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CHIRAL LATTICE-CONTROLLED ASYMMETRIC (β–α)PHOTOISOMERIZATION OF 2-SUBSTITUTED ETHYL COBALOXIME COMPLEXES

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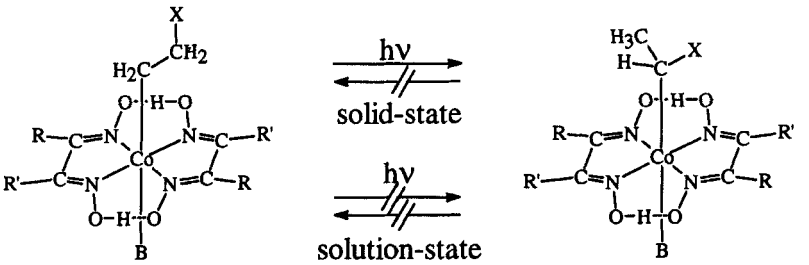
Abstract
Chiral lattice-controlled asymmetric photoisomerization of 2-methoxycarbonylethyl, 2-carbamoylethyl, 2-(*N*-methylcarbamoyl)ethyl and 2-(*N*-phenylcarbamoyl)ethyl cobaloxime complexes was found to occur which afforded corresponding, optically active 1-substituted ethyl cobaloxime complexes in enantioselectivities ranging from 4 to 69%ee.

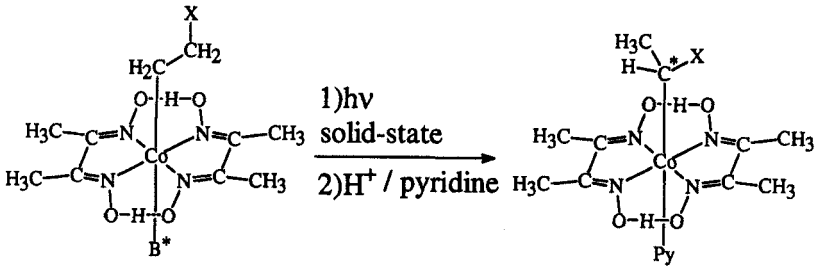
INTRODUCTION

We have previously reported that 2-cyanoethyl and 2-methoxycarbonylethyl cobaloxime complexes isomerize to 1-substituted ethyl complexes unidirectionally in the solid state on visible-light irradiation (Scheme 1).[1] Furthermore, asymmetric induction was found to occur in the photoreaction of 2-cyanoethylcobaloximes having chiral axial ligand as the chiral handle for forming the chiral lattice,[2] and high enantioselectivity (up to 82%ee at room temperature) was obtained (Scheme 2).



X = CN,COOMe
R,R' = Me,Ph
B = various bases

SCHEME 1



X =	CN	
B* =	(*R*)-1-Methylpropylamine	(*S*) ~ 29.8%e.e.
	(*R*)-1-(1-Naphthyl)ethylamine	~ 62.8%e.e.
	(*R*)-2-Phenylglycinol	~ 81.6%e.e.

SCHEME 2

The previous work has, however, had some difficulty in determining the enantioselectivities (in the early stage of the reaction) which were based on the optical rotation of the products. HPLC analysis using a chiral column made it possible to determine enantioselectivity more accurately even in the early stage of the reaction in which the content of alpha-isomer is low.[3]

Present study has been undertaken to extend the applicability of the lattice-controlled asymmetric photoisomerization to a series of 2-methoxycarbonylethyl cobaloximes and a series of 2-carbamoylethyl cobaloximes [2-carbamoylethyl, 2-(*N*-methylcarbamoyl)ethyl and 2-(*N*-phenylcarbamoyl)ethyl cobaloximes], and to scrutinize the time course of the enantioselectivities.

RESULTS AND DISCUSSION

Various chiral base-coordinated 2-methoxycarbonylethyl and 2-carbamoylethyl cobaloxime complexes were easily prepared by ligand displacement of the corresponding aqua, benzylamine or aniline complexes. The aniline coordinated 2-carbamoylethyl cobaloxime complexes were produced by reacting *N*-substituted acrylamide with aniline-coordinated bis(dimethylglyoximato)cobalt(I) under a basic condition. The structures were characterized by IR and NMR spectra.

The powdered samples were irradiated with a solar simulator (flux density:

100mW/cm^2) for a definite time at room temperature. After the reaction the chiral axial bases of the reaction products were displaced by achiral ligands such as methyldi-phenyl-phosphine and dimethylphenylphosphine to afford the corresponding phosphine-coordi-nated complexes which have chiral center only at the carbon coordi-nated to cobalt atom. The concomitantly liberated chiral ligand is able to reuse for preparing the substrate.

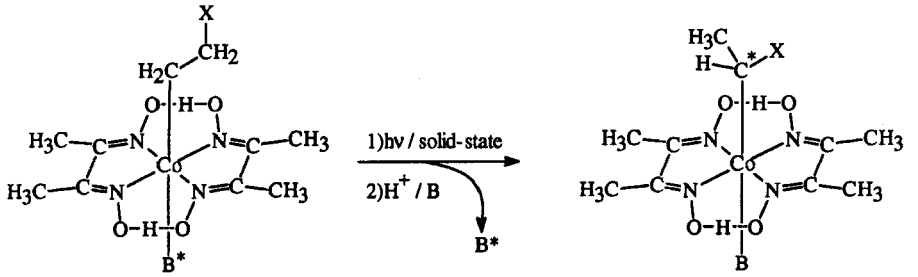


TABLE 1 Rate Constants and Enantioselectivities in the Photoisomerization of β-Substituted Ethyl Cobaloxime Complexes Coordinated with Chiral Amine

	Complexes		Initial rate constants/s^{-1}	Major enantiomer		
	X	B *		B	Max. %ee	Config. (sign of α_D)
1	COOMe	(*R*)-1-(1-Naphthyl)ethylamine	1.09×10^{-4}	$PMePh_2$	0	
2	COOMe	(*R*)-2-Phenylglycinol	8.55×10^{-5}	$PMePh_2$	0	
3	COOMe	Methyl (*S*)-phenylalaninate	2.46×10^{-5}	$PMePh_2$	15	*R* (+)
4	COOMe	(*S*)-Phenylalaninol	1.73×10^{-5}	$PMePh_2$	7	*S* (−)
5	$CONH_2$	(*R*)-1-(1-Naphthyl)ethylamine	3.68×10^{-5}	PMe_2Ph	28.9[a)]	(−)
6	$CONH_2$	Methyl (*S*)-phenylalaninate	4.07×10^{-4}	PMe_2Ph	23.0[a)]	(−)
7	$CONH_2$	(*R*)-2-Phenylglycinol	very slow			
8	CONHMe	(*R*)-2-Phenylglycinol	2.20×10^{-5}	$PMePh_2$	69.1[a)]	(+)
9	CONHMe	(*R*)-1-(1-Naphthyl)ethylamine	very slow			
10	CONHMe	Methyl (*S*)-phenylalaninate	4.34×10^{-5}	$PMePh_2$	18.1[a)]	(+)
11	CONHPh	(*S*)-1-Methylpropylamine	9.94×10^{-5}	$PMePh_2$	4[a)]	(+)
12	CONHPh	(*S*)-Phenylalaninol	very slow			
13	CONHPh	(*R*)-2-Phenylglycinol	very slow			

a) The absolute configuration of the major enantiomer is not yet determined.

The ratios of alpha to betha and the enantioselectivities of the alpha complexes produced were determined by HPLC using CHIRALCEL OD-H. The reaction rate constants were obtained from the first-order rate plots of the ratio of betha/(alpha+betha) of the early stage of the reaction. The rate constants and the maximum enantioselectivities (%ee) are given with the sign of the optical rotation of the major enantiomer in Table 1.

These substrates were all found to isomerize to 1-substituted ethyl complexes, and asymmetric induction was observed in most substrates having chiral axial ligand as the chiral handle for forming the chiral lattice (Table 1). Among them, the reaction of (*R*)-2-phenylglycinol-coordinated 2-(*N*-methylcarbamoyl)ethyl cobaloxime, **8**, gave a relatively high enantioselectivity (69%ee), although those of the others were moderate to low. There is not a complete correlation between the rate constants and the enantioselectivities, but the system with a smaller rate constant, gererally, seems to afford a higher enantioselectivity when compared within a homologous series. This is consistent with one of the conclusions obtained in the studies on the solid-state photoracemization of chiral alkyl cobaloximes[4] that the reaction rate is mainly controlled by the volume of the cavity for the reactive group when no intermolecular interaction exists.

It has been shown in the asymmetric photoisomerization of 2-cyanoethyl cobaloximes that the reactive group in crystals resulting in a relatively high enantioselectivity has a conformational chirality, but the reactive group in crystals giving a lower enantioselectivity has a conformation in which Co, C(alpha), C(betha), and CN are coplanar.[5] This seems to hold for a series of 2-methoxycarbonylethyl and for a series of 2-carbamoylethyl complexes here studied. In fact, preliminary X-ray analyses revealed that

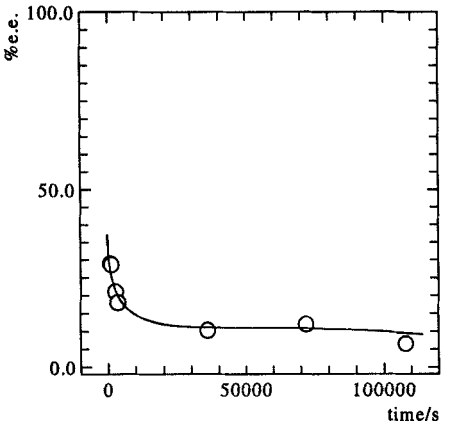


FIGURE 1. Time course of enantioselectivity for isomerization of **5**

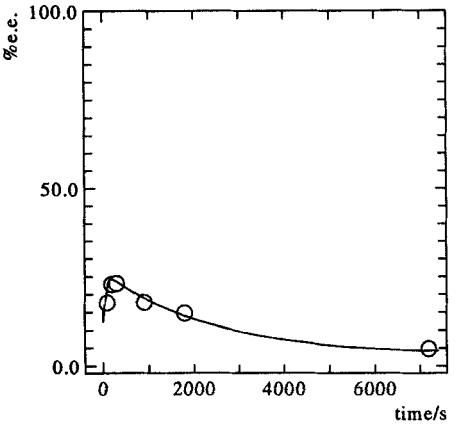


FIGURE 2. Time course of enantioselectivity for isomerization of **6**

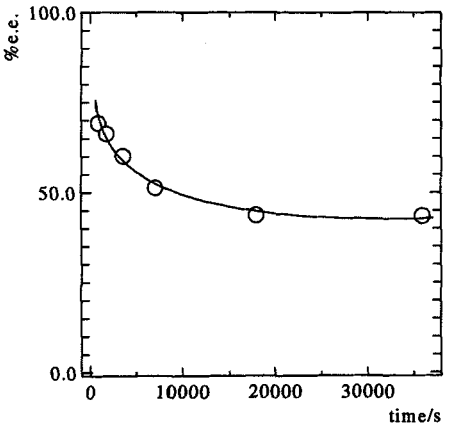


FIGURE 3. Time course of enantioselectivity for isomerization of **8**

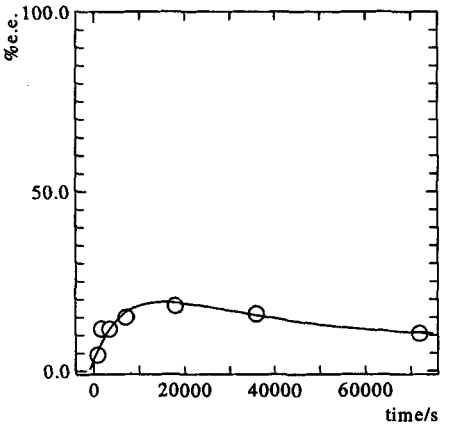


FIGURE 4. Time course of enantioselectivity for isomerization of **10**

crystals of complexes **1, 2, 3, 4, 5, 6, 10,** and **11** have a stretched conformation in which Co, C(alpha), C(betha), and C(carbonyl) are coplanar.[6] Reactive group in crystals of complex **8** is expected to have a chiral conformation enforced by the chiral crystal lattice, and the X-ray crystallographic analysis is now in progress.

The time course of enantioselectivities for complexes **5, 6, 8** and **10** are shown in Figures 1, 2, 3, and 4, respectively. The enantioselectivities for isomerization of complexes **5** and **8** decrease with time. The decrease in enantioselectivity with time can be explained by racemization of the initially formed optically active product. The enantioselectivities for isomerization of complexes **6** and **10** increase with time in the very early stage, and then decrease with time. The increase in the early stage will be considered as follows: the very eary stage of reaction occurring on or near the surface of crystals will afford a lower enantioselectivity due to the disorder, but the reaction in inner part of the crystals (the later stage of reaction) will give the enantioselectivity inherent to the ordered system.

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REFERENCES

1. Y. Ohgo and S.Takeuchi, *J.Chem.Soc. Chem. Commun.*, **1985**, 21.
2. Y. Ohgo, Y. Arai, M. Hagiwara, S. Takeuchi, H. Kogo, A. Sekine, H. Uekusa and Y. Ohashi, *Chem. Lett.*, **1994**, 715.
3. Y. Ohgo, M. Hagiwara, M. Shida, Y. Arai and S. Takeuchi, to be published elswhere.
4. Y. Ohgo, Y. Arai and S. Takeuchi, *Chem. Lett.*, **1991**, 455; Y. Ohgo and Y. Arai, in "Reactivity in Molecular Crystals", edited by Y. Ohashi(Kodansha/VCH, 1993), pp263-273.
5. Y. Ohgo, Y. Arai, M. Hagiwara, S. Takeuchi, H. Kogo, A. Sekine, H. Uekusa and Y. Ohashi, to be published elswhere.
6. The X-ray results will be published later.