

Table 4. Relationship between the volume of the cavity (\AA^3) and the reaction rate k (s^{-1})

	Volume	k ($\times 10^6$)	
Class I			
R-cn-S-mba	14.53	3.06	
S-cn-S-mba	12.23	2.10	
R-cn-tpp	11.31	—	
R-cn-tbp	10.64	—	
Class II			
	(A)	(B)	
S-cn-py	8.89	11.34	2.83
R-cn-cnpy	7.97	10.37	1.65
R-cn-4mepy	11.05	12.61	0.57

around a pseudo inversion center should move cooperatively to form a racemic crystal as observed in the crystal of [(R)-1-methoxycarbonylethyl]-(4-chloropyridine)cobaloxime, R-mce-Clpy (Kurihara, Ohashi, Sasada & Ohgo, 1983). In the present crystal, on the other hand, the A and B cyanoethyl groups contact along the *a*-glide plane. The cavities for the two groups are linked infinitely along the *a* axis as shown in Fig. 7. The joining regions between the two groups in the cavity are very narrow. The cooperative motion of the two groups in the racemization process would be less than those in

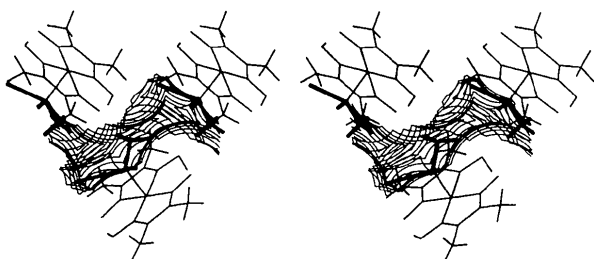


Fig. 7. Infinitely linked cavity along the *a* axis. Contours are drawn in sections separated by 0.1 \AA .

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Crystalline-State Reaction of Cobaloxime Complexes by X-ray Exposure. X. Structural Requirement for the Racemization of the 1-Methoxycarbonylethyl Group

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Abstract

Two crystalline forms of bis(dimethylglyoximate)-[(S)-1-methoxycarbonylethyl][(R)- α -methylbenzylamine]cobalt(III) (dimethylglyoximate is 2,3-butanedione dioximate), $\text{C}_{20}\text{H}_{32}\text{CoN}_5\text{O}_6$, $[\text{Co}(\text{C}_4\text{H}_7\text{O}_2)(\text{C}_4\text{H}_7\text{N}_2\text{O}_2)_2(\text{C}_8\text{H}_{11}\text{N})]$, were obtained

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the crystals of S-cn-py and R-cn-cnpy. In the crystals of the first class, an ordered cyanoethyl group, isolated from the other groups, is converted to the disordered racemates, so that the larger cavity would be necessary as shown in Table 4. The above results suggest that the cooperative motion, as well as the size of the cavity, plays an important role in determining the reaction rate.

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from an aqueous methanol solution and their structures were determined by X-ray analysis. Form (I): $M_r = 497.4$, triclinic, $P1$, $a = 8.637$ (1), $b = 8.955$ (2), $c = 8.094$ (1) \AA , $\alpha = 105.71$ (1), $\beta = 100.18$ (2), $\gamma = 96.23$ (2)°, $V = 585.0$ (2) \AA^3 , $F(000) = 262$, $D_x = 1.412$ g cm^{-3} , $Z = 1$, $\mu(\text{Mo } K\alpha) = 8.11$ cm^{-1} . Form (II): monoclinic, $P2_1$, $a = 8.017$ (3), $b = 16.715$ (6), $c = 8.972$ (3) \AA , $\beta = 101.88$ (3)°, $V = 1176.5$ (7) \AA^3 ,

$D_x = 1.404 \text{ g cm}^{-3}$, $Z = 2$, $\mu(\text{Mo } K\alpha) = 8.04 \text{ cm}^{-1}$. Both structures were solved by direct methods and refined by block-diagonal least squares. The final R values were 0.052 (2646 reflections) and 0.046 (2697 reflections) for forms (I) and (II), respectively. The two different forms result from a conformational change around the Co–C and Co–N bonds. Neither form was racemized by X-rays at room temperature. The chiral methoxycarbonylethyl (mce) group in each crystal is isolated from the other mce groups and the cavity for the mce group is small for the racemization of the bulky mce group. The structures are compared with those of related crystals and the structural requirement for the racemization of the mce group in the crystalline state is discussed.

Introduction

In the serial studies of the crystalline-state reaction of cobaloxime complexes, two kinds of chiral groups bonded to the Co atom, 1-cyanoethyl (cn) and 1-methoxycarbonylethyl (mce) groups, were found to be racemized by X-rays in several crystals with various axial amine and phosphine ligands. In the crystals containing the cn group, two different types of racemization were observed: one chiral cn group in an asymmetric unit is converted to the 1:1 disordered racemic one, and two chiral groups in an asymmetric unit are transformed to the ordered or disordered racemic structure. The crystals belonging to the first type are those containing (*S*)- α -methylbenzylamine (Ohashi, Yanagi, Kurihara, Sasada & Ohgo, 1981), (*R*)- α -methylbenzylamine (Ohashi, Sasada & Ohgo, 1978), tributylphosphine and triphenylphosphine (Kurihara, Uchida, Ohashi, Sasada, Ohgo & Baba, 1983) as axial ligands, whereas the racemization of the second type was observed when the axial ligands are pyridine (Ohashi, Yanagi, Kurihara, Sasada & Ohgo, 1982), 4-pyridinecarbonitrile (Ohashi, Uchida, Sasada & Ohgo, 1983) and 4-methylpyridine (Uchida, Ohashi, Sasada, Ohgo & Baba, 1984).

The mce group, on the other hand, was racemized only in crystals of [(*R*)-1-mce](4-chloropyridine)cobaloxime, *R*-mce-Clpy (Kurihara, Ohashi, Sasada & Ohgo, 1983) and [(*R*)-1-mce](pyridine)cobaloxime, *R*-mce-py (Kurihara, Ohashi & Sasada, 1982; Kurihara, Uchida, Ohashi, Sasada & Ohgo, 1984a), in which two mce groups of the crystallographically independent molecules face each other across a pseudo inversion center. In crystals of [(*R*)-1-mce][(*R*)- α -methylbenzylamine]cobaloxime, *R*-mce-*R*-mba (Ohashi & Sasada, 1977b) and [(*S*)-1-mce](4-pyridinecarbonitrile)cobaloxime, *S*-mce-cnpy (Kurihara, Uchida, Ohashi, Sasada & Ohgo, 1984b), which contain one molecule in an asymmetric unit, the mce group was not converted to the 1:1 disordered racemates as observed in crystals with the cn group. In order to examine the reaction mechanism

of the mce group, crystals of [(*S*)-1-mce]-[(*R*)- α -methylbenzylamine]cobaloxime, *S*-mce-*R*-mba, which is the diastereomer of *R*-mce-*R*-mba, were prepared. Two crystalline forms, triclinic and monoclinic, were obtained under the same conditions. The present paper reports the structures of the two modifications and discusses the reaction mechanism of the racemization.

Experimental

Dark-red plate-like crystals of *S*-mce-*R*-mba were obtained from the mother liquor after the fractional precipitation of *R*-mce-*R*-mba had been carried out from an aqueous methanol solution of *rac*-mce-*R*-mba, which was prepared by the method of Ohgo, Takeuchi, Natori, Yoshimura, Ohashi & Sasada (1981). A preliminary experiment revealed that there were two forms of the crystals, triclinic [*S*-mce-*R*-mba(*T*)] and monoclinic [*S*-mce-*R*-mba(*M*)], in a batch, although they are indistinguishable in appearance. We tried to divide the crystals into the two forms by X-ray diffraction. All the crystals suitable for X-ray work except two had triclinic form. Several attempts to obtain the monoclinic form with different solvents were unsuccessful.

S-mce-*R*-mba(*T*). Crystal $0.3 \times 0.3 \times 0.25 \text{ mm}$. Rigaku four-circle diffractometer, Mo $K\alpha$ radiation monochromated by graphite. Unit-cell dimensions obtained by least-squares technique with 16 reflections in the range $15^\circ < 2\theta < 30^\circ$; determination of the cell dimensions repeated continuously at 293 K; no significant change observed after a week. Three-dimensional intensity data collected using the same crystal. $2\theta < 55^\circ$, $\omega/2\theta$ scan, scan rate $4^\circ(\theta) \text{ min}^{-1}$, scan range $(1.0 + 0.35 \tan \theta)^\circ$. Stationary background counts accumulated for 5 s before and after each scan. 2698 reflections observed; 2646 [$|F_o| > 3\sigma(F_o)$] used for the structure determination. No corrections for absorption or extinction. Structure solved by direct method with *MULTAN78* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) and refined by block-diagonal least squares with *HBLS* (Ohashi, 1975). Positions of most of the H atoms were obtained from a difference map and those of the others were calculated geometrically. Anisotropic and isotropic thermal parameters used for the non-H and H atoms, respectively. $w = [\sigma^2(|F_o|) + (CF_o)^2]^{-1}$, where $C = 0.02$. In the final refinement $(\Delta/\sigma)_{\text{max}} = 0.2$, and $\Delta\rho_{\text{max}} = 0.7 \text{ e } \text{\AA}^{-3}$ (around the Co atom). Final $R = 0.052$ for 2646 reflections. Atomic scattering factors, including anomalous-dispersion terms, from *International Tables for X-ray Crystallography* (1974). Atomic coordinates for non-H atoms are given in Table 1.

S-mce-*R*-mba(*M*). Crystal $0.6 \times 0.4 \times 0.3 \text{ mm}$. 2794 reflections obtained; 2697 considered observed. In the final refinement, $C = 0.015$, $(\Delta/\sigma)_{\text{max}} = 0.2$, $\Delta\rho_{\text{max}} = 0.8 \text{ e } \text{\AA}^{-3}$ (around the Co atom). Final $R =$

Table 1. Final atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters B_{eq} (\AA^2) for non-hydrogen atoms in *S*-mce-*R*-mba(*T*)

$$B_{eq} = \frac{1}{3} \sum_i \sum_j B_{ij} a_i^* a_j^* \cdot a_i \cdot a_j$$

	x	y	z	B_{eq}
Co	-303	-61	71	2.6
N(1)	-775 (5)	-2297 (4)	-659 (5)	3.1
N(2)	-2191 (5)	-325 (5)	917 (5)	2.8
N(3)	74 (5)	2111 (5)	830 (6)	3.4
N(4)	1598 (6)	280 (6)	-697 (5)	4.1
O(1)	319 (5)	-3130 (4)	-1334 (5)	4.4
O(2)	-2810 (5)	849 (5)	1778 (5)	4.7
O(3)	-814 (5)	3029 (4)	1748 (5)	4.2
O(4)	2312 (5)	-983 (5)	-1456 (5)	4.6
C(1)	-2001 (6)	-2934 (5)	-306 (6)	2.9
C(2)	-2876 (7)	-1767 (7)	628 (8)	4.1
C(3)	1392 (8)	2821 (7)	571 (7)	4.6
C(4)	2310 (7)	1678 (6)	-342 (7)	3.4
C(5)	-2469 (9)	-4666 (8)	-753 (9)	5.5
C(6)	-4347 (9)	-2222 (9)	1123 (12)	5.9
C(7)	1927 (10)	4564 (7)	1143 (9)	5.5
C(8)	3898 (8)	2060 (11)	-784 (10)	6.1
N(5)	999 (6)	-230 (6)	2407 (6)	3.9
C(9)	2677 (6)	393 (6)	3257 (7)	3.5
C(10)	3327 (8)	-555 (7)	4488 (7)	4.5
C(11)	2897 (7)	2101 (6)	4210 (6)	3.5
C(12)	1850 (9)	2808 (9)	5183 (8)	5.4
C(13)	2186 (12)	4386 (10)	6073 (10)	7.8
C(14)	3543 (13)	5300 (9)	6134 (11)	7.5
C(15)	4653 (15)	4653 (12)	5238 (15)	8.1
C(16)	4359 (8)	3069 (9)	4308 (9)	5.2
C(17)	-1723 (7)	-52 (7)	-2286 (7)	4.4
C(18)	-2119 (10)	1438 (8)	-2427 (9)	6.0
C(19)	-1282 (7)	-1089 (7)	-3790 (6)	3.8
O(5)	-345 (7)	-571 (8)	-4559 (6)	8.1
O(6)	-1853 (7)	-2599 (5)	-4289 (6)	6.4
C(20)	-1083 (14)	-3527 (12)	-5578 (10)	8.5

Table 2. Final atomic coordinates ($\times 10^5$ for Co; $\times 10^4$ for C, N and O) and equivalent isotropic thermal parameters B_{eq} (\AA^2) in *S*-mce-*R*-mba(*M*)

$$B_{eq} = \frac{1}{3} \sum_i \sum_j B_{ij} a_i^* a_j^* \cdot a_i \cdot a_j$$

	x	y	z	B_{eq}
Co	11514 (6)	20140	21235 (6)	2.4
N(1)	413 (4)	2107 (3)	3990 (4)	3.1
N(2)	1693 (5)	3099 (2)	2502 (5)	3.1
N(3)	1975 (5)	1904 (3)	318 (4)	3.6
N(4)	595 (5)	942 (3)	1736 (4)	3.1
O(1)	-219 (4)	1494 (3)	4656 (4)	4.2
O(2)	2377 (4)	3555 (2)	1572 (5)	4.9
O(3)	2725 (5)	2502 (3)	-283 (4)	5.3
O(4)	-252 (5)	496 (2)	2594 (5)	4.5
C(1)	672 (6)	2799 (3)	4675 (6)	3.8
C(2)	1417 (7)	3383 (3)	3791 (7)	4.2
C(3)	1900 (7)	1196 (4)	-277 (6)	4.5
C(4)	1010 (6)	631 (4)	537 (6)	4.0
C(5)	270 (9)	2959 (5)	6185 (7)	6.2
C(6)	1773 (10)	4222 (4)	4275 (9)	7.2
C(7)	2581 (10)	988 (6)	-1630 (8)	7.0
C(8)	570 (9)	-212 (4)	36 (9)	6.5
N(5)	3569 (4)	1745 (2)	3356 (4)	2.9
C(9)	4006 (6)	999 (3)	4266 (5)	3.2
C(10)	5525 (7)	1157 (4)	5573 (6)	4.7
C(11)	4324 (6)	292 (3)	3329 (5)	3.0
C(12)	5482 (6)	309 (3)	2393 (7)	3.9
C(13)	5849 (7)	-354 (4)	1637 (7)	4.8
C(14)	5035 (7)	-1065 (4)	1777 (8)	5.0
C(15)	3882 (8)	-1102 (4)	2711 (8)	5.3
C(16)	3505 (7)	-425 (3)	3441 (7)	4.1
C(17)	-1148 (5)	2385 (3)	760 (6)	3.4
C(18)	-2063 (7)	1797 (4)	-416 (7)	5.0
C(19)	-2319 (5)	2638 (3)	1723 (5)	3.1
O(5)	-3358 (4)	2225 (2)	2157 (5)	5.2
O(6)	-2197 (4)	3421 (2)	2054 (4)	3.7
C(20)	-3330 (8)	3712 (4)	2964 (8)	5.5

0.046 for 2697 reflections. Other details are as for the triclinic form. Atomic coordinates for non-H atoms are given in Table 2.*

Results and discussion

Molecular structure

A stereoscopic drawing of the molecule in the triclinic form is shown in Fig. 1 with the numbering of the atoms. Bond distances are listed in Table 3. The Co-C(17) distances in the present molecules, 2.080 (7) and 2.086 (5) Å, are slightly longer than that in *R*-mce-*R*-mba, 2.067 (8) Å. Such a difference in the Co-C distances was also found in the crystals of a diastereomeric pair, *R*-cn-*S*-mba, 2.036 (8) Å (Ohashi, Sasada, Takeuchi & Ohgo, 1980a), and *S*-cn-*S*-mba, 2.070 (8) Å (Ohashi, Sasada, Takeuchi & Ohgo, 1980b). The other values are in fair agreement with those in *R*-mce-*R*-mba.

The conformations of the two molecules are different around the Co-C(17) and Co-N(5) bonds. Fig. 2 shows the projection of each molecule onto the mean plane of the cobaloxime moiety, together with the projection of *R*-mce-*R*-mba. The torsion angles C(19)-C(17)-Co-N(1) and N(4)-Co-N(5)-C(9) are -51.7 (5) and 22.7 (5)° for the triclinic form, 5.4 (4) and -30.6 (4)° for the monoclinic form. The conformation of the mce group of the monoclinic form is approximately the mirror image of that of *R*-mce-*R*-mba. The torsion angles C(19)-C(17)-Co-N(4) and N(4)-Co-N(5)-C(9) in *R*-mce-*R*-mba are -15.1 (6) and -39.8 (6)°, respectively. The van der Waals energy was calculated for the various rotation angles around the Co-N(5) bond (Ohashi & Sasada, 1977a). The minimum energy was obtained when the torsional

* Lists of structure factors, anisotropic thermal parameters for non-H atoms, positional and thermal parameters for H atoms and bond angles for the two crystals have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39498 (26 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

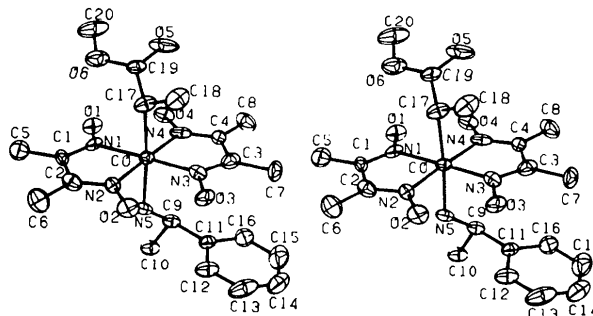
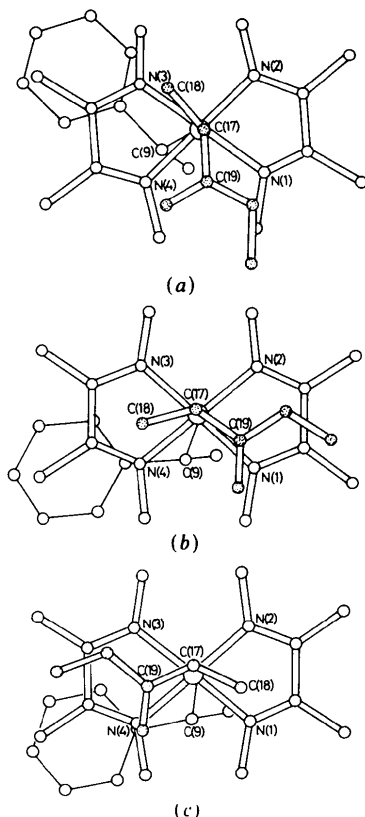


Fig. 1. A stereoscopic drawing of the *S*-mce-*R*-mba(*T*) molecule with the numbering of the atoms. The thermal ellipsoids are shown at the 30% probability level.

Table 3. Bond distances (Å) in the two crystalline forms

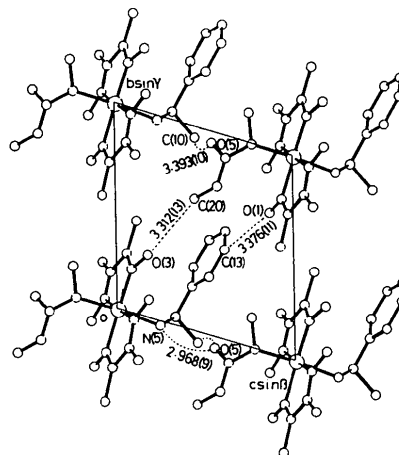
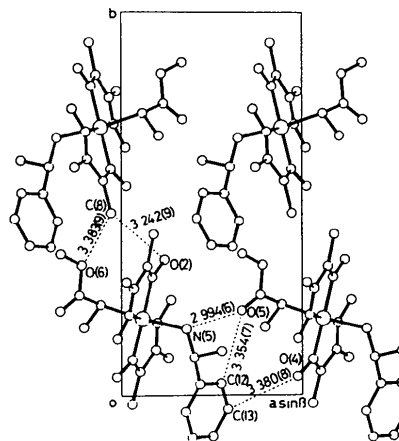
	<i>S</i> -mce- <i>R</i> -mba(<i>T</i>)	<i>S</i> -mce- <i>R</i> -mba(<i>M</i>)
Co–N(1)	1.903 (5)	1.894 (5)
Co–N(2)	1.892 (5)	1.879 (4)
Co–N(3)	1.847 (5)	1.880 (5)
Co–N(4)	1.879 (6)	1.861 (4)
Co–N(5)	2.075 (5)	2.074 (4)
Co–C(17)	2.080 (7)	2.086 (5)
N(1)–O(1)	1.365 (6)	1.338 (7)
N(1)–C(1)	1.262 (7)	1.305 (8)
N(2)–O(2)	1.317 (6)	1.330 (6)
N(2)–C(2)	1.302 (8)	1.310 (7)
N(3)–O(3)	1.350 (7)	1.336 (7)
N(3)–C(3)	1.320 (9)	1.295 (8)
N(4)–O(4)	1.395 (7)	1.351 (6)
N(4)–C(4)	1.267 (8)	1.298 (7)
C(1)–C(2)	1.477 (8)	1.460 (8)
C(1)–C(5)	1.487 (9)	1.481 (10)
C(2)–C(6)	1.448 (12)	1.479 (10)
C(3)–C(4)	1.482 (9)	1.466 (9)
C(3)–C(7)	1.497 (11)	1.472 (12)
C(4)–C(8)	1.504 (11)	1.499 (10)
N(5)–C(9)	1.466 (8)	1.491 (7)
C(9)–C(10)	1.547 (9)	1.530 (8)
C(9)–C(11)	1.489 (8)	1.501 (7)
C(11)–C(12)	1.395 (10)	1.375 (8)
C(11)–C(16)	1.429 (10)	1.381 (8)
C(12)–C(13)	1.374 (13)	1.363 (9)
C(13)–C(14)	1.340 (15)	1.374 (10)
C(14)–C(15)	1.386 (17)	1.371 (10)
C(15)–C(16)	1.385 (15)	1.371 (9)
C(17)–C(18)	1.442 (11)	1.516 (8)
C(17)–C(19)	1.456 (9)	1.463 (7)
C(19)–O(5)	1.229 (10)	1.207 (7)
C(19)–O(6)	1.313 (9)	1.341 (6)
O(6)–C(18)	1.455 (14)	1.425 (8)

Fig. 2. Conformations of the mce group and *R*-mba ligand in (a) *S*-mce-*R*-mba(*T*), (b) *S*-mce-*R*-mba(*M*) and (c) *R*-mce-*R*-mba. Each molecule is projected on to the mean plane composed of four N atoms of cobaloxime.

angle N(4)–Co–N(5)–C(9) was -13.0° . The conformational energies of the present molecules and *R*-mce-*R*-mba are only 0.8 – 1.3 kJ mol $^{-1}$ higher than the minimum energy at -13.0° .

Crystal structure

Fig. 3 shows the crystal structure of the triclinic form viewed along the *a* axis. The molecules are linked *via* hydrogen bonds, N(5) \cdots O(5), along the *c* axis. The mce group is close packed with the cobaloxime moieties and the mba ligands of the neighboring molecules and it has no contacts with the other mce groups. Fig. 4 shows the crystal structure of the monoclinic form viewed along the *c* axis. The N(5) \cdots O(5) hydrogen bonds connect the molecules along the *a* axis. The mce group is also isolated from the other mce groups. There are no unusually short contacts in the two crystal structures.

Fig. 3. Crystal structure of *S*-mce-*R*-mba(*T*) viewed along the *a* axis. Short contacts less than 3.4 Å are shown by dotted lines.Fig. 4. Crystal structure of *S*-mce-*R*-mba(*M*) viewed along the *c* axis. Short contacts less than 3.4 Å are shown by dotted lines.

Reaction cavity

To determine why the present crystals, *R*-mce-*R*-mba and *R*-mce-cnpy, did not reveal crystalline-state racemization by X-ray exposure, the reaction cavity for the mce group in each crystal was drawn and its volume calculated in the same way as reported previously (Ohashi, Uchida, Sasada & Ohgo, 1983). Figs. 5 and 6 show the cavities of *S*-mce-*R*-mba(*T*) and *S*-mce-*R*-mba(*M*), respectively. The cavities of *R*-mce-*R*-mba and *S*-mce-cnpy are drawn in Fig. 7, in which the side views are omitted since they are similar to those in Figs. 5 and 6. Although the shapes of the cavities are slightly different from each other, each mce group is neatly accommodated in its cavity and seems impossible to be racemized without destroying the cavity, *i.e.* the lattice structure.

When the crystals of *S*-mce-cnpy were exposed to X-rays at 353 K, they were gradually decomposed. In order to ascertain whether or not the decomposition is brought about by the racemization of the mce group, the powdered crystals were exposed to X-rays at 353 K and the optical rotation of their CHCl₃ solution was measured. Fig. 8 shows the decrease of the optical rotation with exposure time. Although the measurement points are limited, the racemization would follow first-order kinetics and the rate constant was calculated to be about $2.3 \times 10^{-6} \text{ s}^{-1}$, which is smaller than the rate constant, $6.88 \times 10^{-5} \text{ s}^{-1}$, for the crystalline-state racemization of *R*-mce-Clpy at

353 K. Crystals of *S*-mce-*R*-mba(*T*), *S*-mce-*R*-mba(*M*) and *R*-mce-*R*-mba were also decomposed by X-ray exposure at high temperatures.

The volumes of the four cavities are listed in Table 4, in which the volumes of the two reactive mce groups in *R*-mce-Clpy are also given (Kurihara, Ohashi, Sasada & Ohgo, 1983). Although the crystalline-state

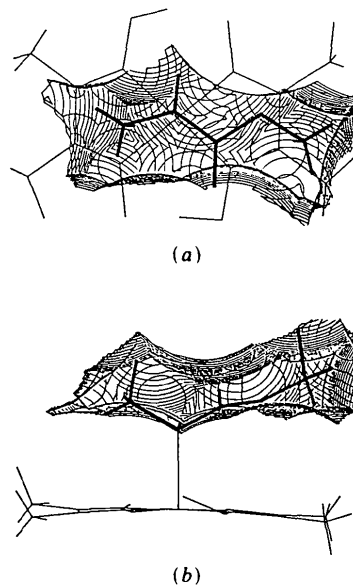


Fig. 6. Cavity for the mce group of *S*-mce-*R*-mba(*M*): (a) projection on to the mean plane of cobaloxime and (b) side view. Contours are drawn in sections separated by 0.1 Å.

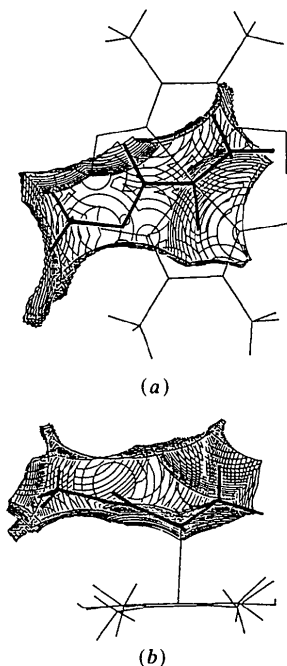


Fig. 5. Cavity for the mce group of *S*-mce-*R*-mba(*T*): (a) projection on to the mean plane of cobaloxime and (b) side view. Contours are drawn in sections separated by 0.1 Å.

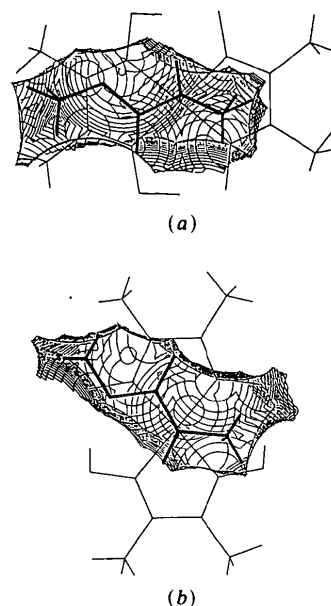


Fig. 7. Cavities for the mce groups of (a) *R*-mce-*R*-mba, and (b) *S*-mce-cnpy. Side views are omitted. Contours are drawn in sections separated by 0.1 Å.

Table 4. Volume (\AA^3) of the cavity for the mce group

	Volume
S-mce-R-mba(T)	24.51
S-mce-R-mba(M)	21.49
R-mce-R-mba	23.83
S-mce-cnpy	18.84
R-mce-Clpy(293 K)	19.01(A)
	20.22(B)

racemization of R-mce-Clpy was observed only at 353 K, the volumes of the two cavities at 353 K are not much greater than those at room temperature, if the expansion of the cell dimensions is taken into account. This indicates that the volume of the cavity is not so different between the reactive and non-reactive mce groups. The two mce groups in the R-mce-Clpy crystal face each other around a pseudo inversion center at the initial stage and would move cooperatively to form the 1:1 disordered racemates as discussed previously (Kurihara, Ohashi, Sasada & Ohgo, 1983). The cooperative motion of the reactive groups seems to be essential for the reaction of the crystals including the mce group. This is distinct from the racemization of the cyanoethyl group, for which one group is converted to the 1:1 disordered racemates independently from the other groups. The

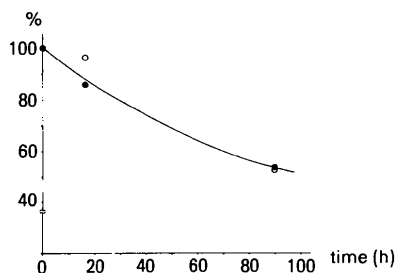


Fig. 8. Change of the optical rotation of the powdered S-mce-cnpy crystals with exposure time. The black and white circles indicate the values obtained with wavelengths 546 and 578 nm, respectively.

bulkiness of the mce group would cause such a difference.

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