Crystalline-State Reaction of Cobaloxime Complexes by X-ray Exposure. 15. Different Reactivity Between Two Crystallographically Independent Molecules

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Abstract

A new type of crystalline-state reaction has been found in [(R)-1-cyanoethyl]bis(dimethylglyoximato)-(piperidine)cobalt(III) (dimethylglyoximato = 2,3-butanedione dioximato). Crystal data at 293 K are as follows: $[Co(C_3H_4N)(C_4H_7N_2O_2)_2(C_5H_{11}N)]$, $M_r = 428 \cdot 4$, $a = 11 \cdot 733$ (2), $b = 31 \cdot 026$ (5), $c = 11 \cdot 311$ (2) Å, $V = 4117$ (1) Å^3, $P2_12_12_1$, $Z = 8$, $D_x = 1 \cdot 383$ g cm^{-3}, $F(000) = 2024$, $\lambda(Mo\ K\alpha) = 0 \cdot 79069$ Å, $\mu = 8 \cdot 06$ cm^{-1}. The final R value was $0 \cdot 062$ for 3573 reflections. The cell dimensions changed gradually on exposure to X-rays at 333 K, although the crystalline-state racemization was not observed at 293 K. Three-dimensional intensity data were collected in the early stages at 333 K (stage I). The cell dimensions before data collection were $a = 11 \cdot 788$ (2), $b = 31 \cdot 146$ (7), $c = 11 \cdot 359$ (2) Å, $V = 4170$ (1) Å^3; and after data collection were $a = 11 \cdot 779$ (2), $b = 31 \cdot 085$ (7), $c = 11 \cdot 368$ (2) Å, $V = 4163$ (1) Å^3. The average dimensions were used for the structure determination: $a = 11 \cdot 784$ (2), $b = 31 \cdot 112$ (7), $c = 11 \cdot 364$ (2) Å, $V = 4167$ (1) Å^3. The structure analyses revealed that one cyanoethyl group of the two crystallographically independent molecules is disordered about the Co—C bond. After 92 h X-ray exposure at 333 K three-dimensional intensity data were collected (stage II) since the changes in cell dimensions became sufficiently small. Average cell dimensions for stage II are $a = 11 \cdot 774$ (2), $b = 31 \cdot 043$ (5), $c = 11 \cdot 379$ (2) Å, $V = 4159$ (1) Å^3. With regard to the disordered cyanoethyl group, 24% was inverted, whereas another crystallographically independent cyanoethyl group remained unaltered. The difference in reactivity between the two groups is explained by the different cavity sizes for the two reactive groups.

Introduction

It has been found that the chiral 1-cyanoethyl (ce) group in crystals of some bis(dimethylglyoximato)-cobalt (cobaloxime) complexes is racemized by X-ray exposure without degradation of the crystal (Ohashi & Sasada, 1977). The racemization processes observed in the related cobaloxime crystals are classified into three modes. In mode 1, the crystal has one molecule in the asymmetric unit and the disordered racemates appear after racemization (Ohashi, Yanagi, Kurihara, Sasada & Ohgo, 1981; Ohashi, Sasada & Ohgo, 1978a,b; Tamura, 1987). The crystals of modes II and III have two crystallographically independent molecules which are related by a pseudoinversion center that becomes a crystallographic center after racemization. In this case the space group changes from chiral to centrosymmetric. In mode II the configuration of one of two crystallographically independent ce groups is fully inverted and the ordered chiral crystal is transformed to the ordered racemic one (Ohashi, Uchida, Sasada & Ohgo, 1983; Ohashi, Yanagi, Kurihara, Sasada & Ohgo, 1982; Uchida, Ohashi, Sasada, Ohgo & Baba, 1984). On the other hand, both of the crystallographically independent ce groups are converted to the disordered racemates in mode III (Tomotake, Uchida, Ohashi, Sasada, Ohgo & Baba, 1985).

In the previous paper, we reported a new type of racemization which belonged to none of the above three classes (Ohashi, Tomotake, Uchida & Sasada, 1986). The crystal, in which the ligand 3-methylpyridine occupies an axial base position, *R*-ce-3mepy, contains two molecules, *A* and *B*, in the $P2_12_12_1$ cell. At an early stage both of the ce groups were inverted to give the disordered racemates, but the ce group of the *A* molecule, the *A* ce group, returned to the

original configuration after about 400 h exposure. Finally, the *B* ce group was fully inverted to the opposite configuration and the *A* ce group was transformed to the original one. The somewhat large size of the reaction cavity of the *A* ce group and the chiral space group after racemization may cause such differences in the racemization process. Recently, we prepared another crystal which had two independent molecules, *A* and *B* (space group $P2_12_12_1$), using piperidine as an axial base ligand (*R*-ce-pip). The racemization process, however, is somewhat different from that of *R*-ce-3mepy. The present paper reports the new type of racemization.

Experimental

R-ce-pip was prepared in a similar way to that previously reported (Ohgo, Takeuchi, Natori, Yoshimura, Ohashi & Sasada, 1981). Dark-red crystals were obtained from an aqueous methanol solution. A Rigaku AFC-4 diffractometer and Mo $K\alpha$ radiation monochromated by graphite were used (45 kV, 20 mA). The cell dimensions were determined by the least-squares technique with 20 reflections in the range $19 < 2\theta < 29°$.

Crystal at 293 K

Three-dimensional intensity data were collected at 293 K using a crystal with dimensions $0.3 \times 0.3 \times 0.3$ mm. Reflections in the range $2\theta < 50°$ ($0 \leq h \leq 13$, $0 \leq k \leq 36$, $0 \leq l \leq 13$) were measured by the $\omega/2\theta$ scan technique with a scan width of $1.0°$, and a scanning rate of $4°$ (ω) min^{-1}. Stationary background counts were accumulated for 5 s before and after each scan. In the course of the data collection the orientation matrix was redetermined if the intensities of three monitor reflections varied by more than 5σ. A total of 3573 reflections with $|F_o| > 3\sigma(|F_o|)$ were used for the structure determination. No corrections for absorption and extinction were made.

The structure was solved by direct methods using *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) and refined by the restrained least-squares method using *SHELX*76 (Sheldrick, 1976). Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV, pp. 99–102, 149). Most of the H atoms were located geometrically. In the final refinement, non-H and H atoms were refined with anisotropic and isotropic temperature factors, respectively. The bond distances between non-H atoms were loosely restrained to the mean values of those corresponding to the related molecules and those of the H atoms were fixed at 1.0 Å. The weighting scheme used was $w = [\sigma(F_o)^2 + CF_o^2]^{-1}$,

Table 1. *Final atomic coordinates* ($\times 10^5$ *for* Co *and* $\times 10^4$ *for* C, N, O) *and equivalent isotropic thermal parameters* [B_{eq} (Å^2)] *at* 293 K

$$B_{eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Co(A)	48492 (8)	12104 (3)	14100 (9)	2·8
N(1A)	4765 (6)	1573 (2)	85 (5)	3·7
N(2A)	3574 (5)	1543 (2)	1870 (5)	3·2
N(3A)	4924 (6)	836 (2)	2712 (5)	3·2
N(4A)	6151 (6)	896 (2)	971 (6)	3·6
O(1A)	5467 (5)	1541 (2)	−841 (5)	5·1
O(2A)	3050 (5)	1488 (2)	2919 (5)	4·2
O(3A)	4204 (5)	870 (2)	3635 (5)	4·4
O(4A)	6724 (5)	969 (2)	−32 (5)	4·9
C(1A)	3950 (7)	1860 (3)	110 (7)	3·7
C(2A)	3280 (7)	1849 (2)	1159 (7)	3·2
C(3A)	5715 (7)	547 (3)	2705 (7)	3·8
C(4A)	6444 (7)	580 (3)	1671 (8)	3·7
C(5A)	3747 (10)	2157 (3)	−920 (9)	6·4
C(6A)	2328 (7)	2154 (3)	1408 (10)	5·1
C(7A)	5905 (10)	235 (3)	3682 (9)	6·2
C(8A)	7431 (8)	292 (3)	1391 (11)	6·2
C(9A)	5849 (7)	1659 (3)	2261 (9)	4·3
C(10A)	6488 (8)	1469 (3)	3188 (11)	3·9
C(11A)	6650 (7)	1922 (3)	1433 (7)	6·4
N(5A)	7057 (6)	1315 (3)	3907 (7)	5·7
N(6A)	3722 (5)	794 (2)	523 (5)	3·3
C(12A)	4262 (8)	528 (3)	−420 (8)	4·8
C(13A)	3327 (9)	279 (3)	−1125 (9)	5·9
C(14A)	2594 (10)	−11 (3)	−340 (9)	5·9
C(15A)	2046 (9)	279 (3)	604 (9)	5·8
C(16A)	2952 (8)	533 (3)	1294 (8)	4·9
Co(B)	48899 (9)	35159 (3)	35091 (9)	2·9
N(1B)	3593 (5)	3151 (2)	3543 (6)	3·4
N(2B)	3763 (5)	3937 (2)	3301 (6)	3·3
N(3B)	6191 (5)	3871 (2)	3470 (5)	3·1
N(4B)	6025 (5)	3088 (2)	3722 (6)	3·8
O(1B)	3684 (5)	2720 (2)	3719 (6)	4·6
O(2B)	4008 (5)	4359 (2)	3140 (5)	4·0
O(3B)	6121 (5)	4301 (2)	3258 (5)	4·2
O(4B)	5775 (5)	2670 (2)	3823 (6)	5·3
C(1B)	2605 (6)	3342 (3)	3474 (7)	3·1
C(2B)	2720 (7)	3801 (3)	3316 (7)	3·5
C(3B)	7166 (6)	3692 (3)	3656 (7)	3·6
C(4B)	7054 (7)	3221 (3)	3833 (7)	3·4
C(5B)	1528 (7)	3091 (3)	3590 (9)	5·2
C(6B)	1745 (8)	4098 (3)	3162 (8)	5·0
C(7B)	8276 (7)	3924 (3)	3632 (9)	5·0
C(8B)	8033 (8)	2918 (3)	4173 (9)	5·5
C(9B)	4925 (7)	3454 (3)	1691 (7)	4·8
C(10B)	6022 (12)	3574 (5)	1215 (11)	4·2
C(11B)	4640 (8)	3020 (3)	1174 (7)	11·3
N(5B)	6873 (7)	3659 (3)	817 (7)	6·1
N(6B)	4678 (5)	3603 (2)	5334 (5)	3·5
C(12B)	5029 (7)	3236 (3)	6101 (7)	4·2
C(13B)	4641 (8)	3299 (3)	7372 (8)	5·6
C(14B)	5074 (9)	3710 (3)	7894 (7)	5·9
C(15B)	4762 (9)	4081 (3)	7098 (8)	5·6
C(16B)	5177 (9)	4004 (3)	5820 (7)	4·9

where $C = 0.0214$. Final R and wR values were 0·062 and 0·053 and S was 0·895, for the 3573 observed reflections. $\Delta\rho_{max}$ and $\Delta\rho_{min}$ were 0·3 and -0.4 e Å^{-3}, respectively, and $(\Delta/\sigma)_{max}$ was 0·03 for non-H atoms. Final atomic parameters for non-H atoms at 293 K are given in Table 1.*

Changes in the cell dimensions were observed when the crystal was warmed to 333 K. Fig. 1 shows

* Lists of anisotropic thermal parameters, H-atom coordinates, bond lengths and angles involving non-H atoms, and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54102 (49 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

the variations of a, b, c and V with exposure time, a crystal of $0.4 \times 0.4 \times 0.3$ mm being used. In the course of measuring the cell dimensions, three-dimensional intensity data were collected at stages I and II as indicated in Fig. 1. Three-dimensional data were collected after 207 h, but the refinement was not successful because of the low quality of the data resulting from damage to the crystal.

Stage I at 333 K

A total of 2759 intensities with $|F_o| > 3\sigma(|F_o|)$ were collectd in the same manner as for the 293 K data, but with $2\theta \le 45°$ ($0 \le h \le 12$, $0 \le k \le 33$, $0 \le l \le 12$). The structure was solved using that at 293 K and refined under the same conditions as the 293 K data. Additional peaks appeared near the B ce group, and were ascribed to the disordered B ce group with the same configuration. The occupancy factor for the new B ce group was refined to a value of 0.35 (2). The H atoms were located geometrically except for those belonging to the disordered B ce groups. At the final stage of the refinement, C was 0.0211, and $\Delta\rho_{max}$, $\Delta\rho_{min}$ and $(\Delta/\sigma)_{max}$ become 0.4, -0.5 e Å^{-3} and 0.2, respectively. Final R, wR and S values were 0.073, 0.090 and 0.864, respectively. The

Fig. 1. Change of the cell dimensions with exposure time at 333 K.

Table 2. *Final atomic coordinates* ($\times 10^5$ *for* Co *and* $\times 10^4$ *for* C, N, O) *and isotropic thermal parameters* [B (Å^2), *for* C(9B), C(10B), N(5B), C(11B), C(10B'), N(5B'), C(11B')] *or equivalent isotropic thermal parameters* [B_{eq} (Å^2)] *for stage* I *at* 333 K

	x	y	z	B or B_{eq}
Co(A)	48550 (11)	12140 (4)	13981 (11)	3·4
N(1A)	4777 (7)	1564 (2)	61 (6)	4·0
N(2A)	3595 (6)	1541 (3)	1856 (7)	3·9
N(3A)	4925 (7)	843 (3)	2712 (6)	3·9
N(4A)	6162 (7)	899 (3)	965 (7)	4·3
O(1A)	5482 (8)	1529 (3)	−862 (7)	5·5
O(2A)	3082 (7)	1496 (3)	2905 (7)	5·0
O(3A)	4213 (8)	877 (3)	3630 (6)	5·5
O(4A)	6748 (7)	977 (3)	−30 (8)	6·6
C(1A)	3981 (9)	1850 (3)	98 (8)	4·7
C(2A)	3280 (8)	1839 (3)	1146 (9)	4·2
C(3A)	5689 (9)	537 (3)	2683 (8)	5·0
C(4A)	6430 (8)	582 (4)	1670 (9)	5·2
C(5A)	3790 (15)	2180 (5)	−850 (12)	7·3
C(6A)	2350 (11)	2161 (4)	1345 (16)	6·7
C(7A)	5890 (14)	236 (4)	3682 (12)	6·9
C(8A)	7414 (11)	302 (4)	1374 (19)	7·7
C(9A)	5866 (9)	1645 (3)	2244 (9)	5·2
C(10A)	6502 (10)	1449 (4)	3203 (10)	4·8
N(5A)	7064 (9)	1324 (4)	3915 (9)	6·0
C(11A)	6671 (12)	1912 (5)	1451 (17)	8·1
N(6A)	3751 (7)	797 (2)	513 (7)	4·1
C(12A)	4269 (10)	525 (5)	−404 (10)	6·7
C(13A)	3388 (13)	285 (5)	−1137 (11)	7·3
C(14A)	2608 (15)	13 (5)	−389 (12)	7·6
C(15A)	2086 (11)	292 (6)	558 (13)	7·9
C(16A)	2980 (10)	536 (4)	1260 (10)	5·4
Co(B)	48944 (11)	35169 (4)	35287 (12)	3·5
N(1B)	3611 (6)	3158 (2)	3557 (9)	4·0
N(2B)	3762 (5)	3938 (2)	3308 (8)	3·9
N(3B)	6178 (6)	3878 (2)	3501 (8)	3·7
N(4B)	6015 (6)	3091 (2)	3742 (10)	4·6
O(1B)	3684 (8)	2734 (2)	3731 (10)	5·5
O(2B)	4017 (7)	4358 (2)	3146 (9)	5·2
O(3B)	6140 (7)	4303 (2)	3285 (8)	4·8
O(4B)	5783 (8)	2670 (2)	3858 (10)	6·1
C(1B)	2628 (6)	3345 (3)	3506 (10)	3·8
C(2B)	2726 (6)	3800 (3)	3306 (9)	3·4
C(3B)	7150 (7)	3693 (3)	3689 (10)	5·3
C(4B)	7037 (8)	3230 (3)	3849 (10)	4·3
C(5B)	1542 (10)	3099 (6)	3562 (15)	8·1
C(6B)	1757 (10)	4112 (4)	3194 (14)	5·7
C(7B)	8253 (10)	3936 (6)	3658 (14)	7·6
C(8B)	8032 (11)	2958 (7)	4147 (14)	8·6
C(9B)*	4959 (9)	3438 (5)	1728 (7)	7·5
C(10B)	6023 (11)	3610 (7)	1244 (15)	3·8 (3)
N(5B)	6850 (12)	3699 (7)	814 (15)	5·0 (3)
C(11B)	4795 (23)	2973 (5)	1291 (22)	6·8 (5)
C(10')	6110 (14)	3400 (12)	1261 (28)	3·8 (3)
N(5')	7013 (17)	3487 (12)	1047 (29)	5·0 (3)
C(11')	4268 (37)	3105 (12)	1028 (37)	6·8 (5)
N(6B)	4717 (7)	3610 (3)	5352 (5)	4·4
C(12B)	5029 (11)	3222 (3)	6069 (8)	5·1
C(13B)	4691 (13)	3285 (4)	7359 (10)	7·1
C(14B)	5032 (15)	3725 (4)	7877 (11)	8·4
C(15B)	4763 (13)	4102 (4)	7086 (9)	6·4
C(16B)	5155 (13)	4021 (3)	5835 (9)	6·1

* Occupancy factors for C(9B), C(10B), N(5B), C(11B) are 0·65, and those of C(10B'), N(5B'), C(11B') are 0·35.
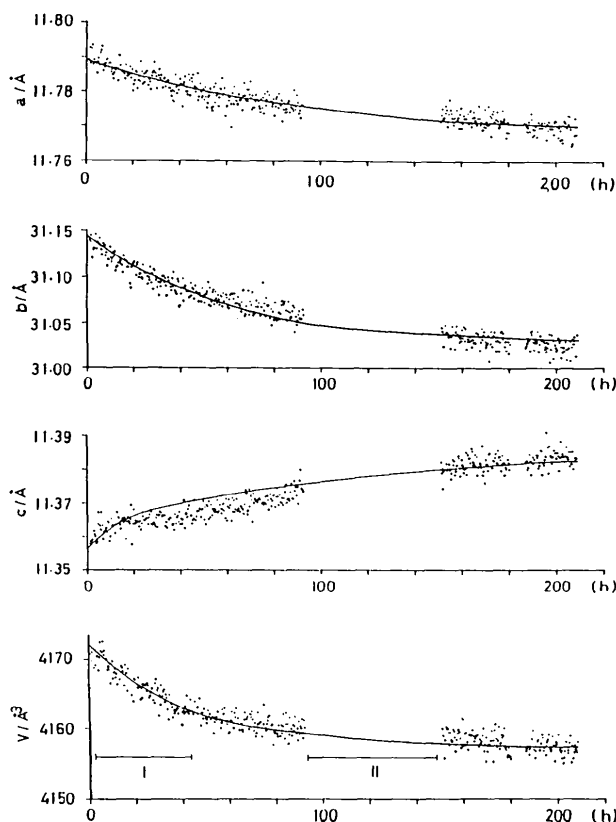
high R values may be the result of disordering of the structure. Final atomic parameters for non-H atoms for stage I at 333 K are given in Table 2.

Stage II at 333 K

A total of 2418 reflections with $|F_o| > 3\sigma(|F_o|)$ were obtained in the same manner as for stage I. Some additional peaks appeared around the B ce group and these were assigned as a ce group with the opposite configuration. The occupancy factor of the

Table 3. *Final atomic coordinates* ($\times 10^5$ *for* Co *and* $\times 10^4$ *for* C, N, O) *and isotropic thermal parameters* [B (Å²), *for* C(11B), C(11C)] *or equivalent isotropic thermal parameters* [B_{eq} (Å²)] *for stage* II *at* 333 K

	x	*y*	*z*	*B* or B_{eq}
Co(*A*)	48600 (14)	12152 (6)	14066 (15)	3·4
N(1*A*)	4798 (9)	1579 (3)	76 (7)	4·4
N(2*A*)	3586 (8)	1543 (4)	1855 (9)	4·4
N(3*A*)	4948 (10)	841 (3)	2711 (7)	4·1
N(4*A*)	6176 (8)	905 (4)	950 (10)	4·3
O(1*A*)	5506 (10)	1547 (4)	−859 (9)	6·0
O(2*A*)	3060 (8)	1493 (4)	2904 (9)	5·4
O(3*A*)	4214 (8)	875 (3)	3612 (8)	5·4
O(4*A*)	6769 (9)	968 (4)	−45 (9)	5·7
C(1*A*)	3986 (12)	1860 (4)	93 (10)	4·3
C(2*A*)	3318 (10)	1861 (4)	1169 (11)	4·4
C(3*A*)	5731 (12)	545 (4)	2705 (11)	5·5
C(4*A*)	6437 (10)	591 (4)	1655 (11)	5·0
C(5*A*)	3865 (19)	2173 (6)	−901 (14)	7·8
C(6*A*)	2354 (11)	2162 (5)	1419 (17)	5·7
C(7*A*)	5868 (17)	224 (6)	3677 (14)	7·7
C(8*A*)	7412 (13)	302 (6)	1307 (21)	8·3
C(9*A*)	5858 (11)	1666 (4)	2226 (11)	4·9
C(10*A*)	6502 (11)	1464 (5)	3176 (11)	4·5
N(5*A*)	7042 (12)	1320 (5)	3899 (11)	6·9
C(11*A*)	6682 (15)	1923 (8)	1445 (22)	9·6
N(6*A*)	3741 (8)	804 (4)	518 (9)	4·7
C(12*A*)	4247 (12)	529 (5)	−405 (12)	6·0
C(13*A*)	3361 (14)	278 (6)	−1095 (14)	6·8
C(14*A*)	2591 (16)	−2 (5)	−358 (15)	7·2
C(15*A*)	2097 (13)	300 (6)	550 (17)	7·8
C(16*A*)	2981 (12)	538 (5)	1269 (12)	5·3
Co(*B*)	49038 (15)	35149 (6)	35250 (15)	3·5
N(1*B*)	3611 (8)	3157 (3)	3593 (12)	4·3
N(2*B*)	3766 (7)	3934 (3)	3304 (11)	3·8
N(3*B*)	6190 (7)	3873 (3)	3477 (12)	3·7
N(4*B*)	6027 (7)	3087 (3)	3747 (13)	5·0
O(1*B*)	3691 (8)	2725 (3)	3726 (11)	5·2
O(2*B*)	4018 (9)	4352 (3)	3129 (10)	5·2
O(3*B*)	6144 (8)	4299 (3)	3299 (10)	4·7
O(4*B*)	5788 (9)	2663 (3)	3841 (12)	6·3
C(1*B*)	2621 (8)	3341 (4)	3483 (13)	3·7
C(2*B*)	2716 (8)	3804 (4)	3318 (11)	3·6
C(3*B*)	7158 (8)	3697 (4)	3716 (11)	4·5
C(4*B*)	7060 (9)	3233 (4)	3867 (12)	4·8
C(5*B*)	1543 (11)	3087 (6)	3585 (19)	6·2
C(6*B*)	1722 (10)	4098 (5)	3205 (15)	5·3
C(7*B*)	8271 (11)	3929 (6)	3608 (18)	7·0
C(8*B*)	8046 (12)	2945 (6)	4182 (15)	6·2
C(9*B*)*	4940	3435	1727	5·7
C(10*B*)	6061 (8)	3541 (5)	1239 (11)	5·1
N(5*B*)	6896 (11)	3648 (5)	852 (12)	7·5
C(11*B*)	4640 (25)	2995 (5)	1184 (24)	9·3 (8)
C(11*C*)	3925 (54)	3357 (33)	901 (69)	9·3 (8)
N(6*B*)	4726 (10)	3602 (3)	5343 (6)	4·1
C(12*B*)	5018 (14)	3236 (4)	6118 (10)	5·5
C(13*B*)	4645 (15)	3298 (6)	7381 (11)	7·7
C(14*B*)	5092 (15)	3718 (6)	7881 (12)	7·1
C(15*B*)	4786 (17)	4090 (6)	7069 (11)	7·5
C(16*B*)	5167 (16)	4015 (4)	5810 (11)	6·2

* Occupancy factors for C(11*B*) and C(11*C*) are 0·76 and 0·24, respectively.

S configuration also refined to 0·24 (3). The H atoms were located geometrically except for those of the *B* ce groups. At the final stage *C* was 0·0020 and $\Delta\rho_{max}$, $\Delta\rho_{min}$ and $(\Delta/\sigma)_{max}$ became 0·4, −0·6 e Å⁻³ and 0·1, respectively. Final *R*, *wR* and *S* values were 0·081, 0·081 and 1·191 respectively. Disordering of the structure may be the cause of the relatively high *R* values. Final atomic parameters for the non-H atoms of stage II at 333 K are in given Table 3. After data collection the temperature was increased to 348 K, but the cell-dimension variations did not change more rapidly. When the crystal was warmed to more than 348 K, it gradually decomposed.

Results and discussion

Crystal and molecular structure at 293 K

Fig. 2 shows the crystal structure at 293 K viewed along the *a* axis. Two crystallographically independent molecules *A* and *B* are not related by any pseudo or local inversion center. Both of the *A* and *B* ce groups are surrounded by moieties other than the ce groups of neighboring molecules and are isolated from each other. These structural features are in marked contrast to those of the mode II and III crystals, and of *R*-ce-3mepy. The N atoms of the *A* and *B* ce groups make hydrogen bonds with the N—H groups of the *B* and *A* piperidine ligands, respectively, and connect the molecules along the [101] direction. The lengths N(5*A*)···N(6*B*) and N(5*B*)···N(6*A*) are 3·203 (9) and 3·142 (8) Å, respectively. The N(5*A*)···H(6*B*)—N(6*B*) and N(5*B*)··· H(6*A*)—N(6*A*) angles are 160·8 (4) and 168·4 (4)°, respectively.

The molecular structure of *A* is essentially the same as that of *B*. Molecule *A* is shown in Fig. 3. Selected bond distances and torsion angles about the
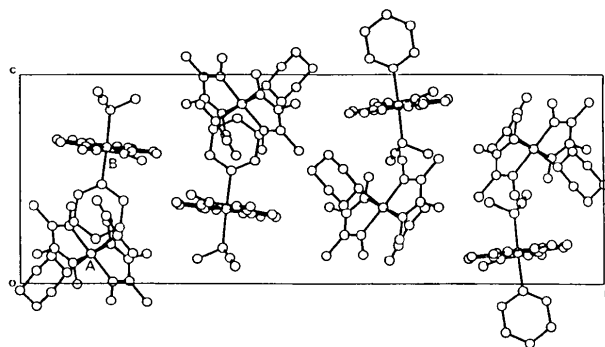

Fig. 2. Crystal structure at 293 K viewed along the *a* axis.
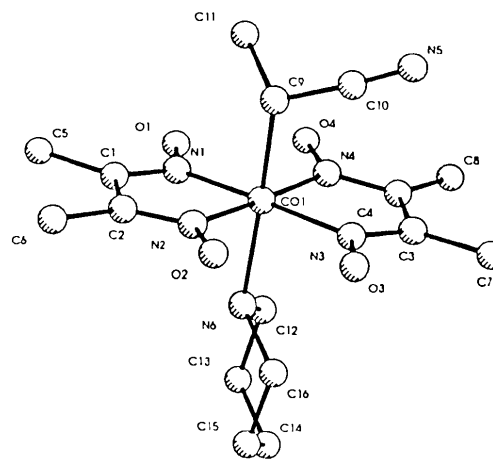

Fig. 3. Molecular structure of *A* at 293 K.

Table 4. *Selected bond distances* (Å) *and torsion angles* (°) *at* 298 K

	A	B
Co—N(1)	1·876 (6)	1·897 (6)
Co—N(2)	1·891 (5)	1·874 (5)
Co—N(3)	1·877 (6)	1·883 (5)
Co—N(4)	1·878 (5)	1·895 (6)
Co—C(9)	2·058 (8)	2·066 (8)
Co—N(6)	2·104 (5)	2·097 (5)
N(1)—Co—C(9)—C(10)	−33·1 (6)	38·3 (5)
N(1)—Co—C(9)—C(11)	−159·0 (9)	−161·8 (7)
N(1)—Co—N(6)—C(12)	77·4 (5)	75·1 (5)
N(1)—Co—N(6)—C(16)	−150·0 (5)	−156·3 (5)

Co—C and Co—N bonds are listed in Table 4. The corresponding values for the *A* and *B* molecules are not significantly different from each other.

Racemization at 333 K

The crystal structure of stage II at 333 K is shown in Fig. 4. The configuration of a part of the *B* ce group, 24%, is inverted whereas the *A* ce group remains unaltered. Fig. 5 shows the *B* ce group viewed along the normal to the cobaloxime plane at 293 K, at stage I at 333 K and at stage II at 333 K. Upon heating the *B* ce group rotates about the Co—C bond and adopts a disordered conformation. On exposure to X-rays at high temperatures, the *B* ce group becomes disordered and gradually inverts its configuration. Ultimately, it would probably become a disordered racemate.

Reaction mechanism

The reaction process of the ce group has been well explained by the size of the reaction cavity for the crystals reported so far. The volumes of the *A* and *B* ce groups for the present crystal at 293 K were calculated to be 7·49 and 11·57 Å^3, respectively. When the ce group is isolated from the other ce groups as observed in the mode I crystals, the critical volume necessary for the racemization was estimated
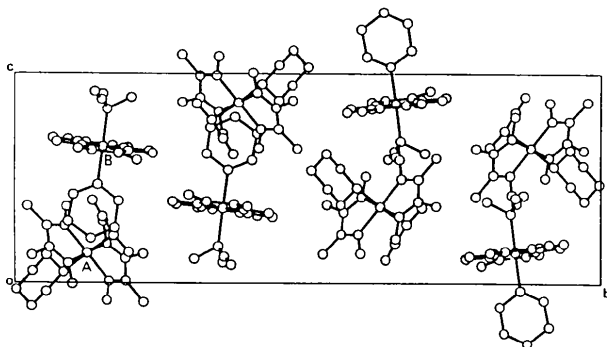
to be 11·5 Å^3 (Ohashi, 1988). The cavity of the *A* ce group is significantly smaller than the critical volume. This causes the nonreactivity of the *A* ce group. The *B* cavity, on the other hand, is approximately the same size as the critical one. Although racemization of the *B* ce group was undetectable within about 400 h at 293 K, it may be possible to observe the disordered racemic structure after infinite exposure to X-rays. When the crystal is warmed to 333 K, the *A* and *B* cavities expand to 7·88 and 14·04 Å^3, respectively. The *A* cavity is still too small for racemization, whereas the *B* cavity is large enough for the disordered racemates. The cavity size
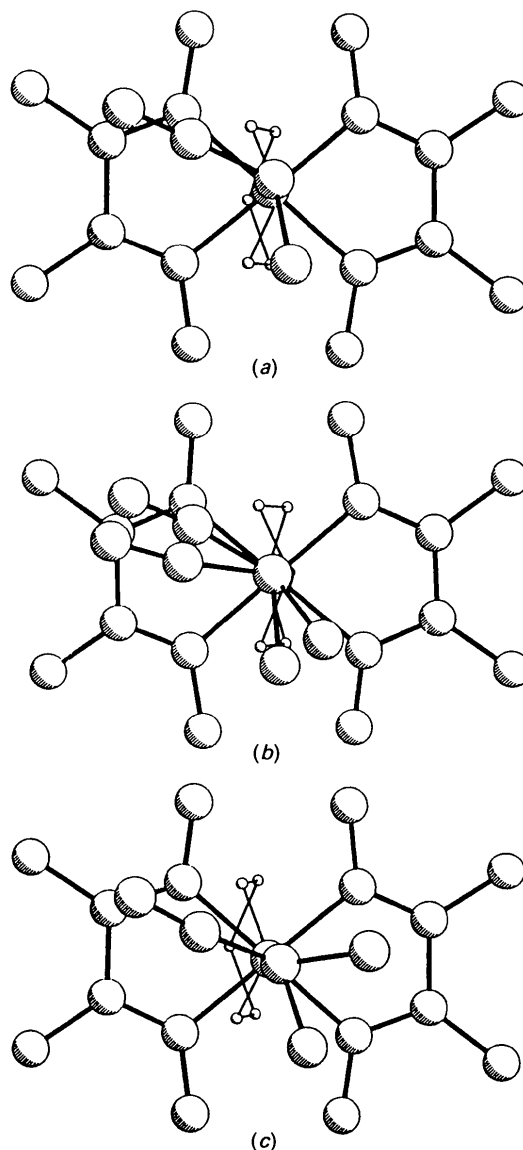

(a)

(b)

(c)

Fig. 5. Molecular structures of *B* at 293 K (*a*), stage I at 333 K (*b*) and stage II at 333 K (*c*).

Fig. 4. Crystal structure for stage I at 333 K viewed along the *a* axis.

of the reactive group explains well the reaction process of the present crystal at both temperatures.

The crystal of *R*-ce-3mepy also belongs to the space group $P2_12_12_1$ and has two crystallographically independent molecules *A* and *B*. However, the two molecules are related by a pseudo inversion center. Moreover, the volumes of the *A* and *B* cavities are 10·24 and 14·29 Å^3, respectively. Since the two ce groups face each other around a pseudo inversion center, not only the *A* but also the *B* ce groups became disordered racemates at early stages. After 400 h exposure, the configuration of the *A* ce group gradually inverted to the original one whereas that of the *B* ce group was inverted to the opposite one. Then the pseudo inversion center became a local inversion center. The cooperative motion of the two ce groups may bring about such a complicated reaction process.

For the present *R*-ce-pip, the cooperative motion of the two reactive groups would be impossible and the two groups should be changed independently by X-ray exposure, since they are isolated from each other. Therefore, the racemization mode of *R*-ce-pip is essentially the same as mode I except that the crystal has two reactive groups.*

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* Recently we have prepared the racemic crystals, *rac*-ce-pip, which have the space group $P2_12_12_1$ and have an isomorphous structure to the present one, *R*-ce-pip. At high temperatures, the crystal revealed a racemic-to-chiral conversion on exposure to X-rays. The reaction process will be reported in detail elsewhere (Osano, Uchida & Ohashi, 1991).

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Complex Between the Subtilisin from a Mesophilic Bacterium and the Leech Inhibitor Eglin-C

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Abstract

The alkaline proteinase from the mesophilic bacterium *Bacillus mesentericus* has been crystallized in a 1:1 complex with the inhibitor eglin-C from the medical leech. The crystals have cell dimensions of $a = 43\cdot0$, $b = 71\cdot9$, $c = 48\cdot3$ Å and $\beta = 110\cdot0°$ and are in the space group $P2_1$. Three-dimensional data to