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Crystalline-State Racemization of Cobaloxime Complexes. 21. Racemization of a Bulky (*R*)-1,2-Bis(ethoxycarbonyl)ethyl Group

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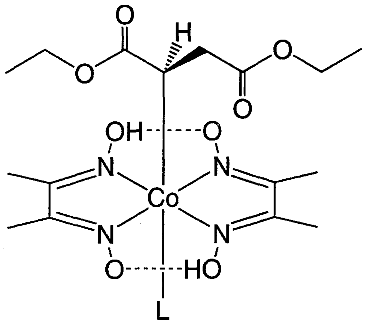
Three cobaloxime complexes with a chiral 1,2-bis(ethoxycarbonyl)ethyl group bonded to the cobalt atom: [(*R*)-1,2-bis(ethoxycarbonyl)ethyl]bis(dimethylglyoximato-*N*,*N*′)[(*S*)-1-phenylethylamine]cobalt(III), **1**, [(*R*)-1,2-bis(ethoxycarbonyl)ethyl]bis(dimethylglyoximato-*N*,*N*′)(pyridine)cobalt(III), **2**, and [(*R*)-1,2-bis(ethoxycarbonyl)ethyl]bis(dimethylglyoximato-*N*,*N*′)(propylamine)cobalt(III), **3**, were analyzed by X-rays. The cell dimensions of **2** were remarkably changed when the crystal was irradiated with a xenon lamp. The structure after the irradiation indicated that the chiral 1,2-bis(ethoxycarbonyl)ethyl group was changed to the disordered racemates retaining the single crystal form. The other two crystals showed no change after the irradiation in the same conditions. Comparing the reaction cavities among four crystals analyzed so far, the shape rather than size of the cavity may play an important role in the crystalline-state racemization.

The crystal structures of bis(dimethylglyoximato-*N*,*N*′)-cobalt(III), cobaloxime, complexes bonded to a alkyl group have been analyzed to elucidate the mechanism of the photo racemization since the crystal of the cobaloxime complex with a chiral 1-cyanoethyl group was found to be racemized on exposure to X-rays or visible light without degradation of the single crystal form.[1,2] Not only 1-cyanoethyl (ce) group but also 1-(methoxycarbonyl)ethyl (mce),[3] and 1,2-bis(methoxycarbonyl)ethyl (bmce)[4] groups bonded to the cobalt atom in the cobaloxime complexes have been found to be racemized on exposure to a xenon lamp with retention of crystallinity. Such racemizations have not been observed for the cobaloxime complexes with bulkier chiral groups such as 1,2-bis(ethoxycarbonyl)ethyl (bece)[5] and 1,2-bis(allyloxycarbonyl)ethyl (bace) groups.[6,7] This may indicate that the bulkier is the chiral alkyl group, the more difficult is the racemization. Although the bmce group is rather bulky, two favorable conditions such as two-step inversion of the chiral group and cooperative motion of the two crystallographically independent molecules may make it possible for the bulky group to be inverted with retention of the single crystal form.[8]

Recently the three cobaloxime complexes with a chiral bece group were synthesized; the axial base ligands are (*S*)-1-phenylethylamine, **1**, pyridine, **2**, and propylamine, **3** (Scheme 1). When the powdered samples of the three compounds were irradiated with a xenon lamp, the sample of **2** showed the racemization very rapidly, whereas those of **1** and **3** were racemized very slowly. This indicated that the crystal of **2** may be racemized with retention of the single crystal form. When a single crystal was irradiated to a xenon lamp on the diffractometer, the cell dimensions gradually changed. The crystal structures before and after enough irradiation were analyzed by X-rays. A half of the bulky chiral groups were inverted to the opposite configuration. The chiral group was transformed to the disordered racemates. This paper reports the mechanism of the photoracemization of the bulky bece group in a crystal and discusses the relation between the crystal structure and the reactivity.



L= **1** (*S*)-1-Phenylethylamine
2 Pyridine
3 Propylamine

Scheme 1. Schematic structures of **1**, **2**, and **3**.

Experimental

The crystals of **1**, **2**, and **3** were kindly supplied from Prof. Ohgo and Dr. Arai. The method of the preparation has been reported.[9]

Structure Analysis. The crystal structures of **1**, **2**, and **3** were analyzed by X-rays. The measurements were performed at 296 K. The crystal data and the experimental details are listed in Table 1. Although the crystal of **1** includes one solvent 2-propanol molecule in an asymmetric unit, it was not decomposed during the data collection without sealing it in a glass capillary. The structures were solved by the direct or Patterson method using the teXsan program package[10] and were refined with SHELXL-97[11] or SHELXL-93.[12] All the non-hydrogen atoms were refined with anisotropic temperature factors. The hydrogen atoms were located geometrically and the parameters including isotropic temperature factors were re-

Table 1. Crystal Data and Experimental Details

	1	**2**	**2′**	**3**
Formula	$C_{24}H_{38}CoN_5O_8 \cdot C_3H_8O$	$C_{21}H_{32}CoN_5O_8$	$C_{21}H_{32}CoN_5O_8$	$C_{22}H_{36}CoN_5O_8$
Formula weight	643.62	541.45	541.45	557.49
Crystal system	Monoclinic	Orthorhombic	Orthorhombic	Orthorhombic
Space group	$P2_1$	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$
a/Å	9.907(3)	16.772(1)	16.801(3)	15.859(6)
b/Å	15.801(2)	16.802(1)	16.963(3)	16.817(1)
c/Å	11.502(2)	9.132(1)	9.142(2)	9.408(2)
β/°	113.10(2)	—	—	—
V/Å^3	1658.8(6)	2573.6(3)	2605.4(9)	2509(1)
Z	2	4	4	4
D_{calc}/g cm^{-3}	1.289	1.397	1.380	1.476
Diffractometer	Rigaku AFC-5R	Rigaku AFC-7S	Rigaku AFC-5R	Rigaku AFC-5R
Radiation/Å	0.71073 (Mo $K\alpha$)	0.71073 (Mo $K\alpha$)	0.71073 (Mo $K\alpha$)	0.71073 (Mo $K\alpha$)
Crystal dimensions/mm^3	0.35 × 0.15 × 0.10	0.35 × 0.30 × 0.15	0.50 × 0.45 × 0.10	0.45 × 0.40 × 0.10
Scan type	ω–2θ	ω–2θ	ω–2θ	ω–2θ
Absorption correction	ψ scans ($0.847 < T < 0.919$)	None	None	ψ scans ($0.857 < T < 1.000$)
θ_{max}/°	27.48	27.50	27.50	27.50
Range of h, k, l	0—12, 0—20, −14—13	0—21, 0—21, 0—11	0—21, 0—22, 0—11	0—20, 0—21, 0—12
No. of measured reflections	3957	3347	3392	3269
No. of independent reflections	3412	3321	3366	3243
No. of observed reflections [$I > 2\sigma(I)$]	2403	2086	1723	1894
$R(F)$ [$I > 2\sigma(I)$]	0.053	0.041	0.064	0.054
$wR(F^2)$	0.123	0.097	0.135	0.107
S	1.018	1.063	1.208	1.140
No. of reflections used in refinement	3412	3321	3366	3243
No. of refined parameters	380	322	293	305
$(\Delta/\sigma)_{max}$	0.024	< 0.001	< 0.001	0.018
$(\Delta\rho)_{max}$/e Å^{-3}	0.27	0.32	0.35	0.50
$(\Delta\rho)_{min}$/e Å^{-3}	−0.37	−0.33	−0.30	−0.36
Flack χ parameter	−0.01(4)	0.01(1)	−0.07(5)	−0.02(4)
Weighting scheme [$P = (F_o^2 + 2F_c^2)/3$]	$1/[\sigma^2(F_o^2) + (0.0439P)^2]$	$1/[\sigma^2(F_o^2) + (0.0520P)^2]$	$1/[\sigma^2(F_o^2) + (0.0666P)^2]$	$1/[\sigma^2(F_o^2) + (0.0504P)^2]$

fined. The absolute structures deduced from the Flack parameter[13] are consistent with those assumed from the optical rotation of the compounds. The coordinates of the non-hydrogen atoms of **1**, **2**, and **3** are listed in Tables 2(a), (b), and (c), respectively.

Table 2. Coordinates and Equivalent Isotropic Displacement Parameters for non-H Atoms

Atom	*x*	*y*	*z*	B_{eq}
(a) (*S*)-1-Phenylethylamine Complex, **1**				
Co	0.48056(8)	0.48495(7)	0.11831(7)	2.8
O1	0.7496(5)	0.5445(4)	0.3042(4)	4.8
O2	0.1896(5)	0.5282(3)	0.0844(5)	4.6
O3	0.2129(6)	0.4158(3)	−0.0571(4)	4.9
O4	0.7733(5)	0.4391(4)	0.1502(5)	5.0
O5	0.5853(6)	0.5444(4)	−0.1436(5)	5.4
O6	0.7138(6)	0.6151(4)	0.0364(5)	5.3
O7	0.3950(6)	0.7280(3)	−0.1615(4)	4.9
O8	0.1825(5)	0.6729(3)	−0.2877(5)	5.8
N1	0.6037(6)	0.5521(4)	0.2544(5)	3.5
N2	0.3322(6)	0.5421(4)	0.1497(5)	3.3
N3	0.3585(7)	0.4165(3)	−0.0182(5)	3.7
N4	0.6266(7)	0.4280(4)	0.0826(5)	3.8
N5	0.4925(7)	0.3885(4)	0.2439(5)	3.4
C4	0.583(1)	0.3762(5)	−0.0117(9)	5.0
C3	0.424(1)	0.3689(5)	−0.0694(8)	4.6
C2	0.3784(9)	0.5959(5)	0.2424(7)	3.9
C1	0.5346(9)	0.6006(5)	0.3036(6)	3.8
C5	0.615(1)	0.6558(6)	0.4174(7)	6.1
C6	0.274(1)	0.6444(6)	0.2818(8)	6.5
C7	0.345(1)	0.3117(7)	−0.1801(8)	7.9
C8	0.685(1)	0.3274(6)	−0.054(1)	8.1
C9	0.4703(7)	0.5836(4)	−0.0029(6)	3.2
C10	0.5915(9)	0.5788(5)	−0.0470(7)	3.9
C11	0.845(1)	0.6074(7)	0.013(1)	8.3
C12	0.906(1)	0.6871(8)	0.004(1)	12.0
C13	0.3231(8)	0.5908(5)	−0.1161(6)	4.1
C14	0.3082(9)	0.6701(5)	−0.1870(7)	3.9
C15	0.151(1)	0.7489(6)	−0.3663(8)	7.5
C16	0.004(1)	0.7407(8)	−0.462(1)	12.2
C17	0.3569(9)	0.3570(5)	0.2616(8)	3.8
C18	0.387(1)	0.2650(5)	0.3096(8)	6.0
C19	0.3181(8)	0.4103(5)	0.3527(6)	4.0
C20	0.4199(9)	0.4360(6)	0.4669(7)	5.4
C21	0.3775(9)	0.4790(8)	0.5529(7)	6.6
C22	0.232(1)	0.4932(9)	0.5239(8)	7.2
C23	0.1302(9)	0.4674(7)	0.4106(8)	7.1
C24	0.1738(9)	0.4276(6)	0.3259(7)	5.6
O1S	0.2181(6)	0.9320(4)	0.5003(5)	5.9
C1S	0.106(1)	1.0196(8)	0.317(1)	11.0
C2S	0.112(1)	0.9374(7)	0.3717(8)	6.7
C3S	0.148(1)	0.8665(7)	0.304(1)	9.9
(b) Pyridine Complex, **2**				
Co	0.00110(5)	−0.02710(3)	0.00499(7)	2.3
O1	0.0493(2)	−0.0932(2)	−0.2676(4)	3.9
O2	−0.1492(2)	0.0372(2)	0.0835(4)	4.0
O3	−0.0476(2)	0.0366(2)	0.2808(4)	3.9
O4	0.1563(2)	−0.0791(2)	−0.0803(4)	4.2
O5	0.0541(3)	−0.1864(3)	0.2568(5)	5.4
O6	0.0674(3)	−0.2267(2)	0.0243(5)	5.4
O7	−0.1247(4)	−0.2767(3)	0.1447(7)	8.8
O8	−0.1852(3)	−0.2183(3)	0.3306(5)	5.8
N1	−0.0111(3)	−0.0614(2)	−0.1897(4)	2.7
N2	−0.1062(2)	0.0011(3)	−0.0200(5)	3.0
N3	0.0125(3)	0.0061(2)	0.2009(4)	3.1
N4	0.1105(2)	−0.0507(3)	0.0283(5)	3.1
N5	0.0296(2)	0.0839(2)	−0.0706(4)	2.6
C1	−0.0791(4)	−0.0492(3)	−0.2496(6)	3.3
C2	−0.1364(3)	−0.0113(3)	−0.1494(6)	3.3
C3	0.0830(3)	−0.0009(4)	0.2573(6)	3.6
C4	0.1410(3)	−0.0328(4)	0.1543(6)	3.8
C5	−0.0990(4)	−0.0669(4)	−0.4062(6)	5.4
C6	−0.2197(3)	0.0118(5)	−0.1863(8)	5.8
C7	0.1023(4)	0.0238(4)	0.4110(6)	5.2
C8	0.2269(3)	−0.0450(4)	0.1904(9)	6.2
C9	−0.0365(5)	−0.1386(3)	0.0741(5)	2.8
C10	0.0321(3)	−0.1843(3)	0.1307(6)	3.9
C11	0.1368(6)	−0.2727(6)	0.064(1)	9.9
C12	0.1554(7)	−0.3276(7)	−0.042(2)	16.2
C13	−0.1016(3)	−0.1376(3)	0.1890(7)	3.8
C14	−0.1370(4)	−0.2183(3)	0.2145(7)	4.2
C15	−0.2252(5)	−0.2931(5)	0.367(1)	8.0
C16	−0.2823(6)	−0.2766(6)	0.482(1)	12.8
C17	0.0664(3)	0.0944(3)	−0.1984(6)	3.6
C18	0.0753(4)	0.1669(3)	−0.2638(6)	4.7
C19	0.0452(5)	0.2328(3)	−0.1961(7)	5.4
C20	0.0095(4)	0.2240(3)	−0.0610(6)	4.4
C21	0.0014(3)	0.1500(2)	−0.0029(5)	3.5
(c) Propylamine Complex, **3**				
Co	0.77274(5)	0.74828(6)	0.32994(8)	2.6
O1	0.7136(3)	0.6951(3)	0.6002(5)	4.0
O2	0.8180(3)	0.9061(3)	0.2486(6)	4.7
O3	0.8327(3)	0.8020(3)	0.0607(5)	4.7
O4	0.7064(3)	0.5971(3)	0.4008(5)	3.9
O5	0.9481(4)	0.7957(3)	0.5653(6)	5.2
O6	0.9781(3)	0.8234(3)	0.3358(6)	4.3
O7	1.0481(3)	0.6334(4)	0.4671(7)	5.8
O8	0.9760(3)	0.5369(3)	0.5744(6)	5.4
N1	0.7445(3)	0.7576(4)	0.5232(5)	3.2
N2	0.7942(4)	0.8578(3)	0.3541(6)	3.5
N3	0.8013(3)	0.7406(4)	0.1357(5)	3.4
N4	0.7424(3)	0.6412(3)	0.3004(6)	3.2
N5	0.6496(4)	0.7778(3)	0.2846(6)	3.9
C1	0.7487(4)	0.8278(5)	0.5795(8)	3.9
C2	0.7786(5)	0.8878(4)	0.4790(8)	3.6
C3	0.7885(5)	0.6720(5)	0.0764(7)	3.6
C4	0.7524(4)	0.6142(4)	0.1720(8)	3.5
C5	0.7209(6)	0.8454(6)	0.7274(8)	6.0
C6	0.7883(5)	0.9736(4)	0.516(1)	5.9
C7	0.8053(6)	0.6562(6)	−0.0790(8)	6.2
C8	0.7266(6)	0.5327(5)	0.129(1)	6.2
C9	0.8940(4)	0.7119(4)	0.3838(7)	2.8
C10	0.9426(4)	0.7800(4)	0.4405(8)	3.5
C11	1.0187(5)	0.8961(5)	0.381(1)	6.5
C12	1.0567(7)	0.9339(7)	0.259(1)	10.4
C13	0.8967(4)	0.6421(4)	0.4851(9)	3.9
C14	0.9824(4)	0.6064(4)	0.5053(8)	3.6
C15	1.0539(6)	0.4925(5)	0.598(1)	7.3
C16	1.0296(7)	0.4174(6)	0.664(1)	10.3
C17	0.6229(6)	0.8004(7)	0.142(1)	8.4
C18	0.5376(6)	0.8244(7)	0.116(1)	7.4
C19	0.5232(7)	0.8485(9)	−0.034(1)	10.1
(d) Pyridine Complex After Irradiation, **2′**				
Co	0.00211(8)	0.47700(6)	−0.52173(9)	3.3
O1	−0.0437(4)	0.4064(3)	−0.2502(7)	5.4
O2	0.1517(4)	0.5412(4)	−0.5992(7)	6.2
O3	0.0487(4)	0.5408(4)	−0.7971(6)	5.8
O4	−0.1515(4)	0.4213(4)	−0.4370(7)	5.3
N1	0.0153(5)	0.4415(4)	−0.3278(7)	4.1
N2	0.1089(4)	0.5067(4)	−0.4962(8)	4.9
N3	−0.0112(4)	0.5118(4)	−0.7165(6)	4.2
N4	−0.1073(4)	0.4519(4)	−0.5437(7)	3.5
N5	−0.0278(4)	0.5861(3)	−0.4423(6)	3.1
C1	0.0822(6)	0.4551(5)	−0.267(1)	4.6
C2	0.1385(6)	0.4958(7)	−0.366(1)	5.6
C3	−0.0820(6)	0.5022(6)	−0.771(1)	5.1
C4	−0.1380(7)	0.4700(6)	−0.669(1)	4.4
C5	0.1034(7)	0.4377(6)	−0.112(1)	7.4

Table 2. (continued)

Atom	*x*	*y*	*z*	B_{eq}	Atom	*x*	*y*	*z*	B_{eq}
C6	0.2215(6)	0.5208(8)	−0.328(1)	8.8	O6B	−0.069(1)	0.275(1)	−0.517(2)	6.6
C7	−0.1003(6)	0.5268(7)	−0.9271(9)	7.1	O7B	0.159(1)	0.211(1)	−0.569(2)	8.2
C8	−0.2241(5)	0.4562(7)	−0.706(1)	7.7	O8B	0.182(1)	0.280(1)	−0.760(2)	7.6
O5A	−0.0507(8)	0.3346(8)	−0.789(1)	5.4	C9B	0.045(1)	0.376(1)	−0.629(2)	4.7
O6A	−0.0430(9)	0.2801(9)	−0.567(2)	6.6	C10B	−0.029(1)	0.341(2)	−0.627(2)	5.4
O7A	0.117(1)	0.2197(9)	−0.656(2)	8.2	C11B	−0.141(2)	0.232(2)	−0.553(4)	9.8
O8A	0.1789(9)	0.281(1)	−0.832(2)	7.6	C12B	−0.149(3)	0.169(3)	−0.437(6)	14.4
C9A	0.038(1)	0.362(1)	−0.578(2)	4.7	C13B	0.114(1)	0.366(1)	−0.548(2)	4.2
C10A	−0.023(1)	0.329(1)	−0.671(2)	5.4	C14B	0.151(1)	0.268(1)	−0.628(2)	4.1
C11A	−0.115(2)	0.233(2)	−0.599(3)	9.8	C15B	0.214(2)	0.204(2)	−0.820(4)	8.0
C12A	−0.128(3)	0.182(3)	−0.468(5)	14.4	C16B	0.281(2)	0.217(3)	−0.926(4)	14.2
C13A	0.1020(9)	0.3610(9)	−0.692(2)	4.2	C17	0.0022(6)	0.6512(4)	−0.5023(8)	4.8
C14A	0.135(1)	0.2799(9)	−0.720(2)	4.1	C18	−0.0067(6)	0.7254(5)	−0.4421(9)	5.7
C15A	0.222(2)	0.212(2)	−0.875(3)	8.0	C19	−0.0466(7)	0.7312(6)	−0.312(1)	6.5
C16A	0.269(2)	0.238(2)	−1.010(4)	14.2	C20	−0.0801(7)	0.6651(6)	−0.251(1)	6.3
O5B	−0.061(1)	0.3075(9)	−0.750(2)	5.4	C21	−0.0690(5)	0.5946(5)	−0.3198(9)	4.3

Exposure to Visible Light. Single crystals different from those used in the above X-ray analyses were irradiated overnight (about 15 h) with a xenon lamp (San-ei SUPER BRIGHT 150) at a distance of 4 cm from the top of the guide tube of the lamp at room temperature. The crystals of **2** and **3** were exposed in open air. The crystal of **1** sealed in a glass capillary was irradiated, since it was decomposed during the irradiation due to desolvation. The cell dimensions of each crystal were measured on the diffractometer to check whether the racemization occurred with retention of the single crystal form. Only the cell dimensions of **2** changed significantly, whereas those of **1** and **3** varied insignificantly.

Structure after Irradiation. The crystal of **2** after the irradiation, termed as **2′**, was analyzed by X-rays at 296 K. The crystal data and the experimental details are also given in Table 1. The structure was solved with teXsan and refined with SHELXL-93. The chiral bece group was changed to the disordered racemates. The non-H atoms except the disordered bece group were refined anisotropically. The disordered atoms of the bece group were refined with isotropic temperature factors, in the refinement of which the occupancy factors of (*R*)- and (*S*)-bece groups were also refined to have the same isotropic temperature factors. The coordinates of the H atoms were calculated geometrically. The coordinates of the non-hydrogen atoms are given in Table 2(d).

The $F_o - F_c$ tables for **1**, **2**, **2′**, and **3** are deposited as Document No. 72004 at the Office of the Editor of Bull. Chem. Soc. Jpn.

Results

Crystal Structure. The crystal structures of **1**, **2**, and **3** are shown in Figs. 1(a), (b), and (c), respectively. In the three crystals, the molecules are packed head-to-tail along the 2_1 axes parallel to the *b*, *b*, and *a* axes, for **1**, **2**, and **3**, respectively. The molecules along the 2_1 axis in **1** are linked by the hydrogen bond between the carbonyl oxygen, O7, of the bece group and the nitrogen atom, N5, of the (*S*)-1-phenylethylamine ligand of the neighboring molecule. The distance of N5···O7(1−*x*, −1/2+*y*, −*z*) is 3.067(8) Å. The solvent 2-propanol molecule makes two hydrogen bonds of O1S···O1(1−*x*, 1/2+*y*, 1−*z*) and N5···O1S(1−*x*, −1/2+*y*, 1−*z*) with the neighboring cobaloxime complex; the distances are 2.788(7) and 3.279(8) Å, respectively. The molecules related by the 2_1 symmetry along the *a* axis in **3** are also linked by the hydrogen bond of N5–H···O7 with the neighboring molecule. The distance of N5···O7(−1/2+*x*, 3/2−*y*, 1−*z*) is 3.206(9) Å.

The molecule in **2**, on the other hand, has no hydrogen bond with the neighboring ones, since it has no hydrogen donor group. Therefore, the molecules in **2** can migrate more easily than those of **1** and **3** when those crystals are irradiated with visible light.

Molecular Structure. The drawings of the molecule structures and the numbering schemes of **1**, **2**, and **3** are shown in Figs. 2(a), (b), and (c), respectively. The selected bond distances, bond angles and torsion angles are listed in Table 3. Since the angles of Co–C9–C10 and the torsion angle of Co–C9–C13–C14 are 111.2(5)° and 169.0(5)° for **1**, 109.9(4)° and 169.3(4)° for **2**, 110.0(4)° and 170.0(5)° for **3**, one of the ethoxycarbonyl group of the (*R*)-bece group (C10, O5, O6, C11, and C12) is nearly parallel to the cobaloxime plane, whereas the other ethoxycarbonyl group (C14, O7, O8, C15, and C16) is almost perpendicular to the plane in each complex. Such a conformation results from the steric repulsion between the two ethoxycarbonyl groups. The average Co–C9 distance, 2.074(6) Å, is nearly consistent with the corresponding one of the bmce complex, 2.064(8) Å. The Co–N5 distance of **2** is smaller than those of **1** and **3**, which is due to the different electronic state of the N5 atoms.

The conformations of the parallel ethoxycarbonyl groups are significantly different among the three complexes, the torsion angles of C10–O6–C11–C12 being 123(1)°, 165.5(3)°, and 177.5(7)° for **1**, **2**, and **3**, respectively. On the other hand, the conformations of the perpendicular groups are nearly the same *trans*; the torsion angles of C14–O8–C15–C16 are 174.7(9)°, 172.1(7)°, and 177.5(7)° for **1**, **2**, and **3**, respectively. The torsion angle of propylamine, N5–C17–C18–C19, 178(1)° is *trans*.

Racemized Structure 2′. The crystal structure after the irradiation is shown in Fig. 3(a), which is essentially the same as that in Fig. 1(b) except for the disordered structure of the bece group. Figure 3(b) shows the molecular structure of the disordered racemates. The *R* and *S* conformers have approximately the same occupancy factors. This indicates that the bece group was changed from *R* configuration to racemates on exposure to visible light with retention of the single crystal form. The conformations of the *R* and *S* isomers

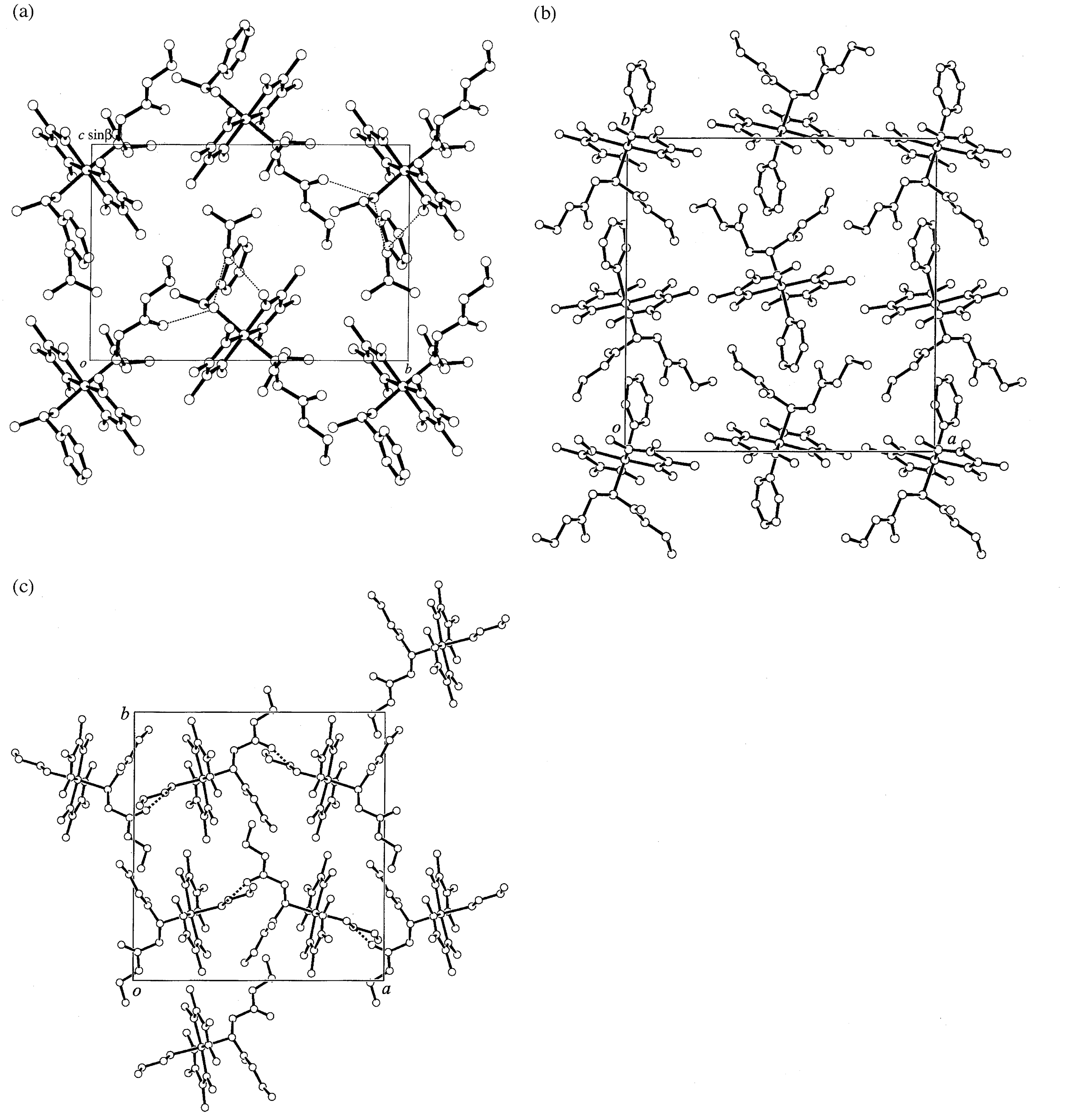


Fig. 1. Crystal structures of (a) **1**, (b) **2**, and (c) **3** viewed along the *a*, *c*, and *c* axes, respectively. The dotted lines show hydrogen bonds.

are drawn viewed down the cobaloxime plane in Fig. 3(c).

Discussion

For the crystalline-state racemization of the bmce group,[8] there are two crystallographically independent molecules which are closely related by a pseudo-inversion center. One of the bmce groups was inverted to the opposite configuration and the other bmce group remained unaltered. Such a cooperative motion of the two molecules around the pseudo-inversion center is an essential factor for such a bulky group in the process of crystalline-state racemization. The pseudo-inversion center became a crystallographic one after the racemization. The crystal of **2**, on the other hand, has only one

Table 3. Selected Bond Distances (Å), Bond and Torsion Angles (°)

	1	**2**	**3**
C9–Co	2.068(7)	2.074(5)	2.080(6)
Co–N5	2.072(5)	2.046(4)	2.060(6)
Co–C9–C10	112.2(5)	109.9(4)	110.0(4)
C9–Co –N5	178.4(3)	175.5(2)	176.0(3)
Co–C9–C13–C14	169.0(5)	169.3(4)	170.0(5)
C10–O6–C11–C12	123(1)	165.3(9)	177.5(7)
C14–O8–C15–C16	174.7(9)	172.1(7)	175.4(8)
C11–O6–C10–C9	173.5(7)	178.5(6)	173.3(6)
C15–O8–C14–C13	178.8(7)	178.8(7)	178.8(6)

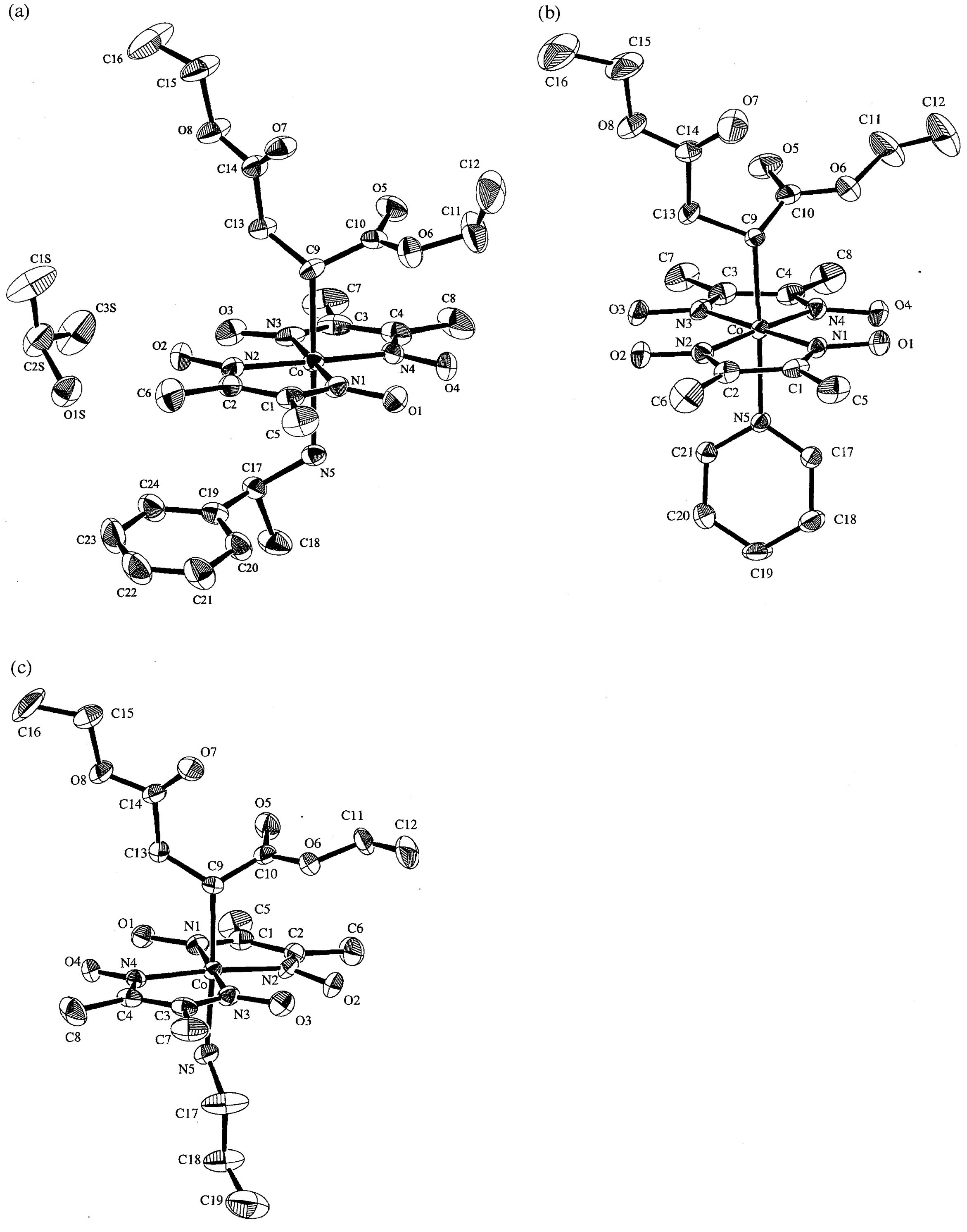


Fig. 2. Molecular structures of (a) **1**, (b) **2**, and (c) **3**. The displacement ellipsoids are drawn at 30% probability level. The H atoms are omitted for clarity.

molecule in an asymmetric unit of $P2_12_12_1$ cell and the bece group is isolated from the other bece groups. It is impossible to assume the cooperative motion of the bece groups.

The inverted group in the bmce crystal has a larger reaction cavity than the non-reactive bmce group. This may suggest that the cavity size should also play an important role. The reaction cavities for **1**, **2**, and **3** were calculated in the same way as reported previously.[1] Figures 4(a), (b), and (c) show the reaction cavities for the bece groups of **1**, **2**, and **3**. The volumes of the cavities for **1**, **2**, and **3** are 68.8, 76.5, and 58.9 Å^3, respectively. The significantly large cavity size of the bece group in **2** is responsible to the racemization without decomposition of the crystallinity. Moreover, the intermolecular hydrogen bonds between the carbonyl group

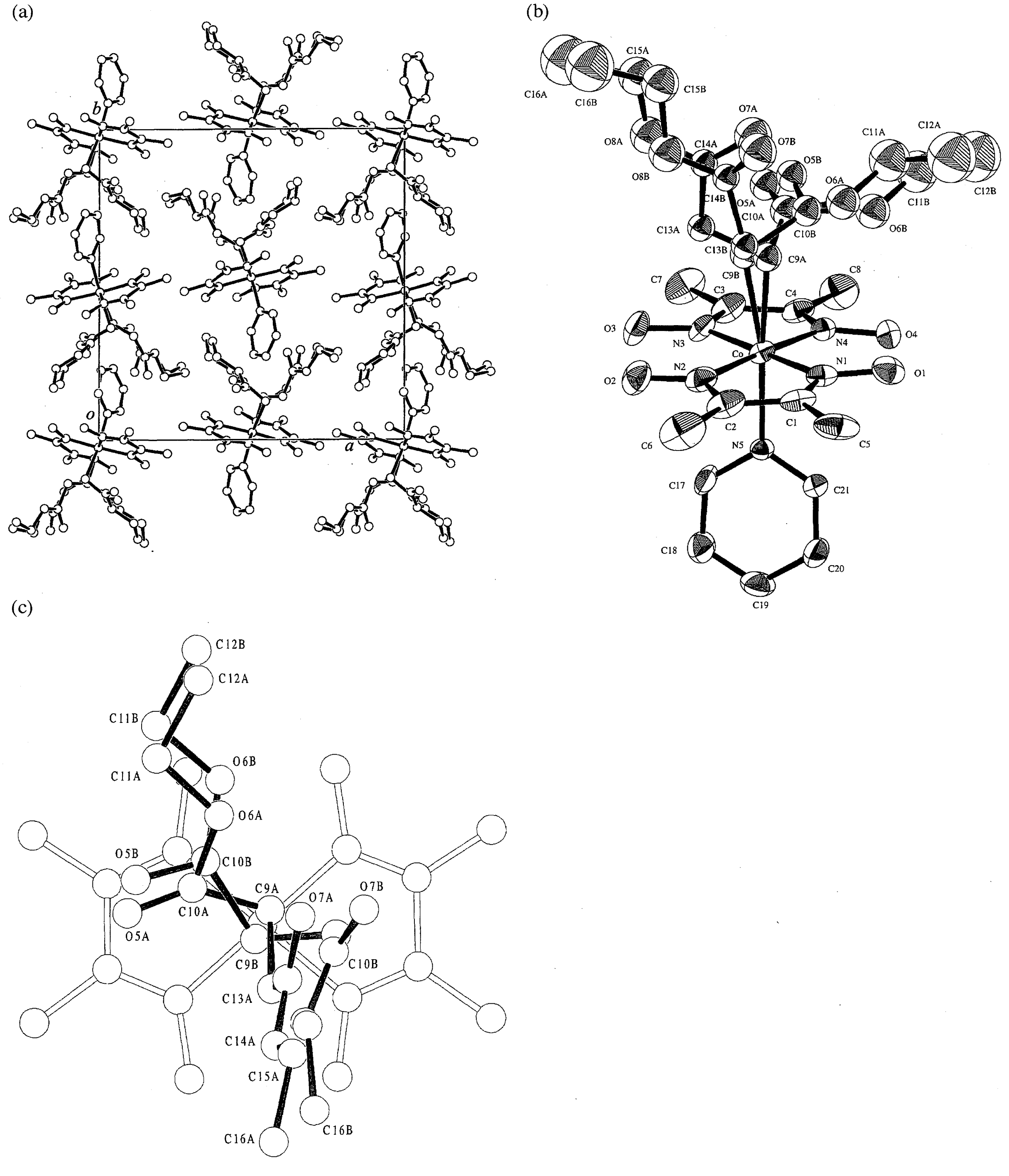


Fig. 3. (a) Crystal structure of **2′** viewed along the *c* axis. (b) Molecular structure of **2′**. (c) The structure of the disordered bece group viewed normal to the cobaloxime plane. Although the chiral carbon atoms of C9A and C9B take the opposite configurations to each other, the ethoxycarbonyl groups of both configurations occupy nearly the same positons.

of the bece groups and the nitrogen atoms of the neighboring molecules in **1** and **3** probably restrict the movement of the bece groups in the crystals and reduce the racemization rates. However, the bece complex with methyldiphenylphosphine as an axial ligand did not reveal racemization despite having almost the same cavity size as **2**, 75.8 Å^3.[5] To explain the difference of reactivity, the shapes of the cavities were compared. Figures 4(b), (d), and (e) show the cavities of **2**, **2′** and the methyldiphenylphosphine complex. There seems to be a wide space for the inverted bece group in the crystal of **2**. The inverted bece group is well accommodated in the cavity of **2′**, which is very similar to that of **2**. For the methyldiphenylphosphine complex, on the other hand, several atoms of the bece group would move outside the cavity when the chiral bece group is inverted to the opposite configuration which is indicated by dotted lines. This would cause a heavy steric effect in its crystalline lattice. This is one reason why such a bulky group can be inverted without degradation of

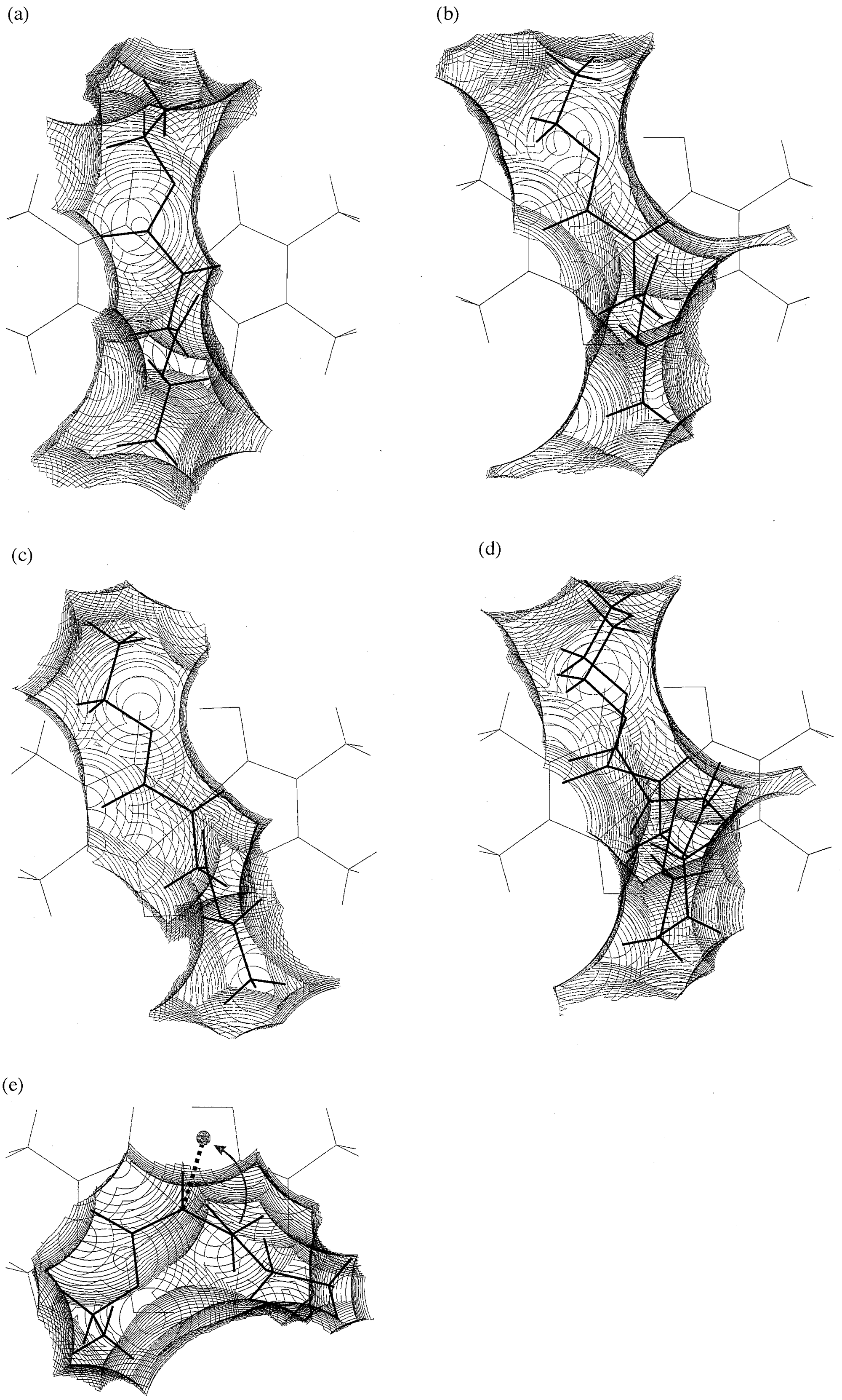


Fig. 4. Reaction cavities of (a) **1**, (b) **2**, (c) **3**, (d) **2′** and (e) methyldiphenylphosphine complex looked down the cobaloxime plane from the bece group. The contour lines are plotted at 0.1 Å intervals.

the crystallinity. In addition to the cooperative motion of the reactive groups, the resemblance in cavity shape before and after the racemization or vacant space for the inverted group before the racemization should be an important factor.

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