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Chiral Lattice-Controlled Asymmetric Photoisomerization of (2-Cyanoethyl)cobaloximes in the Solid State

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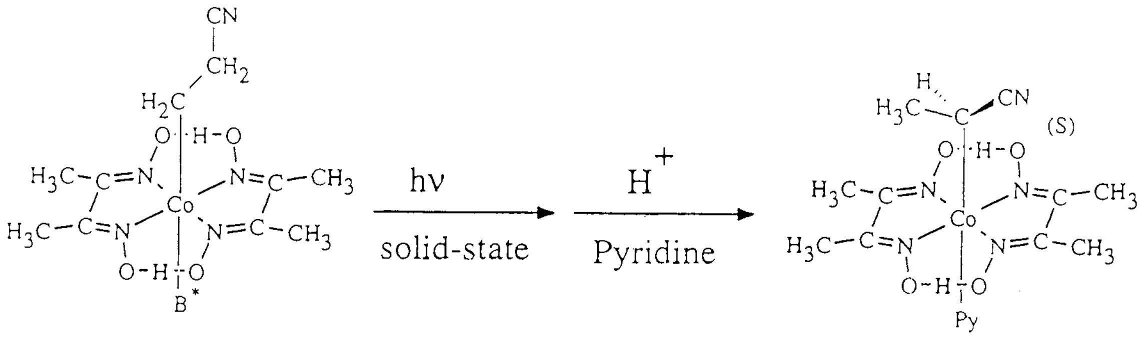
Solid-state asymmetric photoisomerization of 2-cyanoethylcobaloxime complexes occurred to afford optically active 1-cyanoethylcobaloxime complexes with moderate to high enantioselectivities (~82%ee). The X-ray crystal structure analysis of (*R*)-2-phenylglycinol-coordinated complex revealed that the 2-cyanoethyl group is forced to take a chiral conformation by chiral crystal lattice. The enantioselection mechanism is also discussed based on the X-ray results.

Solid-state asymmetric reaction is of importance from both synthetic and prebiological points of view. Several such reactions have been reported in organic photo-reactions involving π-systems.[1-4] However, asymmetric photoreaction of organometallic compounds in the solid-state has not been reported so far to our knowledge. We previously found that 2-substituted ethyl cobalt complexes isomerized to 1-substituted ethyl cobalt complexes unidirectionally on visible light irradiation in the solid-state.[5] The reactive group in the starting material is not chiral but chirality is introduced at the α carbon by the (β-α)photoisomerization. Here, if the crystal lattice is chiral, asymmetric induction can be expected in such a system. In this communication we wish to report an asymmetric photoisomerization of 2-cyanoethylcobaloximes coordinated with chiral axial ligand which has no asymmetric effect on the reactive group at the trans position in the same molecule but serves as the chiral handle for forming the chiral crystal lattice.

The substrates **1**, **2**, and **3** (Fig. 1) were prepared by ligand displacement of aqua(2-cyanoethyl)bis(dimethylglyoximato)cobalt(III)[6] with (*R*)-1-methylpropylamine, (*R*)-1-(1-naphthyl)ethylamine, and (*R*)-2-phenylglycinol, respectively. The crude substrates **1**, **2**, and **3** were recrystallized from methanol/water(1/2), methanol/water(2/1), and ethanol/hexane(1/1), to give yellow plates, yellow columnar crystals, and yellow prisms, respectively. These structures were confirmed by IR and NMR spectra.[6] The finely powdered substrate crystals, suspended in liquid paraffins (6.5 ml) and spreaded onto a petri dish (diameter: 88 mm), were irradiated with a solar simulater (flux density: 100 mW/cm^2) at room temperature for several hours. The chiral bases of each reaction products were displaced by achiral base, pyridine, to give pyridine coordinated complexes. The crude products were chromatographed on a silica gel column which afforded β- (faster fraction) and a mixture of β- and α-isomer(isomerized product:slower fraction). The (α:β) ratios were determined by HPLC using Nova pak C18. From the optical rotation of latter fraction and the (α:β) ratio the optical rotation of the α isomer produced was calculated. The enantioselectivity was determined by reference to the optical rotation of the optically pure α complex.[7] The results are shown in Table 1. All the reactions here examined were found to give (*S*)-(-)-enantiomer predominantly (Fig. 1). Highest enantioselectivity (81.6%ee) was obtained in the reaction with complex **3**.

To elucidate the origin of the enantioselectivity we have investigated the crystal structure of complex **3** by X-ray diffraction method.[8] The crystal structure of complex **3** is shown in Fig. 2. The most remarkable feature is that the cyano group in the reactive group lies in the conformation parallel to the inplane ligand and β-cyanoethyl group is forced to take a chiral conformation by the chiral lattice. The reaction cavity[9] for the reactive group is drawn in Fig. 3a and 3b based on the crystal structure. The conformation of the cyanoethyl



1 B* = (*R*)-1-Methylpropylamine
2 B* = (*R*)-1-(1-Naphthyl)ethylamine
3 B* = (*R*)-2-Phenylglycinol

Fig. 1.

Table 1. The Enantioselectivities in the Solid-state β-α Photoisomerizations of 2-Cyanoethylcobaloximes

Complex No.	Reaction time/h	Ratio of 1-cyanoethyl complex produced/%	Major enantiomer		
			$[\alpha]_D$/°	Configuration	Enantioselectivity/%ee
1	1.7	28.8	-17.9	S	27.9
	3	41.0	-19.1	S	29.8
	15	57.9	-19.1	S	29.8
2	2	35.1	-32.8	S	51.1
	4	55.2	-40.3	S	62.8
	15	88.3	-40.1	S	62.5
3	1	4.9	-52.4	S	81.6
	7.5	53.7	-49.6	S	77.3
	20	79.8	-49.7	S	77.4

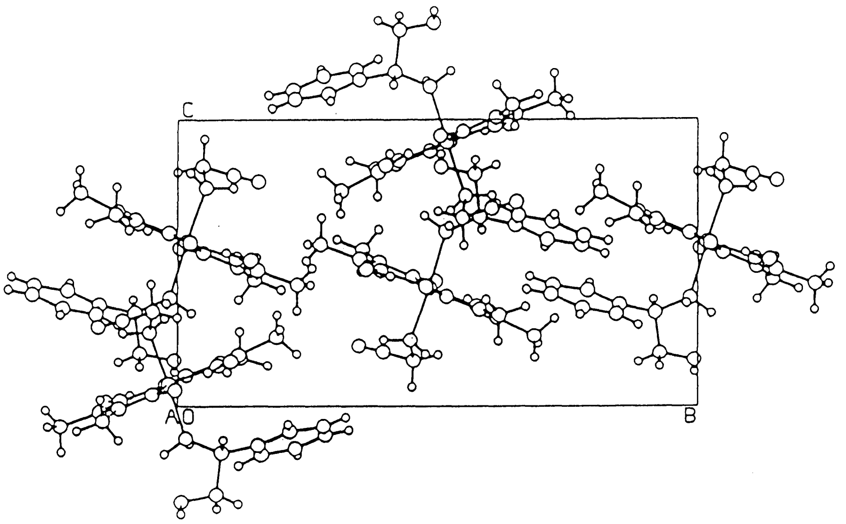
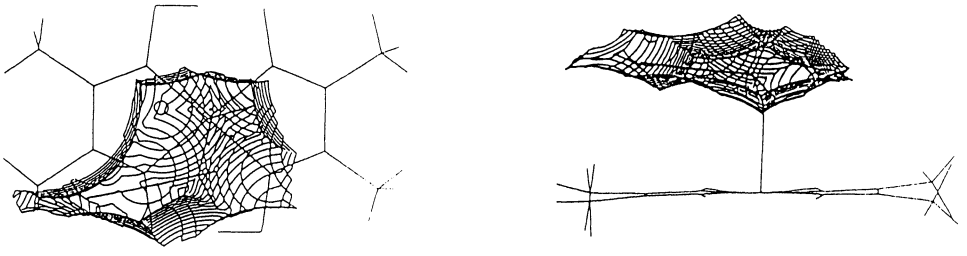


Fig. 2. Crystal structure of complex **3**.



(a) (b)

Fig. 3. The cavity for the cyanoethyl of complex **3** viewed along (a) the normal to the average plane of cobaloxime and (b) its side view.

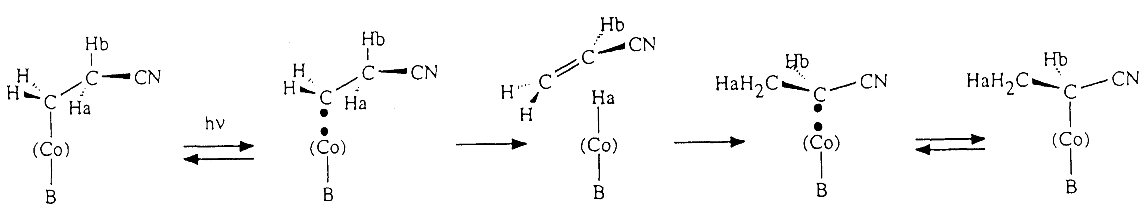


Fig. 4. The mechanism for asymmetric photoisomerization.

group and the shape of the cavity for the group well explain the configuration of the major enantiomer produced and difficulty for racemization. Co-C bond homolysis on visible light irradiation gives 2-cyanoethyl radical and Co(II) species. The Ha(pro-*S*) hydrogen atom on the β carbon of the 2-cyanoethyl radical, which is located nearer the cobalt atom, is abstracted by cobalt(II) species to give acrylonitrile and hydride complex.[10] Since the acrylonitrile molecule formed is freezed in the chiral cavity shown in Fig. 3, H-atom transfer from hydride complex to the methylene of the acrylonitrile and combination of the resulting 1-cyanoethyl radical and the Co(II) species afford (*S*)-α complex. Such a change requires only least movement of alkyl. However, formation of the (*R*)-enantiomer requires rotation of the alkyl group, the radicals or the olefin about the axis through C1 and C2 which seems to be extremely difficult since the space between the bottom and the ceiling of the cavity is too narrow for the rotation (Fig. 3a and 3b). Preliminary X-ray analysis for complex **2** gave the similar result.

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6) **1**: IR(KBr) 3310, 3260, 2240 and 1566 cm^{-1}; ^1H-NMR(200MHz, $CDCl_3$) δ2.30-2.15(m, 1H, HN-C$\underline{H}$-), δ2.26(s, 12H, CH_3 of dmgH), δ2.0-1.2(broad, 2H, -NH_2), δ1.82(t, 2H, J 7.9Hz, -CH_2-CN), δ1.39(t, 2H, Co-CH_2-), δ1,26(m, 2H, CH_2 of amine), δ0.93(d, 3H, J 6.6Hz, H_2N-CH-C$\underline{H}_3$), δ0.74(t, 3H, J 7.3Hz, -CH_2-C$\underline{H}_3$). **2**: IR(KBr) 3299, 3251, 2241 and 1562cm^{-1}; ^1H-NMR(200MHz, $CDCl_3$) δ7.89-7.25(m, 7H, aromatic), δ4.59(m, 1H, H_2N-C$\underline{H}$-), δ2.69(m, 1H, -NH), δ2.08 and 2.03(s, s, 12H, CH_3 of dmgH), δ1.78(t, 2H, J 7.8Hz, -CH_2-CN), δ1.57(broad, 1H, -NH), δ1.42(d, 3H, J 6.6Hz, CH_3 of amine), δ1.36(t, 2H, Co-CH_2-). **3**: IR(KBr) 3367, 3310, 3249, 2242 and 1563cm^{-1}; ^1H-NMR(200MHz, $CDCl_3$)δ7.31(m, 3H, aromatic), δ7.07(m, 2H, aromatic), δ3.75(m, 1H, H_2N-C$\underline{H}$-Ph), δ3.61(dd, 1H, J 4.0Hz and 11.6Hz, -C$\underline{H}$H'-OH), δ3.16(dd, 1H, J 9.7Hz, -CH$\underline{H'}$-OH), δ2.75 and 2.48(m, m, 2H, -NH_2), δ2.03 and 2.01(s, s, 12H, CH_3 of dmgH), δ1.78(t, 2H, J 7.9Hz, -CH_2-CN), δ1.34(m, 2H, Co-CH_2-).
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8) Crystal data for **3**:$C_{19}H_{29}N_6O_5Co$, M=480.41, yellow prismatic crystal 0.5x0.4x0.2mm^3; orthorhombic, space group $P2_12_12_1$, a=11.882(5)Å, b=18.375(7)Å, c=10.276(9)Å, α=90 , β=90 , γ=90 , V=2244(2)$Å^3$, Z=4, Dc=1.42gcm^{-3}, R=0.042, Rw=0.046 for 1979 observed refrections [Io>3σ(Io)]. Intensity data were collected on a Rigaku four-circle diffractometer with graphite-monochromated MoKα radiation, 3 <2θ<55 , ω/2θ scan. The structure was solved with MITHRIL (Gilmore, C.J.,1984) and refined by full-matrix least-squares using TEXSAN Crystallographic Software (Molecular Structure Corporation, 1985).
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10) In solution-state chemistry of organocobaloximes, the Co-C bond homolysis and successive olefin formation steps are widely accepted. F.T.T.Ng, G.L.Rempel, C.Mancuso, and J.Halpern, *Organometallics*, **1990**, 2762 and references cited therein.

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