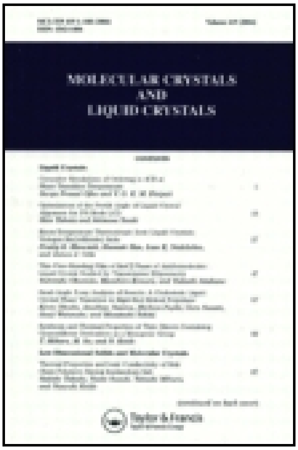

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Photoisomerization of Cobaloxime Complexes in Isostructural Host-Guest Complexes

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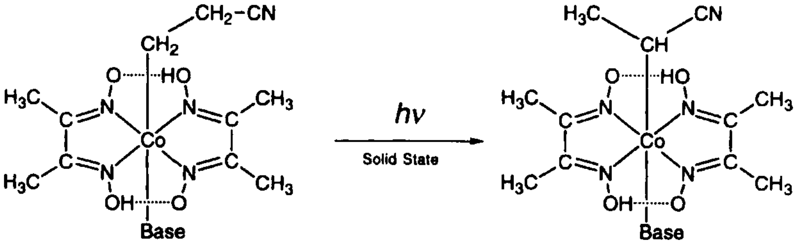
The cobaloxime complex with the β-cyanoethyl group and isonicotinic acid as axial ligands forms host-guest complexes with several kinds of host molecules. Whe the crystals of the host-guest complexes were irradiated with visible light, the β-cyanoethyl group of the guest molecule was changed to the α-cyanoethyl group. The rate of the photoisomerization was controlled by the shape of the host molecule. Designing the host structures, the isotructural host-guest crystals were prepared and the controlled reaction rates were obtained.

Keywords: photoisomerization, host-guest complex, solid-state reaction, X-ray crystal structure analysis, reaction rate

INTRODUCTION

It has been found that the β-cyanoethyl group bonded to the cobalt atom in some cobaloxime complexes is isomerized to the α-cyanoethyl group when the powdered sample of the complex was irradiated with a xenon lamp. This reaction proceeds only in the solid state and the reverse reaction has not been observed[1]. The crystals were decomposed as the reaction proceeded.



SCHEME 1

The reactivity varied when the axial base ligand was replaced with the other bases. The quantitative reaction rate was measured by the change of the absorption specrtra of the stretching vibration mode of C-N triple bond of the β-cyanoethyl group. In order to compare the reactivity quantitatively with the void space around the reactive group, the reaction cavity for the β-cyanoethyl group was calculated for each crystal, since the reaction rate of the crystalline state racemization was well explained by the cavity size[2].

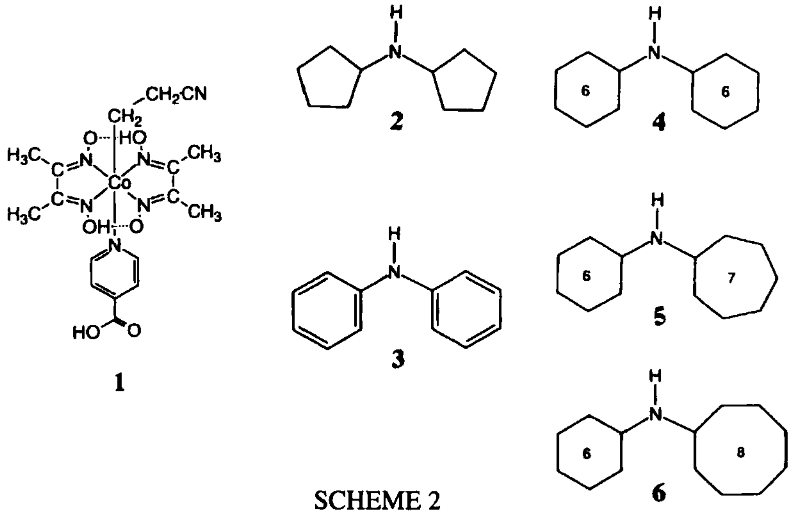
For several cobaloxime complexes with different base ligands, the relation between the reaction rate and the cavity size was examined. Three factors were found to control the reaction rate; the size of the reaction cavity, the conformation of the β-cyanoethyl group and the hydrogen bond between the cyano group and the N-H or O-H group of the neighboring molecules[3].

Although the factors controlling the reaction rate were obtained, it is impossible to make the appropriate crystal structure to show the highest reactivity. We had an idea that one of the effective method to control the crystal structure is the host-guest complex formation, since we have been extensively studied the reactivity of the α-oxoamide in the various host-guest complexes[4,5]. Using the host molecule, the reaction cavity for the reactive group of the guest molecule should be changed. This indicates the reactivity should be controlled by changing the host molecule. This paper reports how to control and design the reactivity in the solid state photoisomerization using the host-guest complex.

HOW TO DESIGN THE HOST MOLECULE

The next problem is how to design the host molecule. The β-cyanoehtyl group of the cobaloxime complex is usually surrounded by the cobaloxime moiety and axial base ligands such as aromatic rings or alkyl groups. It may be adequate that the host molecule has aromatic rings or cycloalkanes. Moreover, it seems impotant that another intermolecular interaction such as the hydrogen bond should be introduced in order to make the host-guest interaction stronger. In practice, the intermolecular hydrogen bond is a very important factor to form the complex between host and guest molecules with quite different characteristics. Before the intermolecular hydrogen bond was not introduced, all trials to obtain the host-guest complexes were in vain. This conditions may be satisfied if the guest molecule has a carboxyl group and the host molecule has an amine. The secondary amine with cycloalkanes or phenyl rings may be good candidates.

The guest molecule , **1**, has isonicotinic acid as an axial base ligand. Two host molecules, dicyclopentylamine, **2**, and diphenylamine, **3**, were prepared. The two host molecules make host-guest complexes with the cobaloxime complex, **1**. The crystal structures of only the guest molecule, **I**, the host-guest complex betwee **2** and **1**, **II**, and the complex of **3** and **1**, **III**, were analyzed.



SCHEME 2

CRYSTAL AND MOLECULAR STRCUTRES

The crystal and molecular structures of the guest only are shown in Figs. 1 and 2, respectively. The β-cyanoethyl group takes a disordered structure and has a conformation almost perpendicular to the cobaloxime plane (perpendicular conformation).

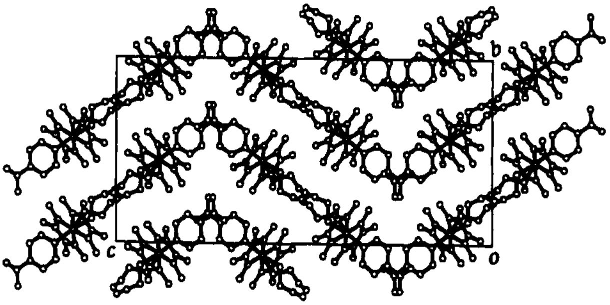


FIGURE 1 Crystal strcuture of I

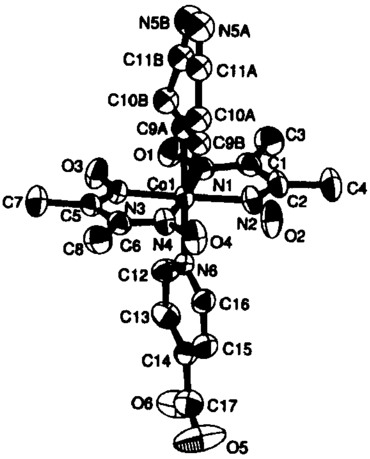


FIGURE 2 Molecular structure of I

The crystal structure of the host-guest complex of **II** is shown in Fig. 3. The molecular structures of the guest is very similat to that in Fig.2. The β-cyanoethyl group takes a perpendicular conformation, but has an ordered structure. One of the cyclopentyl group of the host molecule is disordered.

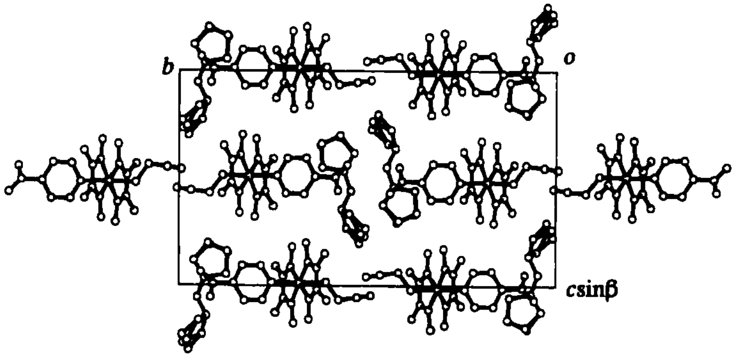


FIGURE 3 Crystal structure of **II**

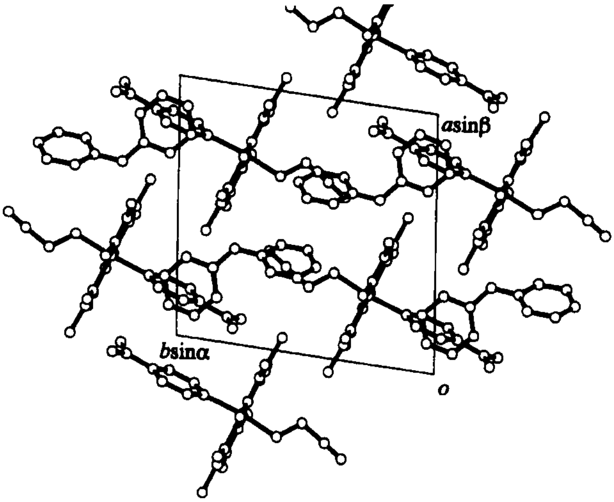


FIGURE 4 Crystal structure of **III**

The crystal structure of the host-guest complex, III, is shown in Fig. 4. The molecular structure of the guest is similar to that in Fig. 2. The β-cyanoethyl group takes a perpendicular conformation and has an ordered structure. The diphenylamine takes an ordered structure.

REACTIVITY AND CAVITY SIZE

In order to compare the void space around the β-cyanoethyl group with those of the related complexes, the reaction cavity was calculated for each crystal[6]. The cavities for the β-cyanoethyl groups in the three crystals are shown in Fig. 5.

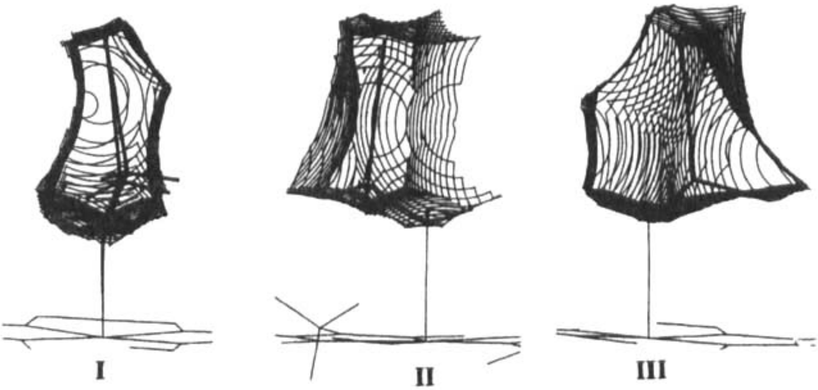


FIGURE 5 Cavities for β-cyanoethyl groups in I, II and III

The quantitative reaction rate was measured by the change of the FT-IR spectra of the stretching vibration mode of the C-N triple bond of the β-cyanoethyl group. The 1% KBr disk of the powdered sample of each crystal was exposed to the xenon lamp and the absorption spectra were observed at a constant interval. When the α-cyanoethyl group was produced, the new absorption of the C-N triple bond of the α-cyanoethyl group appeared at 2200cm^{-1}. The original peak at 2250cm^{-1} decreased and the new peak increased as the reaction proceeded. At early stages the reaction rate is well explained by first-order kinetics and the rate constant can be obtained by the least-squares calculation.

Table I shows the relationship between the cavity size and the reaction rate. The complex of **II** has a smaller reaction cavity and then the reaction rate is smaller than the corresponding one of the crystal of **I**. On the other hand, the complex of **III** has a greater reaction cavity and has a greater reaction rate, compared with the corresponding one of **I**. These results clearly suggest that the reaction rate can be changed, using the various host molecules.

TABLE I Relation between the cavity size and the reaction rate

Crystal	cavity size(Å^3)	reaction rate(x10^{-4} s^{-1})
I	10.6	1.53
II	8.6	1.36
III	15.3	1.80

CONTROL THE REACTIVITY IN ISOSTRUCTURAL CRYSTALS

In the previous examples, we succeeded in changing the reaction rate. However, in order to control the reaction rate and design the adequate host-guest complex, it is very important to be able to estimate how much is the cavity size before the crystal structure is analyzed. We tried to form isostructural crystals. The related host molecules, bis(cyclohexyl)amine, **4**, cyclohexylclcloheptylamine, **5**, and cyclohexylcyclooctylamine, **6**, seemed to be good candidates, in which one of the cycloalkane ring is different among the three hosts, that is 6-, 7- and 8-membered rings, respectively.

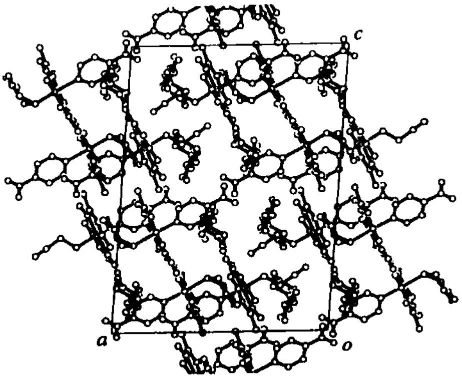


FIGURE 6 Crystal structure of **IV**

The guest molecule, **1**, is the same as before. The host-guest complex crystals between **1** + **4**, **1** + **5**, and **1** + **6** are denoted as **IV**, **V**, and **VI**, respectively.

The crystal structure of the complex of **IV** is shown in Fig. 6. The crystal has two crystallographically independent molecules, A and B. The other two crystals, **V** and **VI**, have isostrcutures to that of IV as shown in Fig. 6.

Figure 7 shows the structures of A and B. The A molecule has a disordered β-cyanoethyl group and a parallel conformation. But the B molecule has an ordered structure and has a perpendicular conformation.

The change of FT-IR spectra were observed at a constant interval. The absorption peak of the C-N stretching vibration mode appeared at 2240 and 2230 cm^{-1}. These spectra correspond to the C-N stretching vibration modes of the β-cyanoethyl groups with the parallel (A) and perpendicular (B) conformations, respectively.

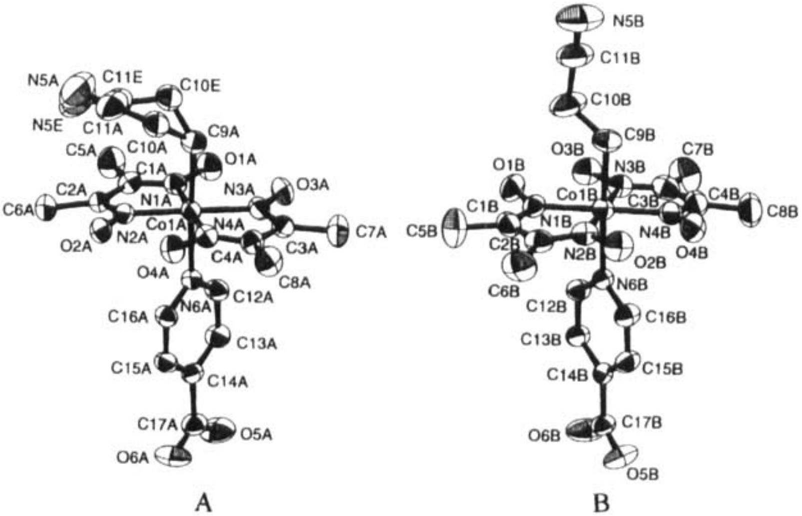


FIGURE 7 Molecular structure of A and B in **IV**

When the reaction proceeded, the new peak due to the α-cyanoethyl group appeared at 2200cm^{-1}, as shown in Fig. 8. The change of the absorption, 2240cm^{-1}, which corresponds to the parallel conformation, is faster than that of 2230cm^{-1}, which corresponds to the perpendicular conformation. For these complexes the reaction rates of the two different conformations were obtained separately. The parallel conformer has much greater reaction rate than that of the perpendicular conformer, which is consistent with the observation in the two crystal forms of the pyridine complex[7]. This is easily explained from the topochemical point of view.

The reaction rates and volumes of the reaction cavities are summarized in Table II. The A molecules have the smaller cavities than the B molecules. However, the reaction rates of A are significantly greater than the corresponding ones of B. Moreover, as the number of atoms in one of the cycloalkane ring increases, the reaction rate increases, which is assumed before the experiment.

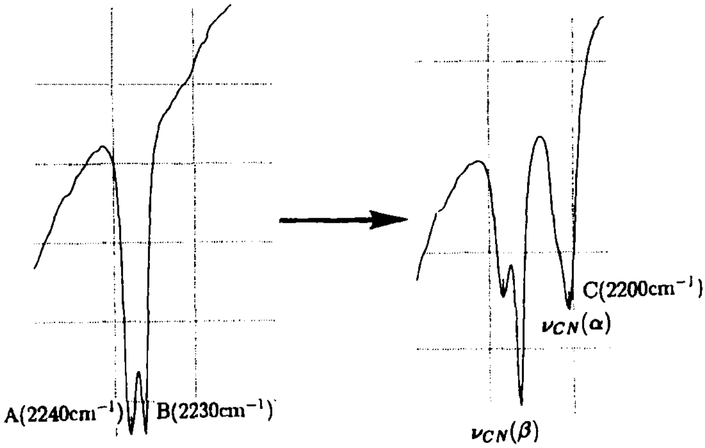


FIGURE 8 Change of the FT-IR spectra

TABLE II Relation between the cavity size (Å^3) and the rate constant (x 10^{-4} s^{-1}) of the two independent molecules, A and B, in **IV**, **V** and **VI**

crystal	A		B	
	cavity	rate const.	cavity	rate const.
IV	15.5	2.00	19.2	1.29
V	16.7	2.93	19.7	1.82
VI	17.2	2.71	17.7	1.84

Summary

The above results suggest that the host-guest complex formation is very attractive method to control the reaction rate in the solid state reaction and the application of a series of host molecules gives us the information how to design the host molecules.

Acknowledgment

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