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Headline Articles

Racemic-to-Chiral Transformation in Cobaloxime Complex Crystals Only by Photoirradiation

Takashi Nemoto# and Yuji Ohashi*

Department of Chemistry and Materials Science, Tokyo Institute of Technology,
O-okayama, Meguro-ku, Tokyo 152-8551

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The cobaloxime complex crystal with the *racemic*-1-cyanoethyl group and piperidine as axial ligands, which has a chiral space group of $P2_12_12_1$, changed its cell dimensions with retention of the single crystal form on exposure to visible light. The chloroform solution of the crystals after irradiation showed the optical rotation ($[\alpha]_D = 30°$). This indicates the racemic-to-chiral transformation occurred in the crystal only by photoirradiation. The crystal before irradiation, analyzed by X-rays, has two complexes with *R*- and *S*-1-cyanoethyl groups in the asymmetric unit. After irradiation, one of the complexes with the *S* group, which has a larger reaction cavity than the *R* group, was partly inverted to create a disordered structure. The *R* : *S* ratio in the crystal changed from 50 : 50 to 70 : 30. The final ratio of 70 : 30 is well explained by the symmetric shape of the reaction cavity after the change. For the cobaloxime complex crystal with the *racemic*-1-cyanoethyl group and pyrrolidine as axial ligands, a similar transformation was observed. The racemic crystal with the space group $P1$ has four complexes in a unit cell, two of which have a *R*-1-cyanoethyl group while the other two complexes have a *S*-1-cyanoethyl group. The complexes with the *S* group, which have larger cavities than those with the *R* group, were partly inverted to create the opposite configuration. This caused optical enrichment in the crystal. Such a racemic-to-chiral transformation will be observed not rarely but commonly if the racemic crystals with chiral space groups will be examined cautiously.

There are two approaches to obtain chiral substances utilizing chiral crystal environment: One is to produce the chiral compounds from the prochiral ones and the other is to obtain the chiral compounds from the racemic ones. The former method is called "absolute asymmetric synthesis", since the asymmetry is introduced from the physical conditions such as the chiral crystal environment. Several examples have been reported,[1] since the chiral polymer was found to be produced in the photo polymerization of the monomer crystal.[2] We observed that a chiral β-lactam was produced from the prochiral oxoamide crystals.[3,4] Recently we found that the chiral 1-cyanoethyl group bonded to the cobalt atom is produced from the prochiral 2-cyanoethyl group in a cobaloxime complex crystal with retention of the single crystal form. Only one enantiomer was observed in the crystal structure after the irradiation.[5] Moreover, the chiral 1-cyanopropyl group is produced from the prochiral 3-cyanopropyl group in a cobaloxime complex with retention of the single crystal form.[6]

On the other hand, there has been no report on the latter method until we found that the racemic crystals of a cobaloxime complex showed optical rotation after the crystals were exposed to visible light.[7] This indicates that only photoirradiation produced chiral substances in a racemic crystal. Fortunately, the racemic-to-chiral transformation occurred with retention of the single crystal form. Since we have found that the chiral alkyl groups such as 1-cyanoethyl,[8] 1-(methoxycarbonyl)ethyl,[9] 1,2-bis(methoxycarbonyl)ethyl,[10] 1,2-bis(ethoxycarbonyl)ethyl,[11] and 1,2-bis(allyoxycarbonyl)ethyl[12] groups bonded to the cobalt atom in some cobaloxime complex crystals are racemized on exposure to visible light with retention of the single crystal form, the racemic-to-chiral transformation appears to be an inverse reaction to the racemization. A solid-state reaction retaining the single crystal form is called a crystalline-state reaction, for which several intermediate structures can be obtained by X-ray analysis and the reaction process can be ascertained on the basis of the structural change. In order to compare the void space around the reactive group with those of the corresponding ones in the other crystals, we define a reaction cavity.[13] A quantitative relationship has been found between the reaction rate and the reaction cavity.[8]

In this report, the reason why the racemic-to-chiral trans-

Present address: Institute of Chemical Research, Kyoto University.

formation occurred in the crystal will be made clear and the processes of the transformation in the two cobaloxime complex crystals with piperidine and pyrrolidine as axial base ligands will be compared.

Experimental

Piperidine Complex. Preparation of the Complex Crystals. (*Racemic*-, *R*- or *S*-1-cyanoethyl)bis(dimethylglyoximato)(piperidine)cobalt(III) was prepared in a way similar to that reported previously.[14,15] The crystals were obtained from aqueous methanol solutions. The mixed crystals with different *R* : *S* ratios were grown from aqueous methanol solutions in which the complexes with the *R*- and *S*-1-cyanoethyl groups were dissolved in the desired proportions. Since the racemic and chiral crystals are isostructural, five kinds of crystals with the *R* : *S* ratios of 50 : 50, 57 : 43, 75 : 25, 87 : 13, and 100 : 0 were prepared; these are abbreviated hereafter as pip-1, pip-2, pip-3, pip-4, and pip-5, respectively. Such crystals with different ratios make it more easy to estimate the final *R* : *S* ratio since complete conversion is difficult even in the crystalline-state reactions.

Determination of *R* : *S* Ratios of the Crystals by X-Ray Analysis. The crystal structures of the five crystals before irradiation were determined by X-rays. Although the cell dimensions of the five crystals were determined by the four-circle diffractometer, Rigaku AFC-4 in the same conditions, the three-dimensional intensity data of the crystals were collected by the four-circle diffractometers: Rigaku AFC-4, AFC-5R, and AFC-7S. The diffractometers were covered with a black sheet to avoid the room light. The absorption correction was not applied. The crystal data are given in Table 1. The initial parameters of the non-hydrogen atoms of pip-5 were taken from the reported ones[16] and refined with the anisotropic temperature factors by the full-matrix least-squares method using the program SHELX76.[17] The hydrogen atoms were refined using the riding model. The isotropic temperature factors were fixed to $B = 6.0$ Å^2. The crystal structures of pip-1 to pip-4 were determined using the parameters of pip-5 as an initial one and refined by the full-matrix least-squares method. The *S*-1-cyanoethyl group of each crystal has a disordered structure, since a part of the group was inverted to have the *R* configuration. The geometries of the disordered *R*- and *S*-1-cyanoethyl groups were fixed in the refinement. The occupancy factors of the *S* and *R* groups were refined to have the same isotropic temperature factors between the corresponding atoms. The other conditions of the refinement were nearly the same as those of pip-5. The details of the refinement are also listed in Table 1. The atomic coordinates of pip-1 are given in Table 2.

Exposure to a Xenon Lamp. Each crystal of pip-1, pip-3, or pip-5 mounted on the diffractometer was irradiated with a xenon lamp, SAN-EI Super Bright 150, using an optical fiber. The cell dimensions were measured at a constant interval of about 40 min. The 2θ values of 20 reflections ($20 < 2\theta < 30°$) were used for the measurement of the cell dimensions. After the changes converged, the intensity data of the crystals, pip-1′, pip-3′, and pip-5′, respectively, were collected again. The crystal structures were refined in the same way as that of pip-3. The cell dimensions and the details of the refinement for pip-1′, pip-3′, and pip-5′ are given in Table 3. The cell dimensions are identical with each other within

Table 1. Crystal Data and Experimental Details for **pip** Crystals before Irradiation

	pip-1	**pip**-2	**pip**-3	**pip**-4	**pip**-5
Formula	$C_{16}H_{29}CoN_6O_4$				
F.W.	428.38				
Space group	$P2_12_12_1$				
Z	8				
a/Å$^{a)}$	11.707(2)	11.717(2)	11.725(2)	11.734(1)	11.743(6)
b/Å$^{a)}$	30.723(7)	30.73(1)	30.790(7)	30.946(5)	31.045(4)
c/Å$^{a)}$	11.414(3)	11.394(4)	11.377(3)	11.339(2)	11.395(3)
V/Å$^{3\ a)}$	4105(2)	4102(2)	4107(2)	4117(1)	4121(2)
D_x/Mg m^3	1.379	1.392	1.367	1.383	1.381
Crystal size	0.5 × 0.4 × 0.2	0.4 × 0.3 × 0.3	0.3 × 0.3 × 0.3	0.4 × 0.4 × 0.3	0.4 × 0.4 × 0.3
Diffractometer	AFC-7S (Rigaku)	AFC-5R (Rigaku)	AFC-7S (Rigaku)	AFC-4 (Rigaku)	AFC-4 (Rigaku)
Radiation	Graphite monochromated Mo $K\alpha$ radiation				
μ/mm^{-1}	0.865	0.868	0.864	0.860	0.861
Measurement temperature	296 K				
Scan mode	ω scan				
θ_{max}	30	27.5	27.5	27.5	27.5
No. of measured reflections	6549	5268	5280	5298	5318
Observed reflections	4077	3041	4180	3768	3948
Criterion	$F > 3\sigma(F)$	$F > 3\sigma(F)$	$F > 3\sigma(F)$	$F > 4\sigma(F)$	$F > 3\sigma(F)$
$R : S$ (in solution)	50:50	57:43	75:25	87:13	100:0
$R : S$ (in whole crystal)	50:50	62:38	74:26	87:13	100:0
$R : S$ (A molecule)	50:0	50:0	50:0	50:0	50:0
$R : S$ (B molecule)	0:50	12:38	24:26	37:13	50:0
R	0.063	0.060	0.045	0.046	0.046
R_w	0.045	0.052	0.040	0.051	0.049
Cavity (A molecule)/Å^3	7.0	6.7	7.0	6.5	5.8
Cavity (B molecule)/Å^3	14.2	11.7	12.9	12.6	12.8

a) Cell dimensions were measured on same condition using Rigaku AFC-4.

Table 2. Atomic Coordinates and the Equivalent Isotropic Temperature Factors for **pip**-1 before Irradiation

Atom	x	y	z	U_{eq}
Co1A	0.48874(7)	0.12233(2)	0.14491(7)	0.038
N1A	0.4869(5)	0.15959(15)	0.0143(4)	0.048
N2A	0.3635(4)	0.15702(17)	0.1895(4)	0.042
N3A	0.4908(5)	0.08521(15)	0.2753(4)	0.045
N4A	0.6173(5)	0.08926(18)	0.1020(5)	0.046
O1A	0.5601(4)	0.15609(14)	−0.0764(4)	0.065
O2A	0.3086(4)	0.15196(15)	0.2912(4)	0.055
O3A	0.4197(4)	0.08865(14)	0.3661(3)	0.059
O4A	0.6782(4)	0.09604(16)	0.0051(4)	0.067
C1A	0.4075(6)	0.1904(2)	0.0130(6)	0.051
C2A	0.3356(6)	0.1889(2)	0.1171(7)	0.047
C3A	0.5700(6)	0.0553(2)	0.2772(6)	0.049
C4A	0.6452(5)	0.0576(2)	0.1736(7)	0.053
C5A	0.3971(6)	0.2210(2)	−0.0860(5)	0.080
C6A	0.2407(5)	0.22009(19)	0.1413(7)	0.071
C7A	0.5856(6)	0.02376(19)	0.3758(5)	0.074
C8A	0.7418(5)	0.02775(17)	0.1473(7)	0.072
C9A	0.5910(6)	0.1667(2)	0.2333(7)	0.060
C10A	0.6574(6)	0.1460(3)	0.3255(6)	0.050
N5A	0.7122(5)	0.1297(2)	0.3936(5)	0.070
C11A	0.6630(6)	0.1951(3)	0.1621(8)	0.100
N6A	0.3752(4)	0.08079(17)	0.0562(4)	0.043
C12A	0.4256(5)	0.0537(2)	−0.0367(5)	0.054
C13A	0.3356(6)	0.0299(2)	−0.1077(6)	0.069
C14A	0.2588(6)	0.0022(2)	−0.0328(6)	0.073
C15A	0.2060(6)	0.0313(2)	0.0613(6)	0.066
C16A	0.2971(5)	0.0541(2)	0.1311(6)	0.056
Co1B	0.49569(8)	0.35003(2)	0.35012(7)	0.037
N1B	0.3800(4)	0.39210(17)	0.3252(5)	0.040
N2B	0.3674(4)	0.31260(18)	0.3604(6)	0.043
N3B	0.6111(5)	0.30797(19)	0.3744(6)	0.051
N4B	0.6236(4)	0.38747(18)	0.3421(5)	0.042
O1B	0.4039(3)	0.43401(14)	0.3037(4)	0.053
O2B	0.3790(3)	0.26930(14)	0.3740(5)	0.056
O3B	0.5889(4)	0.26523(16)	0.3922(5)	0.070
O4B	0.6156(4)	0.43023(15)	0.3169(4)	0.052
C1B	0.2748(5)	0.3778(2)	0.3294(6)	0.042
C2B	0.2689(5)	0.3311(2)	0.3516(7)	0.042
C3B	0.7152(6)	0.3218(3)	0.3846(6)	0.049
C4B	0.7228(5)	0.3690(2)	0.3620(6)	0.047
C5B	0.1754(5)	0.4065(2)	0.3122(6)	0.061
C6B	0.1574(5)	0.30724(19)	0.3614(6)	0.056
C7B	0.8145(5)	0.2942(2)	0.4140(6)	0.077
C8B	0.8342(5)	0.3937(2)	0.3610(6)	0.061
C9B	0.5057(7)	0.3355(2)	0.1749(5)	0.068
C10B	0.6114(6)	0.3490(2)	0.1241(6)	0.047
N5B	0.6949(5)	0.3593(2)	0.0833(5)	0.079
C11B	0.4112(7)	0.3409(3)	0.1026(7)	0.148
N6B	0.4757(5)	0.36142(15)	0.5295(4)	0.045
C12B	0.5228(7)	0.4033(2)	0.5743(5)	0.067
C13B	0.4852(8)	0.4127(2)	0.6992(5)	0.077
C14B	0.5179(8)	0.3751(3)	0.7802(5)	0.088
C15B	0.4709(6)	0.3332(2)	0.7341(5)	0.076
C16B	0.5084(7)	0.32507(19)	0.6093(4)	0.058

the experimental errors.

Converged Structure at 343 K. Another crystal of pip-1 was warmed up to 343 K by the hot-air-flow method and was exposed to the xenon lamp. The cell dimensions were measured continuously. After 15 h exposure, the cell change became insignificantly small and the lamp was turned off. The crystal was cooled to 296 K and the intensity data were collected. The crystal is called pip-1$''$. The structure was refined in the same way as that of pip-1$'$ using the program SHELXL93.[18] The cell dimensions and experimental details are also given in Table 3.

Pyrrolidine Complex. Preparation of the Complex Crystals. (*Racemic*-, *R*- or *S*-1-cyanoethyl)bis(dimethylglyoximato)(pyrrolidine)cobalt(III) was prepared in a way similar to that reported previously.[14,15] The mixed crystals with different $R:S$ ratios were grown from aqueous methanol solutions in which the *R*- and *S*-1-cyanoethyl complexes were dissolved in the desired proportions. For the pyrrolidine complex, four kinds of crystals with the $R:S$ ratios of 50:50, 75:25, 80:20, and 90:10 were prepared; these are abbreviated hereafter as pyrr-1, pyrr-2, pyrr-3, and pyrr-4, respectively. The seed crystals were used in the crystallizations of pyrr-2 to pyrr-4 to obtain the crystals with the desired $R:S$ ratio. The crystal of (*R*- or *S*-1-cyanoethyl)-bis(dimethylglyoximato)(pyrrolidine)cobalt(III) was obtained as the hydrate and the space group is $P2_12_12_1$ and $Z = 4$.[19] If the $R:S$ ratio became more than 90:10 in the solution, the obtained crystal is not isostructural to the racemic one but has the same form as that of the chiral crystal.

Determination of $R:S$ Ratios of the Crystals. The cell dimensions and the intensity data of the four crystals were measured by the four-circle diffractometer, Rigaku AFC-5R, or AFC-7S, in the same conditions as those of the piperidine complexes. The diffractometer was covered with a black sheet to avoid the room light. No absorption correction was applied. The crystal data are given in Table 4. The initial parameters of the non-hydrogen atoms of pyrr-1 were taken from the reported ones.[20] The details of the refinement are nearly the same as those of the piperidine complexes. The hydrogen atoms were refined using the riding model. The isotropic temperature factors of the H-atoms were assumed to be 1.2 times those of the bonded atoms. The crystal structures of pyrr-2 to pyrr-4 were determined using the structure of pyrr-1 as the initial one and were refined. The *S*-1-cyanoethyl group of each crystal has a disordered structure, since a part of the group was inverted to have *R* configuration. The occupancy factors of the *S*- and *R*-1-cyanoethyl groups with disordered structures were refined to have the same isotropic temperature factors between the corresponding atoms. The other conditions of the refinement were nearly the same as those of pyrr-1. The details of the refinement are also listed in Table 4. The atomic coordinates of pyrr-1 are given in Table 5.

Exposure to a Xenon Lamp. Each crystal of pyrr-1 to pyrr-4 was irradiated with the xenon lamp on the diffractometer and the cell dimensions were measured at a constant interval. The experimental details are the same as those for the piperidine complex. After the changes were converged, the intensity data of the four crystals were collected again and the crystal structures were refined in the same way as that of pyrr-2. The crystals after irradiation were abbreviated as pyrr-1$'$, pyrr-2$'$, pyrr-3$'$, and pyrr-4$'$, respectively. The cell dimensions and the details of the refinement for pyrr-1$'$, pyrr-2$'$, pyrr-3$'$, and pyrr-4$'$ are given in Table 6. The cell dimensions of pyrr-2$'$ to pyrr-4$'$ are identical to each other within the experimental errors. The atomic coordinates and the anisotropic temperature factors of non-H atoms, the atomic coordinates and the isotropic temperature factors of H atoms, and bond distances and angles for pip-1 to pip-5, pip-1$'$, pip-3$'$, pip-5$'$, pip-1$''$, pyrr-1 to pyrr-4, and pyrr-1$'$ to pyrr-4$'$ crystals, except the atomic coordinates for pip-1 and pyrr-1, are deposited as Document No. 72039 at the Office of the Editor of Bull. Chem. Soc. Jpn. Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2

Table 3. Crystal Data and Experimental Details for **pip** Crystals after Irradiation

	pip-1′	**pip**-3′	**pip**-5′	**pip**-1″
Formula	$C_{16}H_{29}CoN_6O_4$			
F.W.	428.38			
Space group	$P2_12_12_1$			
Z	8			
a/Å	11.7215(7)	11.725(1)	11.720(1)	11.713(2)
b/Å	30.761(3)	30.754(5)	30.768(5)	30.78(2)
c/Å	11.384(1)	11.384(2)	11.380(2)	11.374(6)
V/Å^3	4105(1)	4105(2)	4104(2)	4100(3)
D_x/Mg m^{-3}	1.367	1.367	1.380	1.381
Crystal size	0.4 × 0.4 × 0.3	0.4 × 0.3 × 0.3	0.4 × 0.4 × 0.3	0.3 × 0.2 × 0.2
Diffractometer	AFC-4 (Rigaku)	AFC-4 (Rigaku)	AFC-4 (Rigaku)	AFC-7S (Rigaku)
Radiation	Graphite monochromated Mo $K\alpha$ radiation			
μ/mm^{-1}	0.846	0.864	0.864	0.859
Measurement temperature	296 K			
Scan mode	ω scan			
$\theta_{\max}$	27.5	27.5	27.5	27.5
No. of measured reflections	5294	5244	5289	5250
Observed reflections	3902	3844	4526	4296
Criterion	$F > 4\sigma(F)$	$F > 4\sigma(F)$	$F > 3\sigma(F)$	$F > 4\sigma(F)$
$R:S$ (in whole crystal)	69:31	69:31	71:29	74:26
$R:S$ (B molecule)	19:31	19:31	21:29	24:26
R	0.055	0.067	0.054	0.035
R_w	0.064	0.072	0.064	wR_2 = 0.083

Table 4. Crystal Data and Experimental Details for **pyrr** Crystals after Irradiation

	pyrr-1[a)]	**pyrr**-2	**pyrr**-3	**pyrr**-4
Formula	$C_{15}H_{27}CoN_6O_4 \cdot 0.1H_2O$			
F.W.	416.16			
Space group	$P1$			
Z	4			
a/Å	11.729(1)	11.7475(8)	11.786(2)	11.788(2)
b/Å	15.640(5)	15.680(2)	15.745(3)	14.796(4)
c/Å	11.142(4)	11.071(1)	11.057(2)	11.004(2)
α/°	98.61(2)	98.879(9)	99.11(1)	99.42(1)
β/°	90.17(2)	90.236(6)	90.32(2)	90.42(1)
γ/°	98.26(2)	98.279(7)	98.21(1)	98.17(2)
V/Å^3	1999(2)	1993.1(3)	2004.3(6)	2000.0(6)
D_x/Mg m^{-3}	1.383	1.387	1.379	1.382
Crystal size	0.3 × 0.3 × 0.3	0.5 × 0.4 × 0.3	0.3 × 0.3 × 0.3	0.3 × 0.2 × 0.2
Diffractometer	AFC-5R	AFC-7S	AFC-5R	AFC-7S
Radiation	Graphite monochromated Mo $K\alpha$ radiation			
μ/mm^{-1}	0.890	0.893	0.888	0.890
Scan mode	$2\theta/\omega$ scan			
$\theta_{\max}$	30	27.5	27.5	27.5
No. of measured reflections	10384	9155	9229	9190
Observed reflections	5810	7976	7971	7515
Criterion	$F > 4\sigma(F)$			
$R:S$ (in solution)	50:50	75:25	80:20	90:10
$R:S$ (in whole crystal)	50:50	76:24	84:16	90:10
$R:S$ (A molecule)	25:0	25:0	25:0	25:0
$R:S$ (B molecule)	25:0	25:0	25:0	25:0
$R:S$ (C molecule)	0:25	10:15	15:10	17:8
$R:S$ (D molecule)	0:25	16:9	19:6	23:2
R ($F > 4\sigma(F)$)	0.085	0.035	0.034	0.042
wR_2	0.202	0.094	0.088	0.118

a) Absolute structure is inverted to have R configuration at A molecule.

Table 5. Atomic Coordinates and the Equivalent Isotropic Temperature Factors for **pyrr**-1 before Irradiation
The Occupancy Factors for C14B = 0.60, C14F, O1W = 0.4, C13D, C14D, C15D, N6D = 0.63, C13H, C14H, C15H, N6H = 0.37

Atom	x	y	z	U_{eg}/U_{iso}	Atom	x	y	z	U_{eg}/U_{iso}
Co1A	−0.79740(5)	−0.75331(4)	−0.68988(5)	0.041	N2C	−0.7954(3)	−0.2150(3)	−0.7830(4)	0.046
N1A	−0.8048(4)	−0.6728(3)	−0.5505(4)	0.065	N3C	−0.5594(3)	−0.2386(3)	−0.8103(4)	0.048
N2A	−0.9071(4)	−0.6895(3)	−0.7424(4)	0.055	N4C	−0.6185(4)	−0.3944(3)	−0.8768(4)	0.055
N3A	−0.7963(4)	−0.8365(3)	−0.8269(4)	0.060	O1C	−0.8711(3)	−0.4576(3)	−0.8888(4)	0.072
N4A	−0.6838(3)	−0.8145(3)	−0.6383(4)	0.054	O2C	−0.7468(3)	−0.1329(2)	−0.7426(4)	0.066
O1A	−0.7403(5)	−0.6705(4)	−0.4458(3)	0.108	O3C	−0.5414(4)	−0.1526(3)	−0.7628(4)	0.066
O2A	−0.9560(4)	−0.7108(3)	−0.8592(3)	0.072	O4C	−0.6644(4)	−0.4798(3)	−0.9114(5)	0.083
O3A	−0.8595(4)	−0.8376(3)	−0.9301(3)	0.079	C01C	−0.9422(4)	−0.3303(3)	−0.8324(4)	0.047
O4A	−0.6362(4)	−0.7920(3)	−0.5240(4)	0.086	C02C	−0.9048(4)	−0.2357(3)	−0.7894(5)	0.050
C01A	−0.8662(3)	−0.6110(4)	−0.55240(19)	0.077	C03C	−0.4719(5)	−0.2786(4)	−0.8359(5)	0.060
C02A	−0.9311(3)	−0.6248(4)	−0.6665(2)	0.069	C04C	−0.5070(5)	−0.3716(4)	−0.8765(5)	0.064
C03A	−0.7260(5)	−0.8959(4)	−0.8251(5)	0.062	C05C	−1.0628(5)	−0.3696(5)	−0.8512(6)	0.072
C04A	−0.6589(4)	−0.8805(4)	−0.7110(6)	0.062	C06C	−0.9888(5)	−0.1718(4)	−0.7539(6)	0.076
C05A	−0.8926(9)	−0.5453(5)	−0.4477(7)	0.126	C07C	−0.3501(5)	−0.2376(6)	−0.8177(7)	0.093
C06A	−1.0130(6)	−0.5660(4)	−0.6966(8)	0.100	C08C	−0.4224(5)	−0.4348(5)	−0.9179(7)	0.097
C07A	−0.7096(8)	−0.9630(5)	−0.9240(6)	0.103	N5C	−0.7234(3)	−0.2812(3)	−1.0053(3)	0.054
C08A	−0.5761(6)	−0.9374(4)	−0.6796(8)	0.093	C09C	−0.6523(8)	−0.2053(6)	−1.0447(6)	0.105
N5A	−0.9278(3)	−0.8327(3)	−0.6236(3)	0.049	C10C	−0.6869(7)	−0.2160(7)	−1.1794(6)	0.161
C09A	−1.0203(5)	−0.8835(5)	−0.7118(7)	0.104	C11C	−0.7146(8)	−0.3083(7)	−1.2257(6)	0.137
C10A	−1.0955(6)	−0.9452(5)	−0.6391(7)	0.100	C12C	−0.7158(8)	−0.3496(6)	−1.1100(5)	0.108
C11A	−1.0212(5)	−0.9532(4)	−0.5294(6)	0.072	C13C	−0.7075(4)	−0.3382(5)	−0.6554(5)	0.077
C12A	−0.9067(6)	−0.8998(4)	−0.5493(6)	0.076	C14C	−0.7836(6)	−0.3005(6)	−0.5664(5)	0.100
C13A	−0.6758(5)	−0.6675(4)	−0.7572(6)	0.069	C15C	−0.5908(5)	−0.3303(4)	−0.6080(5)	0.065
C14A	−0.5957(7)	−0.6071(5)	−0.6657(9)	0.123	N6C	−0.4965(5)	−0.3251(4)	−0.5737(5)	0.095
C15A	−0.6108(4)	−0.7126(4)	−0.8476(4)	0.063	Co1D	−0.29127(5)	−0.73399(4)	−0.19027(5)	0.045
N6A	−0.5559(4)	−0.7492(5)	−0.9196(6)	0.104	N1D	−0.4125(4)	−0.6658(4)	−0.1681(4)	0.063
Co1B	−0.20436(5)	−0.24987(5)	−0.30899(5)	0.047	N2D	−0.4175(4)	−0.8221(4)	−0.2296(4)	0.063
N1B	−0.2052(3)	−0.3333(3)	−0.4509(4)	0.056	N3D	−0.1710(4)	−0.8022(3)	−0.2117(4)	0.052
N2B	−0.3394(3)	−0.3262(3)	−0.2786(4)	0.054	N4D	−0.1660(4)	−0.6455(3)	−0.1507(4)	0.058
N3B	−0.2066(3)	−0.1687(3)	−0.1672(3)	0.053	O1D	−0.3914(4)	−0.5788(3)	−0.1369(4)	0.079
N4B	−0.0675(4)	−0.1769(3)	−0.3355(4)	0.056	O2D	−0.4020(4)	−0.9082(3)	−0.2640(5)	0.098
O1B	−0.1263(4)	−0.3250(3)	−0.5339(4)	0.078	O3D	−0.1872(4)	−0.8889(3)	−0.2511(4)	0.077
O2B	−0.4001(4)	−0.3142(3)	−0.1794(4)	0.073	O4D	−0.1792(4)	−0.5600(3)	−0.1170(5)	0.085
O3B	−0.2838(4)	−0.1719(3)	−0.0846(4)	0.075	C01D	−0.5179(4)	−0.7077(5)	−0.1823(4)	0.063
O4B	−0.0018(3)	−0.1933(3)	−0.4294(4)	0.068	C02D	−0.5179(5)	−0.8005(5)	−0.2200(5)	0.068
C01B	−0.2894(4)	−0.3979(4)	−0.4644(5)	0.054	C03D	−0.0658(4)	−0.7601(4)	−0.1867(4)	0.051
C02B	−0.3661(4)	−0.3932(4)	−0.3612(5)	0.058	C04D	−0.0657(4)	−0.6683(3)	−0.1510(5)	0.052
C03B	−0.1196(5)	−0.1039(4)	−0.1562(5)	0.065	C05D	−0.6217(5)	−0.6640(6)	−0.1717(7)	0.096
C04B	−0.0374(5)	−0.1089(4)	−0.2534(5)	0.061	C06D	−0.6262(6)	−0.8674(6)	−0.2464(7)	0.100
C05B	−0.2999(7)	−0.4673(5)	−0.5725(7)	0.089	C07D	0.0407(5)	−0.8011(5)	−0.2036(6)	0.086
C06B	−0.4702(6)	−0.4589(5)	−0.3543(7)	0.091	C08D	0.0459(6)	−0.6081(5)	−0.1176(7)	0.086
C07B	−0.1095(7)	−0.0331(5)	−0.0410(6)	0.087	N5D	−0.3123(4)	−0.7530(3)	−0.0139(4)	0.056
C08B	0.0742(6)	−0.0476(4)	−0.2561(7)	0.083	C09D	−0.2907(8)	−0.8423(5)	0.0176(7)	0.117
N5B	−0.3071(3)	−0.1862(3)	−0.4066(4)	0.051	C10D	−0.3042(8)	−0.8321(8)	0.1527(7)	0.137
C09B	−0.4053(5)	−0.1492(5)	−0.3401(7)	0.089	C11D	−0.2795(8)	−0.7343(8)	0.1982(6)	0.155
C10B	−0.4569(5)	−0.0981(4)	−0.4320(6)	0.076	C12D	−0.2579(7)	−0.6942(6)	0.0850(5)	0.110
C11B	−0.3530(6)	−0.0708(4)	−0.5082(6)	0.083	C13D	−0.27415(12)	−0.6902(2)	−0.35585(19)	0.0479(16)
C12B	−0.2554(5)	−0.1153(4)	−0.4716(6)	0.075	C14D	−0.3748(2)	−0.7121(8)	−0.4481(3)	0.114(4)
C13B	−0.1124(6)	−0.3245(5)	−0.2153(6)	0.097	C15D	−0.16190(11)	−0.70510(16)	−0.4089(3)	0.0463(15)
C13F	−0.1124(6)	−0.3245(5)	−0.2153(6)	0.097	N6D	−0.07616(17)	−0.7144(3)	−0.4551(4)	0.0721(18)
C14B	−0.0480(9)	−0.3888(7)	−0.3027(9)	0.077(2)	C13H	−0.29457(13)	−0.73328(19)	−0.3671(2)	0.0479(16)
C15B	−0.0285(5)	−0.2671(4)	−0.1298(6)	0.069	C14H	−0.3806(3)	−0.7939(3)	−0.4561(4)	0.114(4)
N6B	0.0414(5)	−0.2238(4)	−0.0657(5)	0.083	C15H	−0.18416(12)	−0.74406(15)	−0.4273(2)	0.0463(15)
Co1C	−0.70661(5)	−0.30545(4)	−0.82940(5)	0.040	N6H	−0.10310(19)	−0.7520(3)	−0.4832(3)	0.0721(18)
N1C	−0.8551(4)	−0.3707(3)	−0.8514(4)	0.049	O1W	−0.4076(17)	−0.0456(8)	−0.9318(19)	0.198

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Table 6. Crystal Data and Experimental Details for **pyrr** Crystals after Irradiation

	pyrr-1′ [a)]	**pyrr**-2′	**pyrr**-3′	**pyrr**-4′
Space group	$P1$			
Z	4			
a/Å	11.7347(7)	11.718(2)	11.713(3)	11.715(3)
b/Å	15.6971(17)	15.654(2)	15.686(4)	15.686(3)
c/Å	11.1241(13)	11.117(2)	11.1121(19)	11.0998(13)
α/°	98.832(9)	98.728(14)	98.817(18)	99.841(12)
β/°	90.245(8)	90.155(16)	90.254(19)	90.223(14)
γ/°	98.419(7)	98.446(13)	98.45(2)	98.524(16)
V/Å^3	2002.2(3)	1993.2(6)	1994.8(8)	1992.5(6)
D_x/Mg m^{-3}	1.383	1.387	1.386	1.387
Crystal size	0.3 × 0.3 × 0.3	0.5 × 0.4 × 0.3	0.3 × 0.3 × 0.3	0.3 × 0.2 × 0.2
Diffractometer	AFC-5R	AFC-7S	AFC-7S	AFC-7S
Radiation	Graphite monochromated Mo $K\alpha$ radiation			
μ/mm^{-1}	0.889	0.893	0.892	0.893
Scan mode	$2\theta/\omega$ scan			
$\theta_{\max}$	30	27.5	30	30
No. of measured reflections	9741	9152	11650	11638
Observed reflections	5968	7415	8263	9006
Criterion	$F > 4\sigma(F)$			
$R:S$ (in whole crystal)	72:28	72:28	72:28	71:29
$R:S$ (A molecule)	25:0	25:0	25:0	25:0
$R:S$ (B molecule)	25:0	25:0	25:0	25:0
$R:S$ (C molecule)	8:17	8:17	8:17	8:17
$R:S$ (D molecule)	14:11	14:11	14:11	12:13
R ($F > 4\sigma(F)$)	0.050	0.037	0.043	0.041
wR_2	0.110	0.098	0.103	0.108

a) Absolute structure is inverted to have R configuration at A molecule.

Results and Discussion

Piperidine Complex Crystal. Optical Rotation after Irradiation. Since the racemic crystal of the piperidine complex has a chiral space group, it has either of the two enantiomeric crystal structures. The absolute structures of twenty crystals obtained from a racemic solution indicated that both of the enantiomeric crystals can be in the same batch. The enantiomeric ratio was 12 : 8. When the seed crystals with one of enantiomeric structures were added in the racemic solution, all the crystals obtained showed the same enantiomeric absolute structure as the seed crystals. The enantiomeric ratio of twenty crystals became 20 : 0. The powdered sample of the same enantiomeric crystals were irradiated with a xenon lamp for 20 h. The specific rotation $[\alpha]_D$ of the chloroform solution became 30°. A racemic-to-chiral transformation can be observed only by exposure to a xenon lamp. Using the seed crystals, one of the enantiomers was selected in all the experiments.

Preparation of Five Kinds of Crystals with Different *R* : *S* Compositions. The racemic piperidine complex crystal is isostructural to that of the chiral one, which was already reported.[16] This brought about an idea that the crystals with the intermediate $R:S$ compositions may show similar results. Therefore, five kinds of crystals with intermediate $R:S$ compositions were prepared. Table 1 shows the compositions and crystal data of the five crystals: pip-1 (50 : 50), pip-2 (57 : 43), pip-3 (75 : 25), pip-4 (87 : 13), and pip-5 (100 : 0). The $R:S$ ratios in the crystals are approximately the same as those in the solutions, except for the pip-2 crystal which has the $R:S$ ratio of 62 : 38, although the $R:S$ ratio in the solution was 57 : 43. Figure 1 shows the relation between the unit-cell volumes and the $R:S$ compositions. The cell volume has a minimum at 62 : 38.

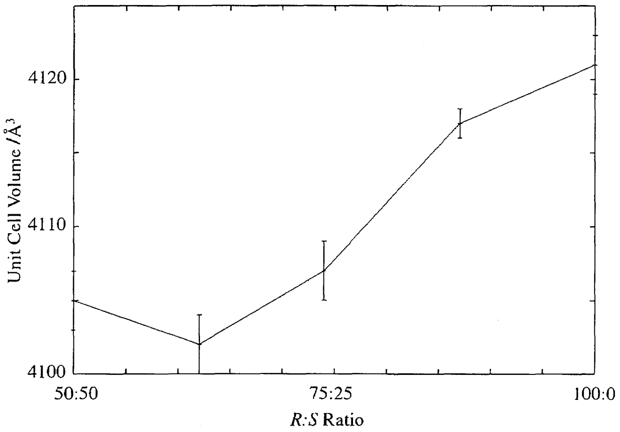


Fig. 1. Relationship between unit cell volume and the $R:S$ composition.

Crystal Structures of pip-1 to pip-5. The crystal structure of pip-1 is shown in Fig. 2(a). The crystal is chiral and the space group is $P2_12_12_1$, although it is racemic. Such a racemic crystal with a chiral space group is very rare, since only seven organic racemic crystals have been reported to have chiral space groups.[21] There are two crystallographically independent molecules, A and B, in an asymmetric unit.

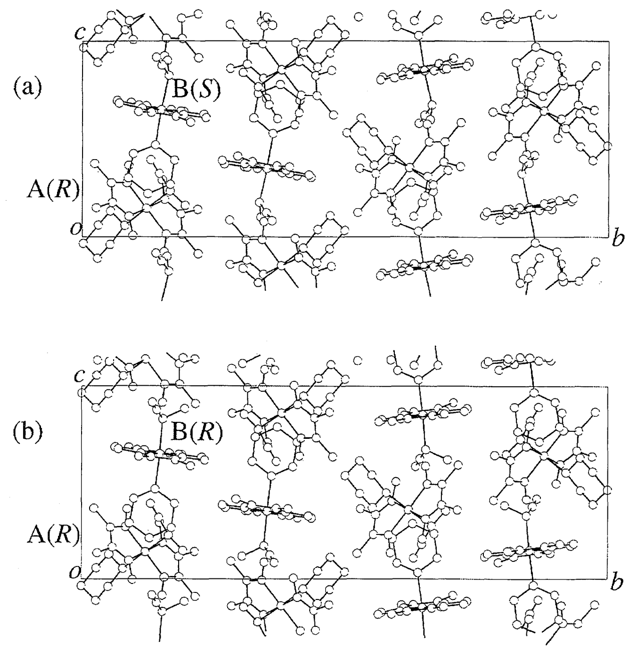


Fig. 2. Crystal structures of (a) pip-1 and (b) pip-5 viewed along the *a* axis.

The A molecule has the cyanoethyl group with *R* configuration whereas the B molecule has the *S* cyanoethyl group. The two molecules have no pseudo symmetry between them. The crystal structure of pip-5 is shown in Fig. 2(b), which is the same as that reported previously.[16] The crystal structures of pip-1 and pip-5 are approximately the same except for the structures of the cyanoethyl groups of the B molecules, since both of the absolute configurations of the A and B cyanoethyl groups are *R* in pip-5. The crystal structures of pip-2, pip-3, and pip-4 are nearly the same as those of pip-1 or pip-5, except the structures of the B cyanoethyl groups. The B cyanoethyl groups of pip-2, pip-3, and pip-4 have disordered structures with the *R* : *S* ratios of 12 : 38, 25 : 25, and 37 : 13, respectively.

Molecular Structures of pip-1 to pip-5. The molecular structures of A and B in the pip-1 crystal are shown in Fig. 3. The A molecules in the five crystals are substantially

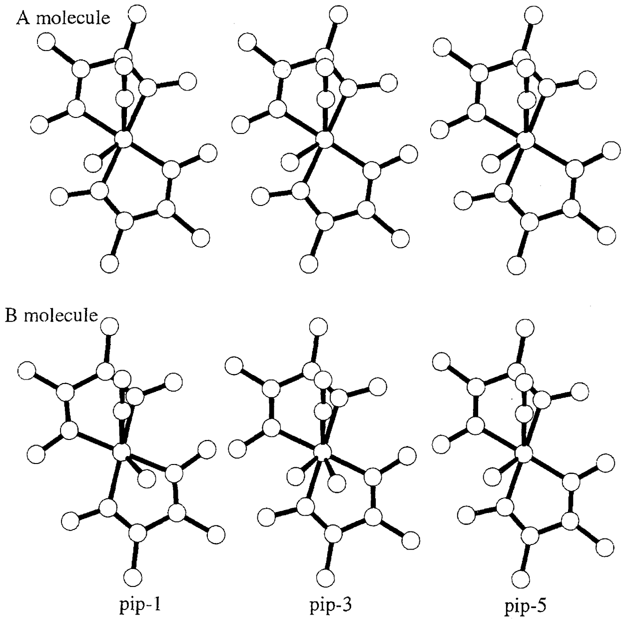


Fig. 4. The structures of the A and B cyanoethyl groups of pip-1, pip-3, and pip-5, viewed along the normal to the cobaloxime plane.

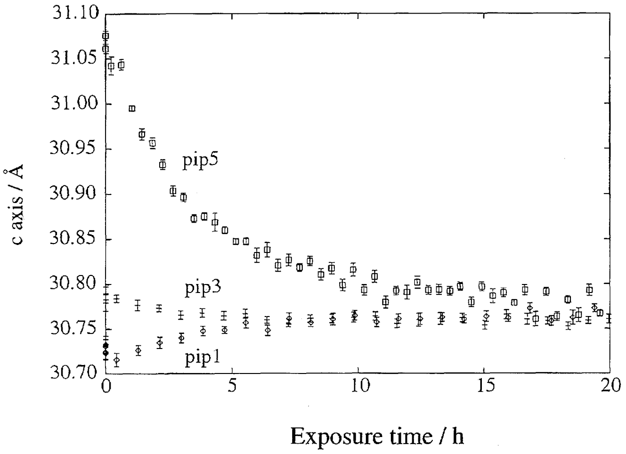


Fig. 5. Changes of the *c* axis lengths of pip-1, pip-3, and pip-5 with the exposure time.

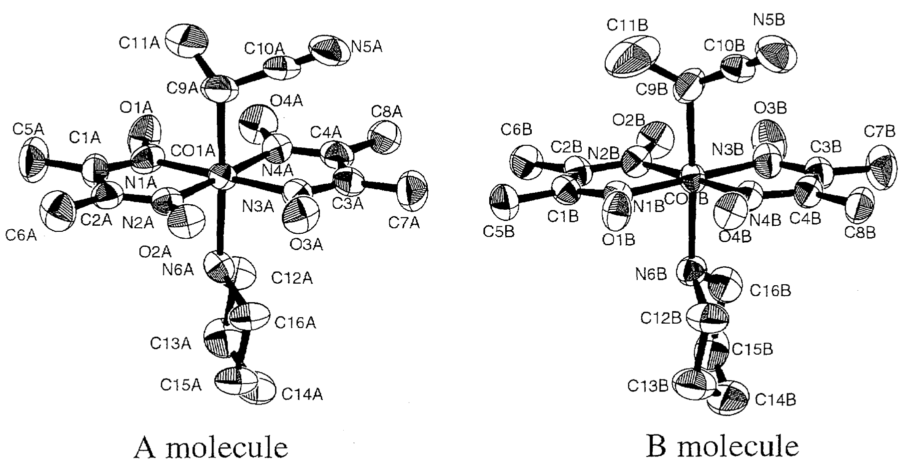


Fig. 3. Molecular structures of A and B in pip-1. Thermal ellipsoids are drawn at the 50% probability level.

the same, while the B molecules are different. The structures of the B molecules viewed normal to the cobaloxime planes in pip-1, pip-3, and pip-5 are shown in Fig. 4. The corresponding structures in pip-2 and pip-4 are the same as that in pip-3 except for the *R* : *S* ratio of the B cyanoethyl group.

Change of Cell Dimensions. Figure 5 shows the changes of the cell dimensions of the three crystals: pip-1, pip-3, and pip-5. It seems adequate to assume that the cell dimensions of the three crystals will reach the same values after infinite exposure to the xenon lamp. The converged values are different from the corresponding ones of pip-3. This means the crystal structure at the final stage is different from that of pip-3.

Crystal and Molecular Structure after Irradiation. Figure 6 shows the crystal structure of pip-1′ (after 40 h exposure) viewed along the *a* axis. The same structures were obtained for pip-3′ and pip-5′. Only the B molecule has the disordered structure with *R* and *S* configurations, while the A molecule retained unaltered. The disordered structure of the B cyanoethyl group in pip-1′, which is the same as those in pip-3′ and pip-5′, is shown in Fig. 7. The *R* to *S* ratios of the B cyanoethyl groups are 19 : 31, 19 : 31 and 21 : 29 for pip-1′, pip-3′, and pip-5′, respectively. These values are identical to 20 : 30 within the experimental error. It must be emphasized that the converged *R* : *S* ratio of the B cyanoethyl group is not 25 : 25 but 20 : 30.

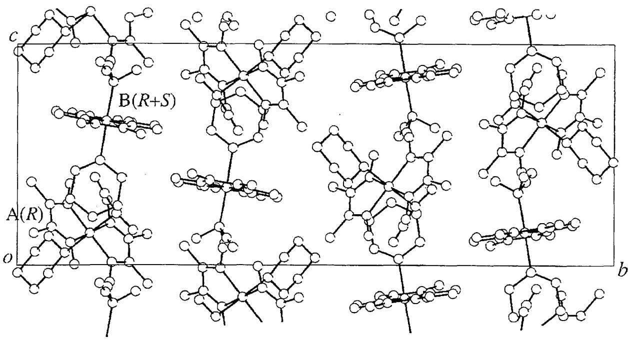


Fig. 6. Crystal structure of pip-1′ viewed along the a axis.

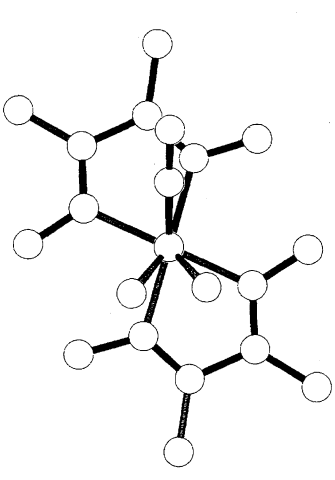


Fig. 7. Disordered structure of the B cyanoethyl group in pip-1′. Approximately the same structures were obtained for the B cyanoethyl groups in pip-3′ and pip-5′.

Racemic-to-Chiral Transformation. The *R* to *S* ratio in the racemic crystal of pip-1 before the irradiation is 50 : 50, since the A and B molecules have *R* and *S* configurations, respectively. After the irradiation, the A molecule has *R* configuration while the B molecule was changed to the disordered structure. The *R* : *S* ratio is 20 : 30. Such a partial racemization brings about the racemic-to-chiral transformation, because the *R* : *S* ratio became 70 : 30 in the crystal. This is the reason why the specific rotatory power of the chloroform solution containing the racemic crystals after irradiation showed 30°.

Final Structure at 343 K. To solve the question of why the final *R* : *S* ratio of B molecule is not 25 : 25 but 20 : 30, the pip-1 crystal was irradiated with the xenon lamp at 343 K under the same conditions as those at 296 K. The change of the cell dimensions was slightly but significantly different from that at 296 K. Although the crystal structure after 15 h exposure at 343 K is approximately the same as that at 296 K, only the *R* : *S* ratio of the disordered B cyanoethyl group is different. The disordered structure of the B cyanoethyl group viewed along the normal to the cobaloxime plane is shown in Fig. 8. The *R* to *S* ratio is not 20 : 30 but 24 : 26, which is 25 : 25 within the experimental error. The final ratio may depend on the environment around the B cyanoethyl group in the crystal structure, which will be discussed later in detail.

Why is Only the Cyanoethyl Group of B Inverted? It must be explained why only the B molecule is partly inverted to create disordered racemates. The most important requirement for the movement of the reactive group is the void space around the reactive group. We defined the reaction cavity for the reactive group in order to estimate the void space quantitatively.[13] Figure 9 shows the reaction cavities for the cyanoethyl groups of A and B. The volumes of the cavities for pip-1 are calculated to be 7.0 and 14.2 Å^3 for the A and B cyanoethyl groups, respectively. The cavities for the A and B cyanoethyl groups are 6.7 and 11.7 Å^3 for pip-2, 7.0 and 12.9 Å^3 for pip-3, 6.5 and 12.6 Å^3 for pip-4, and 5.8 and 12.8 Å^3 for pip-5, respectively. A volume less than 7.0 Å^3 is too small for the inversion of the cyanoethyl group with retention of the single crystal form, whereas 14.2 Å^3 is enough for

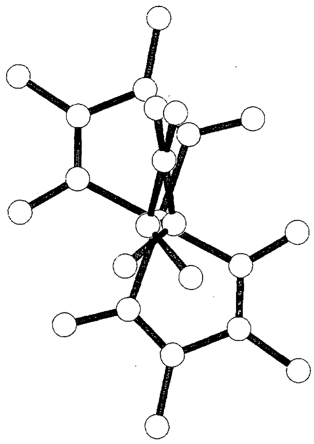


Fig. 8. Disordered structure of the B cyanoethyl group in pip-1″.

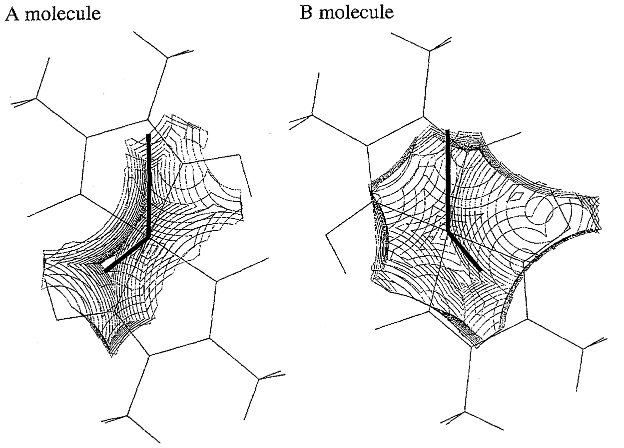
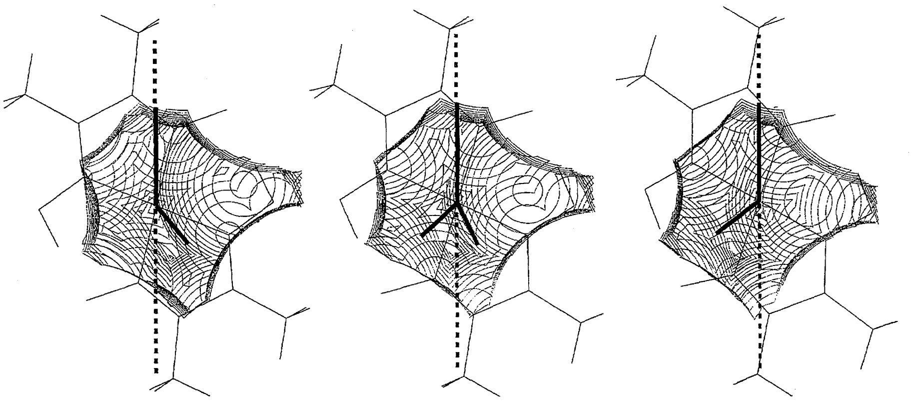


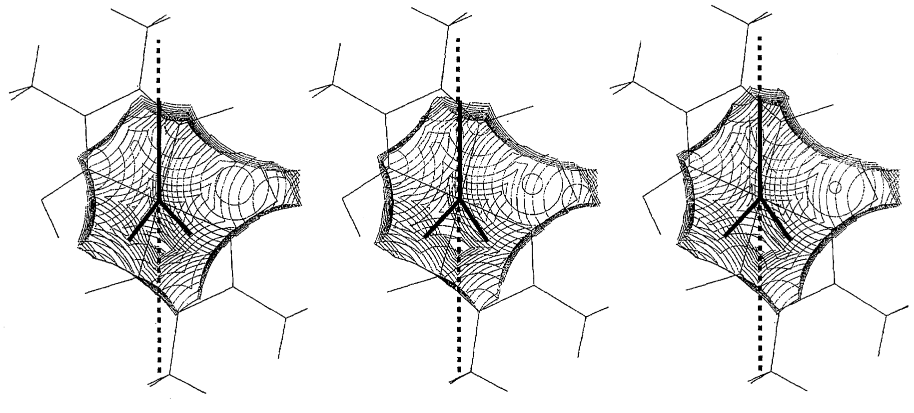
Fig. 9. Reaction cavities for the A and B cyanoethyl groups viewed along the normal to the cobaloxime plane.

the racemization, since the value of 11.5 Å^3 was proposed to be a threshold value for crystalline state racemization in the previous paper.[19] Such different cavity volumes of the A and B cyanoethyl groups clearly explain the different behavior of the two cyanoethyl groups, that is, the A cyanoethyl group remained unaltered while the B cyanoethyl group was partly inverted.

Why is the Converged $R:S$ Not 75 : 25 But 70 : 30? In order to explain the reason why the final $R:S$ ratio of the B molecule is not 25 : 25 but 20 : 30, the reaction cavities of pip-1, pip-3 and pip-5 before and after irradiation are compared in Fig. 10. Each cavity is divided into two parts by the plane composed of Co–C–C–N bond and the volumes of the two parts are calculated. For the pip-1, pip-3, and pip-5 crystals, the $R:S$ ratios before irradiation, 0 : 50, 25 : 25, and 50 : 0, respectively, became 20 : 30 within the experimental error after irradiation. The ratios of the left and right parts of the cavities before irradiation are 45 : 55, 56 : 44, and 63 : 37, respectively. These ratios became 48 : 52, 49 : 51, and 52 : 48, respectively, after irradiation. The ratios after irradiation are 50 : 50 within the experimental error. This suggests that the inversion ratio of the B molecule depends on the symmetry of the cavity. In other words, the inversion ratio is determined by the steric repulsion from the neighboring molecules around the B molecule after irradiation. Since the minimum unit-cell volume is obtained at 62 : 38 (close to 70 : 30 in Fig. 1), the enthalpy term may be responsible to the ratio of 70 : 30. When the crystal after irradiation was warmed up to 343 K, the $R:S$ ratio of the B molecule became



(a) Before irradiation



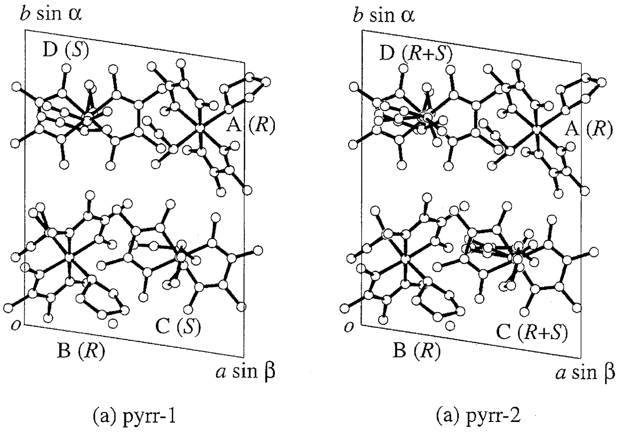
(b) After irradiation

Fig. 10. Reaction cavities of the B cyanoethyl groups in pip-1, pip-3, and pip-5 before and after irradiation. The dotted line indicates the plane including the Co–C–C–N bonds.

25 : 25. Although the reaction cavity at 343 K was not calculated because the precise positions of the hydrogen atoms were not obtained, the reaction cavity has enough size to accommodate the cyanoethyl groups with both configurations and the ratio of the left and right parts of the cavity would become 50 : 50. This means that the entropy term becomes dominant at high temperatures, since the reaction cavity may be enlarged and the enthalpy term has no effect on the $R:S$ ratio.

Pyrrolidine Complex Crystal. Preparation of Four Kinds of Crystals. For the cobaloxime complex with pyrrolidine as an axial base ligand, four kinds of crystals with different $R:S$ compositions were prepared. The crystals of pyrr-1 were obtained from the racemic solution. The pyrr-2 crystals were obtained from a solution which contained the complex with $R:S$ ratio of 75 : 25. The crystals of pyrr-3 and 4 were also obtained from solutions with the $R:S$ ratios of 80 : 20 and 90 : 10, respectively. The cell dimensions of the four crystals are given in Table 4. The X-ray crystal structure analysis indicated that the four crystals are isostructural to each other. From the solutions with the $R:S$ ratio greater than 9 : 1, pure enantiomeric crystals were obtained, which are not isostructural to the above crystals of pyrr-1 to pyrr-4.

Crystal Structures before Irradiation. Figure 11 shows the crystal structures of pyrr-1 and pyrr-2 viewed along the *c* axis before irradiation. There are four crystallographically independent molecules, A, B, C, and D, in one $P1$ cell. In the crystal of pyrr-1, the A, B, C, and D molecules have *R*, *R*, *S*, and *S* configurations, respectively. Therefore, the crystal is racemic. In the crystal of pyrr-2 with the $R:S$ ratio of 75 : 25, on the other hand, the A, B, C, and D molecules have *R*, *R*, $R+S$, and $R+S$ configurations, respectively. The $R:S$ ratios of the C and D molecules are 10 : 15 and 16 : 9, respectively. As a whole, the pyrr-2 crystal has the $R:S$ ratio of 76 : 24, which is identical to the $R:S$ ratio of the solution, 75 : 25, within the experimental error. The pyrr-3 and 4 crystals were also analyzed. The $R:S$ ratios of the A and B molecules are 25 : 0, whereas the $R:S$ ratios of the C and D molecules are 15 : 10 and 19 : 6 for pyrr-3 and 17 : 8 and 23 : 2 for pyrr-4, respectively. These values mean that the $R:S$ ratios of the pyrr-3 and pyrr-4 crystals are 84 : 16 and 90 : 10, respectively, which are very similar to the $R:S$ ratios in the respective solutions.



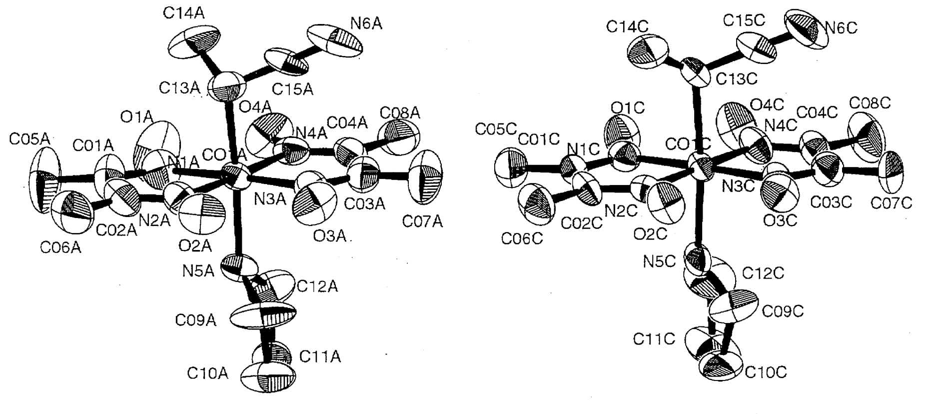
(a) pyrr-1 (a) pyrr-2

Fig. 11. Crystal structures before irradiation viewed along the *c* axis, (a) pyrr-1 and (b) pyrr-2.

Molecular Structures before Irradiation. Figure 12 shows the molecular structures of A and C of pyrr-1. Figures 13 and 14 shows the structures of the 1-cyanoethyl groups viewed along the normal to the cobaloxime planes of the A to D molecules of pyrr-1 and pyrr-2, respectively.

Change of Cell Dimensions. Figure 15 shows the change of the *c* axis lengths of pyrr-1 and -2 with the exposure time to the xenon lamp. The other cell dimensions showed similar changes. The change appears to converge to the same value after the infinite exposure. Probably the crystals of pyrr-3 and -4 will show the same change after the infinite exposure, although the cell changes with exposure time were not examined.

Crystal and Molecular Structure after Irradiation. Figure 16 shows the crystal structure of pyrr-1 after about 40 h exposure. The crystal structure is isostructural to that before irradiation except for the $R:S$ ratios of the cyanoethyl groups of the C and D molecules. The structures of the cyanoethyl groups of C and D viewed along the normal to the cobaloxime plane are shown in Fig. 17. The molecular structures of A and B after irradiation are almost the same as those before irradiation. The $R:S$ ratios became 8 : 17



A molecule C molecule

Fig. 12. Molecular structures of A and C of pyrr-1 before irradiation. Thermal ellipsoids are drawn at the 50% probability level.

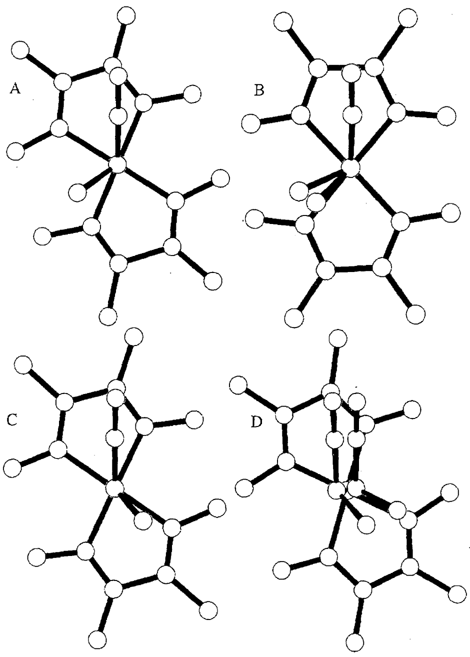


Fig. 13. Structures of the cyanoethyl groups of A, B, C, and D of pyrr-1 viewed normal to the cobaloxime plane before irradiation. Both of the disordered D cyanoethyl group are the same configuration.

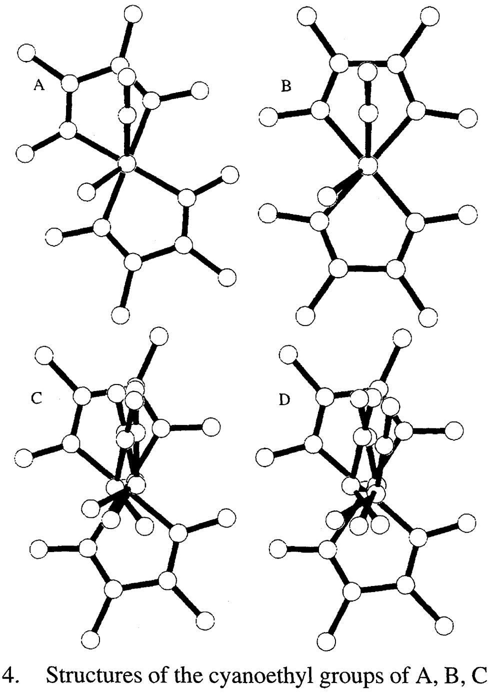


Fig. 14. Structures of the cyanoethyl groups of A, B, C, and D of pyrr-2 viewed normal to the cobaloxime plane before irradiation.

and 14 : 11 for C and D. This indicates that the crystal, as a whole, changed from racemic (R : S = 50 : 50) to chiral (R : S = 72 : 28). The final ratio is 70 : 30 within the experimental error. The R : S ratios of pyrr-2, -3 and -4 crystals after the irradiation became 72 : 28, 72 : 28, and 71 : 29, respectively. The pyrrolidine complex crystals also converged to 70 : 30 after the infinite irradiation.

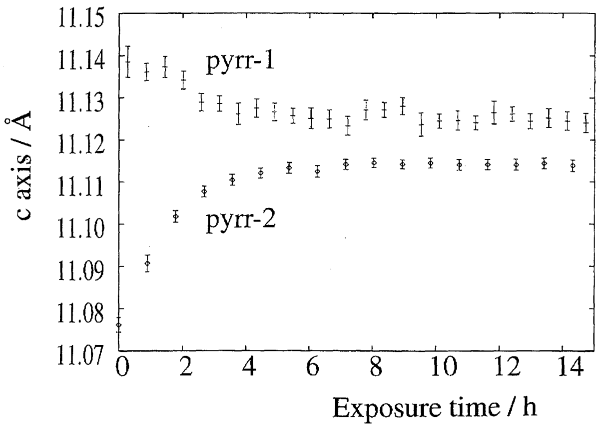


Fig. 15. Changes of the c axis lengths of pyrr-1 and pyrr-2 with exposure time.

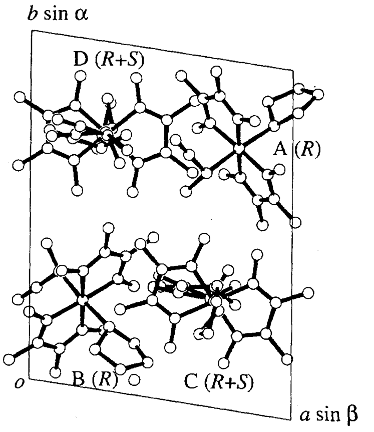


Fig. 16. Crystal structure of pyrr-1′ viewed along the c axis.

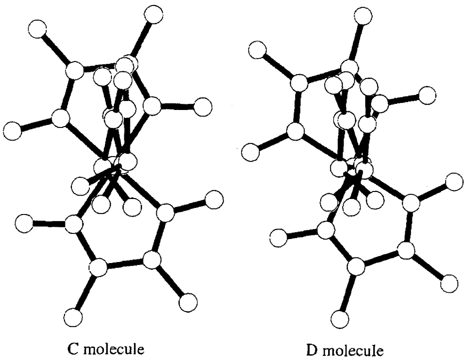


Fig. 17. Structures of the cyanoethyl groups of C and D of pyrr-1′ viewed normal to the cobaloxime plane. The inverted groups are disordered.

Reaction Cavities of A, B, C, and D before Irradiation. In order to explain the reason why only the C and D molecules are partly inverted to the opposite configuration, the reaction cavities for the cyanoethyl groups of the A, B, C, and D molecules in pyrr-1 are drawn in Fig. 18 and the volumes of the cavities were calculated. The volumes of the A and B cavities (9.8 and 9.5 Å^3, respectively) are smaller than the threshold value for racemization, 11.5 Å^3, proposed by the previous paper.[19] On the other hand, the volumes of the C and D cavities (14.5 and 15.9 Å^3, respectively) are significantly

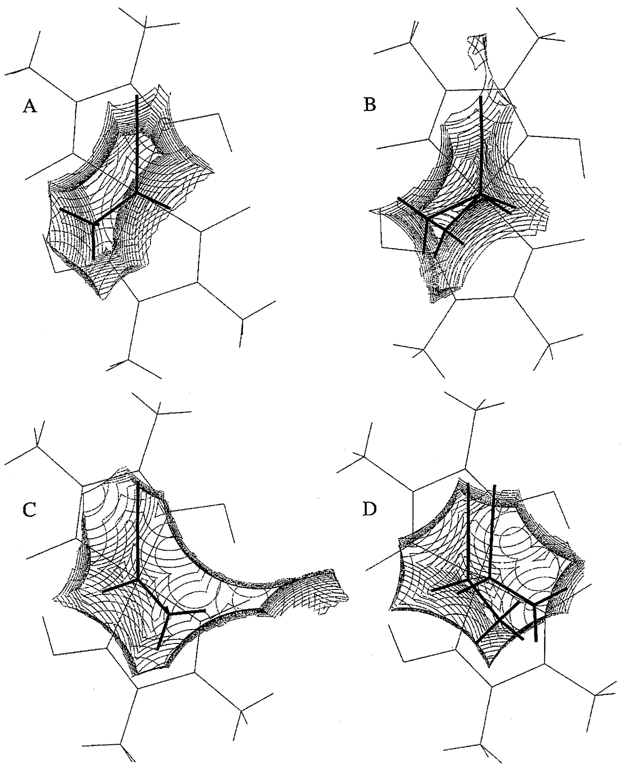


Fig. 18. Reaction cavities for the A, B, C, and D cyanoethyl groups of pyrr-1 viewed normal to the cobaloxime plane before irradiation.

greater than the threshold value. The size of the cavity for the cyanoethyl group well explains the partial racemization.

Change of Reaction Cavity after Irradiation. The next question is why the $R:S$ ratio after irradiation became 70 : 30. The volumes of the reaction cavities for the A, B, C, and D molecules after irradiation were also calculated. They are 10.1, 8.4, 16.9, and 15.0 Å^3, respectively. The cavity volumes are not so different from the corresponding ones before irradiation. However, it is impossible to divide the cavity of C or D into two by a plane composed of the Co–C–C–N bonds, as done in the piperidine complex, because the C and D groups after irradiation take very complicated disordered structures. Probably the ratios of the left and right parts for the C and D cavities may become 50 : 50 after irradiation, although the $R:S$ ratios became 8 : 17 and 14 : 11 for C and D.

Capability of Racemic-to-Chiral Transformation. Both of the racemic crystals of the piperidine and pyrrolidine complexes have chiral space groups before irradiation. The most important requirement for the racemic-to-chiral transformation is that the two molecules with R and S configurations crystallize in a chiral space group. Since the racemic compounds tend to make a pair around an inversion center in the process of crystallization, the racemic crystals, in general, have a center of symmetry. Otherwise, conglomerate crystals may be deposited from racemic solutions. Therefore, only several racemic crystals with chiral space groups have been reported so far.[21] This may be one reason why such a racemic-to-chiral transformation has not been observed till now.

Recently, another complex with *racemic*-1-cyanoethyl group and methyl (*S*)-alaninate as axial ligands was prepared.[22] The crystal belongs to the triclinic and the space group is $P1$. There are two crystallographically independent molecules, A and B, in a unit cell. The A molecule has a *S*-1-cyanoethyl group while the B molecule has a *R*-1-cyanoethyl group. This indicates that the crystal has a pair of diastereomers and the crystal structure well explains why the fractional resolution of the diastereomeric pair of the complex is impossible. When this crystal was exposed to the xenon lamp, the cell dimensions gradually changed. The crystal structure after irradiation indicated that only the B cyanoethyl group was changed to the disordered racemates. Optical enrichment was also observed in the crystal.

These results suggest that the racemic-to-chiral transformation will be commonly observed if the crystallization of the racemic compounds or the compounds with diastereomeric pairs would be extensively studied. Although the racemic-to-chiral transformation only by photo irradiation appears to be strange at first sight, the crystal structure analyses can give a reasonable explanation for the mechanism.

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References

1 J. N. Gamlin, R. Jones, M. Leibovitch, B. Patrick, J. R. Scheffer, and J. Trotter, *Acc. Chem. Res.*, **29**, 203 (1996); T. Suzuki, T. Fukushima, Y. Yamashita, and T. Miyashi, *J. Am. Chem. Soc.*, **116**, 2793 (1994); K. Saigo, M. Sukegawa, Y. Maekawa, and M. Hasegawa, *Bull. Chem. Soc. Jpn.*, **68**, 2355 (1995).

2 L. Addadi, J. van Mil, and M. Lahav, *J. Am. Chem. Soc.*, **104**, 3422 (1982).

3 A. Sekine, K. Hori, Y. Ohashi, M. Yagi, and F. Toda, *J. Am. Chem. Soc.*, **111**, 697 (1989).

4 D. Hashizume, H. Kogo, A. Sekine, Y. Ohashi, H. Miyamoto, and F. Toda, *J. Chem. Soc., Perkin Trans. 2*, **1996**, 61.

5 A. Sekine, H. Tatsuki, and Y. Ohashi, *J. Organomet. Chem.*, **536-537**, 389 (1997).

6 A. Sekine, M. Yoshiike, Y. Ohashi, K. Ishida, Y. Arai, and Y. Ohgo, *Mol. Cryst. Liq. Cryst.*, **313**, 321 (1998).

7 Y. T. Osano, A. Uchida, and Y. Ohashi, *Nature*, **352**, 510 (1991).

8 Y. Ohashi and Y. Sasada, *Nature*, **267**, 142 (1977); Y. Ohashi, *Acc. Chem. Res.*, **21**, 268 (1988), references are therein.

9 A. Sekine, M. Saitoh, D. Hashizume, H. Uekusa, Y. Ohashi, Y. Arai, and Y. Ohgo, *Enantiomer*, **3**, 159 (1998), references are therein.

10 Y. Ohashi, Y. Sakai, A. Sekine, Y. Arai, Y. Ohgo, N. Kamiya, and H. Iwasaki, *Bull. Chem. Soc. Jpn.*, **68**, 2517 (1995), references are therein.

11 H. Sato and Y. Ohashi, *Bull. Chem. Soc. Jpn.*, **72**, 367 (1999), references are therein.

12 H. Sato, Y. Sakai, Y. Ohashi, Y. Arai, and Y. Ohgo, *Acta Crystallogr., Sect. C*, **C52**, 1086 (1996).

13 Y. Ohashi, K. Yanagi, T. Kurihara, Y. Sasada, and Y. Ohgo, *J. Am. Chem. Soc.*, **103**, 5805 (1981); Y. Ohashi, A. Uchida, Y. Sasada, and Y. Ohgo, *Acta Crystallogr., Sect. B*, **B39**, 54 (1983).

14 G. N. Schrauzer and R. J. Windgassen, *J. Am. Chem. Soc.*, **89**, 1999 (1967).

15 Y. Ohgo, S. Takeuchi, Y. Natori, J. Yoshimura, Y. Ohashi, and Y. Sasada, *Bull. Chem. Soc. Jpn.*, **54**, 3095 (1981).

16 Y. T. Osano, M. Danno, A. Uchida, Y. Ohashi, Y. Ohgo, and S. Baba, *Acta Crystallogr., Sect. B*, **B47**, 702 (1991).

17 G. M. Sheldrick, "SHELX76, Program for Crystal Structure Determination," Univ. of Cambridge, England (1976).

18 G. M. Sheldrick, "SHELXL-93, Program for Crystal Structure Determination," Univ. of Göttingen, Germany (1993).

19 Y. Takenaka, Y. Ohashi, T. Tamura, A. Uchida, and Y. Sasada, *Acta Crystallogr., Sect. B*, **B49**, 272 (1993).

20 Y. Takenaka, Y. Ohashi, T. Tamura, A. Uchida, and Y. Sasada, *Acta Crystallogr., Sect. B*, **B49**, 1015 (1993).

21 C. Brock, W. Schweizer, and J. Dunitz, *J. Am. Chem. Soc.*, **113**, 9811 (1991).

22 Y. Ohashi, T. Nemoto, and D. Hashizume, "The 24th Seminar on Science and Technology, Crystallography," ed by F. Iwasaki, Kyowa Insatsu, Abstr., p. 55, (1995).