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Variation of the reaction rate in the solid-state photoisomerization of cobaloxime complexes by forming host–guest complexes

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The 2-cyanoethyl–isonicotinic acid–cobaloxime complex forms host–guest complexes with secondary amines such as dicyclopentylamine and diphenylamine. The 2-cyanoethyl group in the two host–guest complexes as well as the pure guest complex was isomerized to the 1-cyanoethyl group on exposure to a xenon lamp in the solid state. The analyzed structures of the three crystals indicate that the different reaction rates of the three crystals have a quantitative correlation with the volumes of the reaction cavities for the 2-cyanoethyl groups in the crystals. The reaction rate can be altered by forming the host–guest complexes.

Introduction

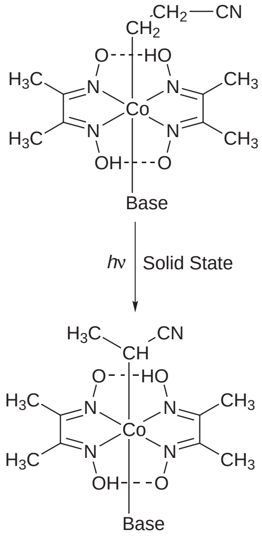
Reactions in the solid state are the most suitable systems for regio- and stereoselective reactions.[1] The control of solid state reactions, however, is very difficult because the design of the crystal structure of the reactant molecule is quite hard. Many efforts have been made to control the crystal 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] Although the process of selectivity induction has been explained based on the crystal and molecular structures of the host–guest complexes, design of the reaction in the crystal has not been achieved yet. This is because the reaction paths are quite complex and the factors determining the selectivity have not been elucidated.

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 relations between the reaction rate and the crystal and molecular structures were vigorously studied. As a consequence of these investigations, the following three factors were found to control the reaction rates: the conformation of the reactive group,[12] the reaction cavity[13] and the hydrogen bond of the reactive group with the neighboring molecule.[14–16]

This gave us the idea that the formation of the host–guest complex crystal is a very effective method for changing the crystal packing around the reactive group. Especially, if the hosts can close up to the reactive group, the reactivity will be easily controlled by changing the hosts. In this paper, we focused on the design of the solid state photoisomerization of the 2-cyanoethyl cobaloxime in the host–guest complex based on the reaction cavity, developing new types of hosts.

Design of hosts

Cobaloxime complexes are soluble in polar organic solvents, for example, methanol, ethanol, acetone and chloroform. This is due to the hydrophilic moieties of the cobaloxime complex, such as the oxime moiety of the dimethylglyoxime. On the other hand, non-polar solvents can barely dissolve cobaloxime complexes although the cobaloxime complexes have hydrophobic moieties. This means that the hosts appropriate to the present work should be soluble in polar solvents and should not form host–guest complexes with solvents.



In the crystal the 2-cyanoethyl group is usually surrounded by the hydrophobic moieties of neighboring molecules. This may indicate that if the host has hydrophobic moieties they will pack around the 2-cyanoethyl group and enable us to change the reaction cavity for the 2-cyanoethyl group by modifying the host.

The host molecules, of course, must be included in the crystalline lattice. This suggests that fairly strong interactions are necessary to form host–guest complexes. One most probable attractive force in forming host–guest complexes is the hydrogen bond. Especially, acid–base interaction is very effective in forming the host–guest complex as well as a good pair of hydrogen bond donor and acceptor since the stoichiometry of the host and guest molecules can be predicted from the valencies of the acid and base.

Considering the conditions, the cobaloxime complex with isonicotinic acid as a base ligand, **1**, and secondary amines were examined as the guest and host, respectively. In this study, dicyclopentylamine, **2**, and diphenylamine, **3**, were examined as hosts.

Hereafter, the crystals of **1**, the host–guest complexes of **1** and **2**, and of **1** and **3** are referred to as **I**, **II** and **III**, respectively.

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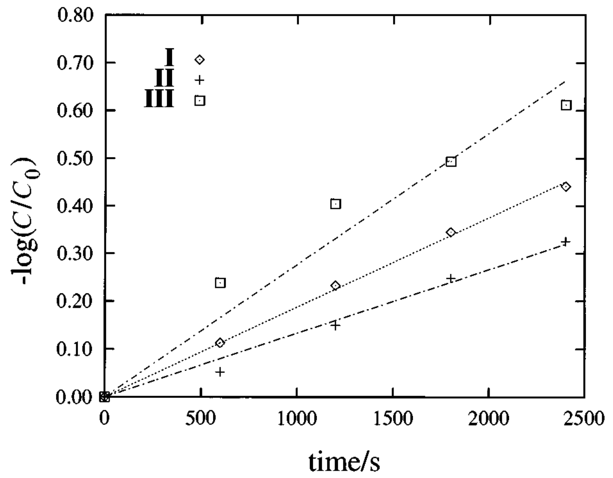
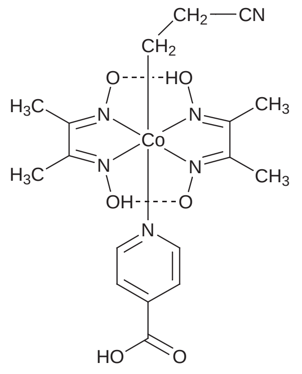


Fig. 1 Log plot of the reaction rates *versus* exposure time for **I**, **II** and **III**



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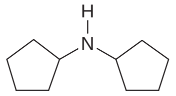

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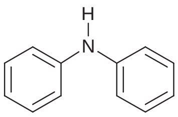

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Results and discussion

Photochemical reaction

A KBr disk which contained 1% of the samples was exposed to a 500 W xenon lamp (Ushio UXL-5S+UI-501C), the distance between the disk and the lamp being 20 cm. The absorption assigned to the stretching vibrational mode of the cyano group of the 2-cyanoethyl complex, ν_{CN}, is at 2250 cm^{-1}, whereas ν_{CN} of the 1-cyanoethyl complex is at 2200 cm^{-1}. The infrared spectra of the KBr disks including the powdered samples of crystals **I**, **II** and **III** were measured at a constant interval of 10 min, using a JASCO A-1000 IR spectrometer. The decrease of the absorption band at 2250 cm^{-1} within 40 min was explained by first-order kinetics for each sample as shown in Fig. 1 and its rate constant was obtained by least-squares fitting. The rates for **I**, **II** and **III** were 1.88, 1.33 and 2.76 × 10^{-4} s^{-1}, respectively.

Crystal and molecular structures

Fig. 2 shows the crystal structure of **I** viewed along the *a*-axis. The hydrogen bonds are formed between the oxygen atom of the dimethylglyoxime and the hydroxy group of the isonicotinic acid, through O(2)···H(6)–O(6). The distances of O(2)···O(6) and O(2)···H(6), and the angle of O(2)···H(6)–O(6) are 2.672(4) Å, 1.55 Å and 164°, respectively. No hydrogen bonds are observed for the 2-cyanoethyl group.

The molecular structure of **1** in **I** is shown in Fig. 3 with the numbering of the atoms. The 2-cyanoethyl group is disordered. Both of the two disordered 2-cyanoethyl groups take *trans* conformations around the C(9)–C(10) bond, which means the C–CN bond is nearly perpendicular to the cobaloxime plane. The *trans* conformation is less favorable for the isomerization than the *gauche* one, since the produced 1-cyanoethyl group has a similar structure to the *gauche* conformation of the 2-cyanoethyl group.[12]

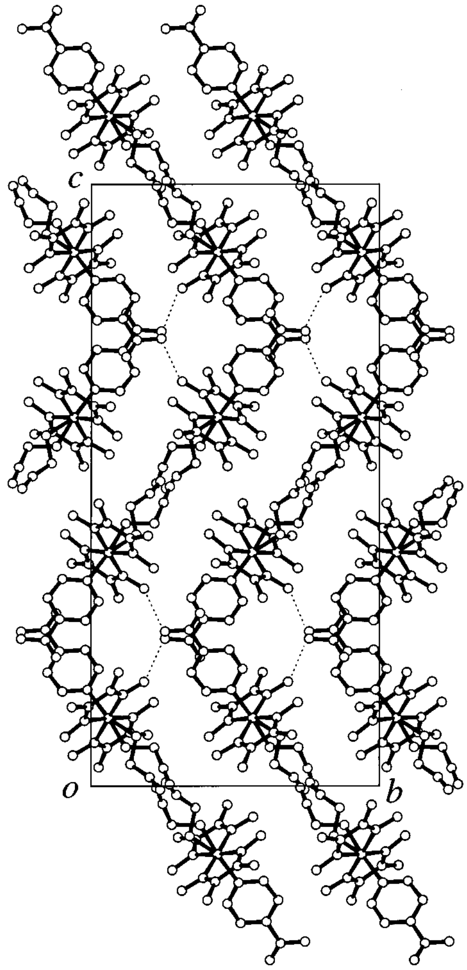

Fig. 2 Crystal structure of **I** viewed along the *a*-axis. Broken lines indicate the hydrogen bonds.

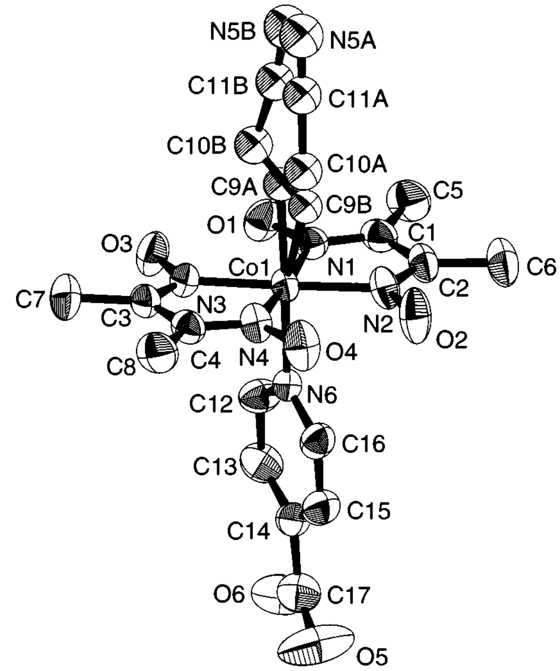

Fig. 3 Molecular structure of **1** in **I** with the numbering of the atoms

Fig. 4 shows the crystal structure of **II** viewed along the *a*-axis. The 1 : 1 host–guest complex was formed in the crystal. The hydrogen bonds are formed between the carboxy group of **1** and the amino group of **2**, through O(5)···H(72)–N(7) and O(6)···H(71)–N(7). The distances of O(5)···N(7) and

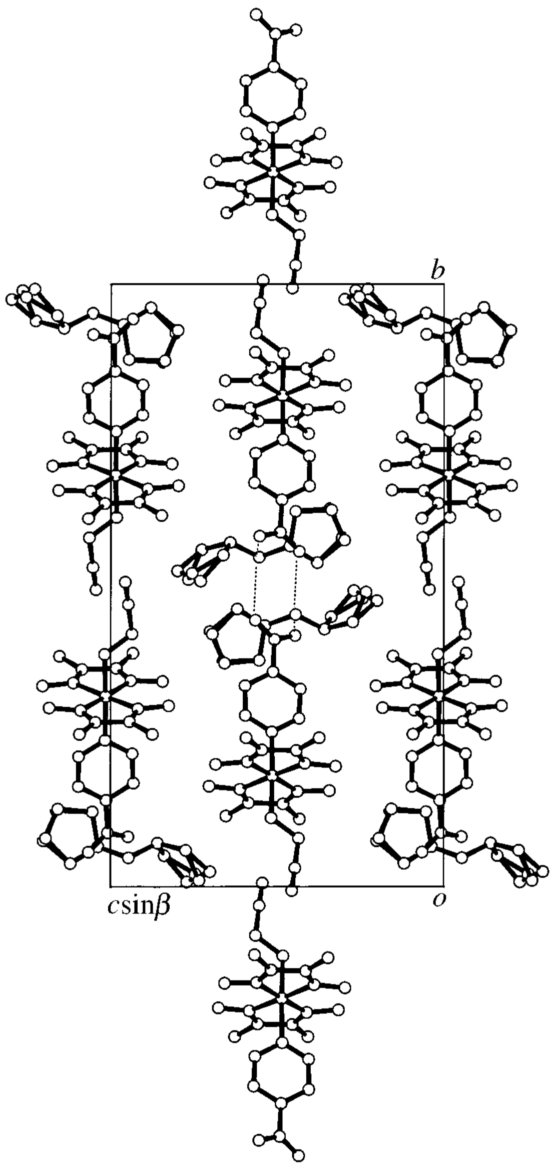

Fig. 4 Crystal structure of **II** viewed along the *a*-axis. Broken lines indicate the hydrogen bonds.

O(5)···H(72) and the angle of O(5)···H(72)–N(7) are 2.776(3) Å, 1.88 Å and 174°, respectively, whereas the distances of O(6)···N(7) and O(6)···H(71) and the angle of O(6)···H(71)–N(7) are 2.726(3) Å, 1.84 Å and 166°, respectively. The cyclopentyl groups of the host, **2**, come close to the 2-cyanoethyl group. This indicates that the environment around the reactive group is controlled by the hosts. No hydrogen bonds are formed with the 2-cyanoethyl group.

The molecular structures of **1** and **2** in **II** are shown in Fig. 5. Although the 2-cyanoethyl group has an ordered structure, the amine, **2**, takes a disordered structure. The conformation of the 2-cyanoethyl group is almost perpendicular to the cobaloxime plane. The molecular structures of **1** in **I** and **II** are very similar to each other.

Fig. 6 shows the crystal structure of **III** viewed along the *c*-axis. The 1:1 host–guest complex is also observed. The hydrogen bond, O(4)···H(104)–N(7), is formed between the oxygen atom of the dimethylglyoxime moiety of **1** and the amino group of **3**. Another hydrogen bond, O(1)···H(103)–O(5), is formed between the carboxy group of **1** and the dimethylglyoxime of the neighboring **1**. The distances and angles of O(1)···O(5), O(1)···H(103), O(1)···H(103)–O(5), O(4)···N(7), O(4)···H(104) and O(4)···H(104)–N(7) are 2.608(2) Å, 1.76(3) Å, 162(3)°, 2.979(3) Å, 2.17(3) Å and 176(2)°, respectively. The pattern of the intermolecular hydrogen bonds is quite different from that of **II**. This may result from the difference in basicity between **2** and **3**. Even though the hydrogen bonding pattern is quite different, phenyl groups of the hosts make contact with the reactive group.

The molecular structures of **1** and **3** in **III** are shown in Fig. 7. The 2-cyanoethyl group of **1** is ordered and its conformation is almost perpendicular to the cobaloxime plane. The structure of **1** is approximately the same as those of **1** in **I** and **II**.

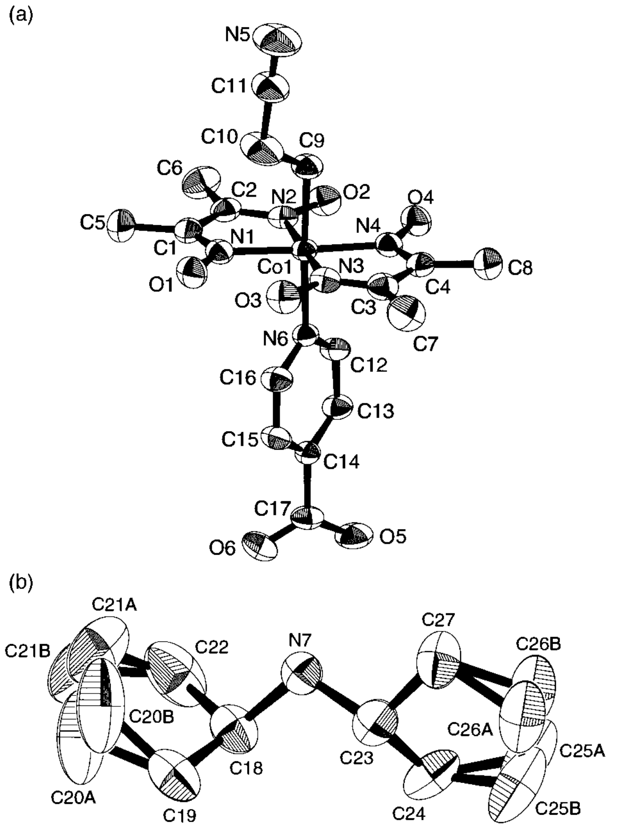

Fig. 5 Molecular structures of (a) **1** and (b) **2** in **II** with the numbering of the atoms

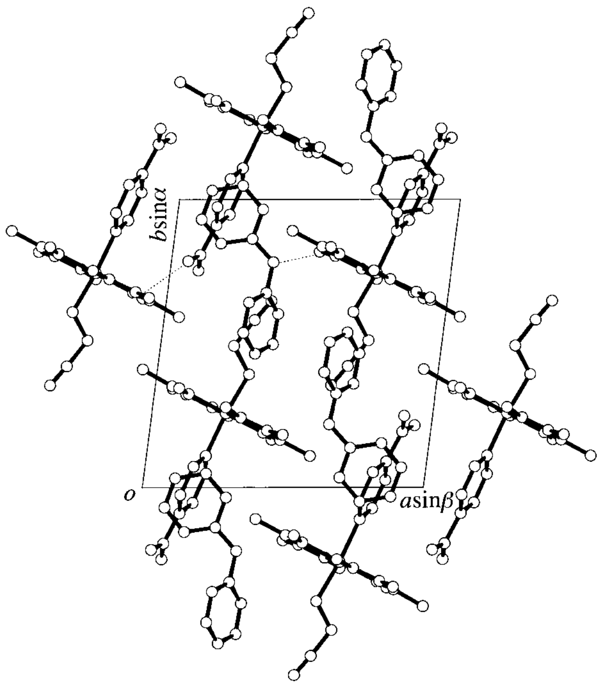

Fig. 6 Crystal structure of **III** viewed along the *c*-axis. Broken lines indicate the hydrogen bonds.

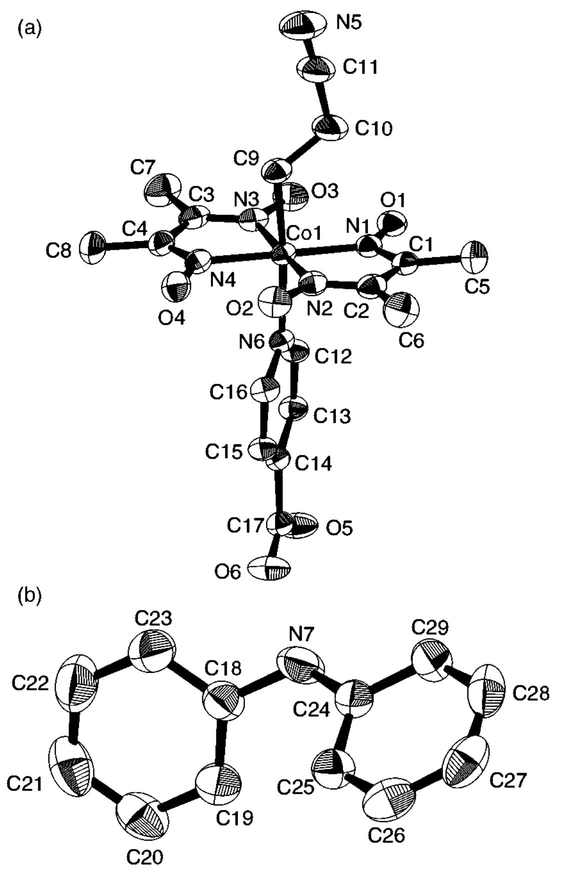

Fig. 7 Molecular structures of (a) **1** and (b) **3** in **III** with the numbering of the atoms

Difference in reactivity

Although the conformations of the 2-cyanoethyl groups of **1** among the three crystals are similar to each other, the reactivities are quite different. The crystal **III** has a greater rate constant than **I**, whereas **II** shows less reactivity than **I**.

In order to explain the differences in reactivity, the reaction cavity for the 2-cyanoethyl group was drawn and the volume was calculated, the definition of which has already been reported.[17]

Fig. 8 shows the reaction cavities for the 2-cyanoethyl groups in the three crystals. Table 1 compares the rate constants and the volumes of the reaction cavities of the three crystals. A good correlation can be seen between the reaction rates and the volume of the reaction cavities. The most reactive crystal **III** has the largest cavity, on the other hand, the least reactive crystal **II** has the smallest cavity. Since the 2-cyanoethyl groups in **II** and **III** are surrounded by the hosts, the difference in reactivity is caused by the selection of the host. This suggests that the reactivity in the solid-state reaction can be controlled by designing the host, even if control of the crystal structure may be impossible.

Experimental

Preparation of the samples

2-Cyanoethyl–isonicotinic acid–cobaloxime. 2-Cyanoethyl–pyridine–cobaloxime[18] (4.22 g, 10 mmol) was dissolved in 150 cm^3 of 80 (v/v)% aqueous methanol and stirred overnight with 25 g of the cation exchange resin, DOWEX 50W-X8. After the resin was filtered, 1.23 g (10 mmol) of isonicotinic acid was added to the filtrate. After being stirred for 1 h, the reaction mixture was concentrated to give a crude product. The recrystallization was carried out from a methanol–acetone solution.

Preparation of the host–guest complexes. The equimolar mixture of 2-cyanoethyl–isonicotinic acid–cobaloxime and the corresponding secondary amine was 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.

Table 1 Relation between the reactivity and the volume of the cavity

	Rate/ 10^{-4} s^{-1}	Volume of cavity/Å^3
I	1.88	10.6
II	1.33	8.6
III	2.76	15.3

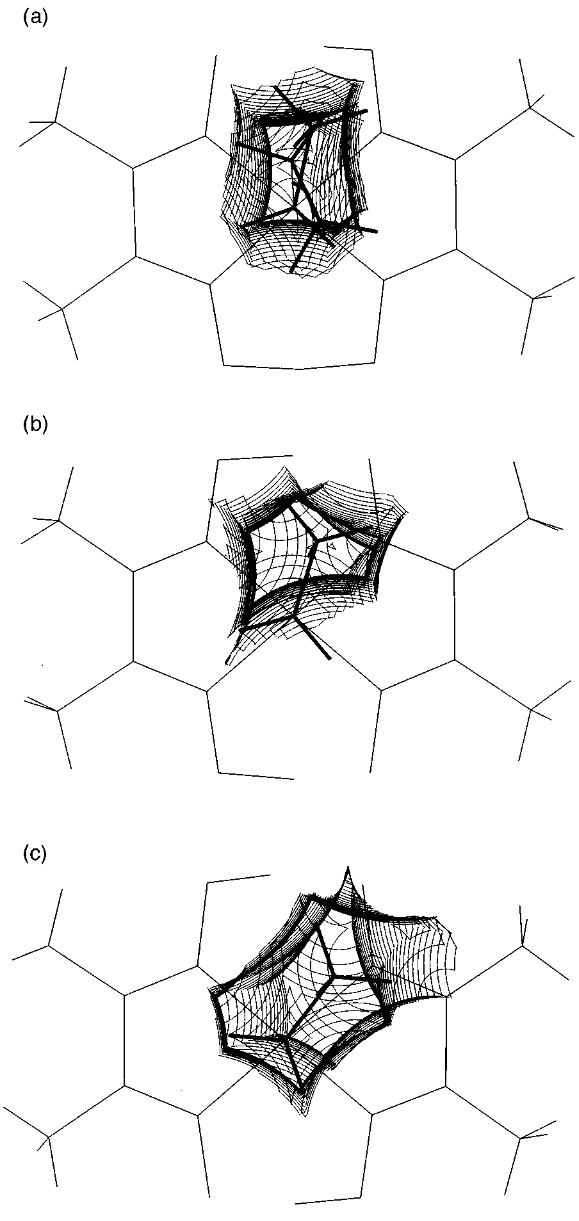

Fig. 8 Reaction cavities for the 2-cyanoethyl group in (a) **I**, (b) **II** and (c) **III**, viewed along the cobaloxime plane

Crystal structure analysis

The crystal data and experimental details of **I**, **II** and **III** are summarized in Table 2. The Lorentz, polarization and absorption corrections were applied to all the crystals and an extinction correction was applied to **I**. The structures were solved by direct methods, using the program SIR-92,[19] and the structures were refined by the full-matrix least-squares method with the program SHELXL-93[20] for all the crystals. The

Table 2 Crystal data and experimental conditions

	I	II	III
Chemical formula	$C_{17}H_{23}N_6O_6Co$	$C_{17}H_{23}N_6O_6Co{\cdot}C_{10}H_{19}N$	$C_{17}H_{23}N_6O_6Co{\cdot}C_{12}H_{11}N$
Molecular weight	466.34	619.61	635.56
Crystal system	Orthorhombic	Monoclinic	Triclinic
Space group	*Pbcn*	$P2_1/c$	$P\bar{1}$
Z	8	4	2
a/Å	8.329(2)	8.280(1)	12.440(1)
b/Å	15.209(3)	25.843(2)	12.893(2)
c/Å	32.055(4)	14.1904(9)	9.4376(9)
α/°	—	—	92.26(1)
β/°	—	93.369(8)	96.081(7)
γ/°	—	—	82.55(1)
V/Å^3	4060(1)	3031.1(5)	1492.0(3)
D_x/Mg m^{-3}	1.526	1.358	1.415
Diffractometer	AFC-5R	AFC-7S	AFC-7S
Radiation		Mo-K$_\alpha$	
λ/Å		0.710 73	
μ(Mo-K$_\alpha$)/mm^{-1}	0.893	0.617	0.630
F(000)	1936	1312	664
Crystal dimensions/mm^3	0.5 × 0.3 × 0.2	0.5 × 0.5 × 0.3	0.5 × 0.5 × 0.3
Colour of crystal		Orange–red	
T/K		296	
$2\theta_{max}$/°		55	
Range of *h*, *k* and *l*	$0 \leqslant h \leqslant 10$	$0 \leqslant h \leqslant 10$	$0 \leqslant h \leqslant 16$
	$0 \leqslant k \leqslant 19$	$0 \leqslant k \leqslant 33$	$-16 \leqslant k \leqslant 16$
	$0 \leqslant l \leqslant 41$	$-18 \leqslant l \leqslant 18$	$-12 \leqslant l \leqslant 12$
Scan technique	ω	ω	$\omega/2\theta$
Scan width/°	$1.2 + 0.35\tan\theta$	$0.89 + 0.30\tan\theta$	$1.57 + 0.35\tan\theta$
Scan rate/°(ω) min^{-1}	16	8	8
Measured reflections	4665	6964	6854
Independent reflections	4665	6964	6854
Observed reflections [$I > 0$]	4134	6326	6393
$R(F)(I > 2\sigma I)$	0.050	0.048	0.039
$wR(F^2)(I > 2\sigma I)$	0.143	0.136	0.106
S	1.07	1.08	1.05
Extinction coefficient	0.0004(2)	—	—
$(\Delta/\sigma)_{max}$	0.00	0.00	0.00
$\Delta\rho_{min}$, $\Delta\rho_{max}$/e Å^{-3}	−0.36, 0.88	−0.37, 0.34	−0.67, 0.29

weighting schemes were $w = [\sigma(F_o^2)^2 + (0.0734P)^2 + 3.2661P]^{-1}$, $[\sigma(F_o^2)^2 + (0.07P)^2 + 0.3579P]^{-1}$ and $[\sigma(F_o^2)^2 + (0.0593P)^2 + 0.3272P]^{-1}$ for **I**, **II** and **III**, respectively, where $P = (F_o^2 + 2F_c^2)/3$. The 2-cyanoethyl group of **1** in **I** the and cyclohexyl groups of **2** in **II** are disordered. The occupancy factors were also refined to have the same temperature factors. The positions of several hydrogen atoms were obtained on difference maps and the others were calculated geometrically. The hydrogen atoms were constrained to have the C–H distances to be 0.96 Å for primary, 0.97 Å for secondary, 0.93 Å for aromatic and the N–H distance to be 0.90 Å. The anisotropic temperature factors were applied to all non-hydrogen atoms, except for the disordered atoms of **I**. For the hydrogen atoms which were not constrained and the disordered atoms of **I**, the isotropic temperature factors were applied. Atomic scattering factors were taken from the International Tables for Crystallography.[21] Full crystallographic details, excluding structure factor tables, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details of the deposition scheme, see 'Instructions for Authors', *J. Chem. Soc.*, *Perkin Trans. 2*, available *via* the RSC Web page (http://www.rsc.org/authors). Any request to the CCDC for this material should quote the full literature citation and the reference number 188/137.

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