

# Modified photoreactivity due to mixed crystal formation. I. Three mixed crystals between isostructural cobaloxime complexes

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Three crystals of 2-cyanoethyl cobaloxime complexes with 3-chloropyridine, 3-bromopyridine and 3-methylpyridine as axial base ligands are isostructural to one another. Three mixed crystals were formed between the pairs: (3-bromopyridine)(2-cyanoethyl)cobaloxime–(2-cyanoethyl)(3-methylpyridine)cobaloxime (0.45/0.55); (3-chloropyridine)(2-cyanoethyl)cobaloxime–(2-cyanoethyl)(3-bromopyridine)cobaloxime (0.61/0.39); (3-chloropyridine)(2-cyanoethyl)cobaloxime–(2-cyanoethyl)(3-methylpyridine)cobaloxime (0.44/0.56). The X-ray crystal structure analysis revealed that the mixed compounds are also isostructural to the component crystals. It was found from the change in IR spectra that the 2-cyanoethyl groups in the three mixed crystals isomerized to 1-cyanoethyl groups on exposure to a xenon lamp, as observed for the 2-cyanoethyl groups in the component crystals. Rate constants for the three mixed and three component crystals, measured under the same conditions, are approximately the same, as the reaction cavities for the 2-cyanoethyl groups in the six crystals have almost the same size. For the mixed crystal between 3-chloropyridine and 3-methylpyridine complexes, the isomerization proceeded with retention of the single-crystal form. The conformation and configuration of the 1-cyanoethyl group that was produced were well explained by the shape of the reaction cavity before irradiation.

## 1. Introduction

It has been reported that the 2-cyanoethyl group, bonded to the Co atom in a cobaloxime complex, photoisomerizes to the 1-cyanoethyl group unidirectionally only in the solid state (Ohgo & Takeuchi, 1985). In general, the rate of photoisomerization of cobaloxime complexes depends on three major factors: volume of the free space around the reactive group, conformation of the reactive alkyl chain, and hydrogen bonding between the CN group and the OH or NH group in the neighboring molecule (Sekine & Ohashi, 1991).

It was also observed that the reaction rate was accelerated when mixed crystals were formed between the reactant compound, the 2-cyanoethyl complex, and its photoproduct, the 1-cyanoethyl complex, since the size of the reaction cavity was enlarged (Uchida *et al.*, 1986).

In a previous paper, the relationship between the reaction rate and the cavity size was compared for the 2-cyanoethyl cobaloxime complexes with 3-chloropyridine (2ce3Clpy), 3-bromopyridine (2ce3Brpy) and 3-methylpyridine (2ce3mepy) as axial base ligands (Sekine & Ohashi, 1996). These three crystals are isostructural to one another and formed mixed crystals with their 1-cyanoethyl complexes. A quantitative relationship was observed between the size of the

reaction cavity and the reaction rate in the solid state and in a single-crystal form as well. This result brought about an idea that three 2-cyanoethyl complexes would also form mixed crystals with one another, since it was reported that chloromethyl interchangeability can be used to form mixed crystals as the size or the volume of the two groups are approximately equal (Theocharis *et al.*, 1984). Further, the rate of photoisomerization should be affected by the size of the reaction cavity for the 2-cyanoethyl group in mixed crystals. Moreover, it was found that for the 2-cyanoethyl group of the cobaloxime complex, with 3-methylpyridine as an axial base ligand, the reaction proceeded with retention of the single-crystal form and a mechanism of the asymmetric induction was proposed (Sekine *et al.*, 1997).

In the present work three mixed crystals between 2ce3Clpy and 2ce3Brpy, **I**, 2ce3Clpy and 2ce3mepy, **II**, and 2ce3Brpy and 2ce3mepy, **III**, were prepared. This paper reports the relation between structure and photoreactivity for the three mixed crystals. Furthermore, the mechanism of the asymmetric induction was examined by analyzing the structure of **II** after irradiation, **II'**.

## 2. Experimental

### 2.1. Formation of mixed crystals

Component complexes of 2ce3Clpy, 2ce3Brpy and 2ce3mepy were synthesized according to the method reported previously (Schrauzer & Windgassen, 1967). Orange-colored mixed crystals of **I**, **II** and **III**, suitable for X-ray analysis, were crystallized from an aqueous methanol solution containing an equimolar mixture of (2ce3Clpy and 2ce3Brpy), (2ce3Clpy and 2ce3mepy), and (2ce3Brpy and 2ce3mepy), respectively, at ambient temperature.

### 2.2. Crystal structure analysis

Three-dimensional intensity data for the three mixed crystals, **I**, **II** and **III**, were collected on a Rigaku-AFC7R diffractometer. Crystallographic data and experimental details are summarized in Table 1.<sup>1</sup> Crystal **II** was exposed to a xenon lamp at ambient temperature (SAN-EI SUPERBRIGHT 150) for 92 h, keeping the distance between the crystal and the lamp at 4 cm. Although the crystallinity became worse after irradiation, three-dimensional intensity data were able to be collected on a SMART CCD diffractometer. The crystal data after irradiation, **II'**, are also given in Table 1. All structures were solved by direct methods using the program *SIR92* (Altomare *et al.*, 1994), and refined by full-matrix least-squares methods using the program *SHELXL97* (Sheldrick, 1997). In the difference Fourier map of crystal **I**, a high peak was found at 1.78 Å from the C13 atom and was assigned as a Cl atom. The C13—Cl bond length was fixed at 1.74 Å using the *DFIX* command and refined. After the refinement, another high peak appeared at about 1.84 Å from the C13 atom and was

assigned as a Br atom. During the refinement the C13—Br bond length was restrained to 1.86 Å. In the Fourier map of crystal **II**, two intense peaks were found at 1.72 Å and 1.45 Å from C13, which were assigned to Cl and methyl C17 atoms, respectively. C13—Cl and C13—C17 bond lengths were restrained at 1.74 Å and 1.51 Å, respectively, in the further refinement. Two peaks were found at 1.86 Å and 1.51 Å away from C13, and assigned to Br and methyl C17 atoms, respectively, in crystal **III**. The C13—Br and C13—C17 bonds were restrained in the further refinement. The sum of the site occupancy factors of the disordered atoms was constrained to be 1.00 in the refinement in all three crystals. In crystals **I** and **II**, H atoms of the hydroxyl groups, pyridine ring and methylene groups were located in the difference Fourier map and their positions, as well as their isotropic temperature factors, were fixed during the refinement, except for the H atoms of the methylene groups, which were refined without restriction. The remaining H atoms (methyl H atoms) were positioned geometrically and refined with the riding model. In crystals **II'** and **III** only the H atoms of hydroxyl groups were found in the difference Fourier map, and their positions were fixed in the refinement. The remaining H atoms, except for those of the disordered alkyl groups, were positioned geometrically and refined with the riding model. The H atoms of the disordered alkyl groups were not observed. Displacement parameters of non-H atoms were refined anisotropically. Further refinement information including data-collection conditions are summarized in Table 1.

In the electron density map of **II'**, new peaks appeared around the 2-cyanoethyl group. They were assigned as atoms of the photoproducted (*R*)- and (*S*)-1-cyanoethyl groups and were refined isotropically. Occupancy factors of the disordered atoms, Cl and methyl C17, were refined to give the sum of the occupancy factors equal to 1.00 and they were restrained geometrically with fixed bond lengths during the refinement. The occupancy factors of the original 2-cyanoethyl group and the produced 1-cyanoethyl group were refined to give a sum of 1.00, and (*R*) and (*S*) methyl groups of the 1-cyanoethyl group were refined to give equal isotropic displacement parameters.

### 2.3. Solid-state photoisomerization

For each mixed crystal, a KBr disc containing 1% of the powdered sample (0.003 g) was prepared and was irradiated at ambient temperature with a 500 W xenon lamp by keeping the distance between the sample disc and the lamp at 4 cm. FT-IR spectra (JASCO, FT/IR 350 spectrophotometer) of the sample disc were recorded at 10 min time intervals. A peak, at 2234 cm<sup>-1</sup>, due to the CN stretching frequency ( $\nu_{\text{CN}}$ ) of the 2-cyanoethyl group gradually decreased and a new peak assigned to the  $\nu_{\text{CN}}$  of the 1-cyanoethyl group appeared at 2196 cm<sup>-1</sup> upon irradiation. The log plot of the reduction of the peak at 2234 cm<sup>-1</sup> against the irradiation time indicated first-order kinetics in the early stages. The rate constant of the 2- to 1-cyanoethyl isomerization was obtained at the early stages for each mixed crystal. In order to compare the rate

<sup>1</sup>Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA0008). Services for accessing these data are described at the back of the journal.

**Table 1**  
Experimental details.

	Mix I	Mix II	Mix II'	Mix III
<b>Crystal data</b>				
Chemical formula	(C <sub>16</sub> H <sub>22</sub> BrCoN <sub>6</sub> O <sub>4</sub> ) <sub>0.39</sub> - (C <sub>16</sub> H <sub>22</sub> ClCoN <sub>6</sub> O <sub>4</sub> ) <sub>0.61</sub>	(C <sub>17</sub> H <sub>25</sub> CoN <sub>6</sub> O <sub>4</sub> ) <sub>0.56</sub> - (C <sub>16</sub> H <sub>22</sub> ClCoN <sub>6</sub> O <sub>4</sub> ) <sub>0.44</sub>	(C <sub>17</sub> H <sub>25</sub> CoN <sub>6</sub> O <sub>4</sub> ) <sub>0.52</sub> - (C <sub>16</sub> H <sub>22</sub> ClCoN <sub>6</sub> O <sub>4</sub> ) <sub>0.48</sub>	(C <sub>17</sub> H <sub>25</sub> CoN <sub>6</sub> O <sub>4</sub> ) <sub>0.55</sub> - (C <sub>16</sub> H <sub>22</sub> CoBrN <sub>6</sub> O <sub>4</sub> ) <sub>0.45</sub>
Chemical formula weight	474.55	445.73	445.76	466.91
Cell setting, space group	Monoclinic, <i>P</i> <sub>2</sub> <sub>1</sub> / <i>a</i>	Monoclinic, <i>P</i> <sub>2</sub> <sub>1</sub> / <i>a</i>	Monoclinic, <i>P</i> <sub>2</sub> <sub>1</sub> / <i>a</i>	Monoclinic, <i>P</i> <sub>2</sub> <sub>1</sub> / <i>a</i>
<i>a</i> , <i>b</i> , <i>c</i> (Å)	23.818 (3), 9.4510 (3), 8.8553 (18)	23.751 (4), 9.4680 (12), 8.8453 (14)	23.7797 (11), 9.5032 (5), 8.8569 (4)	23.82 (2), 9.520 (10), 8.822 (5)
$\beta$ (°)	94.842 (13)	94.672 (13)	94.479 (1)	94.73 (6)
<i>V</i> (Å <sup>3</sup> )	1986.3 (5)	1982.5 (5)	1995.40 (17)	1994 (3)
<i>Z</i>	4	4	4	4
<i>D<sub>x</sub></i> (Mg m <sup>-3</sup> )	1.59	1.594	1.560	1.767
Radiation type	Mo <i>K</i> $\alpha$	Mo <i>K</i> $\alpha$	Mo <i>K</i> $\alpha$	Mo <i>K</i> $\alpha$
No. of reflections for cell parameters	20	20	0	20
$\theta$ range (°)	12.5–15	12.5–15	–	12.5–15
$\mu$ (mm <sup>-1</sup> )	1.771	1.039	1.031	2.905
Temperature (K)	293 (2)	293 (2)	293 (2)	293 (2)
Crystal form, colour	Prismatic, orange	Prismatic, orange	Prismatic, brown	Diamond, orange
Crystal size (mm)	0.5 × 0.4 × 0.2	0.5 × 0.4 × 0.2	0.5 × 0.4 × 0.2	0.7 × 0.2 × 0.2
<b>Data collection</b>				
Diffractometer	AFC-7R-Rigaku	AFC-7R-Rigaku	SMART CCD	AFC-7R-Rigaku
Data collection method	$\omega$ -2 $\theta$ scan scans	$\omega$ -2 $\theta$ scan scans	$\omega$ scans	$\omega$ -2 $\theta$ scans
Absorption correction	$\psi$ -scan	$\psi$ -scan	Multiscan	$\psi$ -scan
<i>T</i> <sub>min</sub>	0.714	0.827	0.76974	0.647
<i>T</i> <sub>max</sub>	0.999	0.998	1.00000	1.000
No. of measured, independent and observed parameters	4852, 4563, 3812	4656, 4547, 3860	13847, 4580, 3677	4886, 4591, 3638
Criterion for observed reflections	>2 $\sigma$ ( <i>I</i> )	>2 $\sigma$ ( <i>I</i> )	>2 $\sigma$ ( <i>I</i> )	>2 $\sigma$ ( <i>I</i> )
<i>R</i> <sub>int</sub>	0.0641	0.0337	0.0296	0.1027
$\theta$ <sub>max</sub> (°)	27.50	27.50	27.53	27.60
Range of <i>h</i> , <i>k</i> , <i>l</i>	-30 → <i>h</i> → 30 0 → <i>k</i> → 12 -11 → <i>l</i> → 0	0 → <i>h</i> → 30 0 → <i>k</i> → 12 -11 → <i>l</i> → 11	-30 → <i>h</i> → 30 -12 → <i>k</i> → 9 -11 → <i>l</i> → 11	-30 → <i>h</i> → 31 -12 → <i>k</i> → 0 -11 → <i>l</i> → 0
No. and frequency of standard reflections	3 every 150 reflections	3 every 150 reflections	–	3 every 150 reflections
Intensity decay (%)	-0.717	0.228	0	-0.334
<b>Refinement</b>				
Refinement on	<i>F</i> <sup>2</sup>	<i>F</i> <sup>2</sup>	<i>F</i> <sup>2</sup>	<i>F</i> <sup>2</sup>
<i>R</i> [ <i>F</i> <sup>2</sup> > 2 $\sigma$ ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	0.0555, 0.1494, 1.136	0.0299, 0.0906, 1.068	0.049, 0.1391, 1.088	0.057, 0.1765, 1.095
No. of reflections and parameters used in refinement	4563, 279	4547, 280	4580, 295	4591, 268
H-atom treatment	Mixed	Mixed	Mixed	Mixed
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0956P)^2 + 0.7262P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0492P)^2 + 0.6457P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0684P)^2 + 2.1437P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0954P)^2 + 3.0983P]$ where $P = (F_o^2 + 2F_c^2)/3$
( $\Delta/\sigma$ ) <sub>max</sub>	0.002	0.002	0.050	0.008
$\Delta\rho_{max}$ , $\Delta\rho_{min}$ (e Å <sup>-3</sup> )	1.622, -0.935	0.41, -0.357	0.697, -0.413	0.765, -0.994

Computer programs used: *TEXSAN* (Molecular Structure Corporation, 2000), *SIR92* (Altomare *et al.*, 1994), *SHELXL97* (Sheldrick, 1997), *SMART* (Siemens, 1995), *SAINT* (Siemens, 1995).

constants of mixed crystals with those of the component crystals, the rate constants of the 2ce3Clpy, 2ce3Brpy and 2ce3mepy crystals were also obtained under the same conditions.

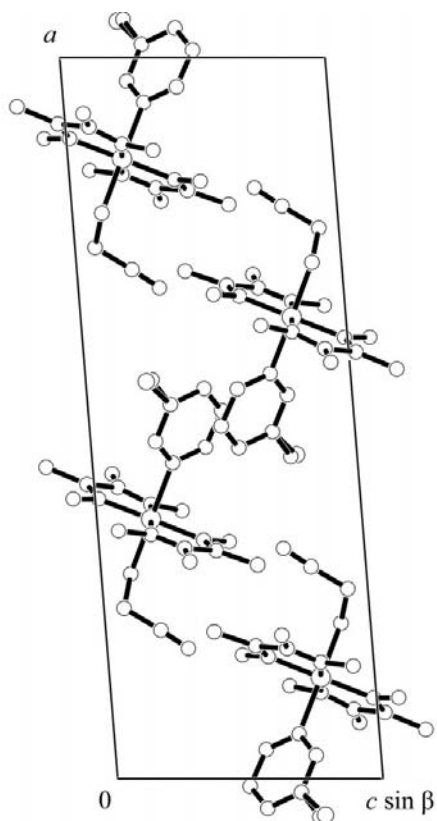
### 3. Results and discussion

#### 3.1. Crystal and molecular structures

All mixed crystal structures are isostructural to one another and to their component crystals and crystallize in *P*<sub>2</sub><sub>1</sub>/*a* with

*Z* = 4. The unit-cell dimensions of the three component crystals are: *a* = 23.89 (1), *b* = 9.486 (3), *c* = 8.823 (4) Å,  $\beta$  = 95.08 (4)°, *V* = 1991 (1) Å<sup>3</sup> for 2ce3Brpy; *a* = 23.714 (5), *b* = 9.408 (2), *c* = 8.858 (3) Å,  $\beta$  = 94.74 (2)°, *V* = 1969.6 (5) Å<sup>3</sup> for 2ce3Clpy; and *a* = 23.761 (5), *b* = 9.496 (2), *c* = 8.815 (3) Å,  $\beta$  = 94.52 (2)°, *V* = 1982.8 (8) Å<sup>3</sup> for 2ce3mepy, and may be compared with those for the mixed crystals given in Table 1. The cell parameters of each mixed crystal lie between the corresponding ones of its component crystals, except for the cell volume of the mixed crystal **III**.

The crystal structure of **II** viewed along the *b* axis is shown in Fig. 1. The reactive 2-cyanoethyl groups form a column along the 2<sub>1</sub> axis and are surrounded by the cobaloxime planes in the crystal structure. Since the disordered 3-Cl, Br and CH<sub>3</sub>



**Figure 1**  
Crystal structure of **II** viewed along the *b* axis.

groups are apart from the reactive group, they may have no direct influence on the reactivity of the mixed crystals.

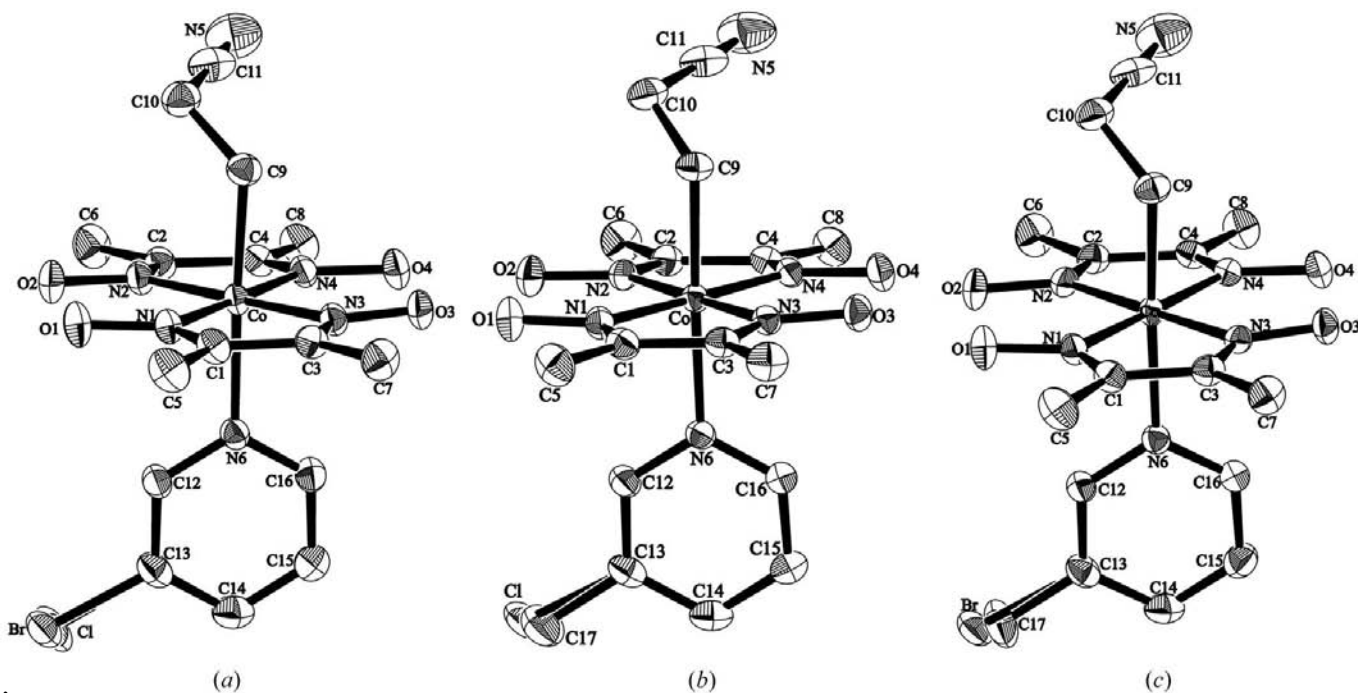
Fig. 2 shows the disordered molecular structures observed in mixed crystals. Except for the 3-Cl and Br atoms and 3-CH<sub>3</sub> group, all the atoms of two component molecules occupy the same positions in each mixed crystal. Bond distances and angles in each mixed crystal are approximately the same as the corresponding ones of component molecules. Moreover, torsion angles around the Co—C9, C9—C10 and Co—N6 bonds are also similar to one another as shown in Table 2.

### 3.2. Reaction cavity and solid-state photoisomerization

In order to compare the reaction rate with the crystal structure, the reaction cavity for the 2-cyanoethyl group was calculated for each mixed crystal. Since the crystal structures of three mixed crystals are isostructural to one another and to the component crystals, the reaction cavities of three mixed crystals and three component crystals are similar in shape and size. The volumes of the reaction cavities and the rate constants for the six crystals are given in Table 3.

There are no significant differences in the cavity volume and the rate constant among the six crystals. With regard to these results it is noteworthy that, when mixed crystals were synthesized between isostructural pairs, no significant difference could be created either in the molecular structure or in the crystal structure. Further, the cavity size of the mixed crystal is intermediate with those of each of the two component crystals. Hence, the reactivity may be improved only in one component.

The above results suggest that if mixed crystals are synthesized from the component molecules with different



**Figure 2**  
Disordered molecular structures of (a) **I**, (b) **II** and (c) **III**. The thermal ellipsoids are drawn at the 30% probability level. H atoms are omitted for clarity.

**Table 2**  
Torsion angles.

Torsion angle	I	II (before)	II' (after)	III	2ce3Brpy	2ce3Clpy	2ce3mepy
N4—Co—C9—C10	78.8 (3)	78.4 (2)	80.0 (1)	78.3 (4)	78.1 (8)	78.0 (4)	78.2 (4)
C16—N6—Co—N4	−129.5 (2)	−129.8 (1)	−130.3 (1)	−129.8 (3)	−129.5 (6)	−129.9 (3)	−129.4 (3)
Co—C9—C10—C11	−81.1 (4)	−81.2 (2)	−82.1 (1)	−81.1 (5)	−79.8 (3)	−80.4 (6)	−81.1 (5)

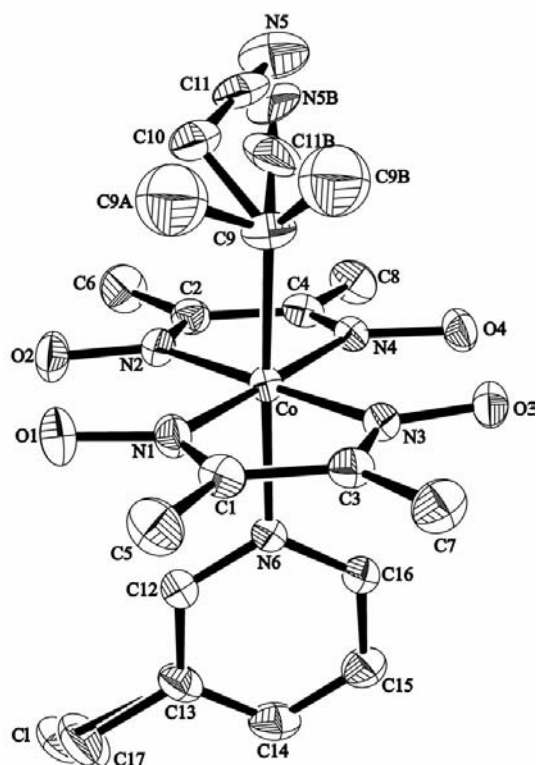
**Table 3**  
Reaction rates and cavity volumes.

	I	II	III	2ce3Brpy	2ce3Clpy	2ce3mepy
Reaction rate (sec <sup>−1</sup> )	$1.4 \times 10^{-4}$	$1.4 \times 10^{-4}$	$1.6 \times 10^{-4}$	$1.6 \times 10^{-4}$	$1.4 \times 10^{-4}$	$1.4 \times 10^{-4}$
Cavity volume (Å <sup>3</sup> )	10.9	10.8	11.0	11.1	10.6	10.1

structures, more enhanced reaction rates will be obtained. Further studies on the mixed crystals composed of quite different molecules are in progress.

### 3.3. Crystal structure of II'

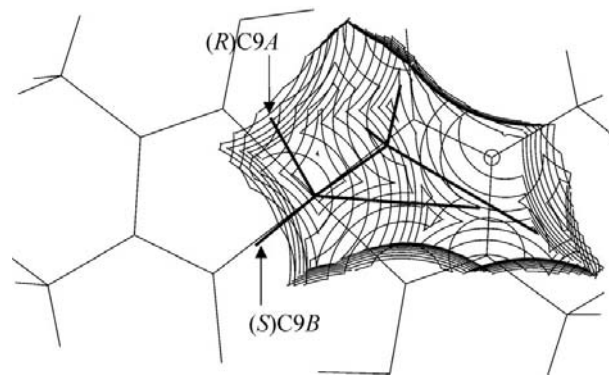
The unit-cell volume for the mixed crystal was increased roughly by 13 Å<sup>3</sup> after irradiation. The molecular structure with the atomic numbers at the original site is shown in Fig. 3. The molecular structure of the photoproducted compound is approximately the same as that of the original one except for the cyanoethyl group. The photoproducted 1-cyanoethyl group has a disordered structure with both *R* and *S* configurations present. The occupancy factors of the disordered cyanoethyl groups in the molecule at the original site were refined to



**Figure 3**  
Molecular structure of II'. The thermal ellipsoids are drawn at the 30% probability level. H atoms are omitted for clarity.

0.798 (2), 0.121 (2) and 0.081 (2) for the 2-cyanoethyl, (*R*)-1-cyanoethyl and (*S*)-1-cyanoethyl groups, respectively. Although the inverted structure is produced at the inverted site around the inversion center, the (*R*)-1-cyanoethyl group is preferentially produced from the 2-cyanoethyl group with the prochiral configuration shown in Fig. 3. The reason why the (*R*) configuration is present in a slightly greater amount than the (*S*) configuration can be clearly understood when the shape of the reaction cavity diagram is drawn (Fig. 4). Here, the shape of the cavity is not symmetric, and there is more space for the C9A methyl group with the (*R*) configuration than that for the C9B with the (*S*) configuration in the cavity before irradiation. In other words, there must be more steric repulsion from neighboring atoms on the methyl group with the (*S*) configuration. Similar results were observed for the photo-isomerization of the component 3-methylpyridine complex, in which the ratio of the produced (*R*) and (*S*) 1-cyanoethyl groups were 0.36 (4) and 0.19 (4), respectively (Sekine *et al.*, 1997). However, since the crystal is centrosymmetric, the reverse occupancy ratio (*R*:*S* = 0.081:0.121) should be found at the inverted site.

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**Figure 4**  
Reaction cavity diagram of II viewed normal to the cobaloxime plane. The contours are drawn in sections separated by 0.20 Å

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