Crystalline-State *trans-cis* Photoisomerization of (*trans*-2-Butenyl)-bis(dimethylglyoximato)(pyridine)cobalt(III)

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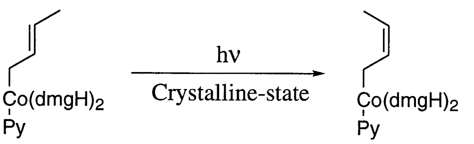
The crystal of (*trans*-2-butenyl)bis(dimethylglyoximato)(pyridine)cobalt(III), **1**, gradually changed its unit cell dimensions on exposure to a high flux xenon lamp. After about 2 hours exposure the change became significantly small. The lengths of a and c axes in the orthorhombic unit cell increased and decreased by 0.25 and 0.39 Å, respectively. The crystal structures before and after the irradiation clearly indicated that only the *trans*-2-butenyl group was transformed to the *cis*-isomer, the other part of the molecule being unaltered.

The crystalline-state reaction, which proceeds in a crystal with retention of the single crystal form, is very interesting and important, since the structural change can be observed by X-ray analysis at any stage of the reaction. Two types of crystalline-state reactions on exposure to visible light or X-rays in some bis(dimethylglyoximato)cobalt(III), cobaloxime, complex crystals have vigorously been studied; one is the racemization of the chiral alkyl groups bonded to the cobalt atom and the other is the β-α isomerization of the achiral alkyl group bonded to the cobalt atom. For the racemization, the chiral 1-cyanoethyl,[1] 1-methoxycarbonylethyl,[2] 1,2-dimethoxycarbonylethyl[3] and 1,2-diethoxycarbonylethyl[4] groups have been found to racemize on exposure to visible light. For the β-α photoisomerization, the 2-cyanoethyl group was transformed to the chiral 1-cyanoethyl group. The asymmetric induction due to the chiral crystal environment was observed for the latter reaction.[5] This paper reports a new type of crystalline-state photoisomerization, which is the *trans-cis* conversion of the 2-butenyl group bonded to the cobalt atom in the cobaloxime complex with pyridine as an axial base ligand.



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The complex of **1** was prepared in a way similar to that reported previously.[6] The red-colored crystals suitable for X-ray work were obtained by recrystallization from an aqueous methanol solution under Ar atmosphere at 5-10°C. The crystal structure before the irradiation was determined by X-rays using a crystal of 0.25 x 0.15 x 0.20 mm. The crystal data are as follows; $C_{17}H_{26}CoN_5O_4$, M_r = 423.36, orthorhombic, space group Cmca, Z = 8, a = 12.017(3), b = 13.036(3), c = 25.982(2) Å, V = 4070(1) Å^3, Dx = 1.382 Mgm^{-3}, MoKα(λ = 0.71073 Å), μ = 0.88 mm^{-1}, T = 296 K, 2453 unique reflections. The structure was solved by direct methods using the program SHELXS-86[7] and was refined by full-matrix least-squares with the program SHELXL-93.[8] Final R(F) and wR(F^2) values became 0.047 and 0.111, respectively.

Since the molecules lie on the mirror plane, a half of the molecule is crystallographically independent. Figure 1 shows the molecular structure with the numbering of atoms. The Co1, C8, N3 and C7 atoms lie on a mirror plane, which passes through the long axis of the cobaloxime moiety. This mirror plane brings about a disordered structure of the *trans*-2-butenyl group.

The crystal was exposed to a high flux xenon lamp (San-ei SUPER BRIGHT 150) on a 4-circle diffractometer and the cell dimensions were determined at an interval of 5 minutes. The light was brought to the crystal with a glass fibre tube, the top of which was apart from 17 mm from the crystal. During the 2θ-angle determinations of 25 reflections the exposure was stopped. Figure 2 shows the typical change of the cell dimensions. At early stages they are expressed by first-order kinetics. After 111 minutes exposure the changes became significantly small and the peak profile of the reflections became broad. The peak intensities decreased to 50-90% of the initial values. The irradiation was

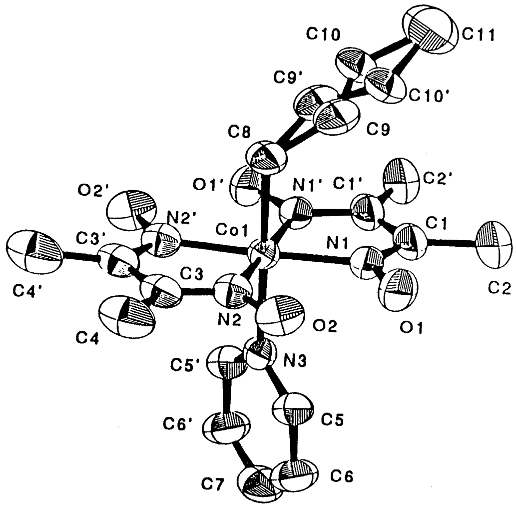

Figure 1. Molecular structure of **1**.

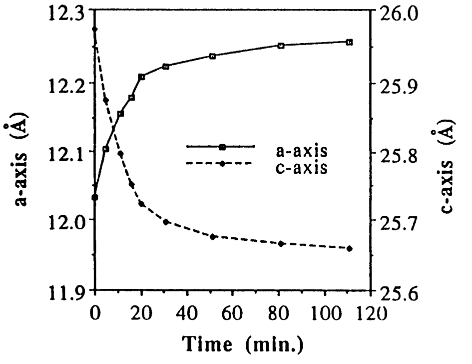

Figure 2. The changes of the cell dimensions during the irradiation.

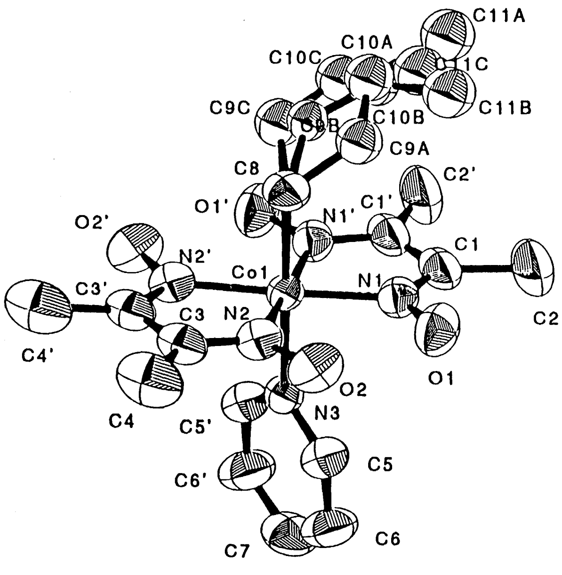

Figure 3. Molecular structure after the irradiation.

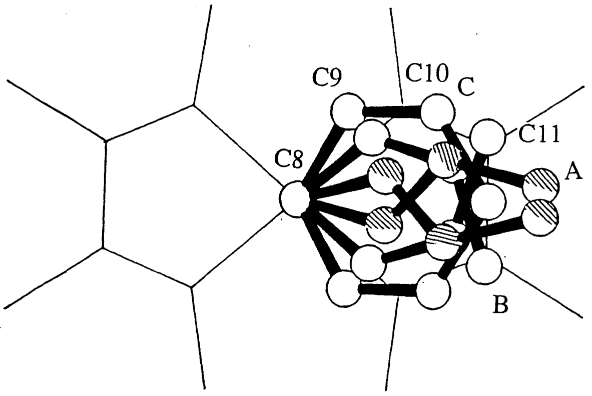

Figure 4. The shapes of 2-butenyl groups after the irradiation. The hatched atoms belong to trans-2-butenyl groups. The mirror images were included.

stopped and the intensity data were collected. The crystal data are as follows; a = 12.270(3), b = 13.020(3), c = 25.597(2) Å and V = 4089(1) Å^3, Dx = 1.375 Mgm^{-3}, 2469 unique reflections. The differences before and after the irradiation are 0.253, -0.016, -0.385 Å and 19 Å^3 for a, b, c and V, respectively. The space group remained unaltered. The structure was solved and refined in the same ways as that before the irradiation (R(F) = 0.060 and wR(F^2) = 0.151).

The crystal structure is essentially the same as that before the irradiation. The molecular structure is shown in Figure 3, in which only a half of the disordered structure of the 2-butenyl groups is drawn and their mirror images are omitted for clarity. In order to examine the disordered structure of the 2-butenyl group, the structure viewed along the normal to the cobaloxime plane is shown in Figure 4. The *trans*-2-butenyl group, C8-C9A-C10A-C11A, has approximately the same conformation as that before the irradiation. The newly appeared peaks are easily assigned as disordered *cis*-2-butenyl groups, C8-C9B-C10B-C11B and C8-C9C-C10C-C11C. The occupancy factors are 0.17(1), 0.24(2) and 0.09(2) for A, B and C 2-butenyl groups, respectively. These results clearly indicate that 66% of *trans*-2-butenyl group is transformed to its *cis* isomer on exposure to the xenon lamp for about 2 hours.

The change of cell dimensions are well explained by the structural change owing to the *trans-cis* conversion. The *trans*-2-butenyl group extends along the c axis whereas the *cis* isomer expands along the a axis. Therefore, the c axis contracts and the a axis expands in the process of the *trans-cis* conversion. Further study to clarify the reason why such a reaction proceeds in a crystal is in progress.

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References and Notes

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