Photoisomerization of (2-cyanoethyl)(isonicotinic acid)cobaloxime complex in a series of isostructural host–guest complex crystals

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A series of host–guest complex crystals has been formed between (2-cyanoethyl)(isonicotinic acid)cobaloxime as a guest and dicyclohexylamine, cycloheptylcyclohexylamine and cyclohexylcyclooctylamine as hosts. The X-ray analyses revealed that the three crystals are isostructural to each other. There are two crystallographically independent molecules in an asymmetric unit of each crystal. One of the cobaloxime molecules, A, has the 2-cyanoethyl group with *gauche* conformation around the central C–C bond while that of the B molecule has the *trans* conformation. When the powdered samples of the crystals were irradiated with a xenon lamp, the 2-cyanoethyl groups were isomerized to the 1-cyanoethyl group. The reaction rate was estimated from the change in the FT-IR spectra of the stretching vibration mode of the C–N triple bond. The reaction rates of the 2-cyanoethyl groups with *gauche* and *trans* conformations were estimated separately from the spectra. The rate constant of the 2-cyanoethyl group with the *gauche* conformation is significantly greater than that with the *trans* conformation in each crystal. The isomerization rate was accelerated as the size of the cycloalkane ring increased. The reaction cavity for the 2-cyanoethyl group expands as the ring size increases. This suggests that it is possible to control the reaction rate if a series of the host–guest complexes are formed and the size of the host molecule is systematically changed.

Introduction

Reactions in the solid state are the most suitable system for a selective reaction.[1] The control of a solid-state reaction, however, is very difficult because the design of the crystal structure of the reactant molecule is quite hard. Many efforts have been made to control the crystal structure.[2] Formation of a host–guest complex which includes a reactant molecule as a guest is one of the most promising methods. Investigations of solid-state photoreactions in the host–guest complexes have been carried out from the viewpoint of stereo- and enantioselective control.[3–11]

The 2-cyanoethyl group bonded to the cobalt atom in the bis(dimethylglyoximato)cobalt(III), cobaloxime, complexes has been found to be isomerized to the 1-cyanoethyl group on exposure to visible light. The reaction proceeds only in the solid state and the reverse reaction has not been observed yet. Several cobaloxime complexes with different axial base ligands were prepared, and the relationship between the reaction rate and the crystal and molecular structures has been vigorously studied. As a consequence of these investigations, three factors were found to control the reaction rate: the conformation of the reactive group,[12] the reaction cavity[13] and the hydrogen bond of the reactive group with the neighbouring molecule.[14–16] This gave us an idea that the formation of the host–guest complex crystal is a very effective method for changing the crystal packing around the reactive group, namely varying the reaction cavity. Especially, if the hosts can get close to the reactive group, the reactivity will be easily controlled by changing the hosts.

In our previous work, we found that the (2-cyanoethyl)cobaloxime complex forms the host–guest complexes with secondary amines, and the host–guest complex formation is quite an effective method for altering the rate of the solid state of β–α photoisomerization of the (2-cyanoethyl)cobaloxime complex.[17] The exchange of the host with others would alter the environment around the reactive group and then the reaction rate would be varied. However, as the crystal structure of the host–guest complex may become quite different if the host molecule is exchanged with others, "control" of the reaction rate has not been achieved. The design of the crystal structure is a difficult subject because the modification of the host causes a different environment around the reactive group.

This problem can be overcome by forming isostructural crystals. The host–guest complexes are effective for making the isostructural crystals, since it is quite common that a small change in the structure of the host molecule gives only a slight change in the crystal structure of the host–guest complex. Since the positions of the atoms are almost the same, the effect of replacing the hosts on the reaction rates can be estimated quantitatively in the isostructural host–guest complexes.

In this paper, we report a procedure for the design of isostructural host–guest complex crystals to control solid-state reactions and the three structures of the designed crystals, and discuss the relation between the reaction rate and structure.

Hereafter, the crystals of the host–guest complexes of **1** and **2**, **1** and **3**, and **1** and **4** are abbreviated as **I**, **II** and **III**, respectively (Scheme 1).

Strategy for design of isostructural crystals

Reasons why the dicycloalkylamines were used as the host molecules and isonicotinic acid was used as an axial base ligand of the guest molecule, **1**, were already reported.[17,18] In order to make isostructural crystals, one of the cyclohexyl groups of dicyclohexylamine, **2**, was exchanged with cycloheptyl, **3**, or cyclooctyl groups. This is because the crystal structure would be varied if both of the cyclohexyl groups were exchanged with the other cycloalkyl groups, as reported in the previous paper.[17] Generally, bulky substituents cause looser packing of the crystal. As the host may locate near the reactive group in the host–guest crystals considering the structures reported in the previous work,[17] such a series of exchange of cycloalkane

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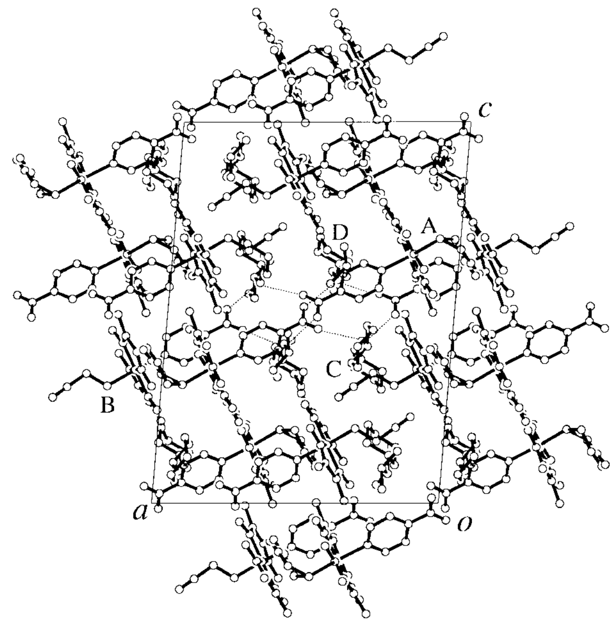
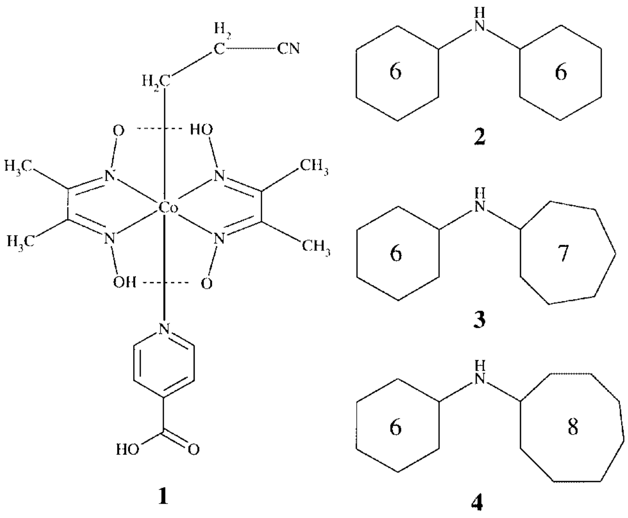


Fig. 1 Crystal structure of **I** viewed along the *b*-axis. Broken lines indicate the hydrogen bonds.



Scheme 1

rings will bring about looser packing around the reactive group, namely the enlargement of the reaction cavity.[19] As the number of the carbon atoms in the cycloalkane ring increases, it would make the reaction faster.

Results and discussion

Crystal and molecular structures

Fig. 1 shows the crystal structure of **I** viewed along the *b*-axis. There are two crystallographically independent guests, A and B, and hosts, C and D, in an asymmetric unit. The protons of the carboxy groups of the guests, **1**, are transferred to the amino groups of the hosts, **2**, to form a pair of the carboxylate anion and the ammonium cation. Strong hydrogen bonds are formed between the anion and the cation. The hydrogen bonds connect the molecules along the *a*-axis. The host molecules locate near the 2-cyanoethyl group. There are no significant contacts of the 2-cyanoethyl groups with the neighbouring molecules as shown in Fig. 2.

Fig. 3 shows the molecular structures of the guests, A and B, and of the hosts, C and D, with the numbering of the atoms. Both of the disordered 2-cyanoethyl groups of A take *gauche* conformations around the C(9A)–C(10A) and C(9A)–C(10E) bonds. The 2-cyanoethyl group of B has an ordered structure and takes a *trans* conformation around the C(9B)–C(10B) bond. All the cyclohexyl rings have chair conformations. Selected bond distances and angles are listed in Table 1. These values are in agreement with the corresponding ones of the related molecules.

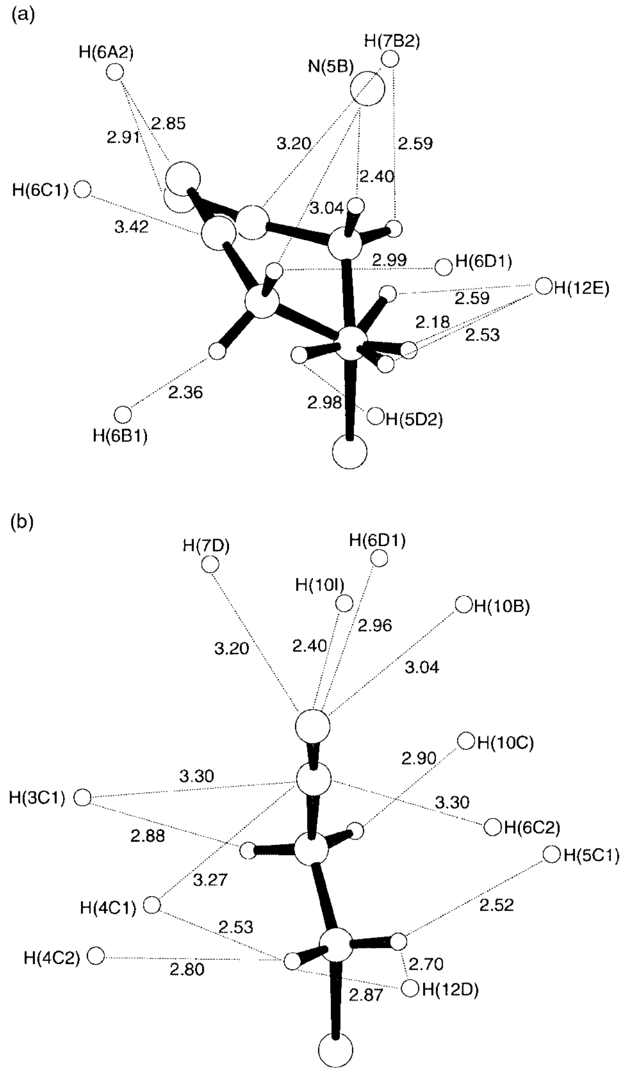


Fig. 2 (a) Intermolecular contacts between the 2-cyanoethyl group of A in **I** and the surrounding molecules. The numbers indicate intermolecular distances in Å. (b) Intermolecular contacts between the 2-cyanoethyl group of B in **I** and the surrounding molecules. The numbers indicate intermolecular distances in Å.

The crystal structures of **II** and **III** are almost the same as that of **I** since they are isostructural to **I**. There are no significant contacts of the 2-cyanoethyl groups with the neighbouring molecules. The protons of the carboxy groups of A and B are transferred to the amino groups as observed in **I**. The same hydrogen bonds as those in **I** are formed in **II** and **III**. Fig. 4 shows the molecular structures of the hosts **3** in **II**, and the hosts **4** in **III**. Selected bond distances and angles are also listed in Table 1. The cyclooctane rings of **4** are disordered, probably due to the ring puckering of the eight-membered ring.

Relation between reaction rate and reaction cavity

Table 2 lists the rate constants of the conversion from the 2-cyanoethyl group to the 1-cyanoethyl group in the crystals of **I**, **II** and **III**. The reaction rates of the 2-cyanoethyl groups of the A and B molecules are observed separately. In each crystal, the reaction rate of the 2-cyanoethyl group in A is greater than that of the 2-cyanoethyl group in B. In order to examine the void space around the 2-cyanoethyl group, the reaction cavity

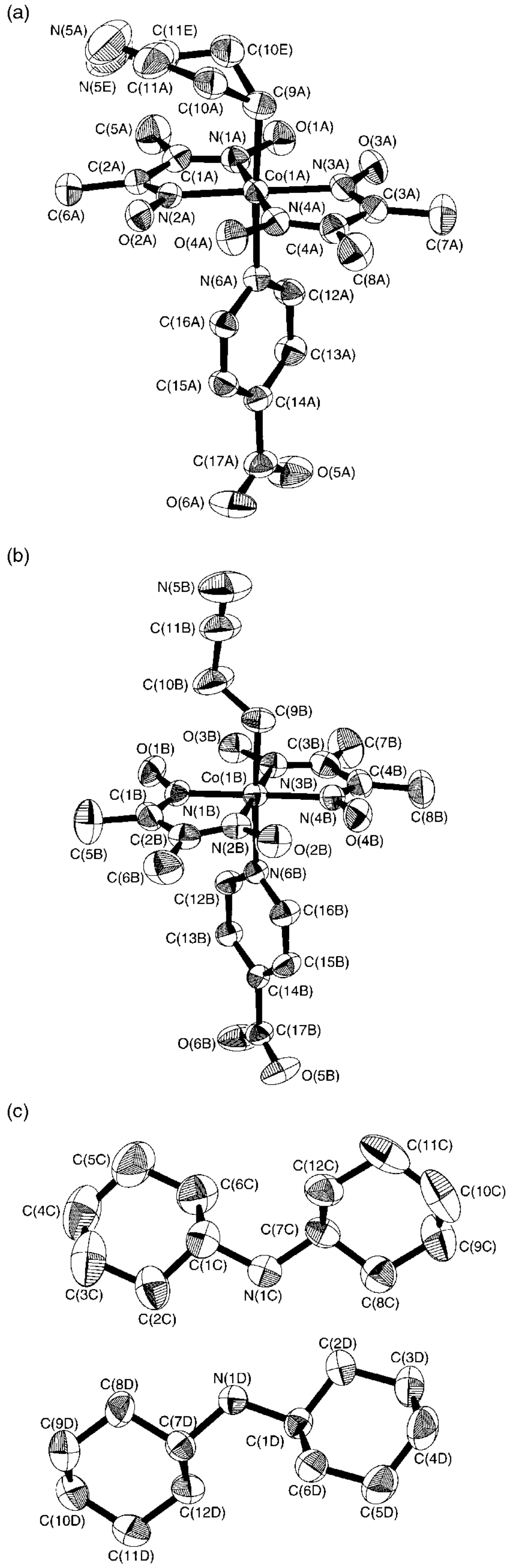


Fig. 3 (a) Molecular structure of 1A in **I** with the numbering of the atoms. Displacement ellipsoids are drawn at 50% probability level. (b) Molecular structure of 1B in **I** with the numbering of the atoms. Displacement ellipsoids are drawn at 50% probability level. (c) Molecular structures of **2** in **I**. Displacement ellipsoids are drawn at 50% probability level.

for the 2-cyanoethyl group was drawn in each crystal and the volume was calculated.[19] Fig. 5 shows the reaction cavities for the 2-cyanoethyl group of the A and B molecules in **I**. Similar

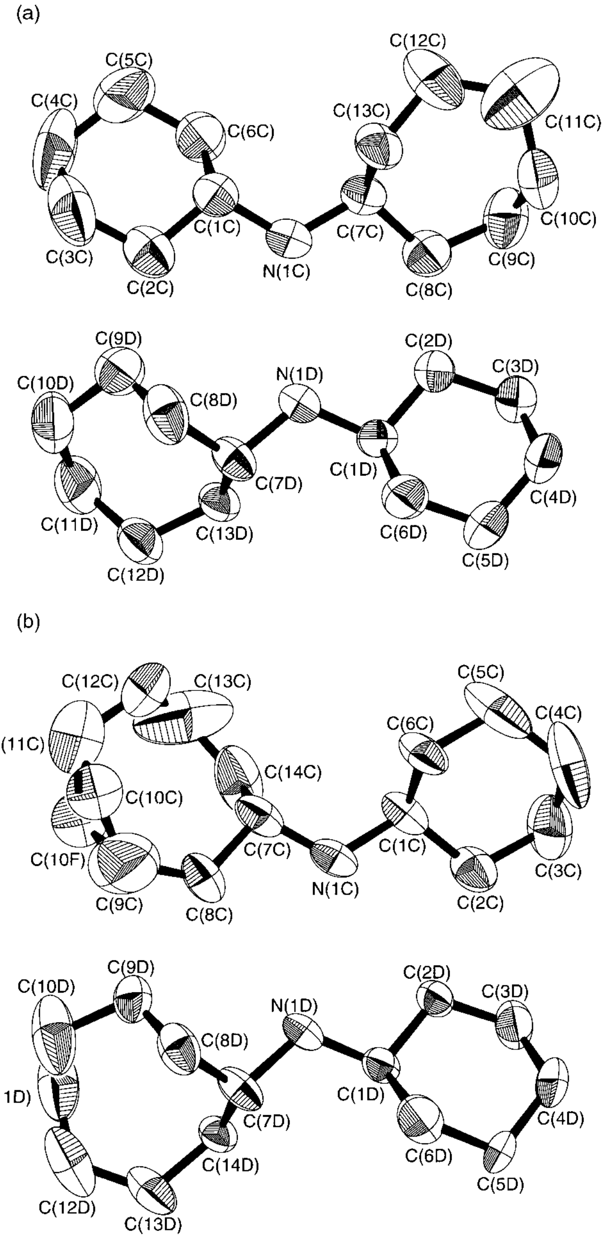


Fig. 4 (a) Molecular structures of **3** in **II**. Displacement ellipsoids are drawn at 50% probability level. (b) Molecular structures of **4** in **III**. Displacement ellipsoids are drawn at 30% probability level.

cavities were observed in the **II** and **III** crystals. The 2-cyanoethyl groups are accommodated in their cavities. This means that the 2-cyanoethyl groups are more than 1.2 Å distant from the van der Waals radii of the surrounding atoms. The right column in Table 2 gives the cavity volume for each 2-cyanoethyl group. The volumes of the cavities are increased as the ring size of the hosts increases except for B in **III**, the reduction of the cavity of B in **III** is attributed to the disordered structures of the hosts as described below.

The reaction rates of A are greater than those of B in the three crystals although the volumes of the cavities of A are smaller than those of B. Such a difference should be caused by a difference in conformations of the 2-cyanoethyl groups in A and B molecules since A has *gauche* conformations whereas B has a *trans* conformation. Such different reaction rates of the two conformers have been observed in the polymorphic crystals of the (2-cyanoethyl)(pyridine)cobaloxime complex.[12] However, since the different crystals are used, the reactions in the polymorphic crystals cannot proceed under exactly the same reaction conditions. However, in this case, as the two types of the conformers exist in a crystal, the condition of the reaction is

Table 1 Selected bond lengths (Å) and angles (°)

	I	II	III		I	II	III
Co(1A)–N(1A)	1.879(2)	1.878(3)	1.884(4)	Co(1B)–N(1B)	1.884(2)	1.883(3)	1.880(5)
Co(1A)–N(2A)	1.866(2)	1.863(3)	1.866(4)	Co(1B)–N(2B)	1.885(2)	1.878(3)	1.869(5)
Co(1A)–N(3A)	1.889(2)	1.882(3)	1.879(4)	Co(1B)–N(3B)	1.874(2)	1.873(3)	1.878(5)
Co(1A)–N(4A)	1.884(2)	1.889(3)	1.869(4)	Co(1B)–N(4B)	1.881(2)	1.878(3)	1.887(6)
Co(1A)–N(6A)	2.055(2)	2.057(3)	2.065(4)	Co(1B)–N(6B)	2.051(2)	2.050(3)	2.059(4)
Co(1A)–C(9A)	2.012(2)	2.002(4)	2.003(5)	Co(1B)–C(9B)	2.001(2)	1.995(4)	1.999(6)
C(9A)–C(10A)	1.484(3)	1.505(6)	1.499(1)	C(9B)–C(10B)	1.504(3)	1.491(6)	1.45(1)
C(9A)–C(10E)	1.472(6)	1.500(1)	1.500(1)				
C(10A)–C(11A)	1.453(5)	1.446(8)	1.471(1)	C(10B)–C(11B)	1.466(4)	1.462(6)	1.47(1)
C(10E)–C(11E)	1.467(6)	1.471(1)	1.470(1)				
C(11A)–N(5A)	1.142(5)	1.117(7)	1.102(1)	C(11B)–N(5B)	1.134(4)	1.129(6)	1.129(9)
C(11E)–N(5E)	1.109(7)	—	—				
C(11E)–N(5A)	—	1.101(1)	1.101(1)				
C(17A)–O(5A)	1.243(3)	1.235(5)	1.234(8)	C(17B)–O(5B)	1.241(3)	1.244(5)	1.218(7)
C(17A)–O(6A)	1.240(3)	1.222(5)	1.238(8)	C(17B)–O(6B)	1.233(3)	1.233(5)	1.226(8)
O(5A)···N(1C)[a]	2.751(2)	2.750(4)	2.750(6)	O(5B)···N(1D)[b]	2.705(2)	2.726(4)	2.720(6)
O(6A)···N(1D)[a]	2.685(2)	2.704(4)	2.726(5)	O(6B)···N(1C)[b]	2.729(2)	2.701(4)	2.709(6)
C(9A)–Co(1A)–N(6A)	177.13(7)	178.3(1)	178.5(2)	C(9B)–Co(1B)–N(6B)	176.88(8)	177.5(2)	177.5(3)
C(9A)–C(10A)–C(11A)	116.2(3)	116.9(5)	115.6(5)	C(9B)–C(10B)–C(11B)	112.2(2)	112.2(4)	112.7(7)
C(9A)–C(10E)–C(11E)	110.3(7)	114.8(8)	117.0(7)				
C(10A)–C(9A)–Co(1A)	120.9(2)	121.6(3)	123.8(5)	C(10B)–C(9B)–Co(1B)	117.4(2)	117.8(3)	119.5(5)
C(10E)–C(9A)–Co(1A)	125.7(3)	128.6(7)	125.8(6)				
C(10A)–C(11A)–N(5A)	177.8(4)	178.8(7)	173(1)	C(10B)–C(11B)–N(5B)	177.2(4)	179.5(8)	178(1)
C(10E)–C(11E)–N(5E)	167.3(9)	—	—				
C(10E)–C(11E)–N(5A)	—	174(1)	176(2)				

Symmetry codes: [a] $x + 1/2, 1/2 - y, z + 1/2$; [b] $x - 1/2, 1/2 - y, z + 1/2$.

Table 2 Relation between the reactivity and the volume of cavities for A and B

		Rate/ 10^{-4} s^{-1}	Volume of cavity/Å^3
A	**I**	2.0	15.5
	II	2.9	16.7
	III	2.7	17.2
B	**I**	1.3	19.2
	II	1.8	19.7
	III	1.8	17.7 (20.5)

exactly the same. It was made clear that the 2-cyanoethyl group with a *gauche* conformation is isomerized to the 1-cyanoethyl group faster than that with a *trans* conformation. This is explained from the topochemical point of view, since the structure of the 2-cyanoethyl group with a *gauche* conformation is similar to that of the 1-cyanoethyl group.[12]

When the reaction rates were compared among the same conformers, there was a significant difference between **I** and **II** and between **I** and **III**. The reaction rate increases significantly as the cavity volume increases except for the B molecule in **III**. The cavity volume of B in **III** is significantly smaller than those in **I** and **II**. Such a small cavity results from the disordered structure of the cyclooctane moiety of the host amine **3**, which is located near the 2-cyanoethyl group of B in **III**. Since each part of the disordered sites cannot exist simultaneously, the real cavity should be greater than the normally calculated one. Then the volume of the cavity of B in **III** was recalculated as a weighted average of the two imaginary cavities, in which one site is occupied by only one of the disordered cyclooctyl groups. The volume was recalculated to be 20.5 Å^3 which is given in parentheses in Table 2. It is clear that the reaction rate increases significantly as the cavity volume increases when **I** is compared with **II** or **III**.

In comparison of the size of the cavity in **I** with that in **II** or **III**, a good correlation between the reaction rate and the cavity size was obtained. On the other hand, a relationship was not found between those of **II** and **III**. These ambiguities may result from the disordered structure of the hosts.

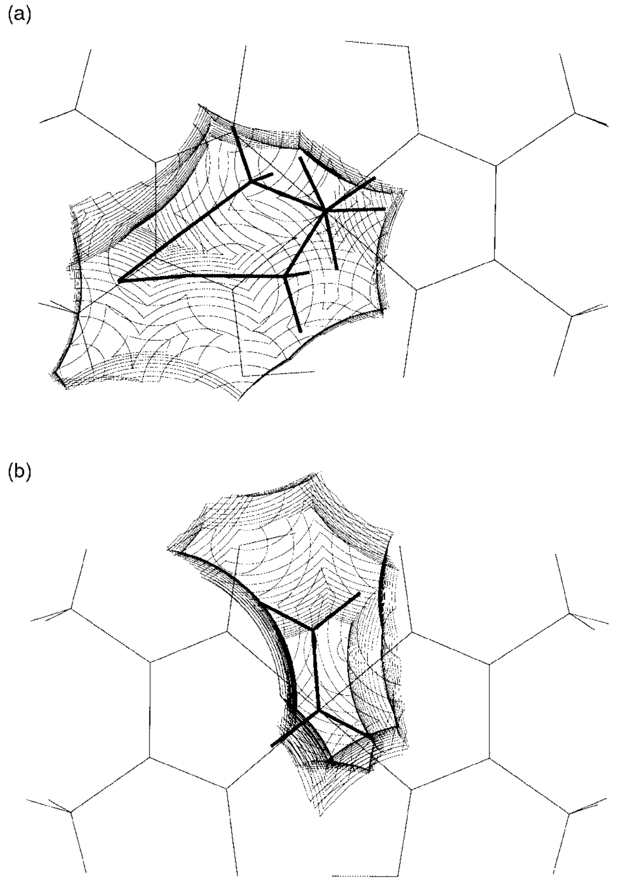


Fig. 5 (a) Reaction cavity for the 2-cyanoethyl group of 1A in **I**. (b) Reaction cavity for the 2-cyanoethyl group of 1B in **I**.

The formation of isostructural crystals using a series of host molecules is effective for the design and control of the solid state reactions. The size of cavities is varied continuously on replacing the host. However, if the crystal has the disordered structure, control may become difficult. The ambiguity remains

Table 3 Crystal data and experimental conditions

	I	II	III
Chemical formula	$C_{17}H_{23}N_6O_6Co{\cdot}C_{12}H_{23}N$	$C_{17}H_{23}N_6O_6Co{\cdot}C_{13}H_{25}N$	$C_{17}H_{23}N_6O_6Co{\cdot}C_{14}H_{27}N$
Formula weight	647.66	661.68	675.71
Crystal system		Monoclinic	
Space group		$P2_1/n$	
Z		8	
a/Å	17.537(2)	17.477(2)	17.556(3)
b/Å	16.113(7)	16.439(2)	16.604(3)
c/Å	23.487(5)	23.606(2)	24.058(3)
β/°	94.81(1)	95.740(7)	95.82(1)
V/Å^3	6613(3)	6748(1)	6977(2)
D_X/Mg m^{-3}	1.301	1.303	1.287
Diffractometer	AFC-7S	AFC-7S	AFC-5R
Radiation, λ/Å		Mo-K$_\alpha$, 0.71073	
μ(Mo-K$_\alpha$)/mm^{-1}	0.569	0.559	0.542
Crystal dimensions/mm	0.5 × 0.5 × 0.2	0.5 × 0.5 × 0.4	0.5 × 0.5 × 0.4
Colour of crystal		Orange–Red	
T/K		296	
$2\theta_{max}$/°		55	
Measured reflections	16233	16565	17117
Independent reflections	15186	15496	15995
Observed reflections [$I > 0$]	12558	13299	13502
R_{int}	0.025	0.029	0.021
$R(F)(I > 2\sigma(I))$	0.057	0.057	0.076
$wR(F^2)(I > 2\sigma(I))$	0.150	0.195	0.222
S	1.02	1.10	1.09
$(\Delta/\sigma)_{max}$	0.01	0.00	0.00
$\Delta\rho_{min}$, $\Delta\rho_{max}$/e Å^{-3}	−0.34, 0.71	−0.97, 0.70	−0.40, 1.00

unsolved. It may be partly solved if a rigid molecule is used as a host.

Experimental

Synthesis of the hosts

Cycloheptylcyclohexylamine **3** and cyclohexylcyclooctylamine **4** were synthesized in the following procedure.

Cyclohexylamine (5.72 cm^3, 50 mmol) and cycloheptanone (5.90 cm^3, 50 mmol) or cyclooctanone (6.04 cm^3, 50 mmol) were added to 100 cm^3 of toluene. The flask was connected to a Dean–Stark water separator which was attached to a reflux condenser, and was refluxed until no more water separated. After cooling to room temperature, the solvent was evaporated in reduced pressure. The residue was dissolved in 100 cm^3 of methanol, and then sodium tetrahydroborate (3.78 g, 100 mmol) was added. After stirring for 2 hours at room temperature, the reaction mixture was concentrated. The solution was added to water and extracted with diethyl ether and dried with anhydrous $MgSO_4$. The ether solution was concentrated and treated with aqueous 6 M HCl. The solution was evaporated to dryness. The crude product of the corresponding ammonium chloride was deposited and washed with ether. The salt of the amine was liberated by addition of an excess of aqueous sodium hydroxide and extracted with ether. After drying with anhydrous $MgSO_4$, the ether was evaporated to give the desired amine.

Preparation of host–guest complexes

Equimolar amounts of (2-cyanoethyl)(isonicotinic acid)cobaloxime[17] **1** and the corresponding secondary amine **2**, **3** or **4** were dissolved in methanol. After filtration, the solution was evaporated under reduced pressure until the crude crystals were deposited. The deposited crystals were filtered and then recrystallized from a methanol solution.

Photochemical reaction

A KBr disk which contained 1% of the sample was exposed to a 150 W xenon lamp (San-ei electric Super Bright 152S), the distance between the disk and the lamp being 1 cm. The absorption assigned to the stretching vibrational mode of the cyano group of the 2-cyanoethyl complex, ν_{CN}, is at about 2250 cm^{-1}, whereas ν_{CN} of the 1-cyanoethyl complex is at 2200 cm^{-1}. The infrared spectra of the KBr disk including the powdered sample of crystal **I** were measured at intervals of 5 minutes, using a JASCO FT/IR-350 spectrometer. The measurement was carried out by setting the resolution at 2 cm^{-1} and 32 times integration. Two peaks appeared at 2240 and 2230 cm^{-1}, which are assigned to ν_{CN} of the *gauche* and *trans* conformations of the 2-cyanoethyl group, respectively. This is due to the fact that the 2-cyanoethyl groups exist in two different environments. The higher wavenumber of ν_{CN} in the *gauche* conformer is caused by the intramolecular interaction between the nitrogen atoms of dimethylglyoxime (butane-2,3-dione dioxime) and 2-cyanoethyl moieties. The N(2A) $\cdots$ N(5A) and N(2A) $\cdots$ N(5E) distances for **I** are 3.611(4) and 3.36(1) Å, respectively, and the distances in **II** and **III** are almost the same as those in **I**. However, there are no such interactions in Bs. The decrease of these absorption bands within 60 minutes was explained by first-order kinetics. The rate constant was obtained independently from these two peaks by least-squares fitting. The same measurements were performed for the crystals **II** and **III**. The reaction rates were 2.0, 2.9 and 2.7 × 10^{-4} s^{-1} for A of **I**, **II** and **III**, and 1.3, 1.8 and 1.8 × 10^{-4} s^{-1} for B of **I**, **II** and **III**, respectively.

Crystal structure analysis ‡

The crystal data and experimental details of **I**, **II** and **III** are summarized in Table 3. The structure of **1** was solved by the direct method with the program SIR-92,[20] and the atomic parameters of **I** were used for the initial values for **II** and **III** since the three crystals have the same space group and very similar cell dimensions to each other. The structures were refined by the full-matrix least-squares method with the program SHELXL-93[21] for the three crystals. The disordered cyanoethyl groups were restrained to be distances of 1.50 Å for C(9A)–C(10A) and C(9A)–C(10E), 1.47 Å for C(10A)–C(11A)

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‡ CCDC reference number 188/175. See http://www.rsc.org/suppdata/p2/1999/1689 for crystallographic files in .cif format.

and C(10E)–C(11E), 1.10 Å for C(11A)–N(5A) and C(11E)–N(5E) for **I** and C(11E)–N(5A) for **II** and **III**. The C–C bond lengths of cycloalkyl groups in **II** and **III** were restrained to be distances of 1.53 Å. The occupancy factors for the disordered moieties were refined to have the same temperature factors. The hydrogen atoms were constrained to have C–H distances of 0.96 Å for primary, 0.97 Å for secondary, 0.93 Å for aromatic and an N–H distance of 0.90 Å. Atomic scattering factors were taken from the International Tables for Crystallography.[22]

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