Crystalline-State Reaction of Cobaloxime Complexes. 19.[1)]
A New Mode of Racemization of the 1-Cyanoethyl Group

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The crystal of [(*R*)-1-cyanoethyl][bis(dimethylglyoximato)](3-hydroxypyridine)cobalt(III) benzene solvate showed racemization along with a retention of the single-crystal form upon exposure to a fluorescent lamp. The crystal data before irradiation are as follows: $[Co(C_3H_4N)(C_4H_7N_2O_2)_2(C_5H_5NO)]\cdot 2C_6H_6$, F.W. = 594.6, triclinic, $P1$, $Z=2$, $a=11.646(3)$, $b=13.267(4)$, $c=11.303(3)$ Å, $\alpha=102.57(2)$, $\beta=101.27(2)$, $\gamma=113.38(2)^\circ$, $V=1485.2(9)$ Å^3, $D_x=1.33$ Mg m^{-3}, $\mu(\text{Mo }K\alpha)=0.624$ mm^{-1}, $F(000)=624$, and $T=296$ K. The structure was solved by the direct method and refined to $R=0.067$, $wR2=0.180$. Upon exposure to a fluorescent lamp, the cell dimensions were gradually changed, and became significantly small after 150 h of irradiation. The cell dimensions became as follows: $a=11.596(4)$, $b=13.287(3)$, $c=11.297(2)$ Å, $\alpha=102.51(2)$, $\beta=101.26(2)$, $\gamma=113.37(2)^\circ$, and $V=1481.1(8)$ Å^3. The analysed structure showed that a crystallographic inversion center appeared between the two molecules, and that the space group changed from $P1$ to $P\bar{1}$. The 1-cyanoethyl groups of the two molecules were transformed to disordered racemates. In the process of racemization, the cyano and methyl groups were exchanged, although the methyl group has been exchanged with hydrogen in the related crystals so far observed. The racemic crystal obtained from a solution showed approximately the same structure as that by photoirradiation. The reason why such a new mode of racemization occurred was clearly explained by the size and shape of the reaction cavities for the two 1-cyanoethyl groups in the structure before irradiation.

The chiral 1-cyanoethyl group, $-C^*H(CH_3)CN$, bonded to the cobalt atom of some bis(dimethylglyoximato)cobalt(III), cobaloxime, complexes, has been found to be racemized by X-ray or visible-light exposure with a retention of the single-crystal form.[2)] Several complex crystals have been prepared by changing the axial base ligands, and the racemization processes have been examined. For complexes with (*S*)-1-phenylethylamine,[3)] (*R*)-1-phenylethylamine,[4)] methyldiphenylphosphine,[5)] and pyrrolidine[6)] as axial base ligands, the chiral 1-cyanoethyl group is changed to the disordered racemates. For complexes with pyridine,[7)] 4-cyanopyridine,[8)] and 4-methylpyridine[9)] as axial base ligands, one chiral group of the two crystallographically independent molecules is completely inverted to the opposite configuration, whereas another chiral group remains unaltered. For a complex with dimethylphenylphosphine[10)] as an axial base ligand, both of the chiral groups of the two crystallographically independent molecules are transformed to disordered racemates, and a crystallographic inversion center appears between the two molecules.

Recently, several complexes having axial base ligands with hydrogen donor groups have been prepared in order to examine the role of hydrogen bonding in racemization. Crystals suitable for X-ray analysis were obtained when 3-hydroxypyridine was used as an axial base ligand (3hp). The analyzed structure, however, showed that the hydroxyl group does not make a hydrogen bond to the nitrogen atom of the chiral 1-cyanoethyl group, but to the oxygen atom of the cobaloxime moiety of the neighboring molecule.

The crystal showed crystalline-state racemization. The structure after irradiation, to our surprise, showed that the methyl group was exchanged with the cyano group during the process of an inversion of the chiral 1-cyanoethyl group, although the methyl was exchanged with hydrogen in all of the crystalline-state racemization (described above). The present paper explains why such a new mode of racemization occurs in this crystal on the basis of the analyzed structures before and after irradiation and racemic crystal.

Experimental

Preparation. The complex of [(*R*)-1-cyanoethyl][bis(dimethylglyoximato)][(*S*)-1-phenylethylamine]cobalt(III) (*S*-pea) was prepared as reported previously.[11)] To a methanol solution of *S*-pea (5.24 g), DOWEX 50W-X12 (2.0 g) was added and stirred overnight. After the solution was filtered 3-hydroxypyridine (1.05 g) was added to the filtrate with stirring. After completion of the ligand exchange, the solution was evaporated and the residue was dissolved in a benzene–methanol solution. Orange crystals of [(*R*)-1-cyanoethyl][bis(dimethylglyoximato)][3-hydroxypyridine]-cobalt(III) (*R*-3hp, 5.64 g, 83% yield) were obtained.

The racemic complex of 3hp was prepared in the same way as that described above, except for using the *S*-pea complex without fractional precipitation. Orange crystals of [*rac*-1-cyanoethyl]-[bis(dimethylglyoximato)][3-hydroxypyridine]cobalt(III) (*rac*-3hp) were obtained.

Crystal Structure Analysis before Irradiation. A crystal was sealed in a glass capillary and mounted on a Rigaku AFC5R four-circle diffractometer with Mo $K\alpha$ radiation ($\lambda=0.71073$ Å). The diffractometer was covered with a black sheet to shut out any room light. Three-dimensional intensity data were collected by means of an ω–2θ scan technique at 16° min^{-1} in 2θ. Three monitored reflections showed no significant deterioration. The reflections with $I > 2\sigma(I)$ were used for a structure determination. Absorption collection was applied. Crystal data and all other experimental details are listed in Table 1. The structure was solved by a direct method with the program SAPI-91 in TEXSAN,[12] and refined by the full-matrix least-squares method with the program SHELXL-93.[13] The absolute structure was determined by the Flack parameter.[14] Atomic-scattering factors were taken from "International Tables for Crystallography".[15] The atomic parameters for non-H atoms are given in Table 2.[#]

Change of Cell Dimensions. After the crystal was exposed to a fluorescent lamp, and the determination of the cell dimensions was repeated continuously using 2θ values of 24 reflections in the $20° < 2\theta < 30°$ range. After a 150 h exposure the change became within the experimental errors.

Crystal Structure Analysis after 150 h Exposure. Three-dimensional intensity data were collected after a 150 h exposure in the same conditions as those of the continuous determination of the cell dimensions. Absorption collection was applied. The crystal data and experimental details are also given in Table 1. The space group was changed to $P\bar{1}$. All of the non-H atoms were refined anisotropically. The 1-cyanoethyl group was treated as a disordered structure under restraint to have the normal bond distances; the site occupancy of the disordered 1-cyanoethyl group was 0.61 : 0.39(1). The atomic parameters are given in Table 3.

Crystal Structure Analysis of *rac*-3hp. No absorption correction was performed. All other conditions were the same as those described above. The crystal data and experimental details are given in Table 1. All the non-H atoms were refined anisotropically. The occupancy factors of N6R and N6S converged to 0.53(1) and 0.47(1), respectively. The bond distances of the disordered 1-cyanoethyl groups were also restrained. The atomic parameters are given in Table 4.

Results

Crystal and Molecular Structure before Irradiation. The crystal structure, viewed along the *a*-axis before irradiation, is shown in Fig. 2. There are two crystallographically independent molecules, (A and B) in a unit-cell. These two molecules are closely related by a pseudo inversion center, except for the chiral 1-cyanoethyl groups, which have an *R* configuration. Between the two molecules there are four benzene molecules [C(C20A–C25A), D(C30A–C35A), E(C20B–C25B), and F(C30B–C35B)] as a crystal solvent.

Table 1. Crystal Data and Details of Refinement

	Initial	After irradiation	Racemic crystal
a/Å	11.646(3)	11.596(4)	11.572(4)
b/Å	13.267(4)	13.287(3)	13.355(4)
c/Å	11.303(3)	11.297(2)	11.283(2)
α/°	102.57(2)	102.51(2)	102.76(2)
β/°	101.27(2)	101.26(2)	100.84(2)
γ/°	113.38(2)	113.37(2)	113.66(2)
V/Å^3	1485.2(9)	1481.1(8)	1481.1(10)
Space group	$P1$	$P\bar{1}$	$P\bar{1}$
Z	2	2	2
No. of independent reflections	6815	5215	5216
No. of parameters	687	396	391
No. of reflections used in refinement	4687	3206	3937
S	1.12	1.07	1.07
$(\Delta/\sigma)_{\text{max}}$	0.003	0.001	0.002
$(\Delta\rho)_{\text{min}}$/eÅ^{-3}	−0.968	−0.282	−0.176
$(\Delta\rho)_{\text{max}}$/eÅ^{-3}	0.918	0.507	0.460
$R1(I > 2\sigma(I))$	0.067	0.051	0.039
$wR(I > 0)$	0.180	0.098	0.093
Crystal dimensions/mm^3	$0.8 \times 0.5 \times 0.08$	$0.8 \times 0.5 \times 0.1$	$0.8 \times 0.5 \times 0.1$
Scan technique	ω–2θ	ω–2θ	ω–2θ
Scan range	$\sin\theta/\lambda \leq 0.65$ Å^{-1}	$\sin\theta/\lambda \leq 0.60$ Å^{-1}	$\sin\theta/\lambda \leq 0.60$ Å^{-1}
	$0 \leq h \leq 15$	$0 \leq h \leq 13$	$0 \leq h \leq 13$
	$-17 \leq k \leq 15$	$-15 \leq k \leq 14$	$-15 \leq k \leq 14$
	$-14 \leq l \leq 14$	$-13 \leq l \leq 12$	$-13 \leq l \leq 12$
Weighting scheme $[P = (F_o^2 + 2F_c^2)/3]$	$1/[\sigma^2(F_o^2) + (0.1388P)^2]$	$1/[\sigma^2(F_o^2) + (0.0299P)^2 + 1.56P]$	$1/[\sigma^2(F_o^2) + (0.0458P)^2 + 0.53P]$

[#] The tables of the anisotropic temperature factor for non-hydrogen atoms, bond distances and angles, the parameters of hydrogen atoms, and the F_o-F_c are deposited as Document No. 68049 at the Office of the Editor of Bull. Chem. Soc. Jpn.

Table 2. The Final Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($U_{eq} \times 10^3$/Å^2)

Atoms	x	y	z	U_{eq}	Atoms	x	y	z	U_{eq}
Co(1A)	2142(1)	1863(1)	−1529(1)	32	C(1B)	−472(13)	−2845(12)	1245(12)	46
O(1A)	333(9)	−277(7)	−3521(8)	57	C(2B)	−1739(14)	−3645(10)	299(13)	56
O(2A)	4885(11)	2607(11)	−204(9)	74	C(3B)	−3783(14)	−935(12)	1883(12)	54
O(3A)	3927(10)	3961(9)	491(9)	63	C(4B)	−2413(16)	−35(12)	2821(11)	60
O(4A)	−559(9)	1066(9)	−2754(11)	71	C(5B)	669(18)	−2970(17)	1340(18)	104
O(5A)	5294(13)	5195(9)	−3018(9)	80	C(6B)	−2087(15)	−4815(10)	−667(11)	71
N(1A)	1626(11)	419(9)	−2718(10)	46	C(7B)	−5023(14)	−762(14)	1655(16)	87
N(2A)	3715(11)	1767(10)	−1174(10)	48	C(8B)	−2329(19)	966(13)	3708(17)	104
N(3A)	2687(10)	3346(6)	−329(8)	38	C(12B)	−3739(13)	−3643(12)	2500(11)	51
N(4A)	539(8)	1932(8)	−1873(9)	33	C(13B)	−4160(13)	−4182(11)	3413(12)	53
N(5A)	2710(9)	2684(9)	−2828(7)	37	C(14B)	−3329(14)	−3709(12)	4625(10)	55
N(6A)	2466(13)	−393(9)	−18(10)	90	C(15B)	−2168(11)	−2682(10)	4910(10)	49
C(1A)	2533(14)	68(11)	−2789(14)	51	C(16B)	−1881(10)	−2177(9)	4020(11)	51
C(2A)	3757(15)	814(12)	−1826(13)	56	C(9B)	−1462(10)	−929(7)	321(8)	45
C(3A)	1882(12)	3733(11)	−325(12)	51	C(10B)	−2154(17)	−261(12)	−34(13)	80
C(4A)	569(16)	2835(16)	−1201(16)	66	C(11B)	−1527(15)	−1742(10)	−873(9)	64
C(5A)	2140(15)	−1119(9)	−3755(12)	77	C(23B)	−10697(14)	−6738(9)	2094(13)	130
C(6A)	4781(15)	466(15)	−1639(16)	94	C(23B)	−11907(11)	−6759(8)	1632(10)	130
C(7A)	2089(24)	4862(16)	445(16)	122	C(21B)	−12097(8)	−5805(10)	−2135(10)	79
C(8A)	−708(14)	2995(16)	−1420(16)	99	C(20B)	−11078(10)	−4830(8)	3099(10)	101
C(12A)	3784(9)	3656(7)	−2499(8)	32	C(25B)	−9868(9)	−4809(9)	3560(9)	99
C(13A)	4154(9)	4193(8)	−3330(8)	34	C(24B)	−9678(10)	−5763(12)	3058(12)	110
C(14A)	3416(12)	3694(10)	−4648(11)	44	C(30A)	−15532(15)	−11883(14)	−5840(11)	260
C(15A)	2260(12)	2688(9)	−5034(8)	42	C(31A)	−16349(11)	−12863(11)	−5607(11)	117
C(16A)	1926(12)	2189(10)	−4091(8)	39	C(32A)	−15983(12)	−13024(9)	−4443(14)	128
C(9A)	1583(11)	1072(8)	−248(10)	47	C(33A)	−14800(13)	−12205(12)	−3513(11)	176
C(10A)	1686(13)	1763(10)	1013(10)	54	C(34A)	−13983(10)	−11225(10)	−3747(12)	104
C(11A)	2089(12)	209(9)	−136(10)	53	C(35A)	−14349(13)	−11064(11)	−4910(15)	162
					C(23A)	−8761(13)	−5205(10)	−3201(12)	123
Co(1B)	−2143(1)	−1864(1)	1529(1)	33	C(22A)	−10005(10)	−5285(8)	−3642(10)	110
O(1B)	621(9)	−1009(10)	2757(9)	63	C(21A)	−10239(10)	−4352(11)	−3160(11)	99
O(2B)	−3918(9)	−3961(7)	−484(8)	49	C(20A)	−9228(14)	−3340(9)	−2238(10)	96
O(3B)	−4848(9)	−2608(9)	229(10)	63	C(25A)	−7984(12)	−3260(10)	−1797(9)	112
O(4B)	−376(10)	264(8)	3449(9)	66	C(24A)	−7750(9)	−4192(13)	−2279(12)	230
O(5B)	−5283(8)	−5178(8)	3053(7)	63	C(30B)	−15050(12)	−7779(9)	−6679(8)	94
N(1B)	−512(13)	−1892(11)	1896(11)	59	C(31B)	−16019(10)	−8750(8)	−6560(9)	110
N(2B)	−2684(10)	−3296(9)	318(9)	44	C(32B)	−15930(10)	−8907(9)	−5376(11)	113
N(3B)	−3751(8)	−1796(9)	1186(9)	37	C(33B)	−14871(12)	−8095(11)	−4310(9)	127
N(4B)	−1558(11)	−378(7)	2728(9)	42	C(34B)	−13902(9)	−7124(10)	−4429(9)	105
N(5B)	−2601(8)	−2636(7)	2852(9)	34	C(35B)	−13992(10)	−6966(8)	−5614(11)	99
N(6B)	−1562(13)	−2278(9)	−1751(8)	99					

Two of the four benzene molecules (C and E, and D and F) are also related by a pseudo inversion. Figure 3 shows the structure around the pseudo inversion center at the origin. Two chiral 1-cyanoethyl groups are contacts with each other, and are surrounded by four benzene molecules. The reason why the crystal is easily broken in air may be due to the structure of the solvent molecules, which are packed as columns. The solvent benzene molecules, therefore, easily leave the crystal, allowing the crystallinity to be deteriorated.

The A and B molecules are connected by fairly strong hydrogen bonds (O5A···O2B and O5B···O2A) around another pseudo inversion center at (0, 0.5, 0), and make a dimer, as shown in Fig. 2. The distances of O5A···O2B and O5B···O2A are 2.66(2) and 2.68(2) Å, respectively.

The molecular structure of A with the numbering system is shown in Fig. 4. The A and B molecules are substantially the same to each other, except for the torsion angles around the Co–C9 and Co–N5 bonds. The N2–Co–C9–C11 and N2–Co–N5–C12 angles are −59.2(11) and −31.8(12)° for A and −42.1(10) and −6.9(12)° for B. The selected bond distances and angles are listed in Tables 5 and 6, respectively. These values are not significantly different from the

Table 3. The Final Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($U_{eq} \times 10^3/\text{Å}^2$)

Atoms	x	y	z	U_{eq}
Co(1)	2140(1)	1862(1)	−1531(1)	38
O(1)	349(3)	−264(2)	−3496(3)	65
O(2)	4874(3)	2613(3)	−202(3)	72
O(3)	3913(3)	3959(2)	478(3)	64
O(4)	−611(3)	1028(3)	−2768(3)	69
O(5)	5301(4)	5182(3)	−3028(3)	75
N(1)	1589(4)	400(3)	−2725(3)	48
N(2)	3750(3)	1777(3)	−1160(3)	50
N(3)	2666(4)	3313(3)	−332(3)	48
N(4)	512(3)	1912(3)	−1894(3)	48
N(5)	2653(3)	2647(3)	−2840(3)	38
C(1)	2498(6)	64(4)	−2795(5)	58
C(2)	3776(5)	873(5)	−1842(5)	63
C(3)	1786(6)	3681(4)	−326(5)	59
C(4)	497(5)	2826(5)	−1246(5)	58
C(5)	2208(7)	−1063(5)	−3725(6)	97
C(6)	4955(6)	662(6)	−1607(6)	108
C(7)	2057(7)	4816(5)	557(6)	94
C(8)	−739(6)	2963(6)	−1407(6)	99
C(12)	3770(4)	3647(3)	−2506(4)	42
C(13)	4165(4)	4189(3)	−3372(4)	45
C(14)	3387(4)	3697(4)	−4633(4)	50
C(15)	2230(4)	2687(4)	−4979(4)	52
C(16)	1895(4)	2187(3)	−4067(4)	45
C(20)	9277(11)	3344(8)	2211(9)	113
C(21)	10284(7)	4319(9)	3134(8)	104
C(22)	10069(9)	5241(7)	3575(7)	108
C(23)	8852(10)	5173(7)	3100(9)	108
C(24)	7891(8)	4197(10)	2211(8)	114
C(25)	8109(10)	3304(8)	1766(7)	117
C(30)	5263(13)	1881(12)	5673(11)	165
C(31)	6144(8)	2841(8)	5543(8)	121
C(33)	4907(9)	2223(8)	3421(8)	115
C(32)	5972(8)	3013(6)	4426(9)	106
C(34)	3999(8)	1262(7)	3568(10)	119
C(35)	4191(11)	1090(9)	4672(13)	149
N(6R)	2385(11)	−421(10)	−42(10)	101
C(9R)	1522(5)	1006(4)	−281(4)	56
C(10R)	1583(24)	1768(14)	948(13)	64
C(11R)	1989(18)	172(15)	−127(24)	80
N(6S)	1527(14)	2269(11)	1728(9)	81
C(9S)	1522(5)	1006(4)	−281(4)	56
C(10S)	2196(21)	286(18)	−7(27)	63
C(11S)	1618(44)	1713(21)	950(30)	80

Table 4. The Final Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($U_{eq} \times 10^3/\text{Å}^2$)

Atoms	x	y	z	U_{eq}
Co(1)	2128(1)	1869(1)	−1530(1)	37
O(1)	362(2)	−266(2)	−3491(2)	64
O(2)	4866(2)	2648(2)	−175(2)	72
O(3)	3877(2)	3978(2)	471(2)	63
O(4)	−623(2)	1004(2)	−2793(2)	68
O(5)	5320(2)	5176(2)	−3024(2)	75
N(1)	1607(2)	406(2)	−2715(2)	47
N(2)	3748(2)	1809(2)	−1139(2)	50
N(3)	2638(2)	3315(2)	−340(2)	48
N(4)	491(2)	1897(2)	−1914(2)	48
N(5)	2653(2)	2649(2)	−2840(2)	37
C(1)	2518(4)	85(3)	−2768(3)	58
C(2)	3791(3)	918(3)	−1799(3)	61
C(3)	1741(4)	3663(3)	−351(3)	58
C(4)	454(3)	2803(3)	−1275(3)	60
C(5)	2253(5)	−1035(3)	−3692(4)	98
C(6)	4982(5)	714(5)	−1559(5)	108
C(7)	2011(5)	4804(3)	535(4)	100
C(8)	−796(5)	2917(4)	−1441(5)	103
C(12)	3778(3)	3646(2)	−2502(2)	42
C(13)	4182(3)	4187(2)	−3365(3)	47
C(14)	3403(3)	3696(2)	−4629(3)	53
C(15)	2239(3)	2685(2)	−4977(3)	51
C(16)	1900(3)	2186(2)	−4068(2)	45
C(20)	9293(8)	3362(5)	2239(6)	114
C(21)	10289(5)	4329(6)	3159(6)	108
C(22)	10078(6)	5263(5)	3594(5)	108
C(23)	8871(7)	5195(5)	3108(6)	108
C(24)	7919(6)	4215(7)	2219(6)	114
C(25)	8109(7)	3322(6)	1792(5)	122
C(30)	5205(9)	1853(8)	5639(7)	155
C(31)	6118(6)	2827(6)	5540(5)	120
C(33)	4912(6)	2199(6)	3391(5)	113
C(32)	5976(5)	3004(4)	4406(6)	105
C(34)	3998(5)	1237(5)	3506(7)	116
C(35)	4151(7)	1069(6)	4614(9)	140
N(6R)	2334(6)	−414(5)	−49(6)	98
C(9R)	1494(3)	1022(3)	−282(3)	54
C(10R)	1606(13)	1784(12)	1009(8)	84
C(11R)	2018(17)	219(13)	−180(16)	68
N(6S)	1497(12)	2259(9)	1733(9)	73
C(9S)	1494(3)	1022(3)	−282(3)	54
C(11S)	1616(23)	1735(25)	947(15)	45
C(10S)	2063(47)	260(34)	92(38)	58

corresponding ones reported so far.

Change of Cell Dimensions and Racemization Rate. Figure 1 shows the change in the cell dimensions (a, b, c, α, β, γ, and V) with the exposure time. These curves are well explained by first-oder kinetics. The rate constants assuming first-order kinetics, were calculated for a, b, and V, since these changes are significantly large. The calculated values by a least-squares fitting are 1.99×10^{-4}, 1.29×10^{-4}, and 2.12×10^{-4} s^{-1} for a, b, and V, respectively. The average value is 1.80×10^{-4} s^{-1}. The rate constant of the crystal of S-pea, which was determined most precisely,3) was also measured under the same conditions. The average value calculated is 2.40×10^{-4} s^{-1}. This indicates that the reaction rates of the two crystals are approximately the same.

Structural Change by Photoirradiation. The crystal structure after irradiation, viewed along the a-axis, is shown in Fig. 5. The chiral 1-cyanoethyl groups of the A and B molecules are changed to disordered racemates, and the

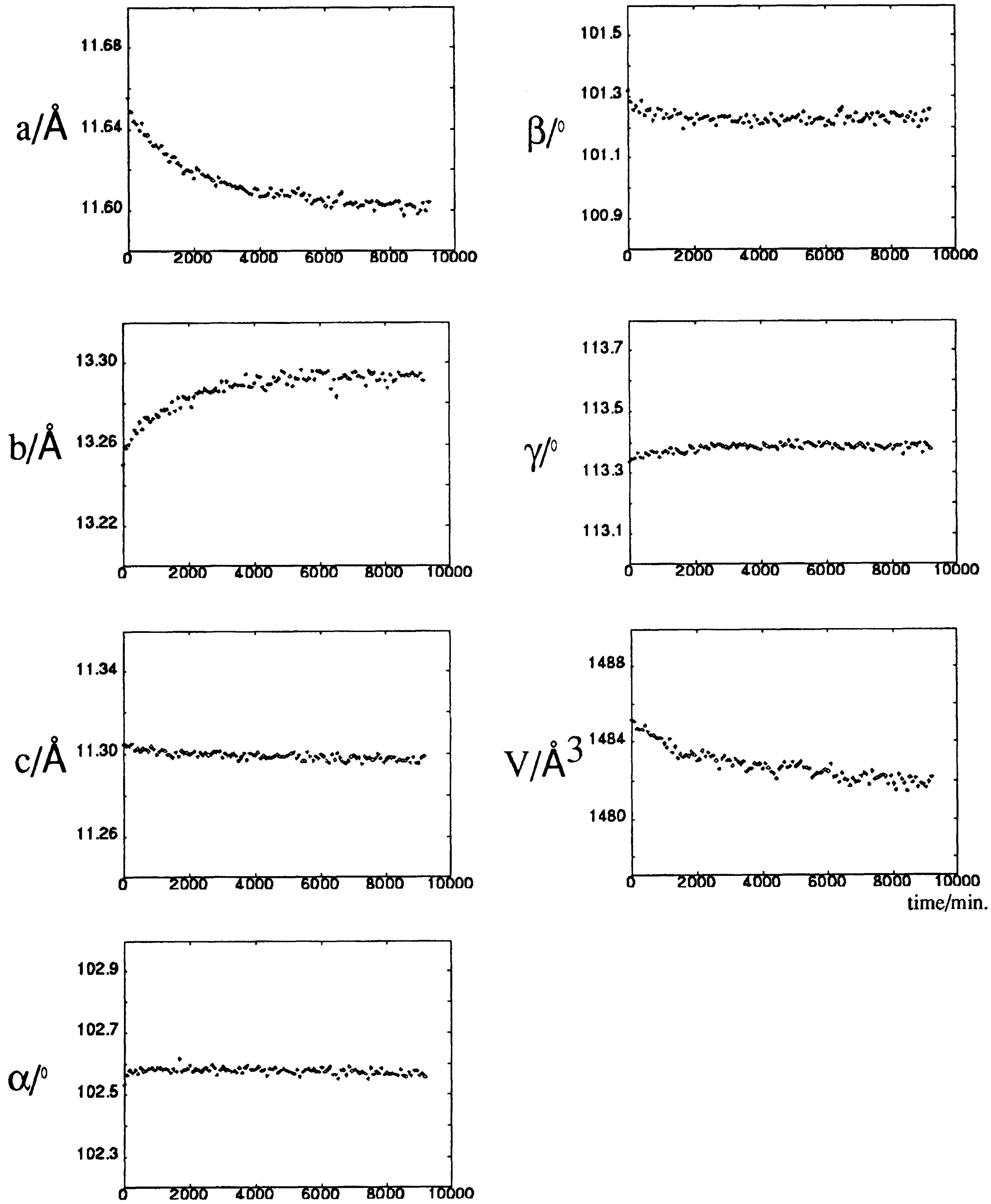


Fig. 1. Change of cell dimensions with exposure time. One cycle of the determination of the cell dimensions is about 30 min.

crystallographic inversion center appears between A and B. The atoms of the other groups, including the solvent benzene molecules, take nearly the same positions as those before irradiation. The structural changes in the A and B 1-cyanoethyl groups are shown in Fig. 6. The inverted 1-cyanoethyl group after irradiation takes a different conformation from those observed in the related crystals; the methyl and cyano groups are exchanged in the 3hp crystal, whereas methyl and hydrogen are replaced by each other in the related crystals. However, such a exchange should occur if the crystallographic inversion center appears between the two molecules in the present crystal structure. This is caused by the different structure before irradiation compared with those observed so far. The occupancy factors of N6R and N6S converged to 0.61(1) and 0.39(1) in the least-squres refinement, respectively.

The racemic crystal, prepared from a solution containing the racemic complex, showed almost the same structure as that after irradiation (Fig. 5). The occupancy factors of N6R and N6S converged to 0.53(1) and 0.47(1) by the refinement, respectively. Each molecule takes a disordered racemate form. The cell dimensions are somewhat different from

Table 5. Selected Bond Distances (Å)

Bond	Initial		After irradiation	Racemic crystal
	A molecule	B molecule		
Co–N1	1.87(1)	1.88(2)	1.888(2)	1.883(4)
Co–N2	1.86(1)	1.86(1)	1.881(2)	1.886(4)
Co–N3	1.90(1)	1.88(1)	1.878(2)	1.880(4)
Co–N4	1.87(1)	1.90(1)	1.881(2)	1.882(4)
Co–N5	2.07(1)	2.03(1)	2.037(2)	2.036(3)
C13–O5	1.37(2)	1.34(2)	1.348(3)	1.351(5)

Table 6. Selected Angles (°)

Angle	Initial		After irradiation[a]	Racemic crystal[a]
	A molecule	B molecule		
Co–C9–C10	120.3(10)	115.4(11)	114.6(8) 113.7(9)	116.0(6) 120.3(17)
Co–N1–C1	118.1(12)	117.3(13)	116.7(3)	117.0(2)
Co–N2–C2	119.2(13)	115.2(11)	117.6(3)	117.6(2)
Co–N3–C3	118.3(11)	117.5(12)	117.2(3)	116.7(2)
Co–N4–C4	115.3(12)	117.0(12)	116.8(3)	117.0(2)
Co–N5–C12	122.3(7)	119.3(12)	121.2(3)	120.9(2)
C10–C9–C11	110.8(12)	109.2(13)	114(1) 107(2)	114(1) 102(2)
C9–C11–N6	178.1(17)	176.0(17)	176(2) 167(5)	174(2) 166(2)
C12–C13–O5	123.9(9)	121.2(14)	122.2(4)	122.4(2)

a) Crystal after irradiation and racemic crystal have disordered structure. There are two groups of reactive 1-cyanoethyl group, *R* and *S*.

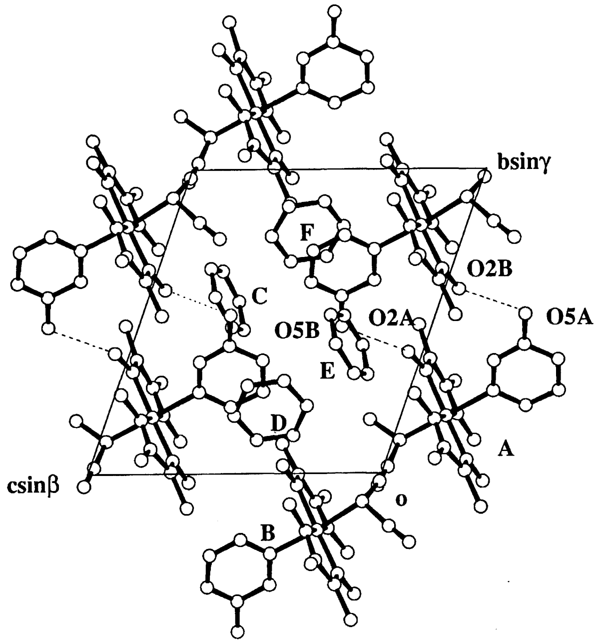


Fig. 2. Crystal structure before irradiation viewed along the *a* axis. Hydrogen bonds are indicated by dotted lines.

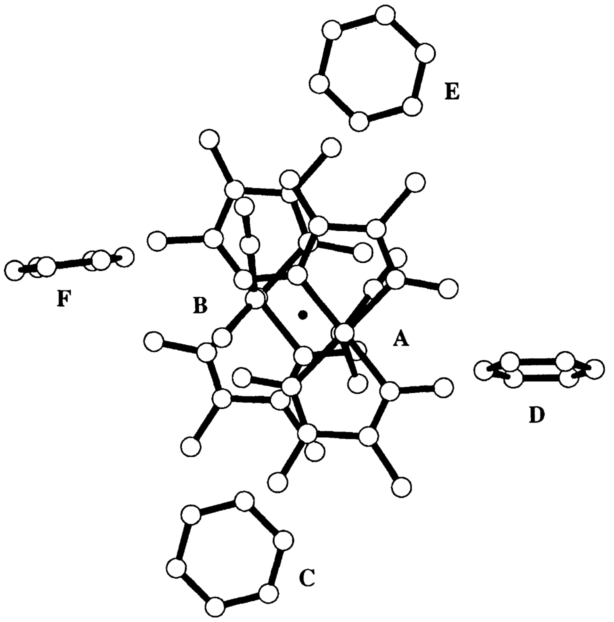


Fig. 3. Structure of the A and B 1-cyanoethyl groups and four benzene molecules around a pseudo inversion center viewed along the normal to the cobaloxime plane.

those after irradiation. The cell dimensions after irradiation take intermediate values between those before irradiation and of racemic crystal (Table 1).

Discussion

In order to explain the reason why such a mode of inversion occurs in the 3hp crystal, the reaction cavity for the 1-cyanoethyl group was calculated in the same way as previously reported.[3] Figure 7 shows the reaction cavities for the A and B 1-cyanoethyl groups in the crystal before irradiation. The volumes of the cavities are 8.0 and 10.4 Å^3 for the A and B 1-cyanoethyl groups, respectively. The crystal of [(*R*)-1-cyanoethyl](4-cyanopyridine)cobaloxime, 4cp, also showed crystalline-state racemization by X-rays or visible light.[8]

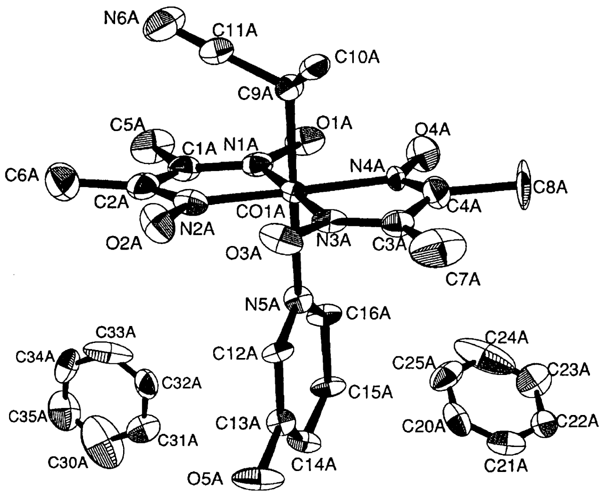


Fig. 4. Molecular structures of A and two benzene molecules before irradiation with the numbering of the atoms.

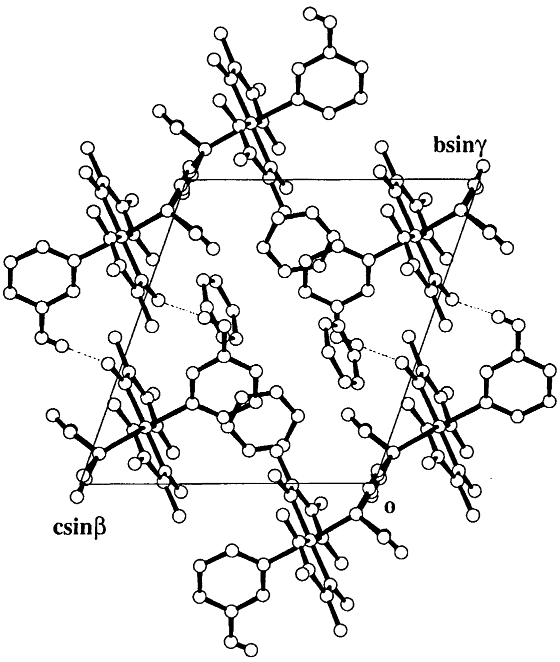


Fig. 5. Crystal structure after 150 h irradiation viewed along the *a* axis. Hydrogen bonds indicated by dotted lines are preserved after the irradiation.

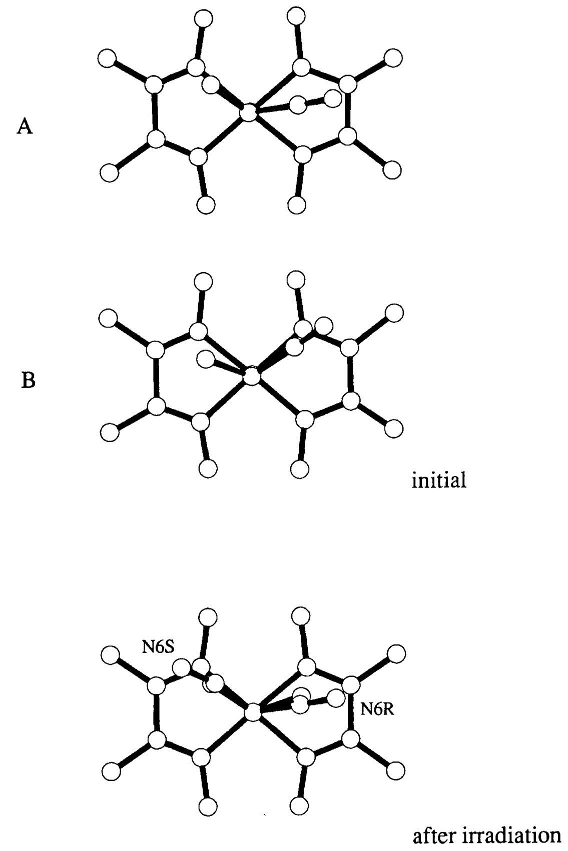


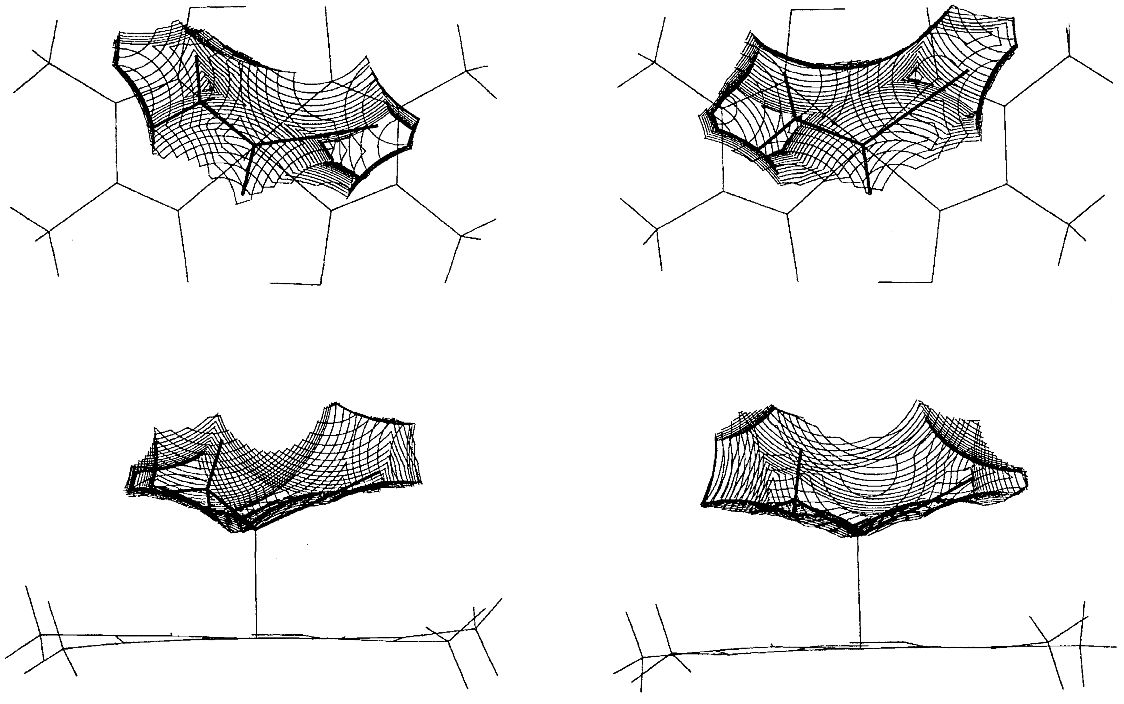
Fig. 6. Conformational and configurational change of the 1-cyanoethyl group viewed along the normal to the cobaloxime plane in the process of racemization.

The crystal has the space group $P1$ before irradiation and two crystallographically independent molecules (A and B) in an unit-cell; after irradiation it was transformed to $P\bar{1}$, and only the B 1-cyanoethyl group was inverted to have an opposite configuration. A crystallographic inversion center appeared between the two molecules. The reaction cavities for the A and B 1-cyanoethyl groups of the 4cp crystal are given in Fig. 8. The volumes of the cavities are 8.0 and 10.4 Å^3 for the A and B 1-cyanoethyl groups, respectively.

Although the 3hp and 4cp crystals have the same space group, similar structures and equivalent volumes of the cavities for the two 1-cyanoethyl groups, and moreover a crystallographic inversion center appears between the two molecules after irradiation, both of the 1-cyanoethyl groups are inverted to have disordered racemates in the former crystal; on the other hand, only B is completely inverted to have the opposite configuration in the latter crystal.

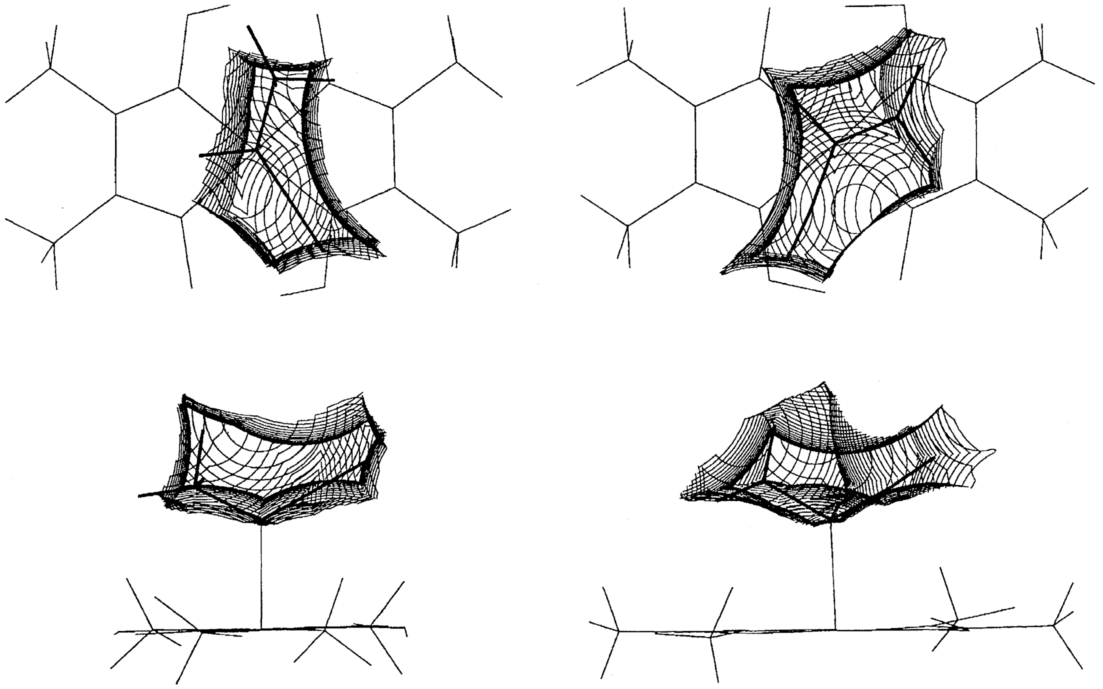
Both the A and B cavities of 3hp have a void space along the C–C(methyl) bond, and the inverted cyano groups can be accommodated in the cavities. However, the A cavity of 4cp has no space around the 1-cyanoethyl group, whereas a void space is found in the position of the B cavity, which would be occupied by the inverted methyl group. The difference in the cavity shape of the two 1-cyanoethyl groups in the 3hp and 4cp crystals may cause the different racemization process. The two benzene solvent molecules surrounding the chiral 1-cyanoethyl group may important role in the process of the racemization, because the cavity wall made by the solvent molecules may be softer than composed of ligid ligands.

In a previous paper we proposed that a cavity size more than 11.5 Å^3 is necessary for an inversion of the 1-cyanoethyl group.[6)] However, all of the cavities of the A and B 1-cyanoethyl groups in the 3hp and 4cp crystals have volumes no longer than the above value. For structures in which two 1-cyanoethyl groups come into contact with each other around the pseudo inversion center, it has been proposed that half of the contact space between the two groups should be added to the usual cavity.[16)] For the 3hp crystal, the cavity including both of the A and B 1-cyanoethyl groups was calculated,



A B

Fig. 7. Reaction cavities for the A and B 1-cyanoethyl groups in 3hp. The upper is a composite drawing viewed along the normal to the cobaloxime plane and the lower is its side view. The contours indicate the section separated by 0.2 Å.



A B

Fig. 8. Reaction cavities for the A and B 1-cyanoethyl groups in 4cp, which are drawn in the same way as those of 3hp.

which is shown in Fig. 9. The volume was calculated to be 35.4 Å^3. Since the contact space is calculated to be (35.4–8.0–10.4)/2, the cavity volumes for the A and B 1-cyanoethyl groups become 16.5 and 18.9 Å^3, respectively. This also indicates that both of the groups should be inverted to the disordered racemates. On the other hand, the contact space of the 4cp crystal is 4.8 Å^3. Therefore, the cavities of the A and B 1-cyanoethyl groups are 12.8 and 15.2 Å^3, respectively. The volume of the A 1-cyanoethyl group is slightly greater than 11.5 Å^3, whereas the B cavity has sufficient size. The

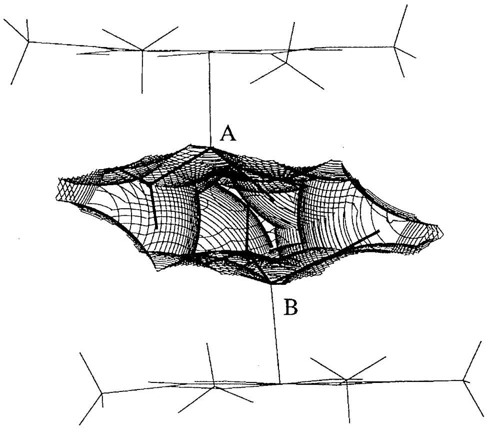


Fig. 9. Reaction cavities for the two 1-cyanoethyl groups viewed along the cobaloxime plane. The contours indicate the section separated by 0.2 Å.

new criterion holds good if the threshold value should be increased for structures in which two reactive groups come into contact with each other.

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