Pergamon

Tetrahedron 56 (2000) 6769–6779

TETRAHEDRON

Asymmetric Induction in Cobaloxime Complex Crystals Due to Chiral Crystal Environment

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Received 1 February 2000; accepted 9 March 2000

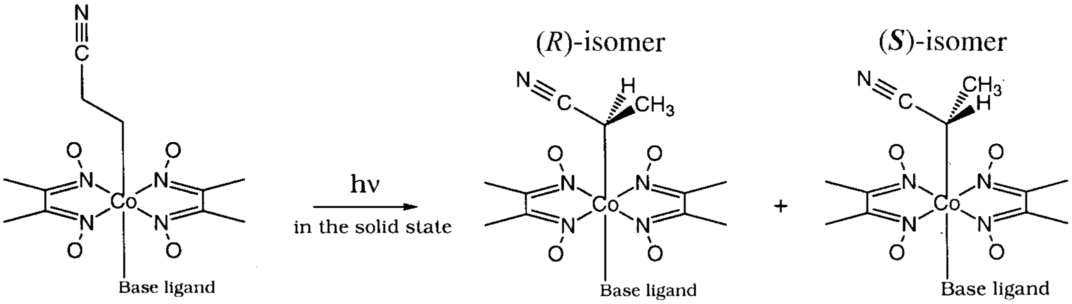
Abstract—The achiral 2-cyanoethyl group of cobaloxime complexes was isomerized to the chiral 1-cyanoethyl group on exposure to a xenon lamp in the solid state. From the crystal structures and the enantiomer or diastereomer excesses of the seven cobaloxime complexes with different axial base ligands, it was found that the chirality of the produced 1-cyanoethyl group depends on the asymmetric shape of the reaction cavity for the 2-cyanoethyl group before irradiation. © 2000 Elsevier Science Ltd. All rights reserved.

Introduction

It was found that the achiral 2-cyanoethyl group bonded to the cobalt atom in some bis(dimethylglyoximato)cobalt(III), cobaloxime, complexes is isomerized to the chiral 1-cyanoethyl group on exposure to visible light in the solid state, as shown in Scheme 1.[1] This photoreaction proceeds only in the solid state and the reverse reaction has not been observed yet. The produced 1-cyanoethyl group has a chiral carbon atom bonded to the cobalt atom. This gave an idea that the asymmetric induction would be observed if the photoisomerization proceeded in the chiral crystal environment.

The 2-cyanoethyl group of the cobaloxime complexes take a *gauche* or *trans* conformation around the C–C bond in the crystal structures reported so far. The averaged torsion angles for *gauche* and *trans* conformations are 83.41 and 175.75°, respectively, which were deduced from the Cambridge Structure Database.[2] Recently it was reported that the 2-cyanoethyl cobaloxime complexes with 3-methylpyridine and 4-methylpyridine as axial base ligands, the 2-cyanoethyl groups of which have *gauche* conformations, were isomerized to the 1-cyanoethyl complexes with retention of the single crystal form on exposure to the xenon lamp. The analyzed structures after irradiation revealed that the produced 1-cyanoethyl groups at one site have not the racemic ones but have the *R* to *S* ratio of 4:7 for the 3-methylpyridine complex and only *R* configuration for the 4-methylpyridine complex. The asymmetric shape of the reaction cavity for the 2-cyanoethyl group at the site before irradiation is responsible for the asymmetric induction.[3]

Since the above crystals have centrosymmetric space groups, the produced 1-cyanoethyl complexes in a whole crystal are racemic. However, the diastereomerically enriched product was obtained due to the chiral crystal environment, when (*R*)-2-amino-2-phenylethanol was used as an axial base ligand. The shape of the reaction cavity for



Scheme 1. Photoisomerization of the 2-cyanoethyl group to the 1-cyanoethyl group in the cobaloxime complexes.

Keywords: asymmetric induction; cobaloxime complex; chiral crystal environment; photoisomerization reaction cavity.

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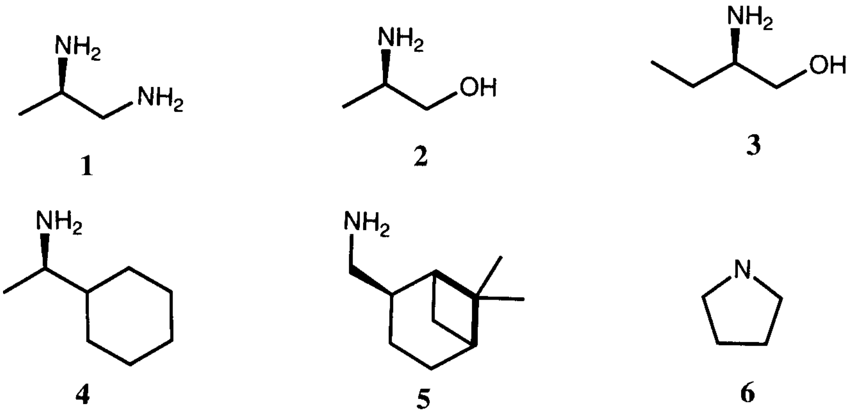
PII: S0040-4020(00)00499-3

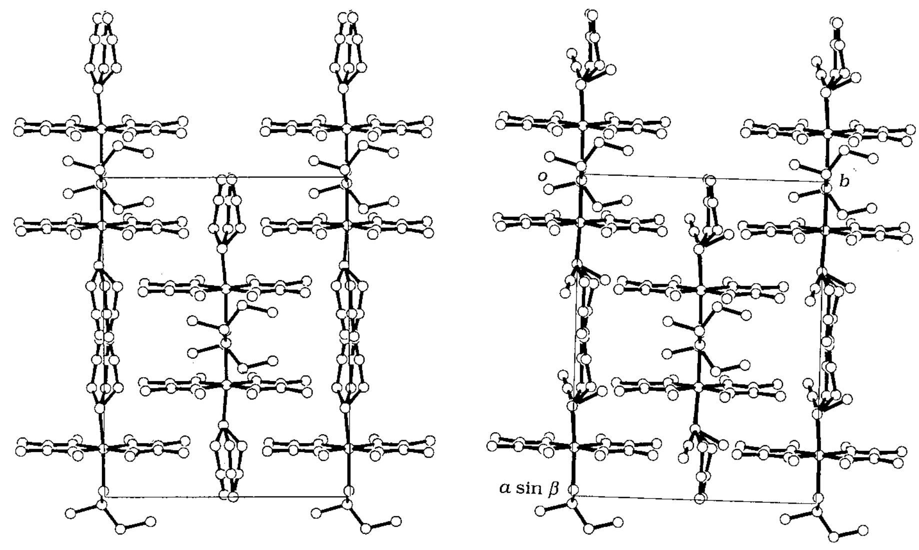


Scheme 2. Axial base ligands of the cobaloxime complexes used in the photoisomerization.

the 2-cyanoethyl group suggested that the configuration of the produced 1-cyanoethyl group was in accord with the asymmetric environment for the 2-cyanoethyl group.[4]

In the previous paper, the asymmetric induction in the powdered sample of [(*S*)-*sec*-butylamine](2-cyanoethyl)-cobaloxime complex was reported. The 2-cyanoethyl group has a *trans* conformation before irradiation. The 1-cyanoethyl group with *R* configuration was preferentially produced in 27% diastereomer excess (d.e.). This result was also explained in term of asymmetric shape of the reaction cavity for the 2-cyanoethyl group. The structure of the produced 1-cyanoethyl group with the lowest packing energy estimated from the molecular mechanics also indicated the *R*-isomer.[5]

Recently it was found after many trials that the photoisomerization of the *sec*-butylamine complex proceeded with retention of the single crystal form. The analyzed structure after the reaction was in good agreement with the estimated structure having the lowest packing energy. This suggested that the asymmetric induction would be estimated by the shape of the reaction cavity before irradiation even if the conformation of the 2-cyanoethyl group is *trans*. In order to ascertain this hypothesis, a series of the 2-cyanoethyl cobaloxime complexes with different amines as axial base ligands were prepared, as shown in Scheme 2; (*R*)-1,2-diaminopropane, **1**, (*S*)-2-amino-1-propanol, **2**, (*S*)-2-amino-1-butanol, 3, (*S*)-1-cyclohexylethylamione, **4**, *cis*-myrtanylamine, **5**, and pyrrolidine, **6**. **1** and **2** are isoelectronic to *sec*-butylamine and **3** is longer by one CH_2 group than **2**, whereas the latter three, **4**, **5** and **6**, have somewhat different structures from those of the former three and *sec*-butylamine. The crystal structure analyses of the six complexes showed that the 2-cyanoethyl groups take *trans* conformations in the crystals with the chiral space group, $P2_12_12_1$. The crystalline powdered samples of the six complexes were irradiated with the xenon lamp and their diastereomer or enantiomer excesses were measured by HPLC. In addition, from the temperature dependence of the diastereomer excesses, thermodynamic parameters were obtained.



(a) (b)

Figure 1. Crystal strucgtures of the (*R*)-*sec*-butylamine complex viewed along the c axis: (a) before, and (b) after irradiation.

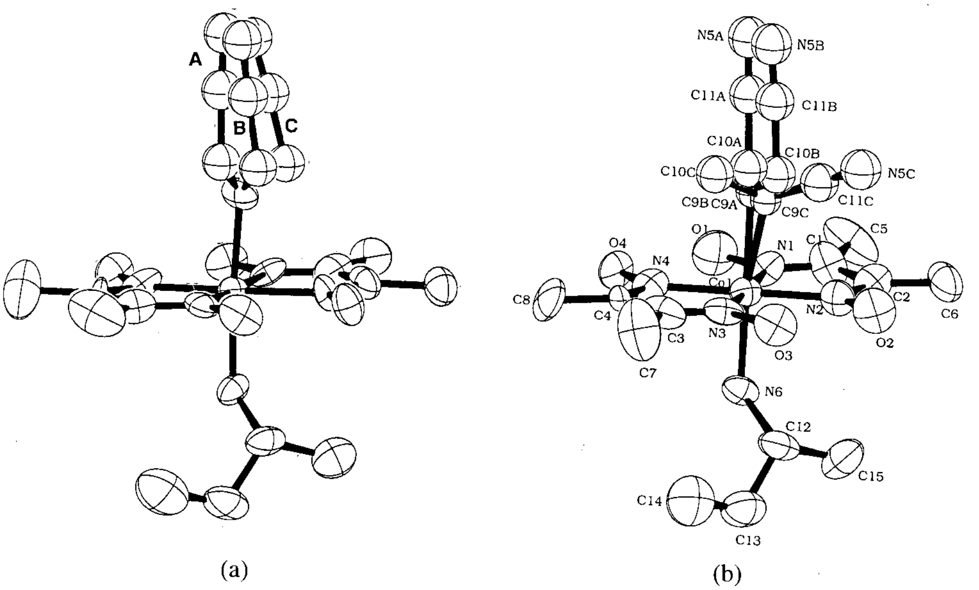


Figure 2. Molecular structures of the (*R*)-*sec*-butylamine complex: (a) before, and (b) after irradiation.

Results and Discussion

Structural change of the cyanoethyl group in the process of photoisomerization of the (*R*)-*sec*-butylamine complex

The crystal structures viewed along the *c* axis before and after the photoirradiation are shown in Fig. 1. Although the crystal with the (*S*)-*sec*-butylamine was used in the previous paper,[5] hereafter the configuration of the amine is inverted to have *R* to compare the structures before and after irradiation, since the crystal with (*R*)-*sec*-butylamine was used in this experiment. Two structures before and after irradiation are essentially the same except for the atoms appeared around the disordered 2-cyanoethyl groups, which were assigned to the atoms of the produced (*S*)-1-cyanoethyl group. The molecular structures with the numbering of atoms before and after photoirradiation are shown in Fig. 2. The 2-cyanoethyl group has three disordered

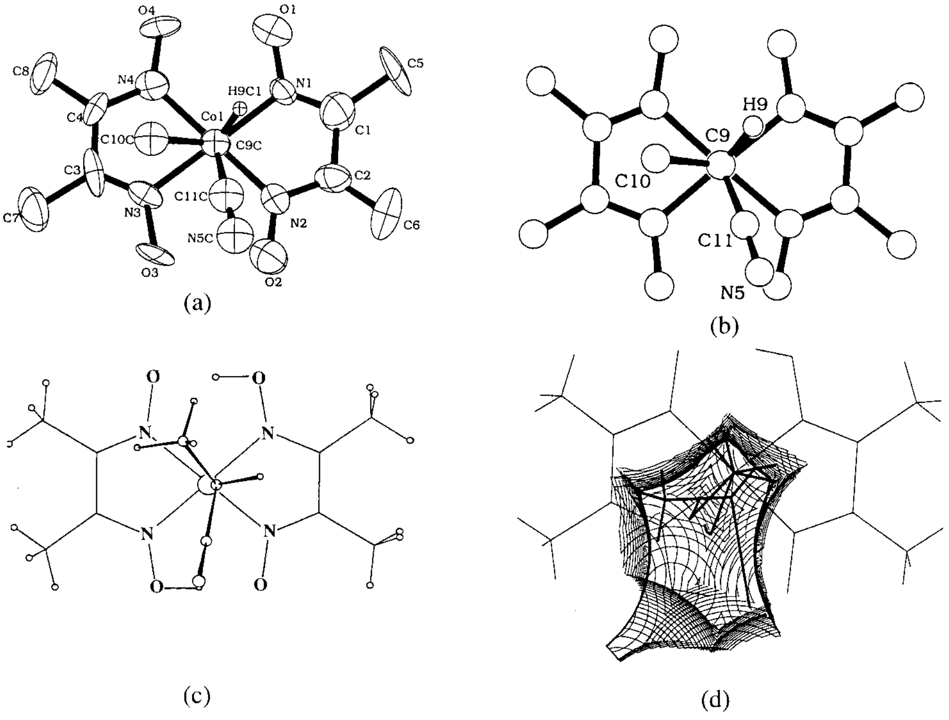


Figure 3. Conformation of the produced (*S*)-1-cyanoethyl group viewed normal to the cobaloxime plane: (a) obtained by crystal structure analysis; (b) estimated by molecular mechanics calculation in the crystal; (c) estimated by molecular mechanics calculation in the gas state; and (d) accommodated in the reaction cavity.

conformations, A, B and C around the Co–C9 bond before irradiation. The occupancy factors are 0.48(2), 0.34(3), and 0.18(3), respectively. After irradiation, the 2-cyanoethyl group takes two disordered positions, A and B, whose occupancy factors are 0.47(2) and 0.40(2), respectively. Moreover the produced 1-cyanoethyl group with *S* configuration appeared as a disordered structure with the original 2-cyanoethyl groups. The occupancy factor is 0.13(1). The 1-cyanoethyl group with *R* configuration was not observed. This is in good agreement with the results of the solid-state asymmetric reaction, in which the major product has the *S* configuration and about 27 % diastereomer excess was observed after 480 min exposure.[5]

The conformation of the produced (*S*)-1-cyanoethyl group is in good agreement with the estimated one from the molecular mechanics calculation. Fig. 3 shows the molecular structures viewed normal to the cobaloxime plane, (a) obtained by photoirradiation and (b) molecular mechanics calculation. This indicates that the photoreaction in the solid state proceeds in the pathway with minimum energy. It must be emphasized that the 1-cyanoethyl group has the lowest energy in the gas state if it has the conformation as shown in Fig. 3(c).[6] Fig. 3(d) shows the reaction cavity after irradiation. The produced 1-cyanoethyl group is accommodated in the cavity although a wide void space is found around the group.

In the previous paper, the reaction cavity for the 2-cyanoethyl group before irradiation was divided into two parts by the average plane comprising the C–C–C–N atoms of the 2-cyanoethyl group in order to examine the asymmetric shape of the cavity. Since the CN group has greater volume than the CH_3 group, it was assumed that the CN and CH_3 groups occupied the greater and smaller parts of the reaction cavity after conversion to the 1-cyanoethyl group. The assumption is valid considering from the structure of the produced 1-cyanoethyl group as shown in Fig. 4. The 2-cyanoethyl groups, A and B, take nearly the same conformations of the corresponding ones before irradiation. If the cavity after the irradiation is divided into two by the average plane composed of the C–C–C–N atoms for the A and B groups, the CN and CH_3 groups occupy the larger and smaller parts of the cavity, respectively, in either group. This well explains the reason why the (*S*)-1-cyanoethyl group is preferentially produced from the (*R*)-*sec*-butylamine complex after photoisomerization. It is clear that the asymmetric shape of the reaction cavity for the reactive group controls the chirality of the produced group. The proposal was examined using the following six complex crystals, although all the crystals were decomposed in the process of the isomerization.

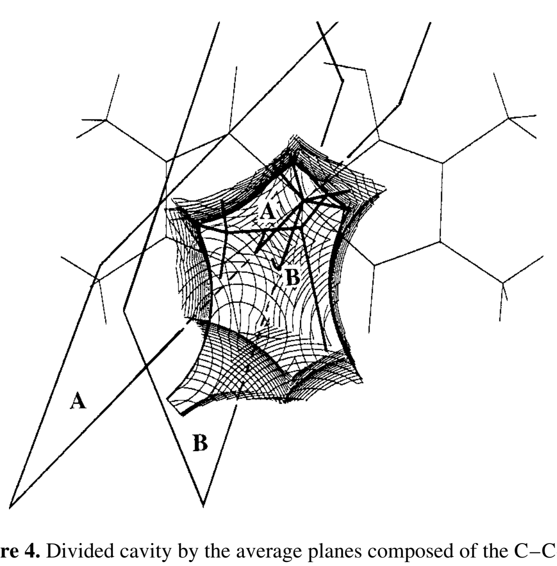


Figure 4. Divided cavity by the average planes composed of the C–C–C–N atoms of the two disordered 2-cyanoethyl groups, A and B. The CN group occupies the larger (left) part whereas the CH_3 group does the smaller (right) part.

Crystal and molecular structures of six complexes

Each crystal belongs to the orthorhombic system and the space group is $P2_12_12_1$ and has one crystallographically independent molecule in the asymmetric unit. The 2-cyanoethyl group in each crystal takes the *trans* conformation around the C–C bond. The crystal data are listed in Table 1. Since the cell dimensions are similar to each other, the similar molecular packings are observed. All the data were collected at 296 K.

(*R*)-1,2-Diaminopropane complex. The crystal structure of (2-cyanoethyl)[(*R*)-1,2-diaminopropane]cobaloxime complex viewed along the *c* axis and the ORTEP drawing of the molecular structure with the numbering of atoms are shown in Figs. 5(a) and (b), respectively. The torsion angle of Co–C9–C10–C11 is 169.45°. The cobalt atom is not coordinated with the secondary amino group, N7, but with the primary amino group, N6. This is probably due to the fact that the more negative charge is localized on N6 than N7,

Table 1. Crystal data for six crystals

	1	**2**	**3**
Chemical formula	$C_{14}H_{28}CoN_7O_4$	$C_{14}H_{27}CoN_6O_5$	$C_{15}H_{29}CoN_6O_5$
Formula weight	417.36	418.35	432.37
Space group	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$
a (Å)	11.079(2)	13.248(3)	13.160(2)
b (Å)	18.833(2)	16.175(3)	16.172(3)
c (Å)	9.456(2)	9.305(3)	9.474(3)
V (Å^3)	1973.1(6)	1993.9(8)	2016.3(7)
Z	4	4	4
D_x (Mg m^{-3})	1.405	1.394	1.424
μ (mm^{-1})	0.903	0.896	0.889
Crystal size	0.4×0.3×0.05	0.3×0.2×0.2	0.4×0.3×0.05
θ_{max} (°)	27.50	27.47	27.50
R	0.049	0.060	0.044
wR	0.125	0.141	0.125
	4	**5**	**6**
Chemical formula	$C_{19}H_{35}CoN_6O_4$	$C_{21}H_{37}CoN_6O_4$	$C_{15}H_{27}CoN_6O_4$
Formula weight	470.46	496.50	414.36
Space group	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$
a (Å)	14.8117(1)	11.270(3)	13.247(2)
b (Å)	18.1398(1)	23.431(7)	16.542(3)
c (Å)	9.7330(1)	9.405(2)	8.882(2)
V (Å^3)	2615.08(3)	2484(1)	1946.4(6)
Z	4	4	4
D_x (Mg m^{-3})	1.195	1.328	0.914
μ (mm^{-1})	0.688	0.728	0.889
Crystal size	0.3×0.3×0.2	0.3×0.3×0.1	0.3×0.2×0.2
θ_{max} (°)	27.82	27.65	27.50
R	0.039	0.069	0.058
wR	0.074	0.203	0.162

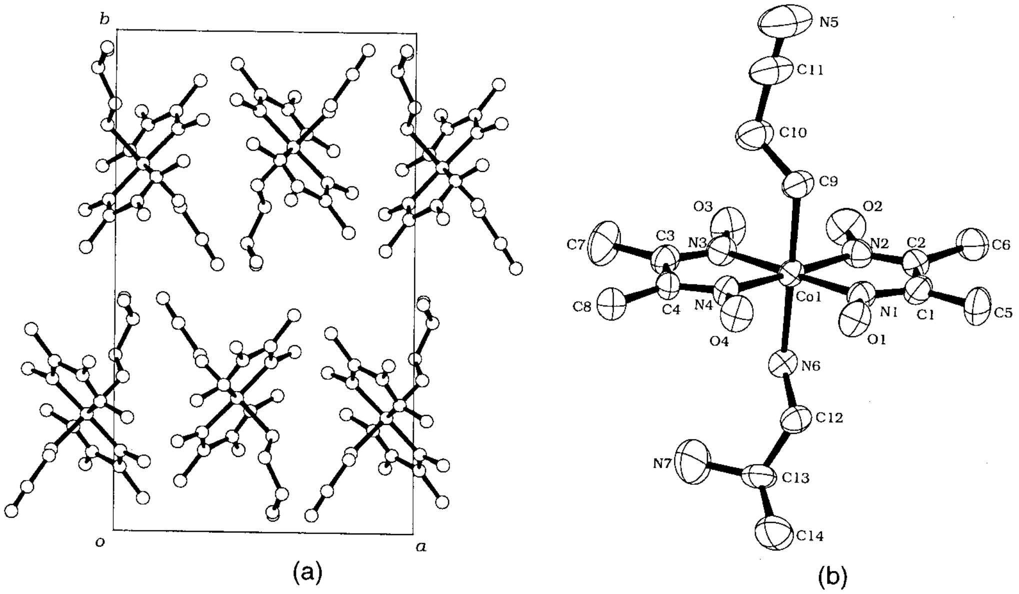


Figure 5. (a) Crystal structure of the (*R*)-1,2-diaminopropane complex viewed along the *c* axis; and (b) ORTEP drawing of the molecular structure.

considered from the ab initio molecular orbital calculation. The 2-cyanoethyl group are sandwiched by the 1,2-diaminopropane ligands and the 2-cyanoethyl groups of the neighboring molecules along the *c* axis. The 2-cyanoethyl group makes no hydrogen bond with the neighboring molecules.

(*S*)-2-Amino-1-propanol complex. The crystal structure of (2-cyanoethyl)[(*S*)-2-amino-1-propanol]cobaloxime complex viewed along the *c* axis and the ORTEP drawing of the molecular structure with the numbering of atoms are shown in Figs. 6(a) and (b), respectively. The 2-cyanoethyl group has three disordered structures, A, B and C, around the Co–C bond, the occupancy factors of which are 0.42(2), 0.36(2) and 0.22(1), respectively. All the disordered ones have *trans* conformation around the C–C bond; the torsion angles of Co–C9–C10–C11 are 178.30, 169.88 and 173.43°, for A, B and C, respectively. The disordered 2-cyanoethyl groups are sandwiched by the 2-amino-1-propanol ligands and the 2-cyanoethyl groups of the neighboring molecules along the *c* axis. The 2-cyanoethyl groups make no hydrogen bond with the neighboring molecules.

(*S*)-2-Amino-1-butanol complex. The crystal structure of (2-cyanoethyl)[(*S*)-2-amino-1-butanol]cobaloxime complex viewed along the *c* axis and the ORTEP drawing of the molecular structure with the numbering of atoms are shown in Figs. 7(a) and (b), respectively. The crystal structure is similar to those of the 1,2-diaminopropane and 2-amino-1-propanol complexes. The 2-cyanoethyl group has two disordered positions, A and B, around the Co–C bond, the occupancy factors of which are 0.84(1) and 0.16(1), respectively. The torsion angles of Co–C9–

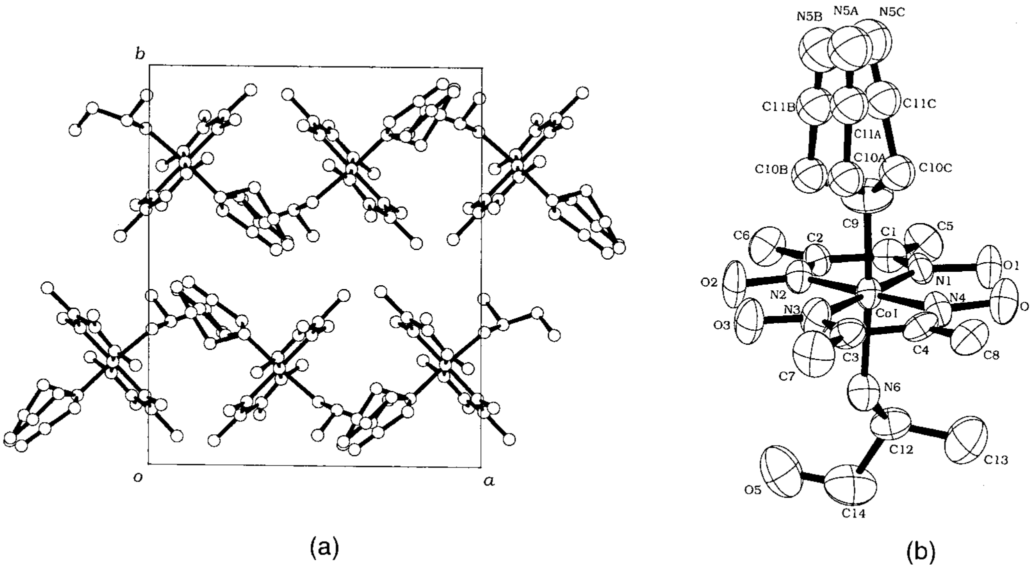


Figure 6. (a) Crystal structure of the (*S*)-2-amino-1-propanol complex viewed along the *c* axis; and (b) ORTEP drawing of the molecular structure.

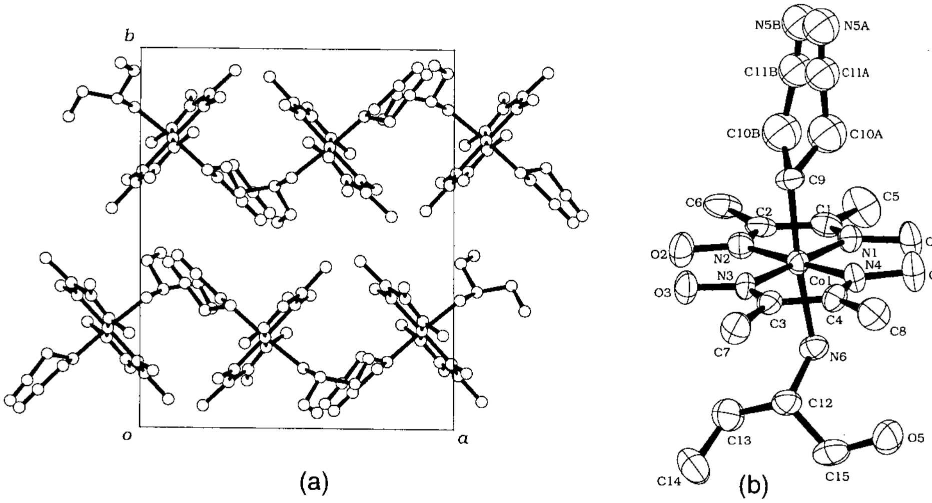


Figure 7. (a) Crystal structure of the (*S*)-2-amino-1-butanol complex viewed along the *c* axis and (b) ORTEP drawing of the molecular structure.

C10–C11 are 177.83 and 156.94° for A and B, respectively. The 2-cyanoethyl groups are also sandwiched by the 2-amino-1-butanol ligands and 2-cyanoethyl groups along the *c* axis and make no hydrogen bond with the neighboring molecules although the amine ligand has a hydroxy group, as observed in the 2-amino-1-propanol complex.

(*S*)-1-Cyclohexylethylamine complex. The crystal structure of (2-cyanoethyl)[(*S*)-1-cyclohexylethylamine]cobaloxime complex viewed along the *c* axis and the ORTEP drawing of the molecular structure with the numbering of atoms are shown in Figs. 8(a) and (b), respectively. Since the 2-cyanoethyl group is surrounded by the 1-cyclohexylethylamine ligands and the cobaloxime moieties of the neighboring molecules, the 2-cyanoethyl groups do not contact with each other. The 2-cyanoethyl group has three disordered structures, A, B and C, around the Co–C bond. The occupancy factors of A, B, and C are 0.40(1), 0.33(1) and 0.27(1), respectively. The torsion angles of Co–C9–C10–C11 are 176.52, 177.65, and 162.71° for A, B and C, respectively. The 2-cyanoethyl groups make no hydrogen bond with the neighboring molecules.

***cis*-Myrtanylamine complex.** The crystal structure of (2-cyanoethyl)(*cis*-myrtanylamine)cobaloxime complex viewed along the *c* axis and the ORTEP drawing of the molecular structure with the numbering of atoms are shown in Figs. 9(a) and (b), respectively. The preliminary crystal structure was already reported.[7] The 2-cyanoethyl group is sandwiched by the *cis*-myrtanylamine ligands along the *c* axis. The 2-cyanoethyl group has an ordered structure and has *trans* conformation around the C–C bond. The torsion angle of Co–C9–C10–C11 is 176.33°. The 2-cyanoethyl group makes no hydrogen bond with the neighboring molecules.

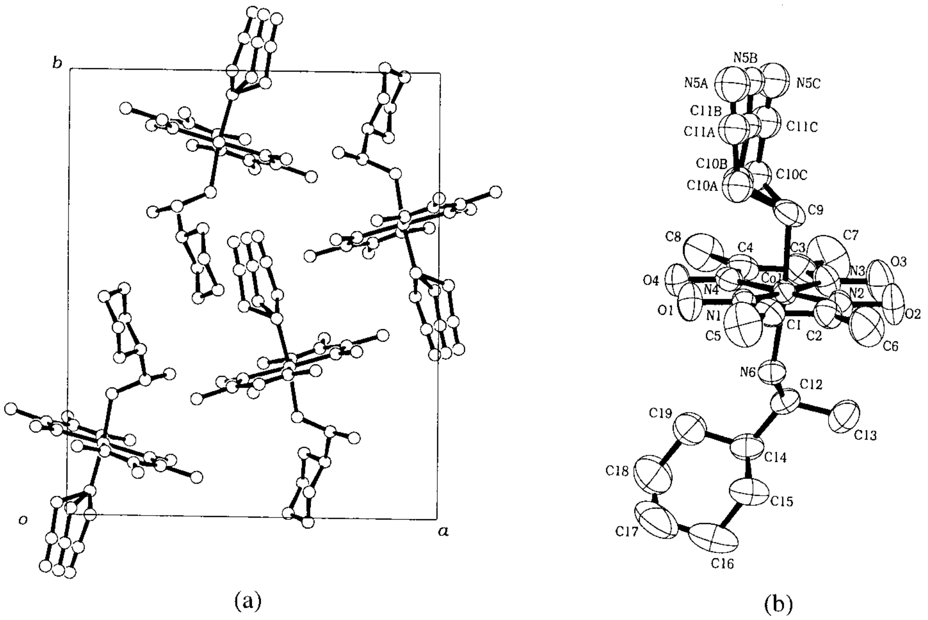
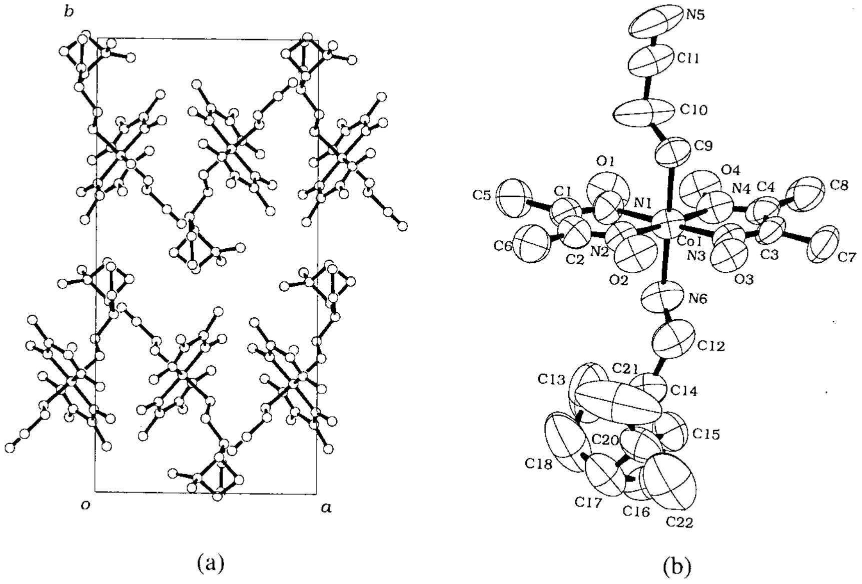


Figure 8. (a) Crystal structure of the (*S*)-1-cyclohexylethylamine complex viewed along the *c* axis and (b) ORTEP drawing of the molecular structure.



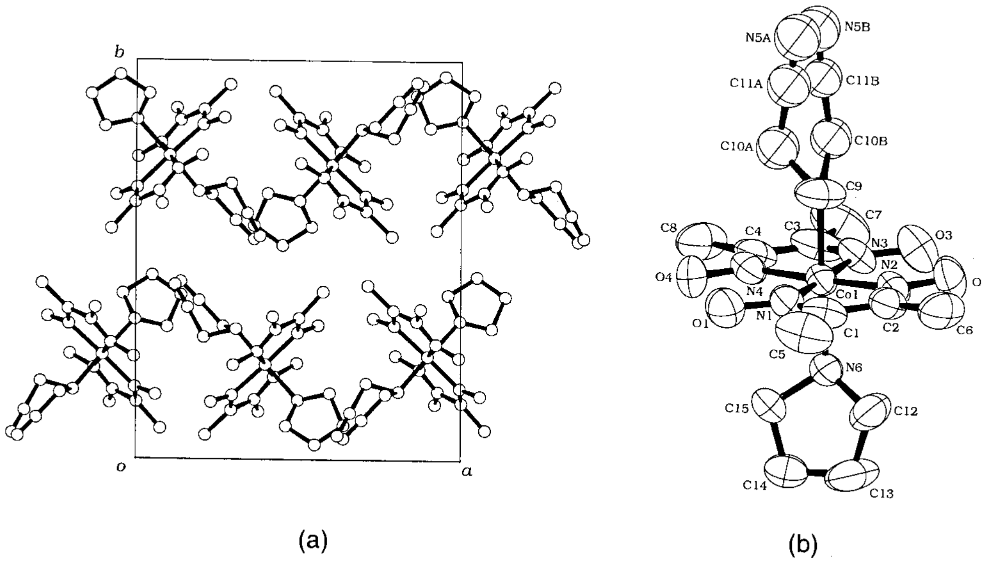
(a) (b)

Figure 9. (a) Crystal structure of the *cis*-myrtanylamine complex viewed along the *c* axis and (b) ORTEP drawing of the molecular structure.

Pyrrolidine complex. The crystal structure of the (2-cyanoethyl)(pyrrolidine)cobaloxime complex viewed along the *c* axis and the ORTEP drawing of the molecular structure with the numbering of atoms are shown in Figs. 10(a) and (b), respectively. The polymorphic crystal structure was already reported, which belongs to the orthorhombic system, the space group is $P2_12_12_1$ with a=12.807(2), b=15.630(2), c=9.699(1) Å and V= 1941.1(4) Å^3, and Z=4.[7] The 2-cyanoethyl group, which is sandwiched by the pyrrolidine ligands along the *c* axis, has two disordered structures, A and B, with *trans* conformation around the C–C bond. The occupancy factors of A and B are 0.52(2) and 0.48, respectively. The torsion angles of Co–C9–C10–C11 are 174.50 and 174.21° for A and B, respectively. The 2-cyanoethyl groups make no hydrogen bond with the neighboring molecules.

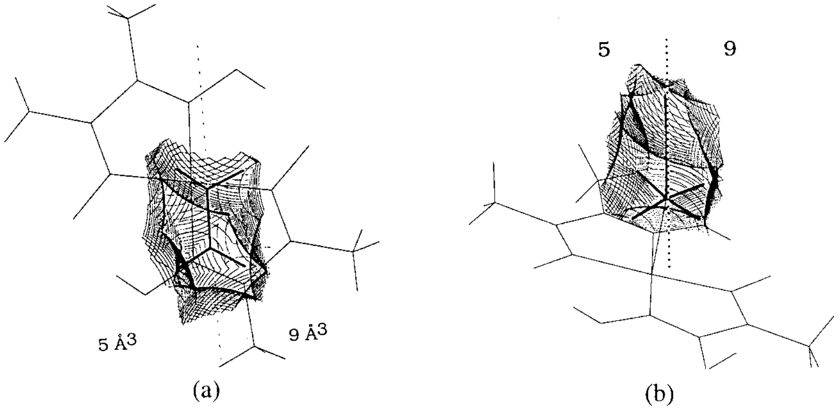
Asymmetric shape of the reaction cavity for the 2-cyanoethyl group

In order to examine the asymmetric environment around the 2-cyanoethyl group in each crystal, the reaction cavity for the 2-cyanoethyl group was drawn in a way similar to that reported previously.[8] The cavity was divided into two parts by the average plane comprising the C–C–C–N atoms of the 2-cyanoethyl group and the volume of each part was calculated. Fig. 11 shows the reaction cavity for the 2-cyanoethyl group of the (*R*)-1,2-diaminopropane complex crystal. The figure is drawn along the C–C–C–N average plane and the C–C–N bond is situated upper side. The volumes of the left and right parts are calculated to be 5.0 and 9.0 Å^3, respectively. For the other five crystals the volumes of left and right parts were calculated in the



(a) (b)

Figure 10. (a) Crystal structure of the pyrrolidine complex viewed along the *c* axis and (b) ORTEP drawing of the molecular structure.



(a) (b)

Figure 11. Cavity for the 2-cyanoethyl group of the (*R*)-1,2-diaminopropane complex divided into two parts by the average plane composed of C–C–C–N atoms, (a) viewed along the C–C–N bonds and (b) viewed normal to the C–C–N bonds.

same way. For the disordered 2-cyanoethyl groups, the cavity was drawn for each conformer and the volumes of left and right parts were calculated. In the calculation of the reaction cavity, the 2-cyanoethyl groups of the neighboring molecules are assumed to occupy all the positions of the disordered structures to simplify the calculation. The 2-cyanoethyl groups loosely contact with each other in each crystal, the approximation may be valid. The volumes of left and right parts of the cavities for the seven crystals including the (*R*)-*sec*-butylamine which was reported previously,[5] are given in Table 2. The averaged volumes of left and right parts, which were calculated as weighted sum of the occupancy factors of the disordered groups are also given.

Asymmetric isomerization

The crystalline powder of each complex was scattered onto a Petri dish and was irradiated with a xenon lamp equipped with UV cut-off filter (TOSHIBA Y-46) at 300 K using the temperature controller. After photoirradiation, the HPLC analysis of the sample was carried out using the chiral stationary phase. Table 3 shows the major configuration of the produced 1-cyanoethyl group and the diastereomer or enantiomer excess and reaction yield for the seven complexes. For the (*R*)-1,2-diaminopropane and (*S*)-1-cyclohexylethylamine complexes, the diastereomer excess gradually decreased as the irradiation time increased. On the other hand, the complexes with the other amines as axial base ligands showed almost constant diastereomer or enantiomer excesses as the irradiation time increased. This may be due to the fact that although the produced 1-cyanoethyl group is packed in the initial reaction cavity for the 2-cyanoethyl group as shown in Fig. 4(d), the cavity has enough size for the racemization or epimerization. It was proposed that the threshold value for crystalline-state racemization of the 1-cyanoethyl group is 11.5 Å^3.[8]

Table 3 also shows the volume ratio of the left part to the right part of the reaction cavity for the 2-cyanoethyl group.

Table 2. Asymmetric shape of the reaction cavity

Base ligand	Conformer	Occupancy	Left (Å^3)	Right (Å^3)
(*R*)-*sec*-butylamine	A	0.48	7	20
	B	0.34	10	17
	C	0.18	18	9
	Average	10.0	17.0	
(*R*)-1,2-diaminopropane		5	9	
(*S*)-2-amino-1-propanol	A	0.42	14	9
	B	0.36	15	8
	C	0.22	13	10
	Average	14.1	8.9	
(*S*)-2-amino-1-butanol	A	0.84	9	7
	B	0.16	8	8
	Average	8.8	7.2	
(*S*)-1-cyclohexyl-ethylamine	A	0.40	15	12
	B	0.33	13	14
	C	0.27	15	12
	Average	14.3	12.7	
cis-myrtanylamine			5	8
Pyrrolidine	A	0.52	9	8
	B	0.48	10	7
	Average	9.5	7.5	

Table 3. Major configuration of the 1-cyanoethyl group, reaction yields, diastereomer or enantiomer excess and volume ratio of the left part to the right part of the reaction cavity

Base ligand	Major configuration	Reaction time(min)	Reaction yield(%)	d.e. or e.e. (%)	V_L/V_R
(*R*)-*sec*-butylamine	*S*		36	28	0.59
(*R*)-1,2-diaminopropane	*S*	30	6	26	0.56
		60	11	19	
		120	14	15	
(*S*)-2-amino-1-propanol	*R*		12	21	1.58
(*S*)-2-amino-1-butanol	*R*		9	32	1.22
(*S*)-1-cyclohexyl-ethylamine	*R*	60	4	11	1.12
		120	7	4	
		240	9	2	
cis-myrtanylamine	*S*	60	7	9	0.63
		120	8	9	
		240	12	9	
Pyrrolidine	*R*	120	1.4	21	1.27
		240	2.9	19	
		480	6.7	20	
		960	6.0	20	
		1920	8.9	17	

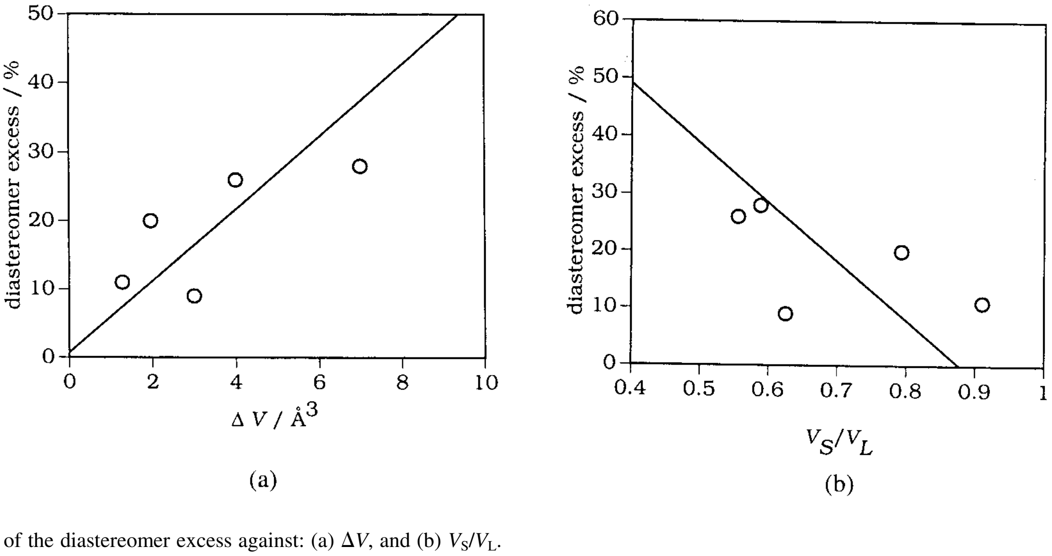
This table clearly indicates that the (*R*)-1-cyanoethyl group is produced preferentially in the solid-state photoisomerization when the left part of the cavity is wider than the right part and vice versa. This result suggests that the stereoselectivity in the solid-state can be controlled by the chiral crystal environment. It was assumed in the previous paper[5] that the CN and CH_3 groups should occupy the greater and smaller parts of the reaction cavity after conversion to the 1-cyanoethyl group. The assumption holds good for the seven complex crystals.

Relation between the diastereomer excess and the asymmetric shape of the reaction cavity

In order to examine the value of the diastereomer excess, the diastereomer excess was plotted against the difference ($V=V_L-V_S$) between the volumes of the larger (V_L) and the smaller (V_S) parts of the reaction cavity and the ratio (V_L/V_S), as shown in Figs. 12(a) and (b), respectively. Both figures may indicate a linear correlation between the diastereomer excess and the asymmetric reaction shape.

Temperature dependence of the diastereomer excess

The temperature dependence of the diastereomer excess observed for the (*R*)-*sec*-butylamine, *cis*-myrtanylamine, and (*R*)-2-amino-2-phenylethanol complexes were given in Table 4. The value of *K* is the ratio of the *R*- to *S*-isomer or vice versa, and is defined as $K=(1+\text{d.e.})/(1-\text{d.e.})$. It is clear that the diastereomer excess significantly decreased as the temperature was raised, which is also observed for the racemization of the chiral 1-cyanoethyl group bonded to the cobalt atom in several cobaloxime complexes.[9,10] Although the irradiation time of the (*R*)-*sec*-butylamine complex is different from those of the other two, the above three cobaloxime complexes showed almost constant diastereomer excess when the irradiation time increased.



(a) (b)

Figure 12. Plots of the diastereomer excess against: (a) ΔV, and (b) V_S/V_L.

Table 4. Temperature dependence of the diastereomer excess

Temperature (K)	(*S*)-*sec*-Butylamine		*cis*-Myrtanylamine		2-Amino-2-phenylethanol	
	d.e. (%)	ln K	d.e. (%)	ln K	d.e. (%)	ln K
270	37.1	0.778	7.0	0.140	84.6	2.49
285	32.7	0.679	9.0	0.180	84.4	2.47
300	28.1	0.577	8.5	0.170	73.8	1.89
315	23.6	0.482	7.3	0.146	73.9	1.90
330	19.8	0.402	7.6	0.153	–	–

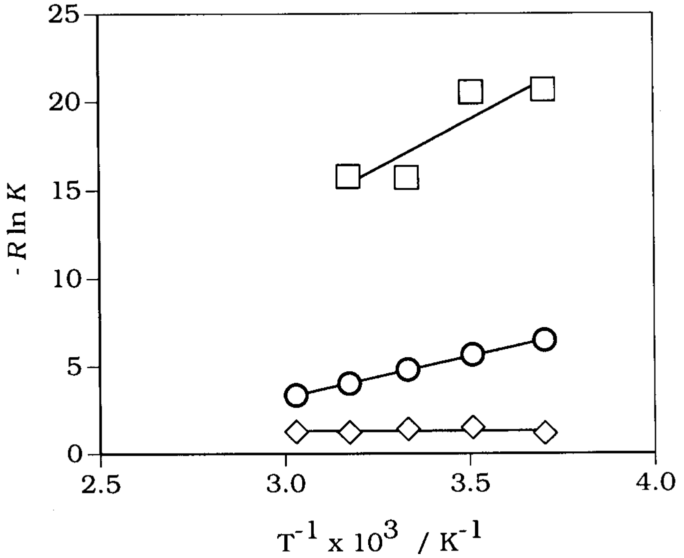


Figure 13. Temperature dependence for the (*R*)-*sec*-butylamine (circle), *cis*-myrtanylamine (diamond), and (*R*)-2-amino-2-phenylethanol (square) complexes.

Fig. 13 shows the Arrhenius plots for the three complexes. The values of $\Delta\Delta H$ and $\Delta\Delta S$ were estimated from the slope and intercept of the Arrhenius plot with the least-squares method. The calculated values of $\Delta\Delta H$(kJ mol^{-1}) and $\Delta\Delta S$(J K^{-1} mol^{-1}) are -4.69 and 11, -0.56 and 0.5, and -11.0 and 19, for (*R*)-*sec*-butylamine, *cis*-myrtanylamine and 2-amino-2-phenylethanol, respectively. Since the ratio of the larger part of the cavity volume to the smaller one, V_L/V_S, of the (*R*)-*sec*-butylamine complex, 1.69, is greater than that of the *cis*-myrtanylamine complex, 1.59, the value of $\Delta\Delta H$ of the (*R*)-*sec*-butylamine complex is significantly greater than that of the *cis*-myrtanylamine. The 2-cyanoethyl group of the 2-amino-2-phenylethanol complex takes a *gauche* conformation around the C–C bond. The gauche conformation gives the greater diastereomer excess than the *trans* conformation, since the transformation proceeds topochemically.[3] This may cause the greater difference in enthalpy between the *R*- and *S*-isomers at the transition state than that of the transformation of the *trans* 2-cyanoethyl group. Therefore, the greatest $\Delta\Delta H$ was observed among the three complexes.

Conclusion

The 2-cyanoethyl group bonded to the cobalt atom in cobaloxime complexes was isomerized to the 1-cyanoethyl group on exposure to visible light. The chirality of the produced 1-cyanoethyl group depends on the chiral environment around the 2-cyanoethyl group in the crystal structure before irradiation. The configuration and conformation of the produced 1-cyanoethyl group after the crystalline-state isomerization of the (2-cyanoethyl)[(*R*)-*sec*-butylamine]cobaloxime complex are in good agreement with the structure estimated from the molecular mechanics calculation. This suggests that the process of the asymmetric induction would be made clear if the chiral environment of the reactive 2-cyanoethyl group is examined. The chiral environment was defined by dividing the reaction cavity into two parts with the average plane comprising the C–C–C–N atoms of the 2-cyanoethyl group and comparing the volumes of the two parts. Since the CN group has a greater volume than the CH_3 group, it is reasonable to assume that the CN and CH_3 groups occupy the greater and smaller parts of the reaction cavity, respectively, after the conversion to the 1-cyanoethyl group. This assumption was confirmed by the asymmetric photoisomerization of the six cobaloxime complexes. Moreover, it was made clear that the degree of the asymmetric induction is caused by the difference in volume of the two parts of the reaction cavity. The temperature dependence of the asymmetric induction was examined for the three cobaloxime complexes. The diastereomer excess increased as the temperature decreased. The difference in activation enthalpy obtained from the Arrhenius plot has positive correlation with the ratio of the larger part of the cavity volume to the smaller one, V_L/V_S. The asymmetric shape of the reaction cavity is a good guide for the asymmetric induction.

Experimental

Preparation

All the cobaloxime complexes were synthesized in a way similar to that reported previously.[11]

The prismatic orange crystals suitable for X-ray analysis were obtained from acetone–hexane solutions.

X-ray structure determination

The three dimensional intensity data were collected on a Rigaku AFC7R diffractometer for the (*R*)-1,2-diaminopropane, (*S*)-2-amino-1-propanol, (*S*)-2-amino-1-butanol, and pyrrolidine complexes, a SMART-CCD diffractometer for the (*S*)-1-cyclohexylethylamine complex, and a Rigaku RAXIS IIcs for the *cis*-myrtanylamine complex, using MoKα radiation monochromated by graphite. The structure was solved by the Patterson method with the program SAPI91,[12] or the direct method with the program SIR 92,[13] and refined with the program SHELXL 97.[14] In the process of the refinement, the bond distances of the disordered 2-cyanoethyl groups were restrained to have fixed values if the group has the disordered conformations around the Co–C bond. All the hydrogen atoms were calculated geometrically and refined with a riding model. Non-hydrogen atoms were refined with the anisotropic temperature factors except for the disordered atoms, which were refined isotropically. The absolute configuration of each crystal was determined with the Flack parameter,[15] which is consistent with that of the chiral amine except the pyrrolidine complex. The atomic scattering factors were taken from International Tables for Crystallography.[16] Other experimental details were given from CIF data, which will be supplied by CCDC.

Photoreaction and HPLC analysis

The crystals scattered onto a Petri dish were irradiated with a xenon lamp equipped with UV cut-off filter (TOSHIBA Y-46) for several hours at 300 K. The temperature controller used was Nisshin Scientific Corporation Model NCP-2215 to obtain the temperature dependence of the diastereomer excess at the range of 270–330 K. After photoirradiation, the HPLC analysis of the samples was carried out using the chiral stationary phase. The HPLC system used was HITACHI L-7000 series system equipped with CHIRALPAK-AD column (F4.6 mm¥250 mm, Daisel Chem., Inc.) maintained at 300 K and with Model L-7420 UV–Vis absorbance detector monitored at 254 nm. The mobile phase consists of hexane with 10% v/v ethanol and its flow rate was 1.0 ml min^{-1}. The quantification was performed integrating the peak area. No leading or tailing around the peaks corresponding to (*R*)- and (*S*)-1-cyanoethyl complexes was observed in the chromatogram. This indicates that the produced 1-cyanoethyl group was not inverted to the opposite configuration when it migrated in the chiral stationary phase of HPLC.

Acknowledgements

This work was partly supported by CREST (Core Research for Evolutional Science and Technology) from Japan Science and Technology Corporation (JST).

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