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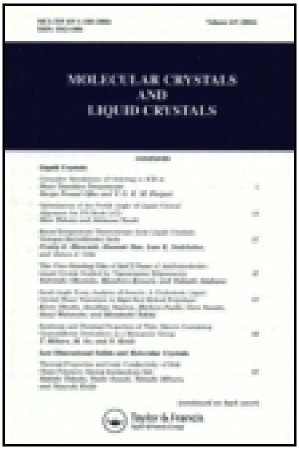

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Optical Enrichment of Chiral Racemic Crystals on Exposure to Visible Light

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OPTICAL ENRICHMENT OF CHIRAL RACEMIC CRYSTALS ON EXPOSURE TO VISIBLE LIGHT

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Abstract The racemic complex of (1-cyanoethyl)(piperidine)cobaloxime crystallizes in an isomorphous structure to its chiral one. In either crystal one of the two crystallographically independent molecules is gradually inverted to have the opposite configuration on exposure to visible light retaining the single crystal form. This brings about optical enrichment for the crystal of racemic complex. The final structures produced by the complete irradiation for the chiral and racemic crystals are converged to the same one. The ratio of the R and S configuration of the partly inverted molecule in the final structure is not 50:50 but 60:40, which is well explained by the shape of the reaction cavities for the cyanoethyl group before and after the partial inversion. Another racemic complex crystal with pyrrolidine instead of piperidine seems to exhibit a similar optical enrichment.

INTRODUCTION

It has been found that a chiral cyanoethyl (ce) group bonded to the cobalt atom in some cobaloxime complex crystals is racemized by X-ray or visible light exposure without degradation of crystallinity,[1] as shown in Fig. 1. This paper reports that such a racemization is able to generate chirality for the racemic crystal and that the mechanism is explained by the reaction cavity for the ce group.

RACEMIZATION OF A CHIRAL PIPERIDINE COMPLEX

When the complex has piperidine as an axial base ligand, the crystal

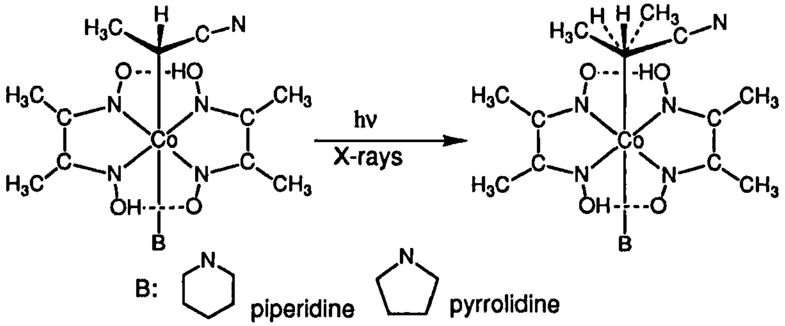

FIGURE 1 Crystalline-state racemization of cobaloxime complexes.

has two crystallographically independent molecules, A and B, in an asymmetric unit and only the chiral ce group of the B molecule, B ce group, is partly inverted to have the opposite configuration on exposure to X-rays at 333 K whereas the A ce group remained unaltered.[2] The crystal structure at the initial stage is shown in Fig. 2. Since the space group is $P2_12_12_1$, the inversion of the B ce group does not seem to bring about the racemic crystal even if the B ce group would be fully inverted to have the opposite configuration.

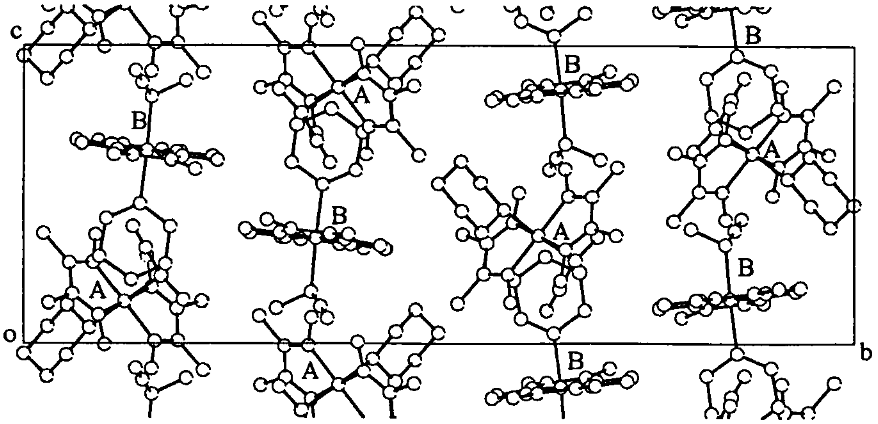

FIGURE 2 Crystal structure of the piperidine complex viewed along the a axis.

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RACEMIZATION OF A RACEMIC CRYSTAL

The racemic crystals were prepared from an aqueous methanol solution containing a racemic mixture of the piperidine complex. The racemic crystal, to our surprise, has the isomorphous structure to the above chiral one except that the B molecule has the opposite configuration. When the racemic crystal was exposed to X-rays or visible light, only the B ce group was partly inverted as observed in the chiral crystal. This causes optical enrichment of the racemic crystal by the irradiation, since the ratio of R to S ce groups are gradually changed from 50:50.[3]

CELL CHANGES OF CRYSTALS WITH DIFFERENT R TO S RATIOS

In order to examine the final structure after the irradiation, five kinds of the complex crystals with different R to S ratios were prepared from the solutions with the ratios of R to S complexes, 50:50(I), 62.5:38.5(II), 75:25(III), 87.5:12.5(IV) and 100:0(V). The I and V crystals are racemic and chiral ones described above. The structures of the five crystals were determined by X-rays shielding the room light. All the structures are isomorphous to that shown in Fig. 2. The A molecule in each crystal is not disordered and has R configuration. The ratios of R to S configurations of the B molecules in five crystals, on the other hand, correspond approximately to those in the solutions, that is, 0:50, 12.5:37.5, 25:25, 37.5:12.5 and 50:0, for I, II, III, IV and V, respectively. The five crystals with nearly the same size were exposed to a Xe lamp in the same conditions and the cell dimensions were determined at constant intervals. Figure 3 shows the changes of the b axis, which shows the most significant variation among the three axes, for the crystals of I, III and V. The converged value for the three crystals, which is significantly different from either of the initial b values of the three crystals, are the same within the experimental error. The b axes of the other two crystals, II and IV, were also converged to the same value.

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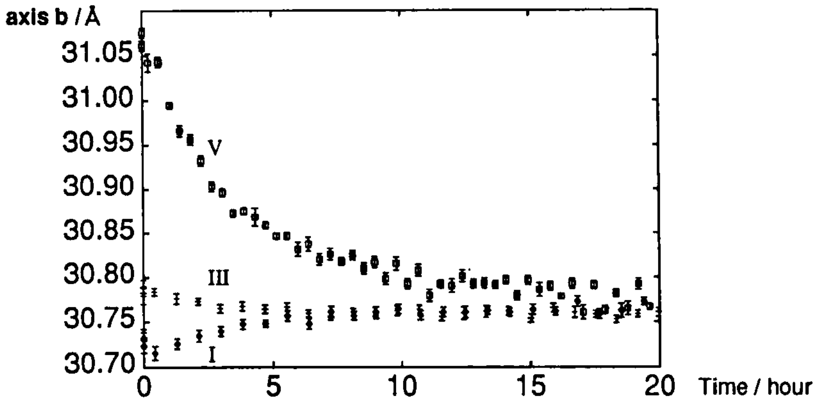

FIGURE 3 Changes of the b axis for the I, III and V crystals with exposure time

RATIO OF R TO S CONFIGURATIONS IN THE FINAL STRUCTURE

After the change became within the experimental errors, the three crystals were determined by X-ray analyses. All the structures are identical to each other including the occupancy factors of the ce groups with R and S configuration. The ratio of R to S ce groups in the B molecule became 20:30 for all the three crystals, contrary to our assumption that it should be 25:25. These results are schematically shown in Fig. 4.

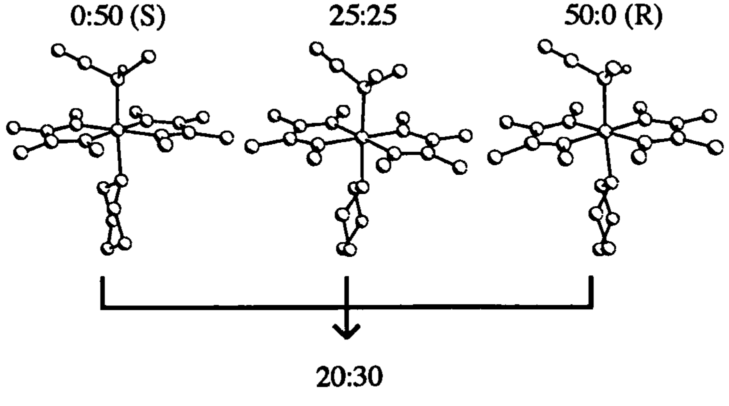

FIGURE 4 Schematic drawing of the partial inversion of the B ce group in the crystals of I, III and V.

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REACTION CAVITY FOR THE B CYANOETHYL GROUP

In order to explain such a strange conversion by visible light, the reaction cavity for the B ce group in each crystal structure was drawn.[4] Figure 5 shows the cavities of the three crystals before the irradiation. The volumes of the three cavities are approximately equivalent to each other, 11.0 Å^3 for I, 12.9 Å^3 for III and 12.8 Å^3 for V. Each cavity was divided into two parts by the plane composed of Co-C-C-N bonds and calculate the volumes of the two parts to compare the shape of the cavities to each other, as shown in Fig. 5. The ratio of the volume in the left side to that in the right side becomes 45:55 in I. The corresponding ratios are 56:44 and 63:37 for III and V, respectively. It must be emphasized that the ratio of III is different from 50:50. This is caused by the chiral environment of the site of the B molecule.

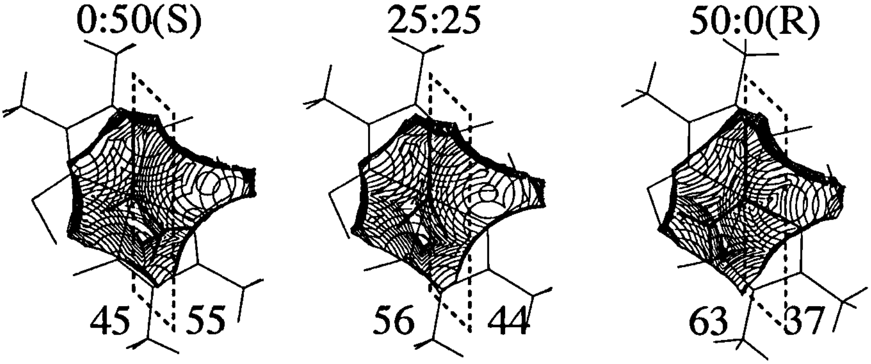

FIGURE 5 Cavities for the ce groups in the crystals of I, III and V.

The cavity in the final structure is shown in Fig. 6. The volume is 11.2 Å^3. The cavity was also divided into two parts. The two parts have the same volumes. These results indicate that the inversion ratio at the B molecule site is influences by the symmetry of the cavity. In other words the steric repulsion from the neighboring molecules should be the same for the R and S ce groups at the position of the final structure.

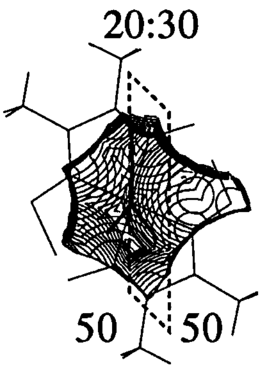

FIGURE 6 Cavity for the B ce group in the final structure.

ANOTHER EXAMPLE OF OPTICAL ENRICHMENT

Recently the racemic complex with pyrrolidine as an axial base ligand was prepared. The crystal obtained from an aqueous methanol solution have four molecules in a P1 cell. Two of the complexes have R ce groups and the other two have S. When the crystal was exposed to visible light, both of the ce groups with S configuration were partly inverted and were changed to the disordered structure. The cavities for the two ce groups have enough space for the partial inversion.[5] The detailed analyses of the inversion are in progress.

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