products are summarized in Table II.

Measurements. CD spectra were obtained with a Jasco J-20 CD spectrophotometer controlled by a Jasco DP-X data processor at a 0.1 mg/mL concentration of peptide at room temperature. The ellipticity, $[\theta]$, is expressed in deg cm^2 dmol^{-1} of amino acid residue by using mean residue molecular weight. The calibration was based on $[\theta]_{304}$ = 11 200 deg cm^2 dmol^{-1} for 0.05% androsterone in dioxane.[26] The IR spectrum was obtained for a KBr disk with a Jasco A-702 spectrophotometer controlled by a Jasco A-330 data processor.

Acknowledgment. This research was partly supported by Grant-in-Aid for Scientific Research (58580095) of the Japanese Ministry of Education, Science, and Culture.

Registry No. Nps-Gly-Gly-Gly-Ile-Phe-Gly-Phe-Leu-Leu-Leu-Leu-Phe-Pro-Gly-OEt, 91295-37-3; Nps-Gly-Gly-Gly-Leu-Phe-Leu-Phe-Leu-Ala-Leu-Leu-Leu-Ala-OEt, 91295-38-4; Nps-Gly-Gly-Gly-Leu-Leu-Leu-Ala-Leu-Gly-Leu-Ala-Leu-Ala-OEt, 91311-02-3.

---

[26] Tuzimura, K.; Konno, T.; Megro, H.; Hatano, M.; Murakami, T.; Kashiwabara, K.; Saito, K.; Kondo, Y.; Suzuki, T. M. *Anal. Biochem.* **1977**, *81*, 167–174.

Crystalline-State Reaction of Cobaloxime Complexes by X-ray Exposure. 7. Structure Analysis of Multistage Racemization

Toshiharu Kurihara,[1a] Akira Uchida,[1a] Yuji Ohashi,*[1a] Yoshio Sasada,[1a] and Yoshiaki Ohgo[1b]

Contribution from the Laboratory of Chemistry for Natural Products, Tokyo Institute of Technology, Nagatsuta 4259, Midori-ku, Yokohama 227, Japan, and Niigata College of Pharmacy, 5829 Kamishinei-cho, Niigata 950-21, Japan. *Received December 23, 1983*

Abstract: A crystal of [(*R*)-1-(methoxycarbonyl)ethyl](pyridine)bis(dimethylglyoximato)cobalt(III) methanol solvate changed its cell dimensions without degradation of the crystallinity at 293 K. After 140 h, the change became so slow that the three-dimensional intensity data were collected. The cell dimensions were varied from a = 9.289 (3) Å, b = 21.059 (6) Å, c = 11.499 (4) Å, β = 94.16 (3)°, and V = 2243 (1) Å^3 to a = 9.296 (3) Å, b = 20.09 (1) Å, c = 11.39 (1) Å, β = 94.27 (8)°, and V = 2121 (3) Å^3. The space group $P2_1$ remained unaltered. The structure analyses before and after the change revealed that the solvent methanol molecules completely went out from the crystal and the conformation of the (methoxycarbonyl)ethyl (mce) group was drastically changed to fill the void space due to the loss of solvent. The absolute configuration of the mce group, however, was conserved. Then the crystal was warmed to 343 K to accelerate the rate of the change. The cell dimensions began to vary again. The change finally stopped after 180 h. The space group was converted from $P2_1$ to $P2_1/n$. The structure at the final stage at 293 K agreed with that reported previously (Kurihara, T.; Ohashi, Y.; Sasada, Y. *Acta Crystallogr., Sect. B* **1982**, *B38*, 2484–2486). The chiral mce group was converted to a disordered racemic structure. Comparison of the three structures at the initial, intermediate, and final stages clearly revealed the atomic process of the multistage racemization of the mce group in the crystalline state.

We have found that the chiral 1-cyanoethyl (cn) group, $-C^*H(CH_3)CN$, bonded to the cobalt atom, in the crystals of several bis(dimethylglyoximato)cobalt (cobaloxime) complexes is racemized by X-ray exposure without degradation of the crystallinity.[2-8] Since the rate of the racemization is closely related with the packing of the cn group in the crystal structure, we have defined the cavity for the cn group and proved that the reactivity has a positive correlation with the volume of the cavity.[7] The chiral 1-(methoxycarbonyl)ethyl (mce) group, $-C^*H(CH_3)CO_2CH_3$, in the crystal of [(*R*)-1-mce](4-chloropyridine)cobaloxime (*R*-mce-Clpy), on the other hand, was racemized only at high temperatures. The mode of the racemization was very complicated; the inversion of configuration of the mce group was accompanied by the rotation around the central $C-CO_2CH_3$ bond.[9] The crystal of [(*R*)-1-mce](pyridine)cobaloxime (*R*-mce-py, Figure 1) also revealed the crystalline-state racemization. Since the rate of the change in the unit-cell dimensions was too rapid to collect the three-dimensional intensity data, only the final racemic structure was determined.[10] It seemed at first sight strange that the

Table I. Crystal Data and Details of Refinement at the Three Stages

	initial		inter-mediate	final[a]
formula	$C_{17}H_{26}CoN_5O_6\cdot CH_4O$	$C_{17}H_{26}CoN_5O_6\cdot CH_4O$	$C_{17}H_{26}CoN_5O_6$	$C_{17}H_{26}CoN_5O_6$
fw	487.40	487.40	455.36	455.36
temp, K	223	293	293	293
space group	$P2_1$	$P2_1$	$P2_1$	$P2_1/n$
a, Å	9.249 (7)	9.289 (3)	9.296 (3)	9.288 (1)
b, Å	20.82 (2)	21.059 (6)	20.09 (1)	19.952 (2)
c, Å	11.45 (1)	11.499 (4)	11.39 (2)	11.397 (1)
β, deg	94.06 (9)	94.16 (3)	94.27 (8)	94.10 (2)
V, Å^3	2201 (3)	2243 (1)	2121 (3)	2106.6 (5)
Z	4	4	4	4
R factor	0.053	0.132	0.104	
N_F[b]	3843	3422	3029	
N_p[c]	691	668	560	
C[d]	0.00386	0.00390	0.02820	

[a] Values taken from ref 10. [b] Number of observed reflections. [c] Number of parameters. [d] Value in the weighting scheme.

---

[1] (a) Tokyo Institute of Technology. (b) Niigate College of Pharmacy.

[2] Ohashi, Y.; Sasada, Y. *Nature (London)* **1977**, *267*, 142–144.

[3] Ohashi, Y.; Sasada, Y.; Ohgo, Y. *Chem. Lett.* **1978**, *457*–460.

[4] Ohashi, Y.; Yanagi, K.; Kurihara, T.; Sasada, Y.; Ohgo, Y. *J. Am. Chem. Soc.* **1981**, *103*, 5805–5812.

[5] Ohashi, Y.; Sasada, Y.; Ohgo, Y. *Chem. Lett.* **1978**, 743–746.

[6] Ohashi, Y.; Yanagi, K.; Kurihara, T.; Sasada, Y.; Ohgo, Y. *J. Am. Chem. Soc.* **1982**, *104*, 6353–6359.

[7] Ohashi, Y.; Uchida, A.; Sasada, Y.; Ohgo, Y. *Acta Crystallogr., Sect. B* **1983**, *B39*, 54–61.

[8] Kurihara, T.; Uchida, A.; Ohashi, Y.; Sasada, Y.; Ohgo, Y.; Baba, S. *Acta Crystallogr., Sect. B* **1983**, *B39*, 431–437.

[9] Kurihara, T.; Ohashi, Y.; Sasada, Y.; Ohgo, Y. *Acta Crystallogr., Sect. B* **1983**, *B39*, 243–250.

[10] Kurihara, T.; Ohashi, Y.; Sasada, Y. *Acta Crystallogr., Sect. B* **1982**, *B38*, 2484–2486.

0002-7863/84/1506-5718$01.50/0

Table II. Final Atomic Coordinates for the Initial Stage at 223 K[a]

atom	x	y	z	B_{eq} or B
Co(A)	0.41260 (7)	0.66125	0.04580 (5)	1.78 ⟨2⟩
O(1A)	0.5838 (4)	0.6617 (2)	0.2604 (3)	2.5 ⟨1⟩
O(2A)	0.1057 (4)	0.6593 (3)	0.0057 (4)	3.5 ⟨1⟩
O(3A)	0.2395 (4)	0.6589 (2)	−0.1714 (4)	3.1 ⟨1⟩
O(4A)	0.7231 (4)	0.6706 (2)	0.0817 (4)	3.0 ⟨1⟩
N(1A)	0.4507 (4)	0.6604 (2)	0.2082 (3)	2.0 ⟨1⟩
N(2A)	0.2195 (4)	0.6585 (2)	0.0869 (4)	2.5 ⟨1⟩
N(3A)	0.3755 (5)	0.6608 (2)	−0.1182 (3)	2.3 ⟨1⟩
N(4A)	0.6057 (4)	0.6658 (2)	0.0033 (4)	2.3 ⟨1⟩
C(1A)	0.3366 (6)	0.6578 (3)	0.2706 (4)	2.7 ⟨1⟩
C(2A)	0.2007 (5)	0.6553 (3)	0.1975 (4)	2.4 ⟨1⟩
C(3A)	0.4879 (6)	0.6662 (3)	−0.1790 (4)	3.0 ⟨2⟩
C(4A)	0.6256 (6)	0.6673 (3)	−0.1081 (4)	3.0 ⟨2⟩
C(5A)	0.3481 (7)	0.6555 (4)	0.4028 (5)	3.9 ⟨2⟩
C(6A)	0.0547 (6)	0.6556 (4)	0.2455 (6)	3.6 ⟨2⟩
C(7A)	0.4738 (9)	0.6698 (4)	−0.3097 (5)	4.2 ⟨2⟩
C(8A)	0.7707 (7)	0.6726 (4)	−0.1591 (7)	4.3 ⟨2⟩
N(5A)	0.4042 (4)	0.7602 (2)	0.0485 (3)	1.8 ⟨1⟩
C(9A)	0.3026 (5)	0.7922 (3)	−0.0206 (4)	2.0 ⟨1⟩
C(10A)	0.2980 (6)	0.8579 (3)	−0.0210 (5)	2.9 ⟨2⟩
C(11A)	0.4032 (6)	0.8926 (3)	0.0451 (5)	3.2 ⟨2⟩
C(12A)	0.5088 (6)	0.8588 (3)	0.1107 (5)	2.8 ⟨1⟩
C(13A)	0.5071 (6)	0.7936 (2)	0.1121 (4)	1.9 ⟨1⟩
C(14A)	0.4232 (5)	0.5612 (2)	0.0371 (4)	2.4 ⟨1⟩
C(15A)	0.2777 (7)	0.5295 (4)	0.0177 (8)	5.2 ⟨2⟩
C(16A)	0.5041 (6)	0.5345 (3)	0.1413 (5)	3.5 ⟨2⟩
O(5A)	0.4504 (6)	0.5161 (3)	0.2292 (4)	4.9 ⟨1⟩
O(6A)	0.6462 (4)	0.5310 (2)	0.1302 (4)	3.6 ⟨1⟩
C(17A)	0.7282 (10)	0.5083 (4)	0.2327 (7)	6.7 ⟨3⟩
Co(B)	0.09007 (7)	0.33784 (4)	0.46060 (6)	2.00 ⟨2⟩
O(1B)	−0.0792 (4)	0.3429 (3)	0.2463 (4)	3.7 ⟨1⟩
O(2B)	0.3991 (4)	0.3423 (2)	0.4977 (4)	3.0 ⟨1⟩
O(3B)	0.2614 (5)	0.3334 (2)	0.6770 (4)	3.2 ⟨1⟩
O(4B)	−0.2172 (4)	0.3379 (3)	0.4232 (4)	3.4 ⟨1⟩
N(1B)	0.0564 (5)	0.3415 (3)	0.2972 (4)	2.8 ⟨1⟩
N(2B)	0.2823 (4)	0.3413 (3)	0.4199 (4)	2.3 ⟨1⟩
N(3B)	0.1286 (5)	0.3338 (2)	0.6243 (4)	2.5 ⟨1⟩
N(4B)	−0.1041 (4)	0.3351 (3)	0.5023 (4)	2.7 ⟨1⟩
C(1B)	0.1650 (6)	0.3418 (3)	0.2363 (4)	3.0 ⟨2⟩
C(2B)	0.3010 (6)	0.3402 (3)	0.3084 (4)	3.0 ⟨2⟩
C(3B)	0.0161 (6)	0.3300 (3)	0.6854 (4)	2.8 ⟨2⟩
C(4B)	−0.1214 (6)	0.3302 (3)	0.6126 (5)	2.7 ⟨1⟩
C(5B)	0.1593 (11)	0.3459 (5)	0.1055 (5)	5.6 ⟨3⟩
C(6B)	0.4492 (7)	0.3451 (4)	0.2621 (7)	4.1 ⟨2⟩
C(7B)	0.0317 (11)	0.3241 (5)	0.8170 (5)	5.3 ⟨3⟩
C(8B)	−0.2656 (7)	0.3307 (4)	0.6652 (7)	4.6 ⟨2⟩
N(5B)	0.0939 (4)	0.2401 (2)	0.4582 (3)	2.3 ⟨1⟩
C(9B)	0.2006 (6)	0.2070 (3)	0.5133 (5)	2.7 ⟨1⟩
C(10B)	0.2102 (7)	0.1415 (2)	0.5154 (5)	2.8 ⟨1⟩
C(11B)	0.1053 (5)	0.1067 (3)	0.4486 (5)	2.7 ⟨1⟩
C(12B)	−0.0040 (7)	0.1403 (3)	0.3862 (5)	3.2 ⟨2⟩
C(13B)	−0.0046 (6)	0.2057 (3)	0.3950 (5)	3.0 ⟨2⟩
C(14B′)	0.0675 (1)	0.4371 (0)	0.4521 (1)	3.1 (2)
C(15B′)	0.1592 (1)	0.4740 (0)	0.3712 (1)	3.5 (2)
C(16B′)	0.0806 (1)	0.4590 (0)	0.5737 (1)	3.6 (2)
O(5B′)	−0.0161 (1)	0.4640 (0)	0.6399 (1)	4.2 (1)
O(6B′)	0.2167 (1)	0.4743 (0)	0.6073 (1)	3.9 (1)
C(17B′)	0.2429 (1)	0.4933 (1)	0.7277 (1)	7.1 (3)
C(14B″)	0.0848 (3)	0.4380 (0)	0.4624 (1)	5.6 (6)
C(15B″)	0.1151 (2)	0.4747 (1)	0.3533 (2)	3.8 (4)
C(16B″)	0.1381 (1)	0.4656 (1)	0.5749 (1)	3.0 (4)
O(5B″)	0.0691 (2)	0.4757 (1)	0.6592 (1)	6.3 (5)
O(6B″)	0.2816 (1)	0.4768 (1)	0.5820 (1)	5.4 (4)
C(17B″)	0.3223 (2)	0.4991 (1)	0.6995 (2)	4.4 (5)
O(M1)	0.1896 (2)	0.9971 (1)	0.1910 (2)	3.2 (4)
O(M2)	0.0950 (2)	1.0535 (1)	−0.0199 (1)	7.1 (4)
O(M3)	0.1461 (2)	0.9736 (1)	0.1779 (1)	2.3 (3)
O(M4)	0.3993 (2)	1.0204 (1)	0.2966 (1)	7.2 (4)
O(M5)	0.4067 (2)	0.9645 (1)	0.5134 (2)	12.0 (7)
C(M1)	0.1147 (2)	1.0135 (1)	0.0820 (2)	6.5 (5)
C(M2)	0.4171 (2)	0.9935 (1)	0.4097 (2)	5.7 (4)

[a] The atoms refined anisotropically have the equivalent isotropic temperature factors, B_{eq}, with esd's in angle brackets. The occupancy factors of the B′ and B″ atoms are 0.685 (8) and 0.315 (8), respectively. The disordered O(M1), O(M2), O(M3), O(M4), O(M5), C(M1), and C(M2) have the occupancy factors of 0.2, 0.4, 0.2, 0.4, 0.4,

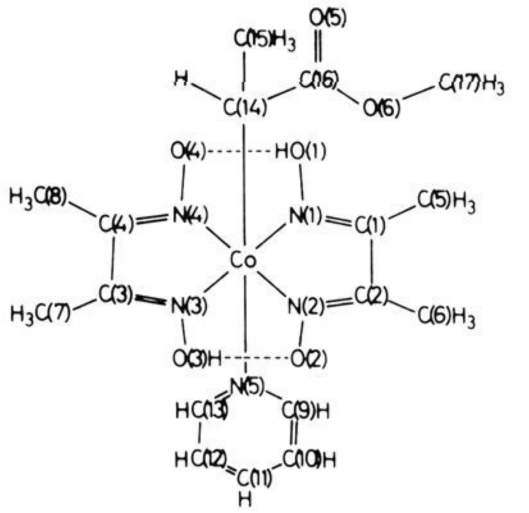

Figure 1. Molecular structure of *R*-mce-py with the numbering of the atoms.

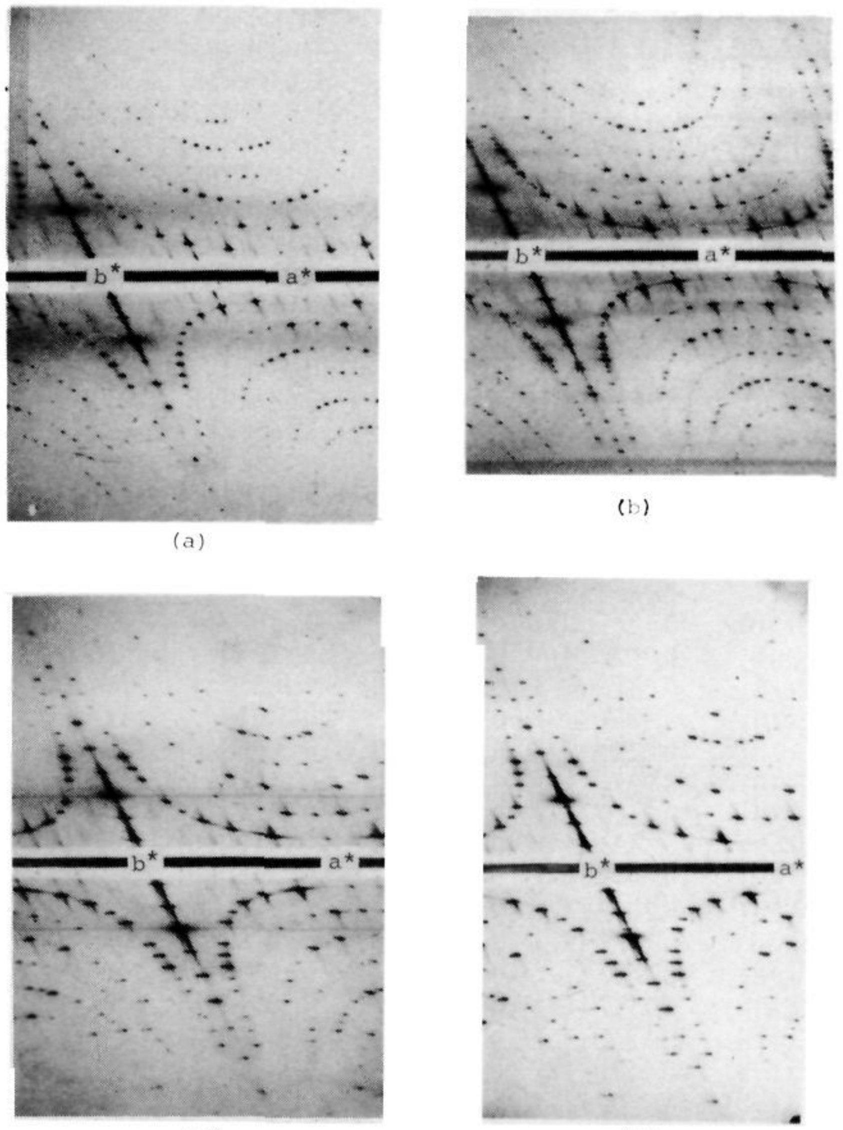

Figure 2. Weissenberg photographs of *hk0* reflections (a) at the initial stage, the crystal being sealed in a capillary tube; (b) at the intermediate stage after 50 h; (c) at the intermediate stage after 140 h; and (d) at the final stage. Fe-filtered Co $K\alpha$ radiation was used. The exposure time for each photograph was about 20 h.

inversion of the bulkier mce group was easier than that of the smaller cn group.

Recently the pure enantiomeric crystals of the pyridine complex containing the mce ligand suitable for X-ray work were obtained. The structure determined at low temperatures indicated that the crsytal contained the solvent methanol. At room temperature, the crystal was changed by X-ray exposure. The rate of the change was very fast at the early stages, but after 140 h it became slow and the diffraction peaks due to the original structure disappeared. The analyzed structure at this stage, to our surprise, indicated that the solvent molecules completely went out from the crystal and the conformation of the mce group greatly changed. The configuration of the mce group, however, was conserved. The temperature was raised, since the change by X-ray exposure was very slow after this stage. The crystal began to change and fully

Table III. Final Atomic Coordinates for the Intermediate Stage

atom	x	y	z	B_{eq}
Co(A)	0.3439 (2)	0.6642	0.1193 (1)	3.53 ⟨5⟩
O(1A)	0.5046 (8)	0.6693 (5)	0.3411 (7)	3.8 ⟨2⟩
O(2A)	0.0393 (8)	0.6685 (6)	0.0770 (8)	5.3 ⟨3⟩
O(3A)	0.1768 (8)	0.6599 (6)	-0.0984 (7)	4.4 ⟨3⟩
O(4A)	0.6492 (9)	0.6645 (7)	0.1608 (8)	5.6 ⟨3⟩
N(1A)	0.3736 (8)	0.6697 (7)	0.2847 (5)	3.5 ⟨3⟩
N(2A)	0.1510 (7)	0.6683 (5)	0.1604 (7)	2.9 ⟨3⟩
N(3A)	0.3120 (8)	0.6632 (6)	-0.0455 (6)	4.0 ⟨3⟩
N(4A)	0.5357 (7)	0.6624 (5)	0.0795 (7)	3.2 ⟨3⟩
C(1A)	0.2620 (9)	0.6687 (8)	0.3456 (7)	3.8 ⟨4⟩
C(2A)	0.1279 (9)	0.6687 (7)	0.2711 (7)	3.3 ⟨3⟩
C(3A)	0.4264 (11)	0.6571 (10)	-0.1061 (8)	5.8 ⟨5⟩
C(4A)	0.5582 (11)	0.6500 (9)	-0.0289 (9)	5.7 (5)
C(5A)	0.2705 (17)	0.6786 (9)	0.4779 (8)	4.5 ⟨4⟩
C(6A)	-0.0201 (12)	0.6723 (9)	0.3169 (14)	5.3 ⟨5⟩
C(7A)	0.4254 (30)	0.6456 (14)	-0.2376 (10)	10.6 ⟨9⟩
C(8A)	0.7012 (15)	0.6502 (12)	-0.0839 (18)	6.7 ⟨6⟩
N(5A)	0.3400 (8)	0.7674 (3)	0.1158 (7)	2.3 ⟨2⟩
C(9A)	0.2440 (11)	0.8001 (5)	0.0439 (9)	3.2 ⟨3⟩
C(10A)	0.2266 (15)	0.8680 (6)	0.0451 (15)	7.0 ⟨6⟩
C(11A)	0.3444 (14)	0.9040 (5)	0.0919 (12)	5.8 ⟨5⟩
C(12A)	0.4524 (13)	0.8726 (5)	0.1624 (12)	5.4 ⟨4⟩
C(13A)	0.4392 (11)	0.8062 (5)	0.1746 (9)	3.9 ⟨4⟩
C(14A)	0.3440 (16)	0.5610 (4)	0.1340 (13)	5.6 ⟨5⟩
C(15A)	0.4767 (20)	0.5292 (9)	0.1935 (21)	9.2 ⟨8⟩
C(16A)	0.2739 (20)	0.5330 (10)	0.0261 (13)	8.4 ⟨9⟩
O(5A)	0.3515 (22)	0.5083 (9)	-0.0422 (12)	11.8 ⟨8⟩
O(6A)	0.1303 (20)	0.5272 (10)	0.0284 (14)	12.1 ⟨8⟩
C(17A)	0.0536 (52)	0.5060 (12)	-0.0793 (27)	14.1 ⟨20⟩
Co(B)	0.1669 (1)	0.3331 (1)	0.3853 (1)	2.58 ⟨4⟩
O(1B)	0.0026 (10)	0.3341 (8)	0.1658 (8)	6.5 ⟨4⟩
O(2B)	0.4724 (8)	0.3296 (6)	0.4343 (8)	4.5 ⟨3⟩
O(3B)	0.3230 (10)	0.3321 (8)	0.6090 (8)	5.9 ⟨3⟩
O(4B)	-0.1423 (9)	0.3360 (8)	0.3413 (10)	6.6 ⟨4⟩
N(1B)	0.1345 (9)	0.3336 (7)	0.2207 (7)	4.5 ⟨3⟩
N(2B)	0.3627 (7)	0.3333 (8)	0.3509 (7)	4.7 ⟨3⟩
N(3B)	0.1951 (9)	0.3419 (6)	0.5503 (6)	3.5 ⟨3⟩
N(4B)	-0.0272 (8)	0.3411 (8)	0.4194 (8)	4.4 ⟨3⟩
C(1B)	0.2516 (10)	0.3305 (8)	0.1636 (8)	3.9 ⟨3⟩
C(2B)	0.3857 (10)	0.3314 (10)	0.2404 (9)	5.0 ⟨4⟩
C(3B)	0.0791 (12)	0.3449 (7)	0.6069 (10)	5.1 ⟨5⟩
C(4B)	-0.0556 (13)	0.3418 (9)	0.5307 (8)	5.0 ⟨4⟩
C(5B)	0.2500 (27)	0.3419 (10)	0.0325 (10)	6.9 ⟨7⟩
C(6B)	0.5335 (14)	0.3400 (9)	0.1947 (16)	5.5 ⟨5⟩
C(7B)	0.0942 (29)	0.3467 (15)	0.7403 (10)	8.9 ⟨9⟩
C(8B)	-0.2053 (17)	0.3523 (13)	0.5710 (17)	8.3 ⟨8⟩
N(5B)	0.1568 (9)	0.2307 (4)	0.3918 (8)	4.0 ⟨3⟩
C(9B)	0.2653 (12)	0.1954 (6)	0.4465 (12)	4.8 ⟨4⟩
C(10B)	0.2572 (12)	0.1281 (5)	0.4582 (10)	3.8 ⟨4⟩
C(11B)	0.1545 (13)	0.0936 (5)	0.3870 (10)	4.2 ⟨4⟩
C(12B)	0.0591 (12)	0.1310 (5)	0.3145 (12)	4.4 ⟨4⟩
C(13B)	0.0606 (11)	0.1982 (5)	0.3210 (9)	3.3 ⟨4⟩
C(14B)	0.1869 (12)	0.4364 (4)	0.3736 (15)	5.3 ⟨5⟩
C(15B)	0.2995 (24)	0.4659 (8)	0.4603 (18)	8.2 ⟨8⟩
C(16B)	0.0434 (15)	0.4659 (10)	0.3733 (11)	7.1 ⟨5⟩
O(5B)	-0.0027 (21)	0.4863 (8)	0.4634 (15)	12.4 ⟨8⟩
O(6B)	-0.0188 (15)	0.4685 (8)	0.2628 (13)	9.7 ⟨6⟩
C(17B)	-0.1621 (20)	0.4921 (15)	0.2309 (33)	15.0 ⟨15⟩

converted to the racemic structure after about 180 h, which has already been reported.[10] To our knowledge, this is the first example that the structure of the intermediate stage in the single crystal-to-single crystal transformation was shown definitely.

The present paper reports details of these quite new findings of the crystalline-state reaction and discusses the possible mechanism of the racemization accompanying the loss of solvent.

Experimental Section

The preparation of *R*-mce-py, which has already been reported,[11] was performed in the dark room to avoid the racemization caused by room light. The complex was dissolved in an aqueous methanol solution and allowed to stand overnight at 278 K in a dark thermostat. Dark red crystals suitable for X-ray work were obtained.

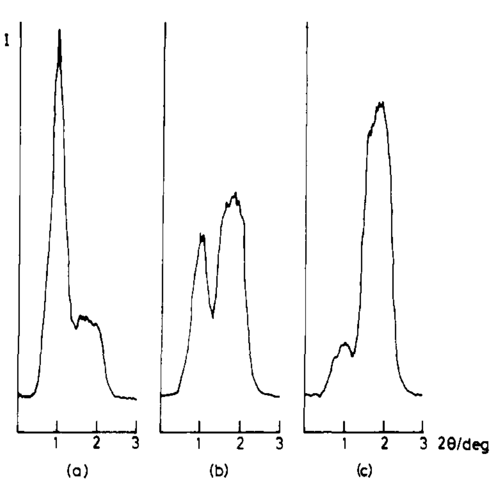

Figure 3. Variation in intensity of 080 reflection, scanned along the ω–2θ direction on the diffractometer: (a) after 0.5 h, (b) after 34 h, and (c) after 85 h. The lower and higher angle peaks, whose absolute 2θ values are 17.03° and 17.88°, indicate the reflections from the initial and intermediate cells, respectively.

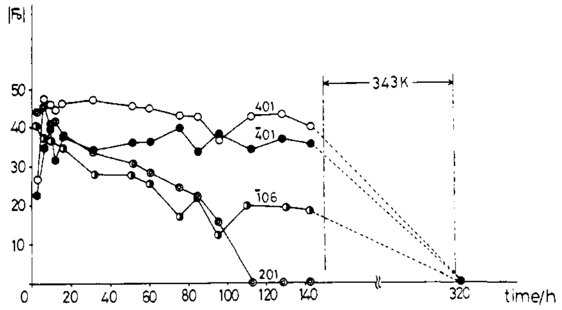

Figure 4. Variation of $|F_o|$'s of four strongest $h0l$ reflections with $h + l$ = odd.

The unit-cell dimensions at the initial, intermediate, and final stages were determined on a Rigaku four-circle diffractometer using the least-squares technique with 12 reflections in the range of 20° $< 2\theta <$ 30°. the low and high temperatures were obtained by the cold-nitrogen-gas-flow and hot-air-flow methods, respectively. Mo Kα radiation monochromated by graphite was used.

The three-dimensional intensity data were collected at the four different stages: the initial stages at 223 and 293 K, intermediate stage at 293 K, and final stage at 293 K. The final structure has been reported.[10]

The intensities at the initial stage at 223 K were measured in the range of $2\theta < 50°$ by the ω–2θ scan, a scanning rate of 4°(θ) min^{-1}, and scan range of (1.0 ± 0.35 tan θ)°, using a crystal of 0.45 × 0.3 × 0.2 mm. Stationary background counts were accumulated for 5 s before and after each scan. In the course of the data collection, the intensities of the three monitor reflections were not significantly changed. The reflections with $|F_o| > 3\sigma(|F_o|)$ were used for the structure determination. No corrections for the absorption and extinction were made.

The intensities at the initial stage at 293 K were collected in the same way as described above, the crystal being sealed in a capillary tube with the mother liquor. Although the reflections of the newly formed cells due to the loss of solvent molecules were not found at all, the crystal was gradually decomposed, which was probably due to the racemization of the mce group by X-ray exposure. When the intensities of the three monitor reflections decreased by 10% of their initial values, the crystal was replaced by another. Two crystals of 0.5 × 0.35 × 0.2 and 0.55 × 0.4 × 0.1 mm were used. About 70 h are necessary for the data collection.

The intensity data at the intermediate stage were also measured with the same method as that at the initial stage, using a crystal of 0.6 × 0.55 × 0.15 mm, which was exposed to X-rays for 144 h at 293 K, not sealed in a capillary tube. The cell dimensions before and after the data collection were not significantly different.

The structures of the three stages were solved by the direct method with the MULTAN 78 program[12] and refined by the constrained full-matrix least-squares with the SHELX 76 program.[13] Since the two crystallo-

---

(11) Ohgo, Y.; Takeuchi, S.; Natori, Y.; Yoshimura, J.; Ohashi, Y.; Sasada, Y. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 3095–3099.

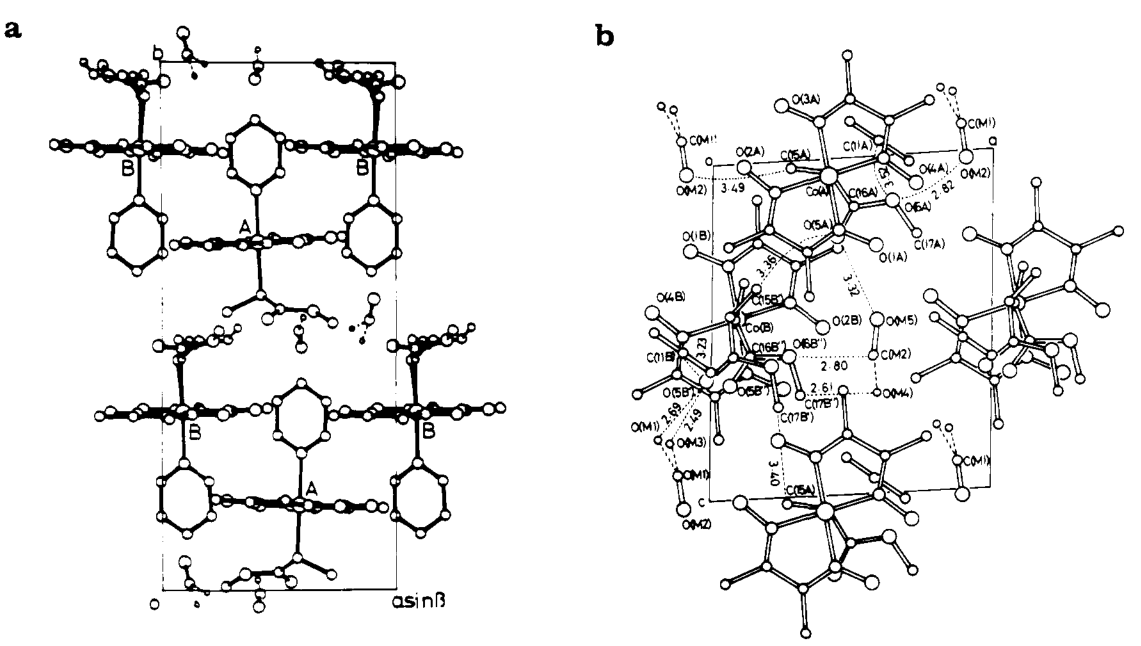

Figure 5. Crystal strucures at the initial stage at 223 K: (a) viewed along the *c* axis and (b) viewed along the *b* axis with short interatomic distances. The disordered methanol bonds are indicated by broken lines.

Table IV. Bond Distances (Å) at the Initial Stage at 223 K

bond	A molecule	B molecule
Co–N(1)	1.868 (5)	1.876 (6)
Co–N(2)	1.879 (5)	1.871 (5)
Co–N(3)	1.885 (5)	1.885 (5)
Co–N(4)	1.886 (5)	1.892 (6)
Co–N(5)	2.063 (4)	2.034 (5)
Co–C(14)	2.088 (5)	2.078 (8)[a]
O(1)–N(1)	1.329 (7)	1.346 (8)
O(2)–N(2)	1.354 (7)	1.351 (7)
O(3)–N(3)	1.359 (7)	1.330 (7)
O(4)–N(4)	1.363 (7)	1.335 (8)
N(1)–C(1)	1.317 (8)	1.263 (9)
N(2)–C(2)	1.293 (8)	1.301 (9)
N(3)–C(3)	1.296 (8)	1.297 (8)
N(4)–C(4)	1.303 (8)	1.288 (9)
C(1)–C(2)	1.461 (9)	1.455 (10)
C(1)–C(5)	1.511 (11)	1.498 (13)
C(2)–C(6)	1.493 (10)	1.507 (10)
C(3)–C(4)	1.462 (10)	1.471 (9)
C(3)–C(7)	1.495 (11)	1.508 (12)
C(4)–C(8)	1.505 (11)	1.502 (11)
N(5)–C(9)	1.359 (7)	1.326 (7)
N(5)–C(13)	1.349 (7)	1.333 (8)
C(9)–C(10)	1.369 (8)	1.366 (8)
C(10)–C(11)	1.392 (8)	1.396 (9)
C(11)–C(12)	1.382 (8)	1.386 (9)
C(12)–C(13)	1.358 (8)	1.364 (9)
C(14)–C(15)	1.501 (11)	1.510 (12)[a]
C(14)–C(16)	1.472 (8)	1.462 (13)[a]
C(16)–O(5)	1.216 (8)	1.218 (13)[a]
C(16)–O(6)	1.331 (8)	1.328 (12)[a]
O(6)–C(17)	1.432 (11)	1.439 (19)[a]

[a] B′ mce group.

graphically independent molecules are closely related to a pseudoinversion center, all the positional parameters were constrained for the bond distances to have the same values as those of the final racemic structure.

In the difference map of the initial structure at 223 K, several peaks were found in the large space between the molecules; interpeak distances are 1.3–1.5 Å. The peaks were assigned as the disordered methanol molecules, since the NMR spectra revealed that the solvent methanol was included in the crystal.[14] Positions of several hydrogen atoms were obtained in the difference map and others were calculated geometrically. Further refinement was performed with the anisotropic and isotropic thermal parameters for non-hydrogen and hydrogen atoms, respectively. The occupancy factors of the methanol molecules were also refined. A weighting scheme of $w = (\sigma^2(|F_o|) + C|F_o|^2)^{-1}$ was applied. The final R value, number of observed reflections, number of parameters, and C value in the weighting scheme are listed in Table I. No peaks other than those of 0.5–0.7 e Å^{-3} around the solvent molecules were found in the final difference map.

In the refinement of the structure at the initial stage at 293 K, many peaks due to the solvent molecules appeared. The largest nine of them were assigned to the atoms of the solvent molecules, and their occupancy factors (0.3) were not refined. There were several peaks of 0.3–0.6 e Å^{-3} around the solvent molecules in the final difference map.

No significant peaks were found between the molecules in the difference map of the intermediate stage. The absolute configuration was determined by Bijvoet's method, using the diffraction intensities of 20 Friedel pairs by Cu Kα radiation.

Atomic scattering factors including the anomalous terms were taken from ref 15. The final atomic coordinates for the non-hydrogen atoms at the initial stage at 223 K and at the intermediate stage are listed in Tables II and III, respectively.[16]

The ^{1}H NMR spectra were measured on JEOL FX-100 spectrometer.

Results and Discussion

Change of the Cell Dimension and Space Group. Figure 2a shows the Weissenberg photograph of *hk*0 reflections using a crystal sealed in a capillary tube with the mother liquor to prevent the loss of solvent molecules. Another crystal, not sealed in a capillary, was exposed to X-rays for 50 h and then the Weissenberg photograph was taken (Figure 2b). The reflection spots are split

---

(12) Main, P.; Lessinger, L.; Woolfson, M. M.; Germain, G.; Declercq, J. P. MULTAN 78 (A system of computer program for the automatic solution of crystal structures from X-ray diffraction data); University of York, England, and Louvain, Belgium, 1978.

(13) Sheldrick, G. M. SHELX 76 (A program for crystal structure determination); University of Cambridge, England, 1976.

(14) The racemic crystal was prepared in a similar way to the present enantiomeric one. The racemic crystal has the same structure as that produced by X-ray exposure and does not contain the solvent molecules. The racemic and enantiomeric crystals were dissolved in CDCl$_3$ solution, respectively, and their ^{1}H NMR spectra were compared with each other. The signal of 3.49 ppm, which is ascribed to the methyl protons of the methoxyl group, is a doublet for the enantiomeric initial crystal, whereas it is a singlet for the racemic crystal. A small amount of methanol was dissolved in the CDCl$_3$ solution of the racemic crystal. The same doublet spectra as those for the enantiomeric crystal were obtained. This indicates that methanol is included in the initial crystal. The integration of the methanol signal suggested that the ratio of methanol to the molecule was about 0.5.

(15) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, pp 72–150.

(16) See paragraph at end of paper regarding supplementary material.

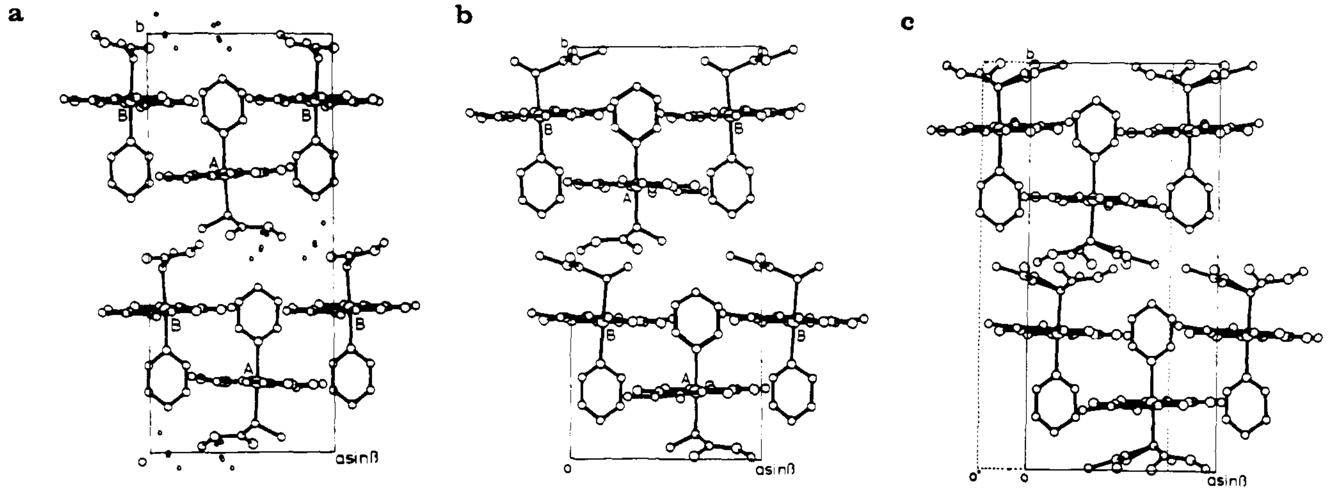

Figure 6. Crystal structures viewed along the c axis: (a) at the initial stage at 293 K and (b) at the intermediate stage. The final racemic structure[10] is shown in (c). In (a) the disordered methanol atoms are drawn with small circles, and in (c) the cell whose origin is coincident with an inversion center is indicated by dotted lines.

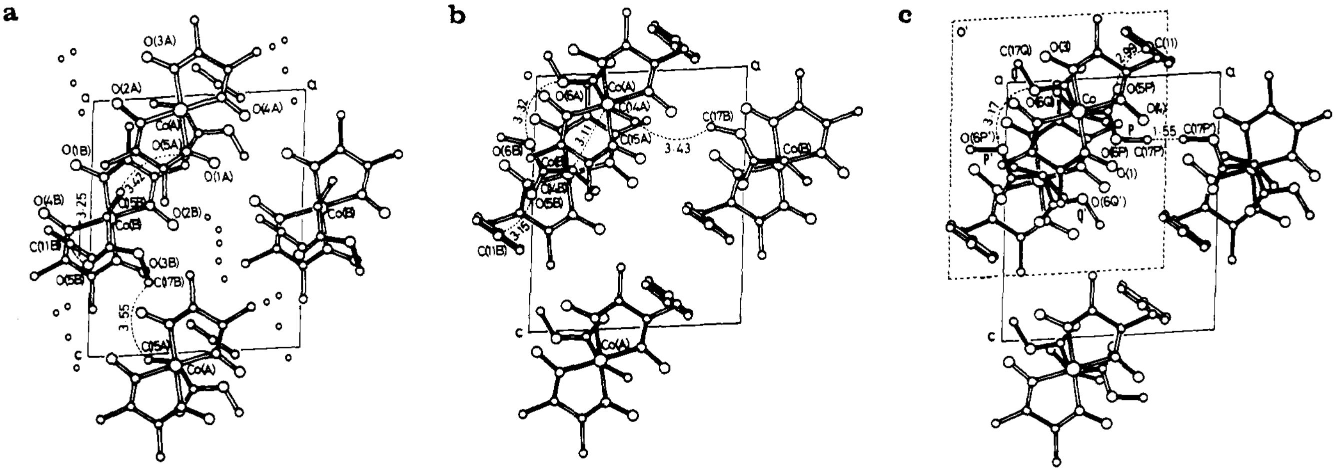

Figure 7. Crystal structures viewed along the b axis: (a) at the initial stage at 293 K, (b) at the intermediate stage, and (c) at the final racemic stage.[10] Several short interatomic distances are shown.

along the b^* axis. Figure 3 shows the change of the 080 reflection, scanned along the $\omega-2\theta$ direction on the diffractometer. The greater is the new peak appearing at higher angle, the smaller is the original peak.

Figure 4 shows the change in the integrated intensities of several strong $h0l$ reflections with $h + l$ = odd. The intensities varied to a great extent at the early stages and after 140 h the change became very slow. Then the crystal was warmed up to 343 K. The intensities of the $h0l$ reflections with $h + l$ = odd decreased and became zero within the experimental error after 180 h. This indicates that the space group of the crystal was converted from noncentrosymmetric $P2_1$ to centrosymmetric $P2_1/n$.

Parts c and d of Figure 2 show the Weissenberg photographs at the intermediate stage after the 140-h exposure and at the final racemic stage, respectively.[17] The two photographs are very similar to each other except the $h00$ reflections with h = odd appearing in Figure 2c.

The cell dimensions at each stage are listed in Table I. It is noteworthy that the values of b and V decrease by 1 Å and 136 Å^3, respectively, which correspond to 5.3% and 6.1% of their initial values.

Initial Structures at 233 and 293 K. Figure 5a shows the initial structure viewed along the c axis at 223 K. The two crystallographically independent molecules A and B are closely related by a noncrystallographic inversion except the chiral mce groups. The cobaloxime planes of the two molecules are approximately perpendicular to the b axis. The mce groups of the A and B molecules, abbreviated hereafter as A and B mce groups, are sandwiched by the two cobaloxime planes. The structure between the two cobaloxime planes viewed along the b axis is shown in Figure 5b, in which some short intermolecular distances (<3.6 Å) are given. The disordered methanol molecules occupy the space around the mce groups. The distance between the two cobalt atoms is 8.877 (1) Å, and the mean separation between the average plane of the two cobaloxime moieties is 6.50 Å.

The B mce group has disordered conformations B′ and B″, whose occupancy factors are 0.685 (8) and 0.315 (8), respectively. Such a disordering is probably brought about by the hydrogen bonds between the carbonyl group of the B′ and B″ mce groups and the disordered methanol molecules. The methyl group and the carbonyl O atom are trans in the B′ and B″ mce groups, whereas they are cis in the A mce group. Such trans and cis conformations were also observed in the crystal of R-mce-Clpy. Bond distances are given in Table IV.

The initial structure at 293 K viewed along the c axis is shown in Figure 6a, and the short interatomic distances are given in Figure 7a. The distance between Co(A) and Co(B) and the mean separation between the two cobaloxime moieties are 8.941 (4) and 6.58 Å, respectively. The structure is essentially the same as that at 223 K, except the conformational ordering of the B mce group. The B mce group takes a stable conformation around the Co–C

---

[17] Two crystals, which were different from those for the data collections, were used for the photographs; one was for Figure 2a and the other was Figure 2b–d. The latter crystal was changed to the intermediate and final stages at nearly the same conditions as for the crystals used for the data collections.

Table V. Torsion Angles (deg) of the mce Group and Pyridine Ligand in the Structures of Four Stages

		initial (223 K)	initial (293 K)	intermediate	final
N(1A)-Co(A)-C(14A)-C(16A)		−21.2 (4)	−19.5 (15)	160.4 (12)	±169.2 (6)[a]
N(3B)-Co(B)-C(14B)-C(16B)	(B′)	−3.9 (6)	−2.2 (15)	−92.1 (13)	±89.4 (8)[b]
	(B″)	11.2 (19)			
N(3A)-Co(A)-N(5A)-C(9A)		40.6 (4)	42.2 (11)	40.8 (8)	±47.3 (7)
N(3B)-Co(B)-N(5B)-C(9B)		−48.7 (5)	−50.7 (14)	−55.5 (10)	

[a] N(1)-Co-C(14)-C(16Q). [b] N(3)-Co-C(14)-C(16P).

bond, since the intermolecular hydrogen bonds between the mce group and the solvent molecules become weak at room temperature.

Intermediate Structure. Figure 6b shows the intermediate structure viewed along the *c* axis. The solvent methanol molecules completely went out from the crystal. The crystal contracts to a great extent along the *b* axis, and the molecules slightly shift to fill the vacant space due to the loss of solvent. The distance between Co(A) and Co(B), 7.542 (3) Å, and the mean separation between the average planes of the two cobaloximes, 6.80 Å, become shorter and longer than the corresponding ones of the initial structure at 293 K, respectively.

The structure around the pseudoinversion center between the A and B molecules is drawn in Figure 7b. Although the loose contacts are observed around the methoxycarbonyl group of the A mce group and the methyl group, C(15B), of the B mce group, the interatomic distances of C(14A)···C(14B) and O(5B)···(C′-(11B) are considerably shorter than the usual van der Waals contacts.

Final Racemic Structure. Figure 6c shows the final racemic structure viewed along the *c* axis.[10] The crystal contracts further along the *b* axis, and the volume of the unit cell decreases by 14 Å^3. This suggests that the molecules in the racemic structure are more closely packed than those in the chiral intermediate structure. The pseudoinversion center between the A and B molecules changed to a crystallographic inversion center. Both of the A and B mce groups take disordered conformations and fill the void space after the loss of solvent.

Figure 7c illustrates the two molecules around an inversion center. There is an approximate mirror plane passing through the two cobalt atoms and normal to the cobaloxime planes. The Co···Co distance becomes 7.856 (2) Å and the separation between the two cobaloxime planes is 6.76 (1) Å.

The two mce groups around the inversion center have four conformations: P, Q, P′, and Q′, as indicated in Figure 7c. Since the shortest contact between the two mce groups, O(6P)···O(6Q′), is 3.17 (7) Å, any of four combinations composed of the two mce groups, (P, P′), (P, Q′), (Q, P′), and (Q, Q′), may be possible around the inversion center. However, there is an unusually short contact, 1.55 (10) Å for C(17P)···C(17P‴), around the other inversion center. This suggests that only the (P, P′) combination depends on whether the combination in the neighboring cells is (P, P′) or not and that the inversion of the mce group occurs cooperatively not only in a unit cell but also among the neighboring cells.

Conformational Change of the mce Group. The torsion angles around the Co–C and Co–N bonds at each stage are listed in Table V. The conformation of the A and B mce groups varies to a great extent at the intermediate and final stages, whereas that of the pyridine ligand has similar torsion angles at each stage. In order to examine the conformational change in the process of loss of solvent, the cobaloxime moieties and mce groups of the A and B molecules at the intermediate stage are superimposed on the structure of the initial stage in Figure 8a, in which the slight change of the cobaloxime moieties between the two stages is ignored. The A mce group rotates by about 180° around the Co–C bond. The B mce group, on the other hand, rotates around the C(14)–C(16) bond to take a cis conformation in addition to the rotation of about 90° around the Co–C bond.

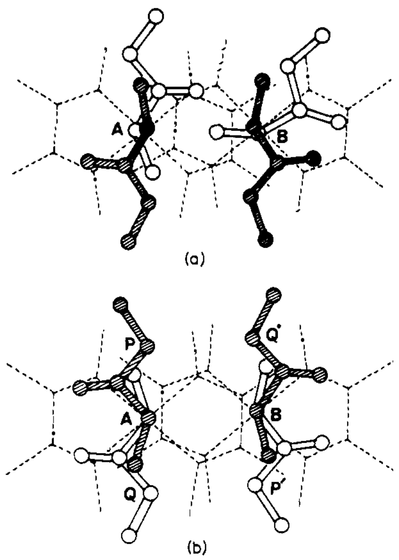

Figure 8. Conformational changes of the mce group: (a) from the initial (unshaded) to intermediate stages (shaded) and (b) from the intermediate (unshaded) to final stages (unshaded and shaded). The structure of the cobaloxime moieties before the change is indicated by broken lines.

Figure 8b shows the superposition of the final racemic structure upon the intermediate one. Each half of the A and B mce groups changes to their mirror image (shaded groups), and each molecule becomes the 1:1 disordered racemates.

Cis–Trans Conversion of the mce Group. At the initial stage, the carbonyl O atom and the methyl group are trans in the B mce group whereas they are cis in the A mce group. The trans conformation is converted to cis at the intermediate and final stages. Such trans and cis conformations of the two independent mce groups at the initial stage were also observed in the crystal of *R*-mce-Clpy, and the trans–cis conversion was proposed to be a factor causing the racemization.[9] Since the rate of the racemization was negligibly small after the trans–cis conversion in the present crystal, this is not a factor for inducting the racemization, although it would be true that the trans conformation is less stable than the cis.

When the present crystals were dissolved in a $CDCl_3$ solution, only the cis conformation was observed in NMR spectra.[18] These results indicate that the methoxycarbonyl group can rotate around the C–C bond in solution and in the crystalline state to relieve the steric repulsion between the methoxyl and methyl groups.

Energy Difference between the Rotation and Inversion. The absolute structure of the crystal at the intermediate stage was determined by using the anomalous dispersion technique, and the configuration of the mce group was proved to be retained in the course of the loss of solvent. This indicates that at 293 K the initial structure is hardly converted to the inverse structure although it is easily changed at 343 K, since the final racemic structure is

---

(18) The doublet signal of 0.398 ppm for the $CDCl_3$ solution of the initial crystals, which is ascribed to the methyl protons of the mce group, was the same as that for the racemic crystal, and no other signals assigned to the methyl protons were observed. Since the signal for the methyl group with trans conformation must be different from that of cis, the conformation of the B mce group seems to be converted to cis immediately after the initial crystals are dissolved in a $CDCl_3$ solution.

very similar to the superposition of the intermediate structure and its mirror image.

The cleavage of the Co–C bond in the mce complexes is considered to be easier than that in the cyanoethyl complexes, since the rate of the racemization of the mce group by visible light is faster than that of the cyanoethyl complexes in an aqueous methanol solution.[19] This suggests that the (methoxycarbonyl)ethyl radical would be formed in the present crystal by X-ray exposure at 293 K, but the rotation of the radical is prohibited. The crystal structure clearly distinguishes the difference between the rotation of the mce radical, as a whole, and that of the methoxycarbonyl group around the Co–C or C–C bond. Further study to clarify the details of this reaction is in progress.

Acknowledgment. We are grateful to Dr. N. Hirayama and Dr. K. Shirahata for measurement of NMR spectra and valuable discussion. This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture, Japan (No. 56430005).

Registry No. *R*-mce-py·CH_3OH, 91328-25-5; *R*-mce-py, 80514-20-1; mce-py, 37824-56-9.

Supplementary Material Available: A table of the final atomic coordinates for non-H atoms of the initial stage at 293 K, a list of bond distances at the initial stage at 293 K and at the intermediate stage, and tables of the observed and calculated structure factors, anisotropic thermal parameters for non-H atoms, and positional and thermal parameters for H atoms at the initial stage at 223 and 293 K and at intermediate stage (57 pages). Ordering information is given on any current masthead page.

---

(19) Ohgo, Y.; Baba, S.; Ohtera, C.; Wada, H.; Takeuchi, S.; Hirata, H. "Abstracts of Papers", Joint Meeting of CSJ and SPSJ, Niigata, Japan, 1981; p 41.

Communications to the Editor

Electrochemistry of Porphyrins Containing a Metal–Metal σ Bond. Reduction of (TPP)In(M(CO)$_3$Cp) Complexes where M = Mo and W

P. Cocolios,[1a] D. Chang,[1a] O. Vittori,[1a,c] R. Guilard,[1b]
C. Moise,[1b] and K. M. Kadish*[1a]

Department of Chemistry, University of Houston
Houston, Texas 77004
and Laboratoire de Synthèse et d'Electrosynthèse
Organométallique associé au CNRS (LA 33)
Faculté des Sciences "Gabriel"
6 Bd. Gabriel, 21100 Dijon, France

Received May 3, 1984

The synthesis and characterization of a promising new class of porphyrin complexes with a bi- or trinuclear framework has recently been reported.[2-4] These compounds are of the form (P)M(M'L) where (P)M is a metalloporphyrin and M'L is an axial ligand of the type $M(CO)_X(\eta^5\text{-}C_5H_5)_Y$. No electrochemical data have ever been reported for metalloporphyrins containing a metal–metal bond but it was expected that the porphyrin ring would be able to stabilize the singly and possibly doubly reduced metal–metal bonded system. This, indeed, is the case as we wish to report in this communication.

We have selected two complexes for our initial electrochemical investigation. These are (TPP)In(Mo(CO)$_3$Cp) and (TPP)In(W(CO)$_3$Cp) where Cp = $\eta^5\text{-}C_5H_5$. For comparison, we have also included the electrochemistry of (TPP)InClO$_4$. The electrochemistry of this compound has never been reported.

(TPP)InClO$_4$ (**1**) was synthesized from (TPP)InCl[5] by metathesis of the axial ligand using a stoichiometric amount of $AgClO_4$ in boiling tetrahydrofuran. The obtained product showed characteristic IR stretching frequencies for a bound perchlorate group[6] at 1140, 1100, 1020, 890, and 625 cm^{-1}. (TPP)In(M(CO)$_3$Cp), where M = Mo, **2**, or M = W, **3**, was prepared by reaction of (TPP)InCl with the $[M(CO)_3Cp]^-$ anion according

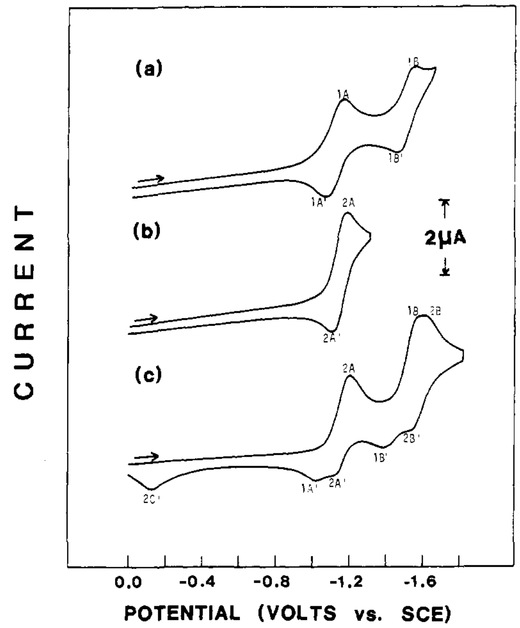

Figure 1. Cyclic voltammograms illustrating (a) two successive reductions of 1.2 × 10^{-3} M (TPP)InClO$_4$, (b) first reduction of 1.1 × 10^{-3} M (TPP)In(Mo(CO)$_3$Cp), and (c) two successive reductions of 1.1 × 10^{-3} M (TPP)In(Mo(CO)$_3$Cp) in CH_2Cl_2, 0.1 M TBAP. Scan rate = 100 mV/s. The numerical part of the peak notation indicates the investigated compound (**1**, **2**, or **3**) while A, B and A',B' indicate the first and second reduction and reoxidation peaks, respectively.

Table I. Half-Wave Potentials for Reduction of (TPP)InClO$_4$, (TPP)In(Mo(CO)$_3$Cp), and (TPP)In(W(CO)$_3$Cp) in CH_2Cl_2, 0.1 M TBAP

	$E_{1/2}$, V vs. SCE	
compd	1st redn	2nd redn
(TPP)InClO$_4$ (**1**)	-1.10	-1.48
(TPP)In(Mo(CO)$_3$Cp) (**2**)	-1.15	-1.54[a]
(TPP)In(W(CO)$_3$Cp) (**3**)	-1.21	-1.57[a]

[a] Potential quoted is at -74 °C.

---

(1) (a) University of Houston. (b) Laboratoire de Synthèse et d'Electrosynthèse Organométallique associé au CNRS (LA 33). (c) On leave from the Ecole Supérieure de Chimie Industrielle de Lyon, France.

(2) Cocolios, P.; Moise, C.; Guilard, R. *J. Organomet. Chem.* **1982**, *228*, C43.

(3) Onaka, S.; Konda, Y.; Toruimi, K.; Ito, T. *Chem. Lett.* **1980**, 1605.

(4) Barbe, J. M.; Guilard, R.; Lecomte, C.; Gerardin, R., *Polyhedron*, in press.

(5) Bhatti, M.; Bhatti, W.; Mast, E. *Inorg. Nucl. Chem. Lett.* **1972**, *8*, 133.

0002-7863/84/1506-5724$01.50/0