) a = 32.09(3), b = 8.912(3), c = 8.851(6) Å, β = 126.15(4)°, V = 2044(5) Å$^3$, $P2_1/a$, Z = 4 and Dx = 1.418 g cm$^{-3}$. It must be emphasized that the b value gradually decreased after 15 hours and converged at 20 hours exposure, whereas a, c and β changed suddenly at 20 hours exposure. The three dimensional intensity data were collected at 340 K without irradiation and after the change by the irradiation.

Figure 4 shows the crystal structures before (a) and after (b) the change. There are two crystallographically independent molecules, A and B, before the change. After the change both of the ce groups of the A and B molecules have the same conformations, which may cause the c axis length to be a half. The above change is essentially the same as the thermal phase transition observed at 343 K. This indicates that the photoinduced phase transition occurred just below the temperature of the thermal transition. The β–α photoisomerization is negligible considering the structure analysis. The crystal after the photoinduced transition was irradiated with the strong light and was warmed up to 346 K, the cell



(a) (b)

FIGURE 4 Crystal structures (a) before and (b) after the phase transition dimensions were gradually changed. After 55 hours exposure, the determined structure clearly indicated that the β–α photoisomerization occurred in the same way as that described in the previous section.

## MECHANISM OF PHOTOINDUCED PHASE TRANSITION

Figure 5(a) shows the conformations of the two β-ce groups of the A and B molecules viewed along the normal to the cobaloxime plane. After the photoinduced transition the β-ce groups becomes the same conformation shown in Fig. 5(b). Figure 5(c) shows the conformation after the thermal transition at 343 K. It is clear that the conformational change produced by the photoinduced transition is incomplete, since the conformation of the B molecule remains.

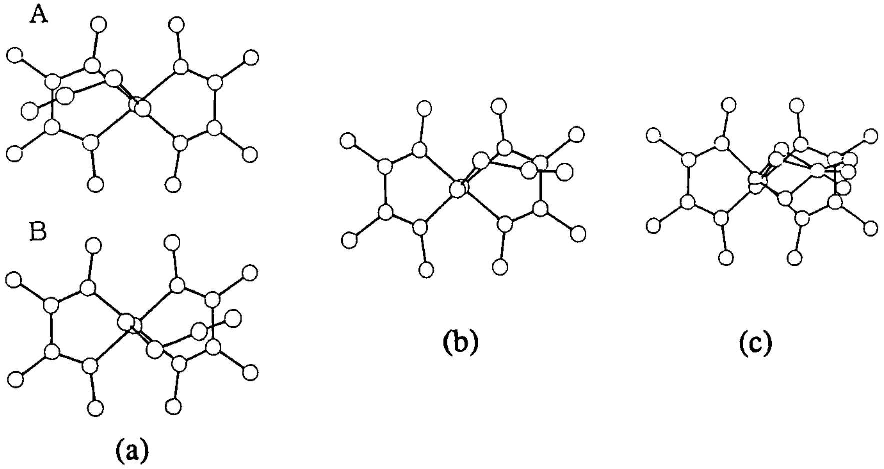


FIGURE 5 Conformation of the β-ce group viewed normal to the cobaloxime plane (a) before the transition, (b) after the photoinduced transition and (c) after the thermal transition.

In order to explain why the transition occurs on exposure to visible light, the crystal structure before the transition viewed along the a axis is shown in Fig. 6(a). The β-ce groups of the A and B molecules are arranged to form ribbons respectively along the b axis. The β-ce group of the A molecule has an extended form along the b axis whereas that of the B molecule takes a bent form. This may indicate that the A ce groups are more closely packed along the b axis than the B ce groups. Figure 6(b) shows the crystal structure after the transition viewed along the a axis. The ce groups (denoted as C) are also arranged along the b axis but they are not so closely packed.

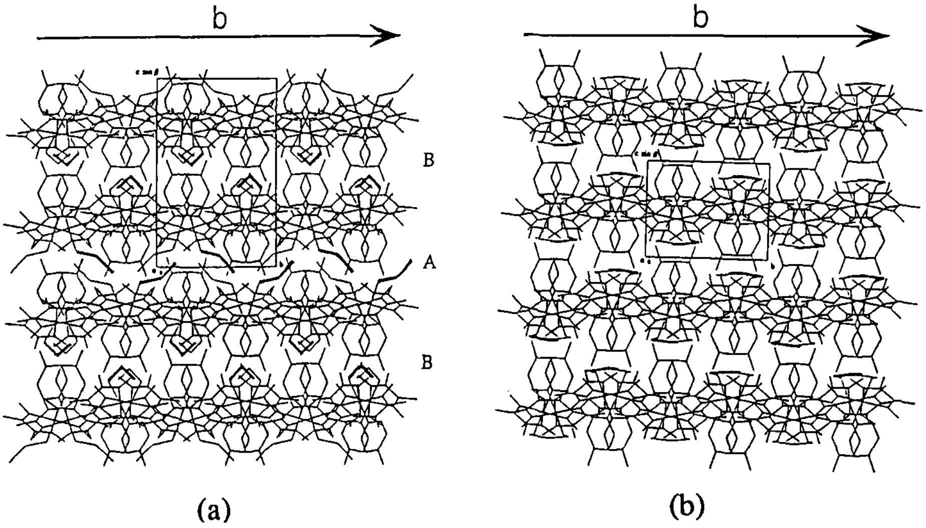
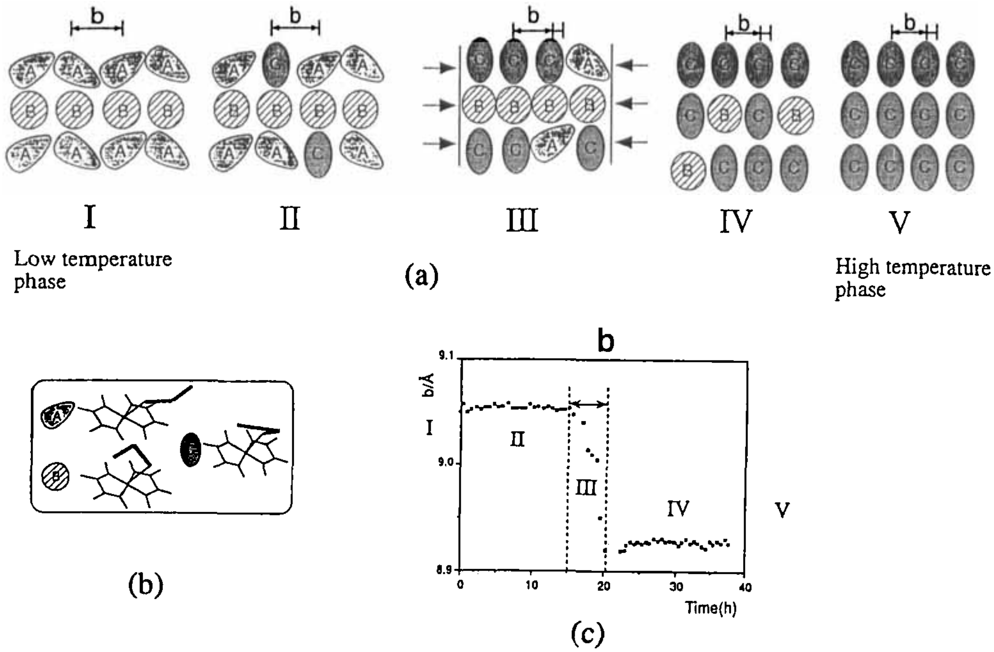


FIGURE 6 Crystal structures viewed along the a axis (a) before the transition and (b) after the transition

When the crystal was irradiated with visible light at 340 K, the length of the b axis gradually changed after 15 hours and converged at 20 hours, whereas other dimensions abruptly changed at 20 hours. This may indicate that the change of the b axis is essential for the photoinduced transition. Figure 7 shows the schematic drawing of the change of the β-ce groups. The A, B and C correspond to the shapes of the A, B and C ce groups, respectively, along the b axis, as denoted in Fig. 7(b). When the crystal was exposed to visible light, the Co-C bond may be cleaved. The A ce group is more easily changed to C after the bond cleavage, since it may be suffered from steric repulsion from the surrounding ce groups. Since the B ce groups are not so closely packed, they may not be changed at early stages, II, which are denoted in Fig. 7(c). Since some part of the A ce groups are changed to C, the b axis is gradually contracted. When the b axis is completely shortened, the accumulated steric repulsion may cause



(a)

(b)

(c)

FIGURE 7 Schematic drawing of the conformational change in the phase transition

the phase transition because considerably large vacant space may appear after the A to C transformation of the ce groups. Since the B ce group has similar length to that of C along the b axis, the B ce group appears as a disordered structure at the IV stage as shown in Fig. 5.

In summary, the process of the thermal transition can be clarified by the photoinduced transition which occurs just below the temperature of the thermal transition.

## REFERENCES

1. Y.Ohgo and S. Takeuchi, *J. Chem. Soc. Chem. Commun.*, **1985**, 21.
2. A. Sekine and Y. Ohashi, *Bull. Chem. Soc. Jpn.*, **64**, 2183 (1991).
3. A. Sekine, Y. Ohashi, E. Shimizu and K. Hori, *Acta Cryst.*, **C47**, 53 (1990).
4. A. Sekine, Y. Ohashi and K Hori, *Acta Cryst.*, **C47**, 525 (1991).
5. A. Uchida, Y.Ohashi and Y. Sasada, *Nature(London)*, **320**, 51 (1986).
6. Akiko. Sekine, Doctor Thesis, Tokyo Institute of Technology (1992).
7. A. Uchida, Y. Sasada and Y.Ohashi, *Acta Cryst.*, **B44**, 249 (1988).