Li site (site symmetry *mm*), two pairs of peaks at 0·4 and 0·5 Å from the atomic center are arranged like a doughnut perpendicular to the B(5)—Li—B(5) plane and parallel to the B(5)—B(5) bond, whereas for the Al site (site symmetry 2/*m*), a pair of peaks at 0·5 Å from the atomic center are arranged like a sandwich approximately along the *a* axis. These peaks are much sharper and closer to the atomic centers than expected for the valence electrons of free metal atoms (2*s* electrons for Li and 3*s*, 3*p* electrons for Al). Further studies on related compounds will clarify whether these peaks represent real deformations of valence electrons or some other characteristics of the metal sites such as positional disorder. It is interesting to note that the shortest Al—Al distance (2·92 Å) is comparable to that (2·86 Å) in metallic aluminum, and the shortest Li—Li distance (3·36 Å) is a little longer than that (3·03 Å) in metallic lithium.

Calculations were performed on a FACOM M200 computer of this Institute using the *UNICS* III program system (Sakurai & Kobayashi, 1979) unless otherwise stated. We are grateful to Professor Y. Saito and Dr S. Ohba of Keio University for allowing us to use the computer programs *CHAR* and *RADIEL*. Our thanks are also due to Professor W. N. Lipscomb of Harvard University for his encouragement; in fact, he has correctly predicted a large amount of charge transfer from the metal to B(5) atoms, and also the bends in the highly strained B—B bonds.

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Crystalline-State Reaction of Cobaloxime Complexes by X-ray Exposure. V. A New Type of Racemization Caused by the Cooperative Motion of Two Reactive Groups

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(*Received* 18 *September* 1982; *accepted* 1 *November* 1982)

Abstract

Crystalline-state racemization has been found at 353 K for a crystal of (4-chloropyridine)bis(dimethylglyoximato)[(*R*)-1-methoxycarbonylethyl]cobalt(III) (dimethylglyoximato = 2,3-butanedione dioximato), $C_{17}H_{25}ClCoN_5O_6$, $[Co(C_5H_4ClN)(C_4H_7N_2O_2)_2(C_4H_7O_2)]$. When the temperature is lowered to 293 K, the racemization is no longer observed. The crystal at the initial stage at 293 K is monoclinic, space group $P2_1$, with a = 14·946 (2), b = 9·227 (1), c = 15·956 (3) Å, β = 103·95 (2)°, V = 2135·5 (6) Å^3, M_r = 489·8, D_m = 1·52, D_x = 1·523 g cm^{-3} for Z = 4 and μ(Mo $K\alpha$) = 10·06 cm^{-1}. The unit-cell dimensions gradually vary with or without X-ray irradiation at 353 K and the space group changes to $P2_1/n$. The reaction follows approximate first-order kinetics. The rate constant is 6·88 × 10^{-5} s^{-1} at 353 K. The crystal structures at the initial and final stages at 293 K were solved by the direct method and refined by constrained least squares to R = 0·076 for 3383 reflections and R = 0·12 for 2572 reflections, respectively. The two crystallographically independent molecules at the initial stage are related by a pseudo inversion, which becomes

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0567-7408/83/020243-08$01.50

a crystallographic one after the racemization. Each of the two independent methoxycarbonylethyl (mce) groups is inverted to produce a disordered racemic structure. However, the two mce groups around an inversion center must take a pair of different configurations; otherwise the two groups with the same configuration would have very short contacts. This indicates that the crystal undergoes racemization as a result of the cooperative motion of the two neighboring reactive groups.

Introduction

We have been studying crystalline-state reactions of cobaloxime complexes [cobaloxime is an abbreviation of bis(dimethylglyoximato)cobalt], which proceed without degradation of crystallinity, by X-ray exposure. In crystals of [(*R*)-1-cyanoethyl][(*S*)-α-methylbenzylamine]cobaloxime (Ohashi & Sasada, 1977*a*; Ohashi, Sasada & Ohgo, 1978*a*; Ohashi, Yanagi, Kurihara, Sasada & Ohgo, 1981) and [(*S*)-1-cyanoethyl][(*S*)-α-methylbenzylamine]cobaloxime (Ohashi, Sasada & Ohgo, 1978*b*) (*R*-cn-*S*-mba and *S*-cn-*S*-mba, respectively), the ordered enantiomers of the cyanoethyl group, $-CH(CH_3)CN$, were converted into disordered racemates. In crystals of [(*S*)-1-cyanoethyl](pyridine)cobaloxime (Ohashi, Yanagi, Kurihara, Sasada & Ohgo, 1982) and [(*R*)-1-cyanoethyl](4-pyridinecarbonitrile)cobaloxime (Ohashi, Uchida, Sasada & Ohgo, 1983) (*S*-cn-py and *R*-cn-cnpy, respectively), on the other hand, one of the two chiral cyanoethyl groups changed to have the opposite configuration and a center of symmetry appeared between the two groups: ordered enantiomeric crystals are transformed into ordered racemic ones.

In order to examine this new kind of solid-state reaction more extensively, the reacting group was replaced by 1-methoxycarbonylethyl (mce), $-CH(CH_3)CO_2CH_3$; that is, the cyano group was substituted by the bulkier methoxycarbonyl group. Three cobaloxime complexes were prepared: [(*R*)-1-methoxycarbonylethyl][(*R*)-α-methylbenzylamine]cobaloxime (*R*-mce-*R*-mba), [(*R*)-1-methoxycarbonylethyl](pyridine)cobaloxime (*R*-mce-py) and [(*R*)-1-methoxycarbonylethyl](4-chloropyridine)cobaloxime (*R*-mce-Clpy). It has been found that X-ray exposure gives rise to crystalline-state racemization of *R*-mce-py at room temperature, and of *R*-mce-Clpy only at high temperatures. The *R*-mce-*R*-mba crystal remains intact even at high temperatures. Since the change of the *R*-mce-py crystal was too fast to collect the three-dimensional intensity data at the initial stage, only the final racemic structure has been analyzed (Kurihara, Ohashi & Sasada, 1982). The structure of a crystal of *R*-mce-*R*-mba has already been reported (Ohashi & Sasada, 1977*b*). The present paper reports the new type of racemization in the crystal of *R*-mce-Clpy and discusses the possible mechanism of the change.

Experimental

R-mce-Clpy was prepared in a way similar to *R*-mce-py (Ohgo, Takeuchi, Natori, Yoshimura, Ohashi & Sasada, 1981). Dark-red plate-like crystals were obtained from an aqueous methanol solution. Preliminary unit-cell dimensions and space group were obtained from photographs. A crystal 0·5 × 0·2 × 0·1 mm was mounted on a Rigaku four-circle diffractometer. Mo $K\alpha$ radiation monochromated by graphite was used (45 kV, 20 mA, $\lambda = 0{\cdot}71069$ Å). The unit-cell dimensions were obtained by means of the least-squares technique with 15 reflections in the range $20° < 2\theta < 30°$. The determination of the unit-cell dimensions was repeated continuously at 293 K. No significant change was observed after 12 h.

Three-dimensional intensity data were collected using the same crystal. A total of 3999 reflections in the range $2\theta \le 50°$ were measured by an $\omega/2\theta$ scan; the scanning rate was $8°(2\theta)\ \mathrm{min}^{-1}$ for the scan range $(1{\cdot}0 + 0{\cdot}35 \tan \theta)°$. Stationary background counts were accumulated for 5 s before and after each scan. 3383 reflections with $|F_o| \ge 3\sigma(F_o)$ were used for the structure determination. No corrections for absorption and extinction were made.

The structure was solved by the direct method with the *MULTAN* 78 program (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) and refined by constrained least squares with the *SHELX* 76 program (Sheldrick, 1976) in order to avoid parameter interaction between the two crystallographically independent molecules. The final refinement, however, was carried out with no constraints using the modified *HBLS* program (Ohashi, 1975) with unit weight for all reflections. No significant peaks, except those around the Co atoms (0·6–0·8 e Å^{-3}), were found in the final difference map. The atomic scattering factors were

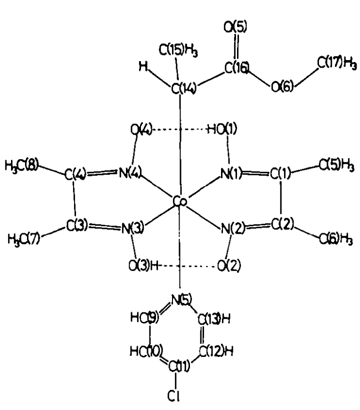

Fig. 1. The numbering of the atoms of *R*-mce-Clpy.

taken from *International Tables for X-ray Crystallography* (1974). The final R value was 0·076 for 3383 reflections. The numbering of the atoms is shown in Fig. 1. Atomic coordinates for non-hydrogen atoms are given in Table 1.

The crystal was warmed by the hot-air gas-flow method at 353 K. The unit-cell dimensions increased anisotropically and they changed gradually with X-ray exposure. The cell dimensions at the initial and final stages are given in Table 2. Fig. 2 shows the changes of a, b, c, β and V with exposure time at 353 K. After 144 h the changes were within experimental error. The temperature was then lowered to 293 K. The cell dimensions decreased anisotropically and showed different values from the corresponding ones before the high-temperature experiment. The crystal turned black. The peak and integrated intensities of five strong reflections, which have approximately the same $|F_c|$ values before and after the racemization, dropped to about 70 and 80% of their initial values. The structure of the crystal surface is probably destroyed by X-ray irradiation.

The intensities of 3750 reflections were collected at 293 K. The experimental conditions were the same as those at the initial stage. 2572 reflections with $|F_o| \geq 3\sigma(F_o)$ were used for the structure determination. The intensities of $h0l$ reflections with $h + l$ odd became zero within experimental error. This indicates that the space group has changed from the noncentrosymmetric $P2_1$ to the centrosymmetric $P2_1/n$. The structure was solved by the direct method and refined by constrained least squares. After several cycles of refinement, the difference map revealed that the mce groups with R and S configurations were disordered. The occupancy

Table 1. *Final atomic coordinates and equivalent isotropic thermal parameters B_{eq} (Å^2) for non-hydrogen atoms at the initial stage*

$$B_{eq} = \tfrac{8}{3}\pi^2 \textstyle\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j.$$

	x	y	z	B_{eq}
Co(*A*)	0·2489 (1)	0·4299 (2)	0·0212 (1)	3·2
O(1*A*)	0·0749 (5)	0·2838 (9)	−0·0349 (5)	5·1
O(2*A*)	0·3045 (6)	0·6442 (11)	0·1527 (5)	4·9
O(3*A*)	0·4216 (6)	0·5719 (9)	0·0765 (5)	5·5
O(4*A*)	0·1979 (5)	0·2143 (9)	−0·1091 (5)	4·1
N(1*A*)	0·1284 (6)	0·3818 (11)	0·0210 (5)	3·7
N(2*A*)	0·2348 (7)	0·5577 (11)	0·1102 (5)	4·0
N(3*A*)	0·3730 (6)	0·4737 (10)	0·0227 (5)	4·9
N(4*A*)	0·2666 (7)	0·3000 (10)	−0·0649 (6)	3·1
C(1*A*)	0·0922 (7)	0·4441 (11)	0·0785 (7)	5·1
C(2*A*)	0·1540 (10)	0·5518 (14)	0·1294 (7)	3·9
C(3*A*)	0·4095 (7)	0·4005 (13)	−0·0321 (7)	4·0
C(4*A*)	0·3456 (8)	0·3015 (13)	−0·0840 (7)	3·5
C(5*A*)	0·0009 (9)	0·4111 (16)	0·0919 (10)	6·3
C(6*A*)	0·1272 (11)	0·6327 (18)	0·2002 (8)	5·7
C(7*A*)	0·5066 (8)	0·4167 (17)	−0·0352 (8)	7·2
C(8*A*)	0·3668 (10)	0·2127 (17)	−0·1553 (8)	5·1
Cl(*A*)	0·1253 (3)	0·9254 (4)	−0·2777 (2)	7·0
N(5*A*)	0·2063 (6)	0·5893 (9)	−0·0722 (5)	3·7
C(9*A*)	0·1523 (9)	0·5549 (12)	−0·1484 (7)	3·7
C(10*A*)	0·1287 (7)	0·6561 (13)	−0·2112 (7)	5·2
C(11*A*)	0·1595 (9)	0·7990 (13)	−0·1966 (7)	4·1
C(12*A*)	0·2107 (7)	0·8314 (13)	−0·1177 (7)	5·4
C(13*A*)	0·2401 (7)	0·7228 (14)	−0·0550 (7)	3·9
O(5*A*)	0·2647 (9)	0·0373 (12)	0·0545 (7)	8·8
O(6*A*)	0·1733 (7)	0·1304 (11)	0·1329 (6)	6·2
C(14*A*)	0·2939 (10)	0·2757 (15)	0·1180 (7)	4·3
C(15*A*)	0·3993 (10)	0·2510 (16)	0·1464 (8)	7·1
C(16*A*)	0·2456 (10)	0·1360 (14)	0·0944 (8)	5·8
C(17*A*)	0·1202 (15)	0·0042 (24)	0·1222 (13)	9·8
Co(*B*)	0·2455 (1)	0·1168 (2)	0·4885 (1)	3·3
O(1*B*)	0·4173 (6)	0·2640 (10)	0·5479 (5)	4·7
O(2*B*)	0·2048 (6)	−0·0938 (9)	0·3521 (5)	5·4
O(3*B*)	0·0750 (5)	−0·0300 (11)	0·4249 (6)	5·3
O(4*B*)	0·2959 (5)	0·3172 (8)	0·6254 (5)	4·3
N(1*B*)	0·3711 (6)	0·1624 (9)	0·4933 (6)	4·1
N(2*B*)	0·2666 (7)	−0·0020 (10)	0·3977 (6)	3·9
N(3*B*)	0·1246 (7)	0·0669 (12)	0·4820 (7)	3·6
N(4*B*)	0·2293 (6)	0·2354 (9)	0·5790 (5)	4·0
C(1*B*)	0·4085 (9)	0·1031 (17)	0·4381 (7)	3·4
C(2*B*)	0·3468 (8)	0·0031 (13)	0·3820 (7)	4·6
C(3*B*)	0·0840 (7)	0·1247 (12)	0·5364 (8)	4·2
C(4*B*)	0·1456 (7)	0·2271 (12)	0·5944 (7)	4·3
C(5*B*)	0·5026 (9)	0·1342 (19)	0·4282 (9)	6·0
C(6*B*)	0·3734 (10)	−0·0913 (18)	0·3147 (8)	6·5
C(7*B*)	−0·0120 (10)	0·1072 (20)	0·5414 (11)	5·3
C(8*B*)	0·1193 (9)	0·3093 (14)	0·6632 (9)	5·8
Cl(*B*)	0·3701 (3)	−0·3975 (5)	0·7766 (2)	5·6
N(5*B*)	0·2911 (6)	−0·0482 (10)	0·5745 (6)	3·1
C(9*B*)	0·3448 (7)	−0·0213 (13)	0·6533 (7)	4·5
C(10*B*)	0·3738 (10)	−0·1230 (16)	0·7194 (7)	3·9
C(11*B*)	0·3411 (8)	−0·2619 (14)	0·6994 (7)	4·5
C(12*B*)	0·2862 (10)	−0·2989 (12)	0·6196 (9)	3·6
C(13*B*)	0·2691 (8)	−0·1940 (12)	0·5627 (7)	4·0
O(5*B*)	0·2679 (10)	0·5031 (11)	0·4543 (7)	8·5
O(6*B*)	0·3106 (7)	0·3798 (11)	0·3503 (6)	6·2
C(14*B*)	0·1905 (8)	0·2828 (13)	0·4045 (7)	5·2
C(15*B*)	0·1421 (11)	0·2347 (20)	0·3165 (11)	5·9
C(16*B*)	0·2557 (11)	0·4000 (15)	0·4068 (7)	5·3
C(17*B*)	0·3847 (14)	0·4855 (23)	0·3528 (11)	10·1

Table 2. *The cell dimensions at four stages*

	Initial 293 K	Initial 353 K	Final* 353 K	Final* 293 K
a (Å)	14·946 (2)	15·045 (4)	15·314 (3)	15·259 (6)
b (Å)	9·227 (1)	9·238 (3)	9·209 (2)	9·179 (4)
c (Å)	15·956 (3)	15·937 (6)	15·618 (4)	15·551 (8)
β (°)	103·95 (2)	103·19 (4)	102·52 (3)	102·71 (6)
V (Å^3)	2135·5 (6)	2157 (1)	2150·3 (8)	2125 (2)

* After 144 h.

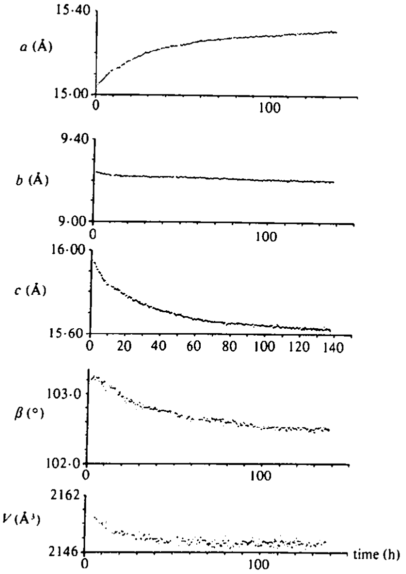

Fig. 2. The change of the unit-cell dimensions with X-ray exposure at 353 K. After 144 h the change was within experimental error.

Table 3. *Final atomic coordinates and equivalent isotropic thermal parameters* B_{eq} (Å^2) *for non-hydrogen atoms at the final stage*

	x	*y*	*z*	B_{eq}
Co	0·4987 (1)	0·6620 (1)	0·2691 (1)	3·5
O(1)	0·3344 (5)	0·5142 (8)	0·2065 (5)	5·5
O(2)	0·5358 (6)	0·8837 (8)	0·4003 (5)	6·1
O(3)	0·6643 (5)	0·8085 (8)	0·3340 (5)	6·0
O(4)	0·4575 (5)	0·4501 (7)	0·1336 (4)	4·6
N(1)	0·3777 (6)	0·6136 (9)	0·2629 (6)	4·6
N(2)	0·4749 (7)	0·7887 (9)	0·3575 (5)	4·6
N(3)	0·6197 (6)	0·7100 (9)	0·2774 (6)	4·4
N(4)	0·5215 (6)	0·5366 (8)	0·1807 (5)	3·5
C(1)	0·3370 (8)	0·6805 (11)	0·3179 (8)	4·8
C(2)	0·3942 (8)	0·7838 (12)	0·3722 (8)	4·9
C(3)	0·6604 (7)	0·6410 (11)	0·2219 (7)	4·1
C(4)	0·6020 (8)	0·5409 (10)	0·1671 (7)	4·0
C(5)	0·2408 (6)	0·6479 (9)	0·3236 (5)	7·6
C(6)	0·3640 (5)	0·8763 (9)	0·4434 (5)	7·1
C(7)	0·7583 (7)	0·6652 (8)	0·2230 (5)	6·9
C(8)	0·6283 (5)	0·4541 (8)	0·0952 (5)	5·4
Cl	0·3804 (3)	1·1698 (4)	−0·0281 (2)	7·7
N(5)	0·4605 (5)	0·8234 (8)	0·1767 (5)	3·4
C(9)	0·4078 (8)	0·7948 (10)	0·0990 (7)	4·4
C(10)	0·3820 (9)	0·8967 (12)	0·0347 (8)	4·8
C(11)	0·4135 (9)	1·0398 (11)	0·0524 (8)	5·0
C(12)	0·4659 (8)	1·0698 (13)	0·1306 (7)	4·7
C(13)	0·4899 (8)	0·9617 (11)	0·1922 (7)	4·1
O(5*P*)	0·4998 (23)	0·2698 (21)	0·3025 (16)	12·6
O(6*P*)	0·4274 (16)	0·3780 (22)	0·3926 (15)	8·8
C(14*P*)	0·5431 (22)	0·5093 (33)	0·3647 (19)	8·8
C(15*P*)	0·6415 (25)	0·4724 (52)	0·3867 (23)	11·6
C(16*P*)	0·4945 (22)	0·3679 (31)	0·3466 (25)	7·1
C(17*P*)	0·3640 (31)	0·2489 (45)	0·3800 (25)	13·9
O(5*Q*)	0·6811 (12)	0·4966 (24)	0·4306 (12)	7·9
O(6*Q*)	0·5917 (12)	0·6360 (21)	0·4914 (12)	7·2
C(14*Q*)	0·5273 (15)	0·5035 (23)	0·3667 (16)	5·1
C(15*Q*)	0·5265 (18)	0·3455 (26)	0·3340 (15)	6·4
C(16*Q*)	0·6074 (14)	0·5421 (23)	0·4337 (13)	3·8
C(17*Q*)	0·6687 (19)	0·6982 (36)	0·5536 (17)	8·6

factors for the two structures were also refined. The H atoms of the disordered mce groups could not be located in the difference map. The final refinement was carried out with no constraints except for the H atoms of cobaloxime, for which a fixed C—H distance was introduced. The weighting scheme $w = [\sigma^2(F_o) + 0{\cdot}000094F_o^2]^{-1}$ was employed. Several peaks of about 0·7 e Å^{-3} were found in the final difference map. The occupancy factors were 0·53 (1) and 0·47 (1) for the two disordered structures of the mce group: *P* and *Q*, respectively. The final *R* value was 0·12 for 2572 reflections. Atomic coordinates for non-hydrogen atoms are given in Table 3.*

Results and discussion

Initial structure

Fig. 3 shows the crystal structure viewed along the *b* axis at the initial stage. The two crystallographically independent molecules, *A* and *B*, are closely related by a pseudo inversion except for the methyl groups of the mce groups. The *A* and *B* molecules form their respective sheets parallel to the *ab* plane and the sheets are stacked alternately along the *c* axis.

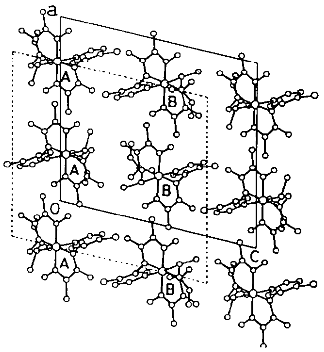

Fig. 3. Packing of the molecules viewed along the *b* axis at the initial stage. The unit cell at the final stage is indicated by broken lines.

Fig. 4 shows the two independent molecules around a pseudo inversion center. The mce groups face each other and are sandwiched by the two cobaloxime planes at an interval of 6·56 (9) Å. The distance between the two Co atoms is 8·008 (2) Å. The distance of O(6*A*)···C(15*B*) is shorter than the usual van der Waals contacts, although the others are relatively long. The mce group of the *B* molecule (the *B* mce group) has a different conformation from the *A* mce group; that is, in the *A* mce group the methyl group and carbonyl O are *cis* about the C—C bond, whereas they are *trans* in the *B* mce group.

Final structure

Fig. 5 shows the crystal structure viewed along the *b* axis at the final stage. The crystallographic inversion center appears between the two molecules which were related by a pseudo inversion in the initial structure. Each mce group has a disordered structure with the *R* and *S* configurations, so that the reaction proceeds with a conversion from the enantiomeric ordered structure to the racemic disordered one.

Fig. 6 shows the two molecules around the inversion center, which corresponds to Fig. 4. The distance between the mean plane of the two cobaloxime moieties is 6·72 (1) Å, longer by 0·16 (9) Å than that of the initial structure. However, the Co···Co distance is 7·772 (3) Å, shorter by 0·236 (4) Å than the initial one. The two mce groups around an inversion center have four conformations: *P*, *Q*, *P′* and *Q′* as shown in Fig. 6(*b*). The absolute configuration of *P* and *Q′* is *R* whereas that of *Q* and *P′* is *S*.

The conformation of *P* is nearly the same as that of the *A* mce group at the initial stage. *P′* is brought about by the inversion of the *B* mce group, the methoxy-

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* Lists of structure factors, anisotropic thermal parameters for non-hydrogen atoms, positional and thermal parameters for hydrogen atoms and bond angles at the initial and final stages have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38222 (30 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

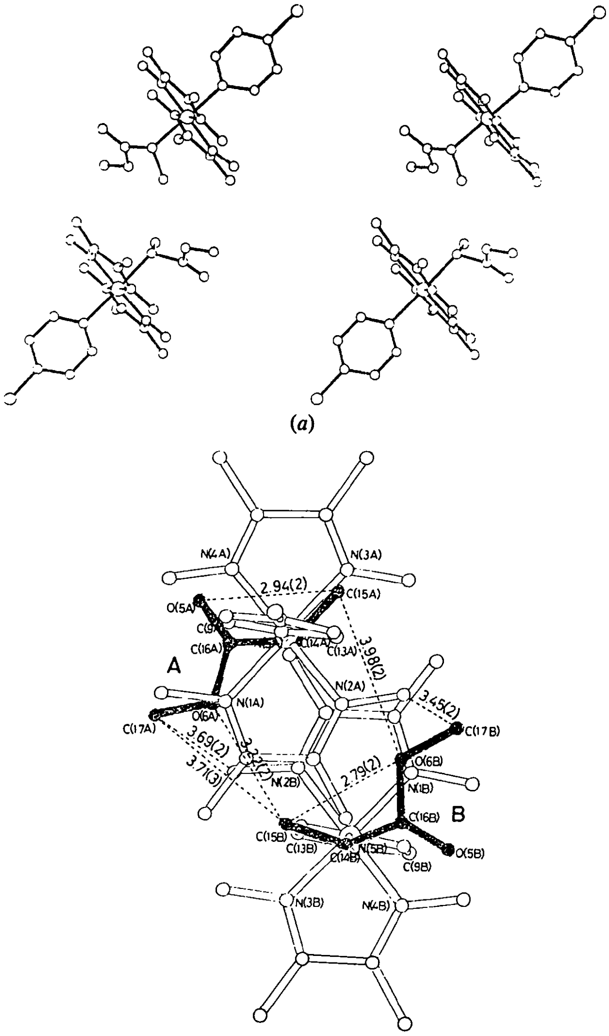

Fig. 4. The two independent molecules around a pseudo inversion center at the initial stage. (*a*) A stereoscopic drawing viewed along the *a* axis and (*b*) a view down the normal to the mean plane of the *A* cobaloxime moiety. The shaded groups are reactive mce, which are sandwiched by the cobaloxime plane. (Distances are in Å.)

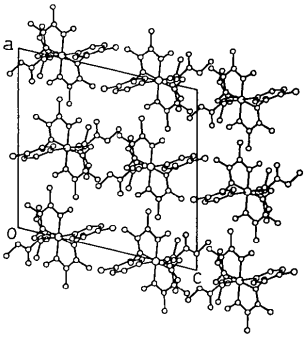

Fig. 5. Packing of the molecules viewed along the *b* axis at the final stage.

carbonyl group being fixed. On the other hand, *Q* and *Q'* are not produced by the minimum shifts of the atoms. The distance between the methoxy groups of *P* and *Q'* or *Q* and *P'* is very short, while the contacts between *P* and *P'* or *Q* and *Q'* are usual van der Waals approaches. This indicates that the two mce groups around an inversion center must form a pair, *P* and *P'* or *Q* and *Q'*, and such pairs are disordered throughout the crystal.

Reaction rate and thermal effect

Fig. 2 indicates that the racemization follows first-order kinetics. Significant changes were observed for *a*, *c* and *V*. The rate constants k_a, k_c and k_V were calculated to be $7{\cdot}77 \times 10^{-5}$, $6{\cdot}52 \times 10^{-5}$ and $6{\cdot}40 \times$

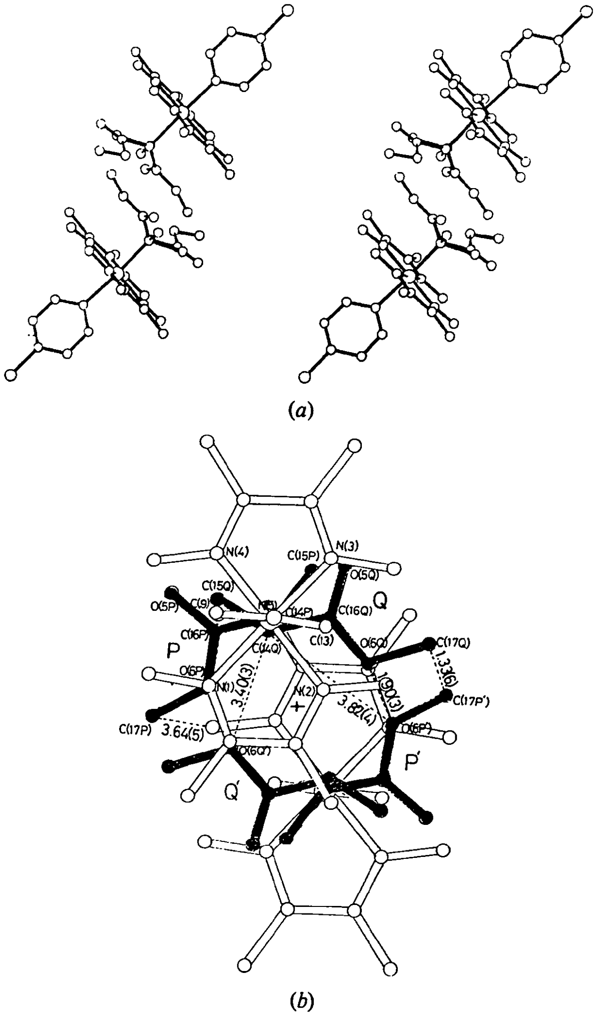

Fig. 6. The two disordered molecules around a crystallographic inversion center at the final stage. (*a*) A stereoscopic drawing viewed along the *a* axis and (*b*) a view down the normal to the mean plane of cobaloxime. The disordered pair of mce groups (shaded) is sandwiched by the two cobaloxime planes and face each other. The + denotes an inversion center. (Distances are in Å.)

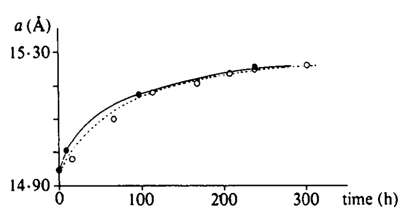

Fig. 7. The change of *a* when the crystal was kept in a dark thermostat at 353 K (white circles and a dashed curve) and when it was exposed to X-rays at the same temperature (black circles and a solid curve). These values were obtained at room temperature.

10^{-5} s^{-1}, respectively. The average, $6{\cdot}88 \times 10^{-5}$ s^{-1}, is slightly larger than the corresponding value, $5{\cdot}06 \times 10^{-5}$ s^{-1}, of the *S*-cn-py crystal at 353 K, which was decomposed at the final stage.

In order to confirm whether or not the crystal can be racemized without X-rays at high temperatures, it was kept in a dark thermostat at 353 K. The unit-cell dimensions were determined every two days on the diffractometer at 293 K. The change of *a* with time is shown in Fig. 7, in which the corresponding change with X-ray exposure is also shown. The rate of racemization is nearly the same as that produced by X-rays. This observation indicates that the racemization is mainly induced thermally for the present crystal, although about half an hour of X-ray exposure necessary for the determination of the accurate cell dimensions may leave the active species as trigger of the reaction. It is noteworthy that the *S*-cn-py crystal was not racemized thermally even if it was kept for a week at 353 K in the same conditions.

Conformational change of the molecule

Bond distances in the initial and final molecules are given in Table 4. Corresponding values in the three molecules are identical within experimental error, although the estimated standard deviations are somewhat large.

The *B* mce group has a different conformation from that of the *A* mce group and is converted to the same conformation as *A* at the final stage. The interatomic distance C(15*B*)···O(6*B*) is 2·79 (2) Å whereas C(15*A*)···O(5*A*) is 2·94 (2) Å. This suggests that the conformation of the *B* mce group is less stable energetically than that of *A*. Such a steric repulsion is probably a factor causing the racemization. The same conformation as the *A* mce group has been observed in the crystal of *R*-mce-*R*-mba.

The torsion angles around the Co—C and Co—N bonds in the *A*, *B* and final molecules are listed in Table 5. When the crystal is racemized, the Co—C bond of *A* rotates counterclockwise by 6 (3)° in Fig. 4(*b*), whereas that of *B* rotates clockwise by 20 (3)° in addition to the shift of the C(15*B*) methyl group. On the other hand, the pyridine ligands of *A* and *B* rotate counterclockwise by 4 (1) and 6 (1)°, respectively, around their Co—N bonds.

Table 4. *Bond distances* (Å) *of the initial A and B molecules and of the final one including the disordered P and Q mce groups*

	A	*B*	Final	
Co—N(1)	1·85 (1)	1·91 (1)	1·88 (1)	
Co—N(2)	1·90 (1)	1·90 (1)	1·90 (1)	
Co—N(3)	1·89 (1)	1·84 (1)	1·87 (1)	
Co—N(4)	1·89 (1)	1·87 (1)	1·88 (1)	
Co—N(5)	2·08 (1)	2·05 (1)	2·06 (1)	
N(1)—O(1)	1·38 (1)	1·35 (1)	1·34 (1)	
N(2)—O(2)	1·36 (1)	1·33 (1)	1·34 (1)	
N(3)—O(3)	1·34 (1)	1·36 (1)	1·34 (1)	
N(4)—O(4)	1·35 (1)	1·32 (1)	1·35 (1)	
N(1)—C(1)	1·31 (2)	1·28 (2)	1·32 (2)	
N(2)—C(2)	1·32 (2)	1·28 (2)	1·30 (2)	
N(3)—C(3)	1·32 (2)	1·29 (2)	1·33 (1)	
N(4)—C(4)	1·29 (1)	1·34 (2)	1·29 (2)	
C(1)—C(2)	1·46 (2)	1·45 (2)	1·43 (2)	
C(1)—C(5)	1·46 (2)	1·48 (2)	1·52 (2)	
C(2)—C(6)	1·49 (2)	1·51 (2)	1·55 (2)	
C(3)—C(4)	1·43 (2)	1·48 (2)	1·43 (2)	
C(3)—C(7)	1·47 (2)	1·47 (2)	1·51 (2)	
C(4)—C(8)	1·50 (2)	1·46 (2)	1·50 (1)	
C(11)—Cl	1·73 (1)	1·74 (1)	1·72 (1)	
N(5)—C(9)	1·33 (2)	1·34 (2)	1·32 (1)	
N(5)—C(13)	1·33 (2)	1·39 (2)	1·35 (1)	
C(9)—C(10)	1·35 (2)	1·40 (2)	1·36 (2)	
C(10)—C(11)	1·40 (2)	1·38 (2)	1·41 (2)	
C(11)—C(12)	1·34 (2)	1·38 (2)	1·33 (2)	
C(12)—C(13)	1·41 (2)	1·31 (2)	1·37 (2)	
			P	*Q*
Co—C(14)	2·09 (1)	2·07 (1)	2·05 (3)	2·08 (2)
C(14)—C(15)	1·55 (2)	1·49 (2)	1·50 (6)	1·54 (4)
C(14)—C(16)	1·48 (2)	1·45 (2)	1·49 (5)	1·47 (3)
C(16)—O(5)	1·18 (2)	1·20 (2)	1·15 (5)	1·21 (3)
C(16)—O(6)	1·37 (2)	1·37 (2)	1·37 (5)	1·30 (3)
O(6)—C(17)	1·40 (2)	1·47 (3)	1·52 (5)	1·47 (4)

Table 5. *Torsion angles* (°) *of the* Co—C *and* Co—N *bonds*

Initial	
N(1*A*)—Co(*A*)—C(14*A*)—C(16*A*)	48·9 (10)
N(4*A*)—Co(*A*)—N(5*A*)—C(9*A*)	40·5 (9)
N(1*B*)—Co(*B*)—C(14*B*)—C(16*B*)	−22·7 (11)
N(4*B*)—Co(*B*)—N(5*B*)—C(9*B*)	−38·3 (9)
Final	
N(1)—Co—C(14*P*)—C(16*P*)	43·1 (24)
N(3)—Co—C(14*Q*)—C(16*Q*)	32·5 (16)
N(4)—Co—N(5)—C(9)	44·0 (9)

Reaction mechanism

Comparison between the initial and final structures suggests that the *B* mce group relieves its conformational instability by changing its absolute configuration from *R* to *S*. Migration of the methyl group brings about a closer approach of the two molecules around the inversion center, since the C(15*B*) group has an unusually short contact with O(6*A*) in the initial structure. As the *A* and *B* molecules are stacked alternately along the *c* axis, the crystal contracts along this axis and the volume of the unit cell decreases. This process is essentially the same as that of the racemization of the *S*-cn-py crystal.

However, this inversion process in the present crystal is accompanied by disordering. For interpretation, we have defined the cavity for the two mce groups as concave space (Ohashi, Uchida, Sasada & Ohgo, 1983). Any point in the cavity is then considered to be accessed by the centers of the atoms of the two mce groups. Fig. 8 shows the cavity at the initial stage projected (*a*) along the normal to the *A* cobaloxime plane and (*b*) along the long axis of the cobaloxime. Although the two groups have a very close contact between C(15*B*) and O(6*A*), there is a wide space between the two groups. The void space does not seem to disappear fully even if C(15*B*) is shifted to the position of C(15*P*′), since the other contacts between O(6*A*) and H(14*B*) bonded to C(14*B*) and between O(6*B*) and H(14*A*) prevent sufficient approach of the two molecules. Fig. 9 compares the cavities at the initial and final stages. The side views are omitted since they are almost identical owing to approximately the same distances between the two cobaloxime planes. As can easily be seen from Fig. 9, the disordered mce groups, *Q* and *Q*′, occupy the void space.

The volumes of the initial and final cavities were calculated in the same way as reported previously (Ohashi, Yanagi, Kurihara, Sasada & Ohgo, 1981): these are 57·95 and 57·93 Å^3, respectively. In the *R*-cn-*S*-mba crystal, the cavity of the disordered racemic cyanoethyl group is greater than that of the initial enantiomeric one. In the *S*-cn-py crystal, on the other hand, the cavity of the ordered racemic group is smaller than that of the initial enantiomer. For the present crystal, the increase in volume of the cavity due to disordering is compensated by the approach of the two molecules. This is probably the reason why such a bulky substituent as the mce group is racemized without destroying the crystallinity.

One question remains unsolved: how are the disordered mce groups, *Q* and *Q*′, formed from the initial *A* and *B* mce groups? A probable explanation is the rotation around the Co—C bond and around the C(14)—C(16) bond. Fig. 8 indicates, however, that the cavity is too narrow to allow the latter rotation. The cavity may be expanded to a large extent along the normal to the cobaloxime plane at higher temperatures.

It is noteworthy that an mce group must occupy either of the disordered positions depending on the configuration of the other mce group opposite to the inversion center. If the *A* mce group migrates to *P*, the *B* mce group must become *P*′, or if *A* is transformed to *Q*, *B* must become *Q*′. The two mce groups around a pseudo inversion center move cooperatively to form a racemate crystal. Otherwise, there would be very short contacts. This is distinct from the racemization of the *R*-mce-py crystal, in which no unusual van der Waals contacts are observed between neighboring mce groups, so that one mce group can occupy either of the disordered positions independently of the neighbor.

The crystal of *R*-mce-*R*-mba cobaloxime was not racemized even at high temperatures. This crystal lacks two favorable conditions seen in the present crystal: the crystal contains only one molecule, which has a stable conformation of mce, in the asymmetric unit of the $P2_1$ cell and the mce group is surrounded very tightly by the cobaloxime and mce moieties.

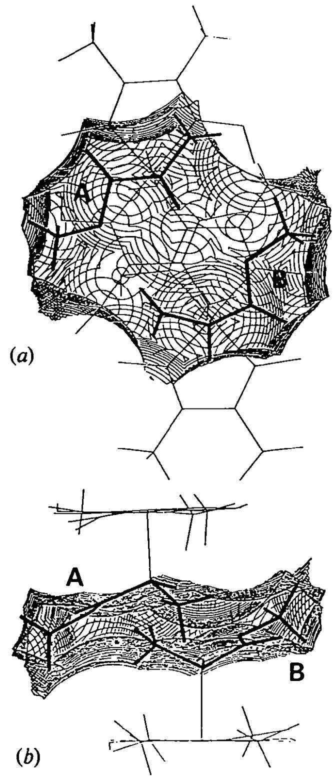

Fig. 8. The cavity for the two mce groups at the initial stage projected (*a*) along the normal to the *A* cobaloxime plane and (*b*) along the long axis of cobaloxime. The contours are drawn in sections separated by 0·1 Å.

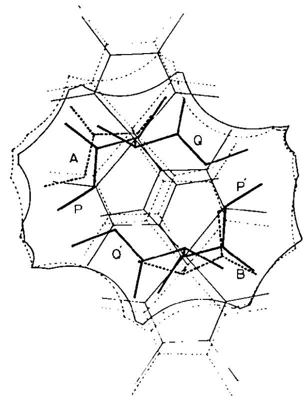

Fig. 9. Comparison of the two cavities at the initial and final stages. The broken and solid lines indicate the initial and final structures, respectively. The broken and solid concaves are the peripheries of the cavities at the initial and final stages, respectively.

This work was partly supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture, Japan. The cost of the high-temperature facility was partly defrayed by a grant from RCA Research Laboratories, Inc.

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The Molecular Symmetry of Glutaminase-Asparaginases: Rotation Function Studies of the *Pseudomonas* 7A and *Acinetobacter* Enzymes

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(*Received* 23 *February* 1982; *accepted* 22 *July* 1982)

Abstract

The molecular symmetry of crystalline *Pseudomonas* 7A glutaminase-asparaginase (orthorhombic, $P2_12_12_1$, $a = 118{\cdot}0$, $b = 131{\cdot}2$, $c = 85{\cdot}1$ Å), which contains one 139 000 g mol^{-1} tetramer per asymmetric unit, has been studied with Patterson rotation techniques. The results are completely consistent with 222 point-group symmetry. The relative orientations of the crystalline *Acinetobacter* glutaminase-asparaginase (orthorhombic, $I222$, $a = 96{\cdot}7$, $b = 112{\cdot}4$, $c = 70{\cdot}9$ Å), which contains one subunit per asymmetric unit, and the *Pseudomonas* 7A enzyme have been established with the so-called locked and cross-rotation functions. The presence of 222 symmetry in these tetramers is consistent with several previous investigations of the asparaginases.

Introduction

The administration of L-asparaginase (L-asparagine amidohydrolase, EC 3.5.1.1) produces the regression of

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