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Modified photoreactivity due to mixed crystal formation. II. Enhanced reactivity upon conformational mimicry and cavity enlargement

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The 2-cyanopropyl (β-cyanopropyl) group in the cobaloxime complex of (2-cyanopropyl)(3-methylpyridine)bis(dimethylglyoximato)cobalt(III) takes a *trans* conformation around the Co—C—C—CN bond in the crystal and undergoes isomerization to the 1-cyanopropyl (α-cyanopropyl) group with a low reaction rate when the powdered crystals are irradiated with a xenon lamp. When the complex was mixed with (2-cyanoethyl)(3-methylpyridine)bis(dimethylglyoximato)cobalt(III) or (2-cyanoethyl)(3-ethylpyridine)bis(dimethylglyoximato)cobalt(III), a mixed crystal, Mix-I or Mix-II, was obtained. The cell parameters of Mix-I and Mix-II were considerably different. When the crystals of Mix-I and Mix-II were irradiated with the xenon lamp, the 2-cyanopropyl group and the 2-cyanoethyl group isomerized to the 1-cyanopropyl and 1-cyanoethyl groups, respectively, in the crystalline state as well as in the solid state. The isomerization rates of the 2-cyanopropyl and 2-cyanoethyl groups of the mixed crystals became significantly higher than the corresponding rates in the component crystals. For the 2-cyanopropyl group, the conformational change from *trans* to *cis* in the mixed crystals caused reaction rates to be enhanced, and the expanded volume of the reaction cavity in the mixed crystals increased the reactivity for the 2-cyanoethyl group, when compared with the reactivity of each component crystal. A quantitative discussion of the increased rate constants is presented, which is based on the crystal structures. The shapes of the reaction cavities for the reactive groups undergoing isomerization control the conformation and configuration of the produced 1-cyanoethyl and 1-cyanopropyl groups.

1. Introduction

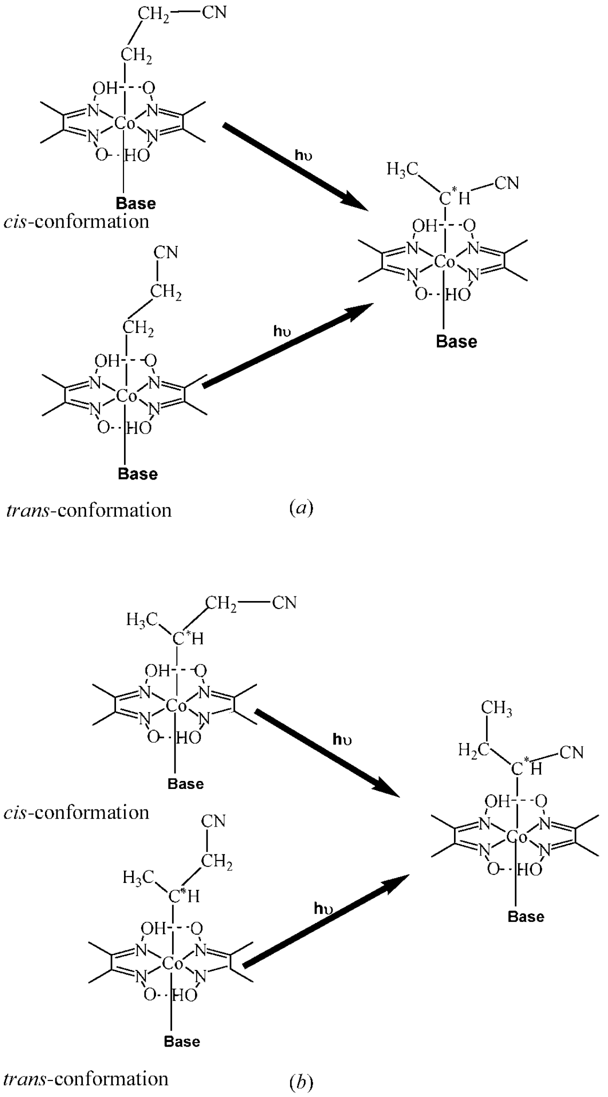
For the past two decades many researchers have been studying mixed-crystal formation under different subjects (Nakanishi *et al.*, 1979; Hasegawa *et al.*, 1989; Braga *et al.*, 2001). Further, some difficulties associated with the reactivity of some organic molecular crystals have been overcome by the formation of mixed crystals; this process is known to be an effective crystal-engineering method (Theocharis *et al.*, 1984). In a series of studies of photoreactive bis(dimethylglyoximato)cobalt(III), cobaloxime, complex crystals, we found that (1-cyanoethyl) cobaloxime complex (product) formed mixed crystals with (2-cyanoethyl)cobaloxime complex (reactant) in different molar ratios. In these mixed crystals the 2-cyanoethyl group underwent photoisomerization to the 1-cyanoethyl group in the single crystal form and the reactivity was increased noticeably when compared with the reactivity of the 2-cyanoethyl group in pure crystals (Uchida *et al.*, 1986; Sekine, 1992; Sekine & Ohashi, 1996).

A powdered sample of the 2-cyanoethyl (β-cyanoethyl group) in cobaloxime complexes was found to be isomerized to the 1-cyanoethyl (α-cyanoethyl group) as shown in Scheme 1(*a*) (Ohgo & Takeuchi, 1985). The 2-cyanoethyl group has two conformations, *trans* and *cis*, which have different torsion angles around the Co—C—C—CN bond. The isomerization rate of the (2-cyanoethyl)cobaloxime complex crystal with the *cis* conformation was significantly greater than that with the *trans* conformation (Ohashi *et al.*, 1990). Recently, a quantitative relationship between the isomerization rates and the structures of the 2-cyanoethyl groups in three mixed cobaloxime crystals with different axial base ligands was investigated (Vithana *et al.*, 2002). However, striking changes in the reactivity were not observed, because the mixed crystals were composed of isostructural compound pairs and had structures similar to their parent crystals.

Recently, it was reported that the 2-cyanopropyl (β-cyanopropyl) groups of cobaloxime complexes also isomerize to the 1-cyanopropyl (α-cyanopropyl) groups in the solid state, as shown in Scheme 1(*b*). The torsion angles of Co—C—C—CN in various (2-cyanopropyl)cobaloxime complexes are either 160–175° (*trans* conformation) or 77–83° (*cis* conformation) (Yoshiike, 1998), which are nearly the same as those angles observed in the (2-cyanoethyl)cobaloxime complexes (Sekine, 1992). The isomerization rate of the 2-cyanopropyl group with a *trans* conformation is significantly smaller than that of the 2-cyanopropyl group with a *cis* conformation (Yoshiike, 1998). Such a difference in reactivity between *trans* and *cis* conformations was also observed in the 2-cyanoethyl complexes (Uchida *et al.*, 1991; Sekine, 1992). Conversely, it was reported that when a mixed crystal was formed between two molecules with significantly different molecular conformations, the minor component adopted the molecular conformation of the major (Theocharis *et al.*, 1984).

This behavior suggested that the 2-cyanopropyl complex would form a mixed crystal with the 2-cyanoethyl complex, if the two groups have the same conformation, because the only difference between the two groups is the methyl group of 2-cyanopropyl. Furthermore, since the conformations of the 2-cyanoethyl groups in the crystal structures of (2-cyanoethyl)(3-methylpyridine)cobaloxime, 2ce3mpy, and (2-cyanoethyl)(3-ethylpyridine)cobaloxime, 2ce3epy, are *cis* (Uchida *et al.*, 1987; Sekine *et al.*, 1991), it was assumed that the conformation of the 2-cyanopropyl group would become *cis* if the above two 2-cyanoethyl complexes form mixed crystals with the (2-cyanopropyl)cobaloxime complex, even if the 2-cyanopropyl group takes a *trans* conformation in the pure complex crystal.

When the complexes of 2ce3mpy and 2cp3mpy and the complexes of 2ce3epy and 2cp3mpy were mixed in aqueous acetone and methanol solutions, mixed crystals Mix-I and Mix-II were obtained, respectively. Although the 2-cyanopropyl group takes a *trans* conformation in 2cp3mpy, the conformation of the 2-cyanopropyl group in either Mix-I or Mix-II is *cis*, and the reaction rates of the 2-cyanopropyl groups in Mix-I and Mix-II were significantly increased compared with those of the parent 2-cyanopropyl complex crystal. Moreover, both mixed crystals showed photoisomerization without damaging the single-crystal form. This paper describes such structural changes in the 2-cyanopropyl groups in the two mixed crystals and the relationship of these changes to the subsequent photochemical behavior in the powdered sample (solid state) and in a single crystal (crystalline state).



2. Experimental

2.1. Preparation

Complexes (2-cyanoethyl)(3-methylpyridine)bis(dimethylglyoximato)cobalt(III) (2ce3mpy), (2-cyanopropyl)(3-methylpyridine)bis(dimethylglyoximato)cobalt(III) (2cp3mpy) and (2-cyanoethyl)(3-ethylpyridine)bis(dimethylglyoximato)-cobalt(III) (2ce3epy) were synthesized *via* the method reported by Schrauzer & Windgassen (1967). An equimolar mixture of 2ce3mpy and 2cp3mpy was recrystallized from a

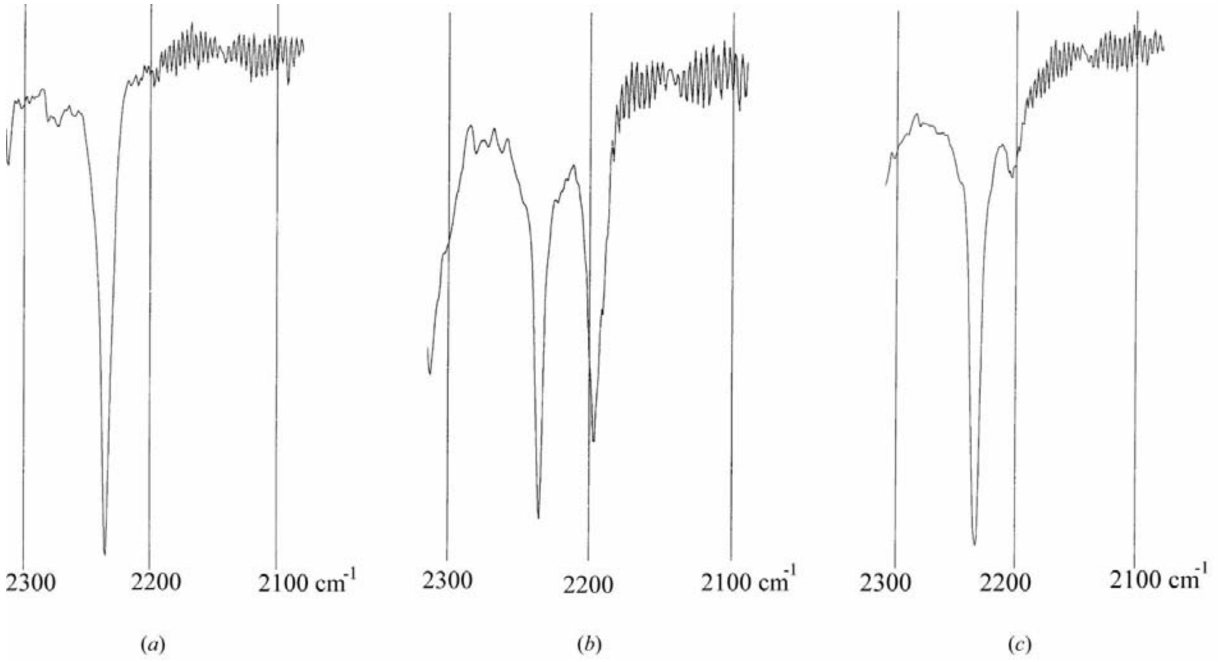


Figure 1
IR spectra of the 2-cyanoethyl group (*a*) before and (*b*) after irradiation, and (*c*) the 2-cyanopropyl group after irradiation.

hot acetone solution at ambient temperature to obtain very thin dark-yellow plate-like crystals, Mix-I. The compounds 2ce3epy and 2cp3mpy were recrystallized in a 1:1 molar ratio from a hot methanol solution at ambient temperature to obtain very thin yellow plate-like crystals, Mix-II, by slow evaporation of the solvent.

2.2. Solid state and crystalline state photoisomerization

For each of 2ce3mpy, 2ce3epy, 2cp3mpy, Mix-I and Mix-II, KBr discs that consisted of 1% of the powdered sample (0.003 g) were prepared separately and were irradiated with a xenon lamp (HOYA–SCHOTT Mega light 100). To suppress the oxidation of the sample, the KBr discs were irradiated in a transparent vessel in an argon atmosphere at ambient temperature; the distance between the lamp and the KBr disc was maintained at 1.5 cm. The FT/IR spectra were recorded at a constant time interval of 5 min. The CN stretching frequency of the 2-cyanoethyl group appeared at 2235 cm^{-1}, as shown in Fig. 1(*a*). However, the evaluation of the reactivity took into account the increase in the intensity of the peak at 2196 cm^{-1} upon irradiation. This peak is due to the CN stretching frequency of the 1-cyanoethyl group for the 2ce3mpy and 2ce3epy compounds, as shown in Fig. 1(*b*). In 2cp3mpy before irradiation, the peak corresponding to the CN stretching frequency of 2-cyanopropyl was at 2235 cm^{-1}. The increase in the intensity of the peak at 2203 cm^{-1}, which was due to the CN stretching frequency of the 1-cyanopropyl group, was considered to provide an estimate of the rate constant of pure 2cp3mpy, as shown in Fig. 1(*c*). Assuming first-order kinetics during the early stages (within the initial 30 min), the rate constants for each sample were calculated with the help of a log plot of the peak intensity against the irradiation time. In the Mix-I and Mix-II crystals, however, the CN stretching frequencies of both 2-cyanoethyl and 2-cyanoproyl groups appeared at 2235 cm^{-1} before light exposure, and the peak that was observed at 2198 cm^{-1} on irradiation is responsible for the CN stretching frequencies of the 1-cyanoethyl and the 1-cyanopropyl groups. The average reaction rates were estimated from the increase in the intensities of the peaks that were due to the products of those reactions.

Well defined single crystals of Mix-I and Mix-II were irradiated with the xenon lamp for 40 h and 60 h, respectively. The crystals after irradiation were called Mix-I′ and Mix-II′, respectively, and their structures were analyzed by X-ray techniques.

2.3. Crystal structure analysis

Three-dimensional intensity data collection of 2cp3mpy, Mix-I, Mix-II, Mix-I′ and Mix-II′ was performed on a SMART-CCD diffractometer. The crystal structures of 2ce3mpy and 2ce3epy have already been reported (Uchida *et al.*, 1987; Sekine *et al.*, 1991). The other crystal data and experimental details are listed in Table 1. Structures of all the crystals were deduced using direct methods (*SIR*92; Altomare *et al.*, 1994) and refined by the full-matrix least-squares method with the program *SHELXL*97 (Sheldrick, 1997).[1]

All non-H atoms of 2cp3mpy were located on the difference-Fourier map. The methyl group of 2-cyanopropyl is disordered, and atoms C15 and C15*B* have occupancy factors of 0.9:0.1. The atomic parameters of non-H atoms were refined with anisotropic temperature factors, except for C15*B*, which

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[1] Supplementary data for this paper are available from the IUCr electronic archives (Reference: DE0020). Services for accessing these data are described at the back of the journal.

Table 1
Experimental details.

	2cp3mpy	Mix-I	Mix-I′	Mix-II	Mix-II′
Crystal data					
Chemical formula	$C_{18}H_{26.712}CoN_6O_4$	$C_{17.48}H_{21}CoN_6O_4$	$C_{17.50}H_{19}CoN_6O_4$	$C_{18}H_{21}CoN_6O_4$	$C_{18}H_{18}CoN_6O_4$
Chemical formula weight	450.08	438.09	436.31	444.33	441.31
Cell setting, space group	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/n$
a, b, c (Å)	15.5525 (1), 7.5711 (1), 18.1578 (1)	11.5388 (2), 9.3751 (2), 19.2929 (4)	11.5432 (9), 9.3978 (4), 19.5033 (16)	11.7299 (4), 9.2358 (3), 19.8561 (6)	11.5090 (4), 9.4410 (3), 20.0330 (7)
β (°)	98.4	92.204 (1)	90.992 (4)	91.082 (1)	95.875 (2)
V (Å^3)	2115.01 (3)	2085.51 (7)	2115.4 (3)	2150.73 (12)	2165.28 (13)
Z	4	4	4	4	4
D_x (Mg m^{-3})	1.41	1.40	1.37	1.37	1.35
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	0.848	0.858	0.845	0.833	0.827
Temperature (K)	293 (2)	293 (2)	293 (2)	293 (2)	293 (2)
Crystal form, colour	Plate, orange	Plate, yellow	Plate, orange	Plate, yellow	Plate, orange
Crystal size (mm)	0.50 × 0.35 × 0.05	0.40 × 0.30 × 0.04	0.40 × 0.30 × 0.04	0.50 × 0.45 × 0.05	0.50 × 0.45 × 0.05
Data collection					
Diffractometer	SMART CCD	SMART CCD	SMART CCD	SMART CCD	SMART CCD
Data collection method	ω scans	ω scans	ω scans	ω scans	ω scans
Absorption correction	Multi-scan	Multi-scan	Multi-scan	Multi-scan	Multi-scan
T_{min}	0.7094	0.7264	0.5027	0.3802	0.7932
T_{max}	1.0000	1.0000	1.0000	1.0000	1.0000
No. of measured, independent and observed reflections	14434, 4814, 4163	14242, 4761, 3427	14831, 4856, 2223	14428, 4876, 3259	15233, 4998, 2565
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
R_{int}	0.0338	0.0477	0.0873	0.0670	0.0802
θ_{max} (°)	27.45	27.52	27.53	27.52	27.55
Range of h, k, l	$-18 \rightarrow h \rightarrow 20$ $-9 \rightarrow k \rightarrow 9$ $-23 \rightarrow l \rightarrow 14$	$-14 \rightarrow h \rightarrow 14$ $-12 \rightarrow k \rightarrow 12$ $-22 \rightarrow l \rightarrow 25$	$-12 \rightarrow h \rightarrow 14$ $-12 \rightarrow k \rightarrow 12$ $-25 \rightarrow l \rightarrow 21$	$-15 \rightarrow h \rightarrow 15$ $-11 \rightarrow k \rightarrow 10$ $-25 \rightarrow l \rightarrow 22$	$-14 \rightarrow h \rightarrow 14$ $-12 \rightarrow k \rightarrow 11$ $-16 \rightarrow l \rightarrow 26$
Refinement					
Refinement on	F^2	F^2	F^2	F^2	F^2
$R[F^2>2\sigma(F^2)]$, $wR(F^2)$, S	0.0374, 0.0997, 1.063	0.0613, 0.1663, 1.04	0.1101, 0.317, 1.045	0.0809, 0.2169, 1.123	0.0763, 0.2095, 1.061
No. of reflections, parameters and restraints used in refinement	4814, 281, 1	4761, 280, 16	4856, 294, 20	4876, 280, 10	4998, 281, 9
H-atom treatment	Mixed	Mixed	Mixed	Mixed	Mixed
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0534P)^2 + 0.674P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0795P)^2 + 1.695P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.1163P)^2 + 7.8125P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0832P)^2 + 2.7552P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$	0.001	0.036	0.048	0.005	0.011
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.463, −0.425	0.865, −0.519	0.708, −0.581	0.613, −0.952	0.501, −0.667

Computer programs used: *TEXSAN* (Molecular Structure Corporation, 2000), *SIR*92 (Altomare *et al.*, 1994), *SHELXL*97 (Sheldrick, 1997), *SMART* (Siemens, 1995), *SAINT* (Siemens, 1995).

was refined isotropically. H atoms of the hydroxyl groups of the equatorial ligands were found in the difference-Fourier map and refined with isotropic parameters. The remaining H atoms were added geometrically and refined with the riding model.

For Mix-I, several new peaks appeared around the 2*ce* and 2*cp* groups in the difference electron-density map. When the peaks were named as C17*B*, C18*B* and N6*B*, the *R* value was reduced to 0.173. The two peaks that were observed about 1.43 Å away from either side of the C16 atom were labeled as C15 and C15*B*, the *R* and *S* methyl groups of the 2*cp* chain. Furthermore, two other peaks, of intensity greater than 0.6 e Å^{-3}, were found in the difference map close to the C17*B*—C18*B*—N6*B* chain, and they were assigned as C17*A*

Table 2
Cell dimensions and cavity volumes of the component and mixed crystals.

Cell parameters	*a* (Å)	*b* (Å)	*c* (Å)	*β* (°)	*V* (Å^3)	Space group	*Z*	Cavity volume (Å^3)
2ce3mpy(*α*)	8.815 (3)	9.496 (2)	24.684 (5)	106.34 (2)	1982.8 (8)	$P2_1/n$	4	10.1
2ce3mpy(*β*)	11.507 (2)	9.28 (2)	21.413 (3)	117.70 (2)	2026.2 (9)			11.5
2cp3mpy	15.552 (4)	7.565 (3)	18.181 (3)	98.33 (1)	2116.5 (9)	$P2_1/n$	4	25.3
Mix-I	11.526 (3)	9.340 (4)	19.275 (8)	92.21 (3)	2073.5 (12)	$P2_1/n$	4	12.6
2ce3epy	11.637 (5)	9.286 (1)	19.556 (3)	92.42 (2)	2111.3 (9)	$P2_1/n$	4	13.5
Mix-II	11.728 (4)	9.232 (3)	19.810 (6)	90.66 (3)	2144.6 (11)	$P2_1/n$	4	15.1

and C18*A* of another disordered group, in which the N6 atom is common for two chains. Disordered atoms were refined isotropically and independently with some restrained bond lengths, and the site occupancy factors of the three chains were normalized to sum to unity. C15 and C15*B* were refined independently to have equal isotropic temperature factors. The remaining non-H atoms were refined with anisotropic temperature factors. After several cycles of least-squares refinement, the *R* value converged to 0.0679. Finally, H atoms were introduced geometrically and refined with the riding model, except for the hydroxyl and methine H atoms, which were located from the difference-Fourier map; their positions were refined freely to have a final *R* value of 0.061.

After 40 h of irradiation, the crystallinity of Mix-I became worse, and the $R_{\rm int}$ value of Mix-I′ became 0.09. After the first refinement cycle with isotropic temperature factors, new peaks were found in the electron-density map of Mix-I′. They were named as N6, C18, C17, N6*B*, C18*B* and C17*B* of the C—C—N groups; C15 and C15*B* were again identified as the *R* and *S* groups of the 2*cp* group. Further refinement was performed with restrained bond lengths, and the *R* value was reduced to 0.24. The *R* and *S* methyl groups of the 1-cyanoethyl chain and the *S* methyl group of the 1-cyanopropyl chain, atoms C16, C16*A* and C15*A*, respectively, appeared more clearly in the electron-density map, with peaks of intensity greater than 0.6 e Å^{-3}. The occupancy factors of C15, C15*A*, C15*B*, C16*A* and C16 were allowed to refine freely by balancing their isotropic temperature factors until they were almost identical. The other ordered non-H atoms were refined anisotropically. The hydroxyl and methine H atoms were located on the difference-Fourier map and their positions were refined freely. Finally the remaining H atoms were introduced geometrically and refined with the riding model. The final *R* value converged to 0.11.

For Mix-II, a similar process was applied to separate the disordered atoms. After several refinement cycles, the *R* value was lowered to 0.14. The methyl group of the 3-ethylpyridine ligand was also found to be disordered (C15 and C15*B*). The methyl groups of the *R* and *S* configurations of the 2-cyanopropyl group, C16 and C16*B*, were refined to have the same isotropic temperature factors. Finally non-H atoms, except for C15, C15*B*, C16, C16*B*, C18, C18*B*, C19, C19*B*, N6 and N6*B*, were refined with anisotropic temperature factors. Besides the methine and hydroxyl H atoms that were found in the electron-density map, all other H atoms were added geometrically and refined with the riding model to obtain a final *R* value of 0.08.

The initial structure analysis of Mix-II′ revealed that all the high-intensity peaks in the reactive alkyl region were at completely different sites from those in Mix-II. The three peaks with the highest intensity were assigned to the N6, C18 and C19 atoms of the 1-cyanoethyl and the 1-cyanopropyl groups, which are superimposed. The other new peaks in the reactive alkyl region were assigned to the atoms of the (*R*)- and (*S*)-1-cyanoethyl and -1-cyanopropyl groups, and the two peaks that were observed closer to C14 were named as disordered methyl groups of the 3-ethylpyridine group, C15 and C15*B*. All these disordered atoms were refined iostropically. After several refinement cycles, the *R* value was reduced to 0.13. Finally, all other non-H atoms, including the N6, C18 and C19 atoms, were treated with anisotropic temperature factors. Geometrically fixed H atoms, except for the hydroxyl H found in the Fourier map, were allowed to refine with the riding model. With all these changes, in the last refinement cycle the *R* value became 0.076. Further refinement information about all of the crystals is summarized in Table 1.

3. Results and discussion

3.1. Molecular and crystal structures of 2cp3mpy, Mix-I and Mix-II

Table 2 gives the cell dimensions of the mixed crystals, Mix-I and Mix-II, and their component crystals. There are two polymorphs for 2ce3mpy, form I and II (Uchida *et al.*, 1987). Although the two crystals are indistinguishable morphologically, the 2-cyanoethyl groups in the two crystals are different; the ordered and disordered structures in form I and II, respectively, are shown in Fig. 2. Since the structure of the 2-cyanoethyl group in both mixed crystals is disordered, only form II is considered hereafter. The crystal and molecular structures of 2cp3mpy are shown in Figs. 3 and 4, respectively. There are *R* and *S* configurations of 2-cyanopropyl groups with the ratio of 9:1. Only the methyl groups, C15 and C15*B*, take different positions in the two enantiomers. The torsion angle, Co—C16—C17—C18, of the 2-cyanopropyl group is 164.94 (2)°. Therefore, both enantiomers have *trans* conformations.

As shown in Table 2, the cell dimensions of the 2cp3mpy crystal are considerably different from those of either crystal form of 2ce3mpy, although the space group and *Z* value are the same. Moreover, the unit-cell volume of 2cp3mpy is 90 Å^3 greater than that of 2ce3mpy. There are a handful of examples (Theocharis *et al.*, 1984; Hasegawa *et al.*, 1987) in which two

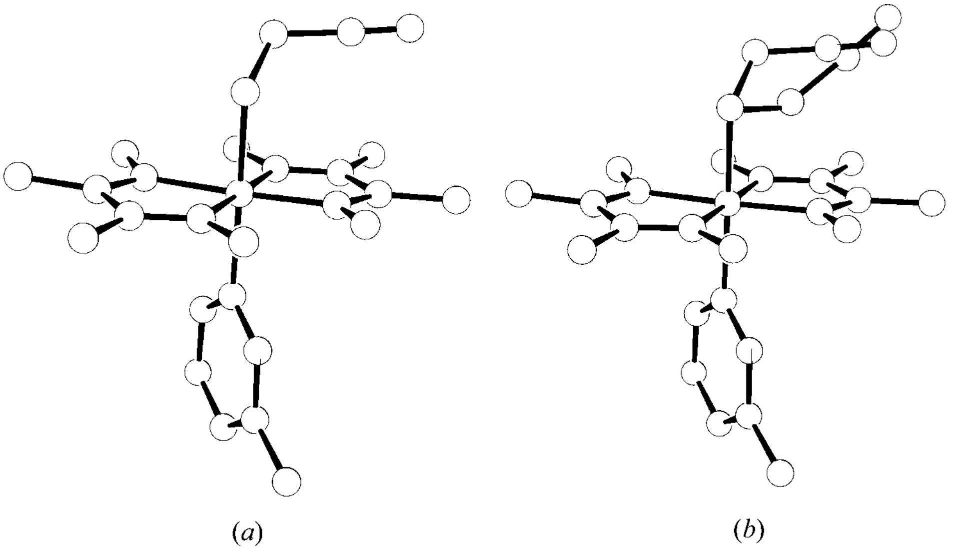
(*a*) (*b*)

Figure 2
Molecular structures of the (*a*) I and (*b*) II forms of 2ce3mpy.

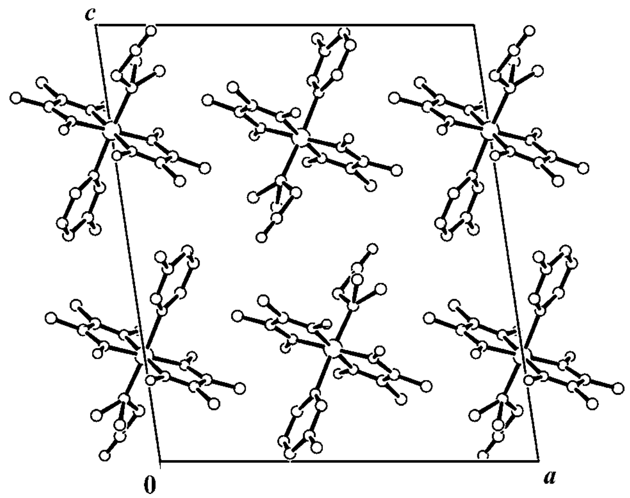

Figure 3
Crystal structure of 2cp3mpy viewed along the *b* axis.

compounds have different crystal structures and/or cell parameters but still form mixed crystals that contain two components. However, only in one example was the discrepancy between the unit-cell volumes of the two component crystals greater than 90 Å^{3} (Ding *et al.*, 2001). The Co—C—C—CN conformation of 2ce3mpy is nearly *cis*, −81.91 (5)°, while that of 2cp3mpy is almost *trans*, as shown in Fig. 4.

Despite the above incompatibilities, the two compounds formed the mixed crystal Mix-I. The cell parameters lie in between those of the two component crystals; the crystal structure, which is shown in Fig. 5, differs from that of either of the two components. The molecular structure of Mix-I is shown in Fig. 6. The disordered 2-cyanopropyl groups have the same C—C—CN conformations as the two disordered 2-cyanoethyl groups. Hence, only the methyl groups of the enantiomeric 2-cyanopropyl groups, C15 and C15*B*, take independent positions, and their occupancy factors are 0.13 and 0.35, respectively. There are three conformations for the C—C—CN moiety, C16—C17—C18—N6, C16—C17*A*—C18*A*—N6 and C16—C17*B*—C18*B*—N6*B*, and their occupancy factors are 0.45, 0.15 and 0.40, respectively. Most importantly, the disordered conformations of the Co—C—C—CN [72.16 (7), −80.90 (4) and −68.52 (5)] of the 2-cyanopropyl groups are *cis* in Mix-I while the conformations are *trans* in the pure 2cp3mpy crystal. This fact clearly indicates that the conformation of the 2-cyanopropyl group was induced to adopt the same conformation as its partner component, the 2-cyanoethyl group, in the process of mixed crystal formation.

As shown in Table 2, the cell parameters of Mix-II, which is composed of 2ce3epy and 2cp3mpy, are closer to those of 2ce3epy than to those of 2cp3mpy. The 2-cyanoethyl group of 2ce3epy has a *cis* conformation. The torsion angle of Co—C—C—CN is −77.2 (9)° (Sekine *et al.*, 1991). In the disordered molecular structure of Mix-II, the 2-cyanoethyl groups as well as the 2-cyanopropyl groups take *cis*

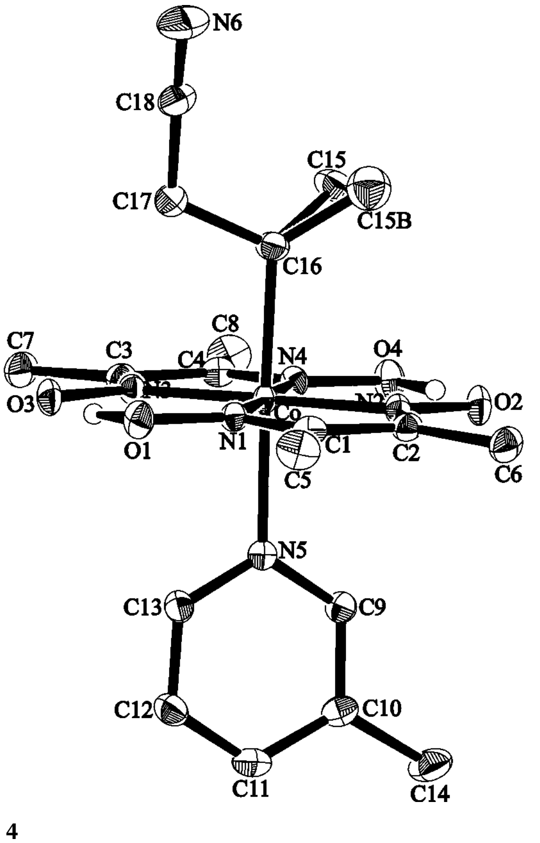

Figure 4
Molecular structures of (*R*)- and (*S*)-2cp3mpy. The thermal ellipsoids are drawn at the 30% probability level. H atoms are omitted for clarity. The occupancy factors of the two disordered methyl groups, C15 and C15*B*, are 0.90 and 0.10, respectively.

conformations, in which the Co—C—C—N torsion angles are 80.8 (8)° and 79 (2)°, as revealed in Fig. 7. A similar conformational change was observed in the crystal of Mix-I.

Since the occupancy factors of C16 and C16*B* are 0.36 and 0.14, respectively, in Mix-II, the occupancy factors of the (*S*)- and (*R*)-2-cyanopropyl groups should be in the same ratio. In contrast, the C—C—C—N moieties of the two enantiomeric 2-cyanopropyl groups occupy the same positions as the disordered 2-cyanoethyl groups. Therefore, the ratio of the two disordered 2-cyanoethyl groups, C17—C18—C19—N6 and C17—C18*B*—C19*B*—N6*B*, becomes 0.14:0.36, if we take into account the total occupancy ratio, 50:50, of the C18—C19—N6 and C18*B*—C19*B*—N6*B* moieties. The crystal structure viewed down the *b* axis is given in Fig. 8, and the packing pattern in Mix-II is similar to that in pure 2ce3epy.

Therefore, in Mix-I and Mix-II, the structures of 2ce3mpy and 2ce3epy have a great influence on the molecular structure of the partner, 2cp3mpy, and change the conformation of the 2-cyanopropyl group from *trans* to *cis*. Such a structural change is called conformational or structural mimicry, and very few related examples have been reported so far. Although the molecular geometry of the minor component is dominated by the major component, wherein the composition of the major component is closer to 0.70 or greater (Sacconi *et al.*, 1965; Jones *et al.*, 1983), conformational mimicry was observed in Mix-I and Mix-II in a 1:1 molar ratio.

3.2. Molecular structures of Mix-I′ and Mix-II′

The crystal structure of Mix-I′ (Mix-I after 40 h of irradiation with a xenon lamp) is approximately the same as that of Mix-I, although the unit-cell volume of Mix-I′ is about 30 Å^3

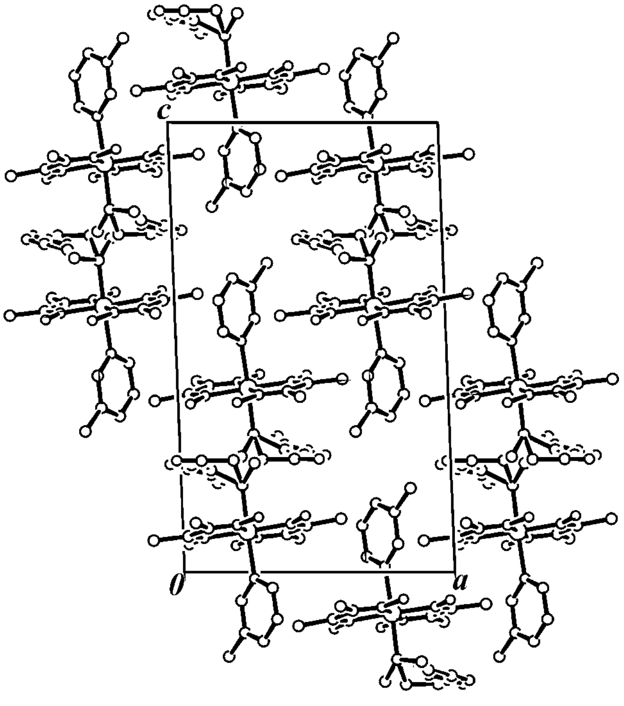

Figure 5
Crystal structure of Mix-I viewed along the *b* axis.

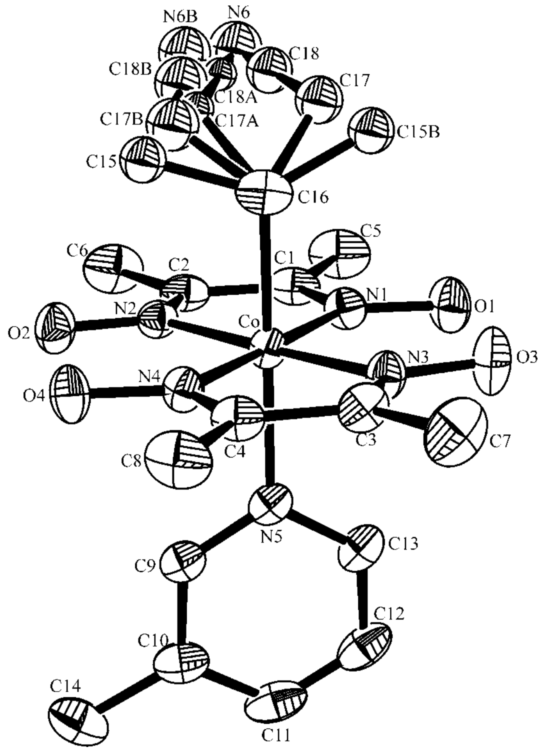

Figure 6
Disordered molecular structure of Mix-I. The thermal ellipsoids are drawn at the 30% probability level. H atoms are omitted for clarity. The occupancy factors of 2ce3mpy and 2cp3mpy are 0.52 and 0.48, respectively.

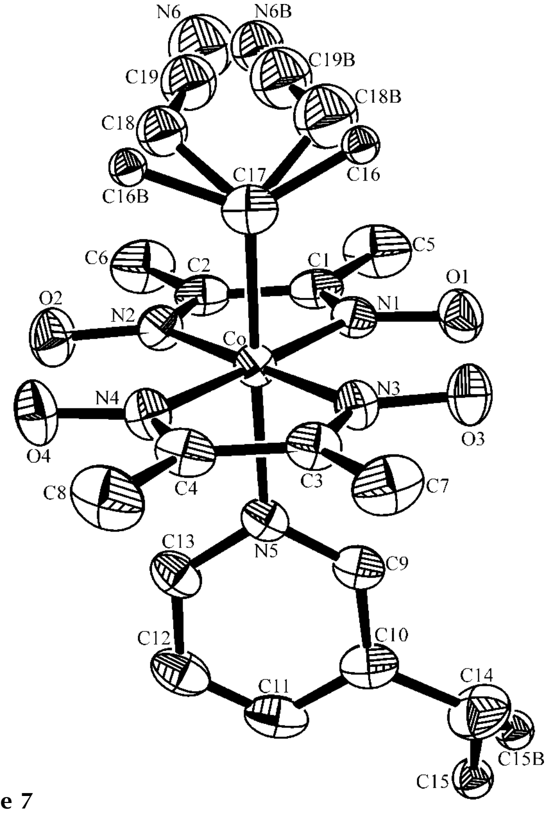

Figure 7
Disordered molecular structure of Mix-II. The thermal ellipsoids are drawn at the 30% probability level. H atoms are omitted for clarity. The occupancy factors of 2ce3epy and 2cp3mpy are 0.50 and 0.50, respectively.

larger than that of Mix-I. The molecular structure of Mix-I′ is given in Fig. 9. As the structures of the original and produced alkyl groups are too complicated, the changes in the 2-cyanoethyl and 2-cyanopropyl groups after irradiation are shown separately in Figs. 10(*a*) and 10(*b*), respectively. The disordered 2-cyanoethyl groups were transformed to the 1-cyanoethyl group with *R* and *S* configurations as shown in Fig. 10(*a*). The occupancy factors of *R* and *S* enantiomers were estimated, from the occupancy factors of C16*C* and C16*A*, to be 0.11 (1) and 0.05 (1), respectively. The disordered 2-cyanopropyl groups with *R* and *S* configurations were changed to the (*S*)-1-cyanopropyl group only, as illustrated in Fig. 10(*b*), at this stage. The occupancy factor of the (*S*)-1-cyanopropyl group, 0.20 (1), is obtained from the occupancy factor of C15*A*. Since the C16*A* position is occupied by two atoms of the (*S*)-1-cyanoethyl and (*S*)-1-cyanopropyl groups, the total occupancy factor of C16*A*, 0.25 (1), was divided into two factors, 0.05 and 0.20, for the (*S*)-1-cyanoethyl and (*S*)-1-cyanopropyl groups, respectively. The C17*A* and C18*A* atoms between the two main C—C—N chains in Mix-I disappeared after irradiation, and the CN groups of the produced 1-cyanoethyl and 1-cyanopropyl groups, which were overlapped, appeared there. The total occupancy factor of the overlapped CN group is 0.358 (9).

The crystal structure of Mix-II′ (Mix-II after 60 h irradiation) is substantially the same as that of Mix-II, although the unit-cell volume was increased by about 15 Å^3 after light exposure. The molecular structure of Mix-II′ is shown in Fig. 11. The original 2-cyanoethyl and 2-cyanopropyl groups totally disappeared and only the products were observed. The structural changes of the 2-cyanoethyl and 2-cyanopropyl groups are given separately in Figs. 12(*a*) and 12(*b*), respectively. Both of the produced 1-cyanoethyl and 1-cyanopropyl groups are disordered with *R* and *S* configurations.

The C—C—N moieties of the two groups occupy the same positions, C18, C19 and N6. Moreover, the methyl C atom of the (*S*)-1-cyanoethyl group and the methylene C atom of the (*S*)-1-cyanopropyl group occupy the same position, C17. The occupancy factors of the (*R*)- and (*S*)-1-cyanopropyl groups were estimated, from the occupancy factors of C16*A* and C16, to be 0.35 (1) and 0.16 (1), respectively. The occupancy factors of the (*R*)- and (*S*)-1-cyanoethyl groups were estimated, from the occupancy factors of C17*B* and C17, to be 0.35 (2) and 0.14 (1). The latter value was deduced by subtracting the occupancy factor of the (*S*)-1-cyanopropyl group from that of C17 (0.30 − 0.16 = 0.14). It is noteworthy that the ethyl groups of the two 1-cyanopropyl groups have nearly parallel conformations to the cobaloxime plane. Such parallel conformations are easily explained on the basis of the shape of the reaction cavity shown in Fig. 13. It seems difficult for the ethyl groups to take conformations perpendicular to the cobaloxime plane as there is not enough space in the reaction cavity perpendicular to the plane of the alkyl groups. A similar conformation was observed in the produced (*S*)-1-cyanopropyl group in Mix-I′.

3.3. Photoreactivity in solid and crystalline states

To investigate the structure–reactivity correlation of the mixed and component crystals quantitatively, the IR spectral changes on photoirradiation were measured for each crystal of 2ce3mpy, 2ce3epy, 2cp3mpy, Mix-I and Mix-II. Rates of isomerization are plotted in Fig. 14. The estimated first-order

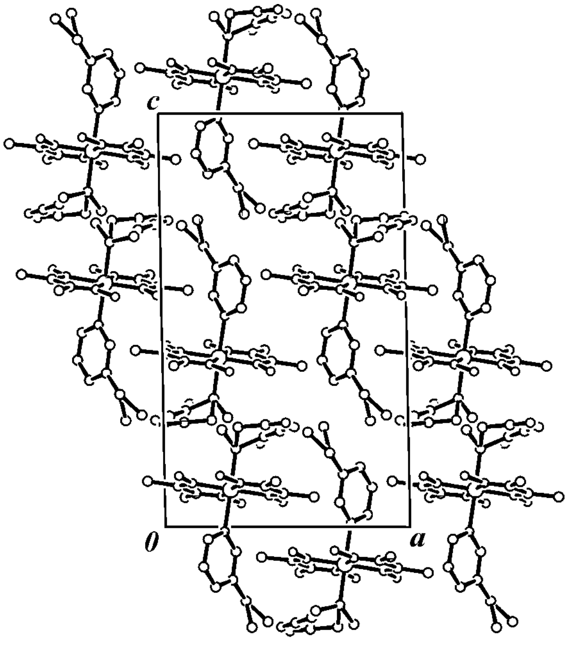

Figure 8
Crystal structure of Mix-II viewed along the *b* axis.

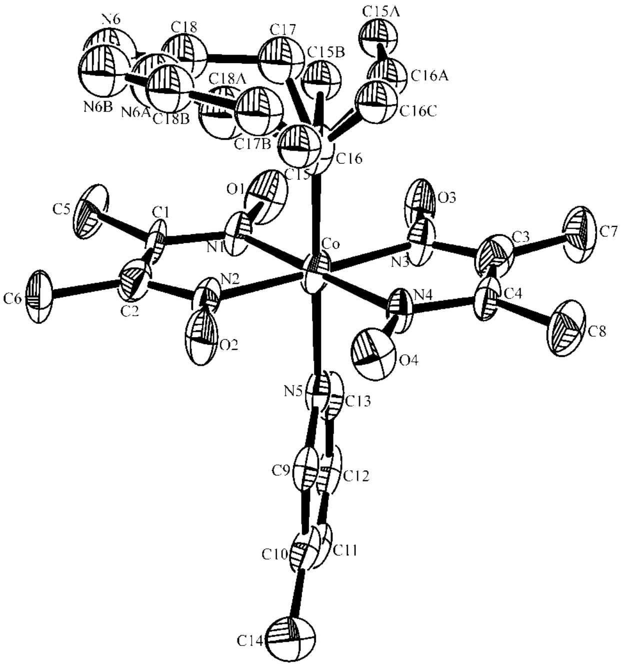

Figure 9
Disordered molecular structure of Mix-I′. The thermal ellipsoids are drawn at the 30% probability level. H atoms are omitted for clarity. The occupancy factors of 2ce3mpy and 2cp3mpy are 0.50 and 0.50, respectively.

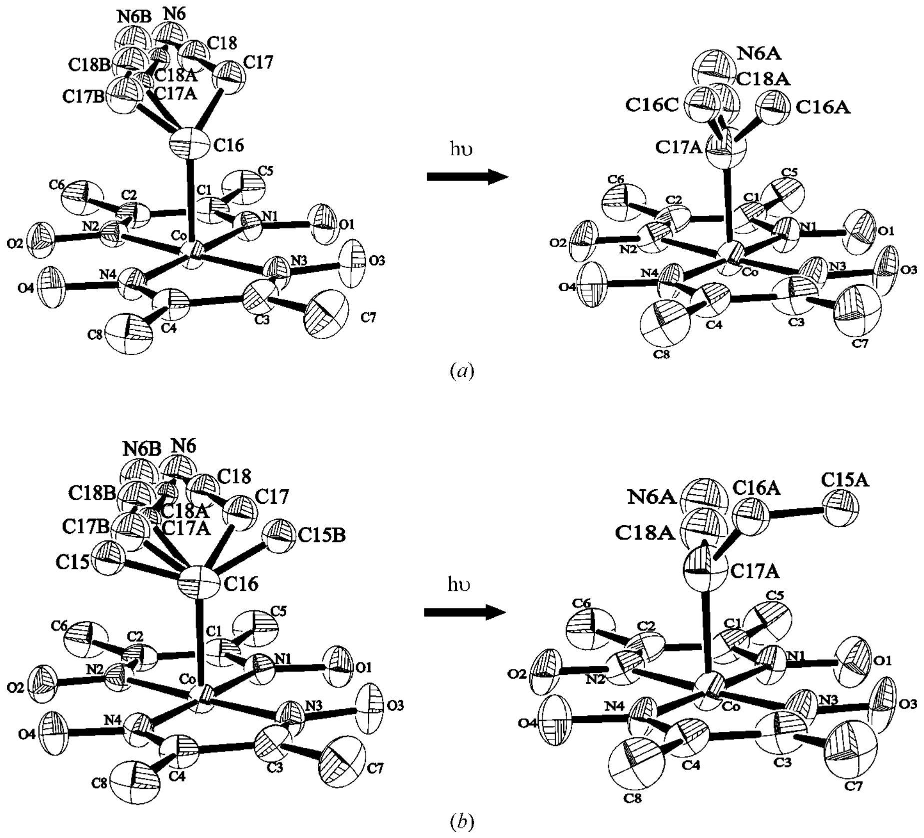

Figure 10

Transformation of (*a*) the 2-cyanoethyl group to the 1-cyanoethyl group and (*b*) the 2-cyanopropyl group to the 1-cyanopropyl group in Mix-I′.

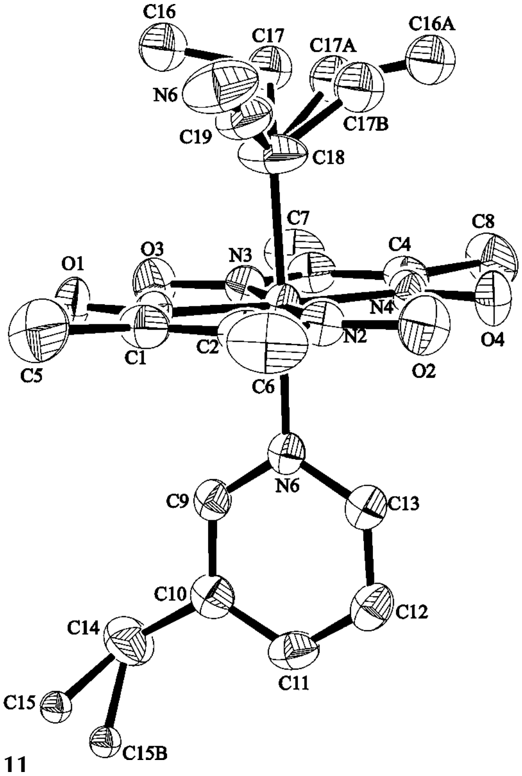

Figure 11

Disordered molecular structure of Mix-II′. The thermal ellipsoids are drawn at the 30% probability level. H atoms are omitted for clarity. The occupancy factors of 2ce3epy and 2cp3mpy are 0.51 and 0.49, respectively.

rate constants within 30 min were calculated to be 5.29×10^{-4}, 6.88×10^{-4} and $0.46 \times 10^{-4}\,s^{-1}$ for 2ce3mpy, 2ce3epy and 2cp3mpy, respectively. The rate constant of 2cp3mpy is much lower than that of 2ce3mpy or 2ce3epy, because the conformation of the 2-cyanopropyl group is *trans*, whereas the conformations of the 2-cyanoethyl groups of 2ce3mpy and 2ce3epy are *cis*. In a previous paper (Uchida *et al.*, 1991), we observed that the *trans* conformer of the 2-cyanoethyl group has a significantly smaller rate constant than the *cis* conformer. This difference can be explained on the basis of the topochemical principle. Hence, a similar explanation is probably applicable to rationalize the small rate constant of the *trans* conformer of 2cp3mpy.

For the mixed crystals, too, the reaction rates are well explained by first-order kinetics; here the rates are $10.73 \times 10^{-4}\,s^{-1}$ and $14.05 \times 10^{-4}\,s^{-1}$ for Mix-I and Mix-II, respectively. Since it is impossible to estimate first-order rate constants of 2ce3mpy, 2ce3epy and 2cp3mpy separately in each mixed crystal from the IR spectroscopy data alone, the reaction rates in the crystalline-state isomerization also have to be considered. The populations that were observed for reactants and products in the Mix-I′ and Mix-II′ crystals were used to estimate the rough reaction rates of the two components in each mixed crystal. In Mix-I′, the population ratio of the produced 1-cyanoethyl group to the 1-cyanopropyl group is nearly 1:1 after 40 h of irradiation, which indicates that both of the components have nearly equal reaction rates in Mix-I.

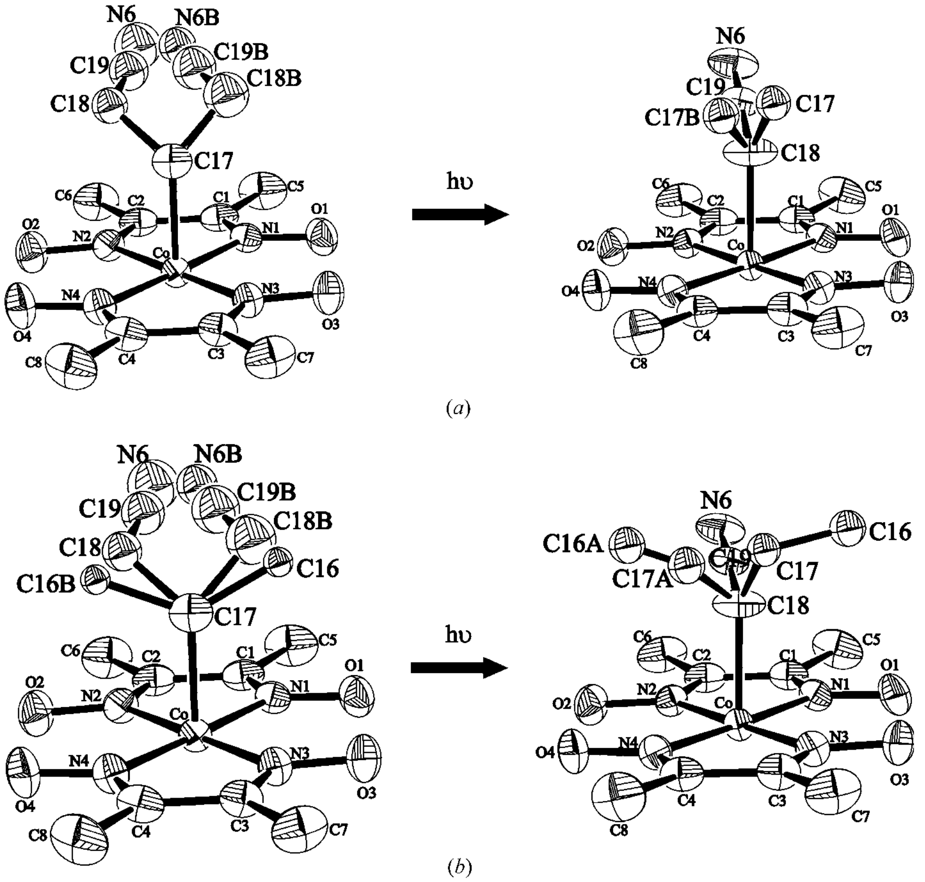

Figure 12
Transformation of (*a*) the 2-cyanoethyl group to the 1-cyanoethyl group and (*b*) the 2-cyanopropyl group to the 1-cyanopropyl group in Mix-II′.

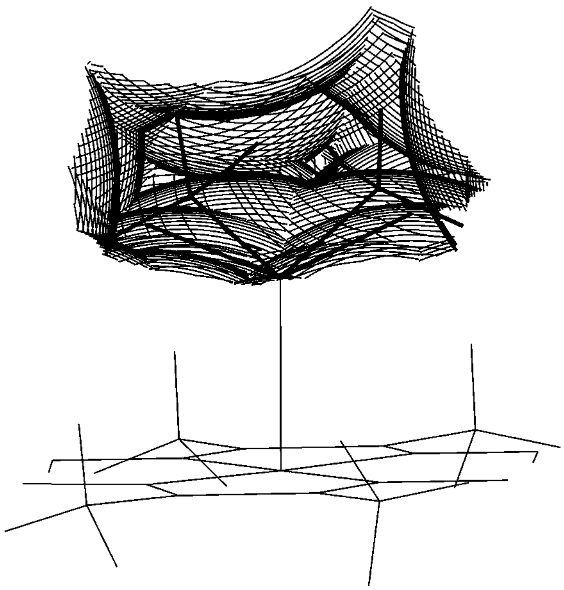

Figure 13
Side view of the reaction-cavity diagram of Mix-II. The contours are drawn in sections and are separated by 0.20 Å.

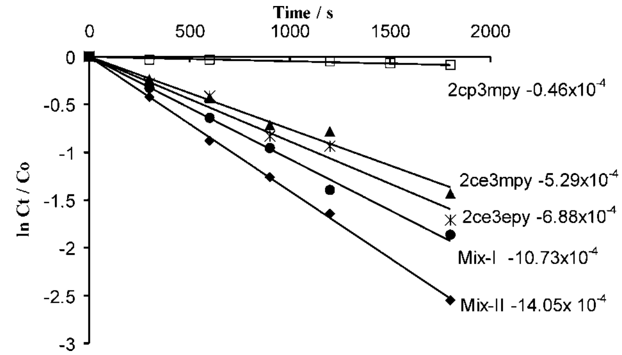

Figure 14
The first-order reaction rates observed for the 2ce3mpy, 2ce3epy, 2cp3mpy, Mix-I and Mix-II crystals. The increase in intensity of the IR peaks that are due to the CN stretching frequencies of the cyano groups is considered to give an estimate of the reaction rates. The values of C_0 and C_t indicate the concentration of the 1-cyanoethyl and/or 1-cyanopropyl complex(es) at the irradiation times 0 and t, respectively.

In Mix-II′, both components have isomerized completely after 60 h of irradiation, which may indicate that the reaction rates might be the same for the two components. Hence, the rate constants of Mix-I and Mix-II were divided by two to estimate the rate constants for the two components. The rate constants of 2ce3mpy and 2cp3mpy in Mix-I would be thus be 5.37×10^{-4} s^{-1}, and the corresponding rates of 2ce3epy and 2cp3mpy in Mix-II must be 7.03×10^{-4} s^{-1}. The rate constants of 2cp3mpy in the two mixed crystals, 5.37×10^{-4} and 7.03×10^{-4} s^{-1} in Mix-I and Mix-II, respectively, are significantly greater than that of the pure 2cp3mpy crystal,

0.46×10^{-4} s^{-1}, which is about one tenth of the rate constant observed in the mixed-crystal form.

The reaction cavities for the 2-cyanoethyl and 2-cyanopropyl groups in the component crystals and the corresponding cavities for the disordered 2-cyanoethyl and 2-cyanopropyl groups in the mixed crystals were calculated (Ohashi *et al.*, 1981; Weiss *et al.*, 1993) and the volumes are listed in Table 2. The cavity volume of the 2-cyanopropyl group in the component crystal, 25.3 Å^3, became noticeably smaller when the 2-cyanopropyl group was included in the mixed crystals: 12.6 and 15.1 Å^3 for Mix-I and Mix-II, respectively. However, the reaction rate was increased by a factor of ten. This is because the conformation was changed from *trans* to *cis* when the 2-cyanopropyl group was included in the mixed-crystal form.

Further, the enhancements in the reaction rates that are observed for the 2-cyanoethyl groups of 2ce3mpy and 2ce3epy can be explained by the expansion of the cavity volumes that occurs when the 2-cyanoethyl groups are included in the mixed crystals. The cavity volume of the 2-cyanoethyl group was expanded by 1.1 Å^3 in Mix-I and by 1.6 Å^3 in Mix-II. The rate constant of Mix-I is smaller than that of Mix-II. Since the reaction cavities of Mix-I and Mix-II have volumes of 12.6 and 15.1 Å^3, respectively, the lower rate constant of Mix-I can be explained by the smaller reaction-cavity size. Finally, note that the reactivity and the reaction-cavity size correlate in the mixed crystal too.

4. Concluding remarks

Two mixed crystals, Mix-I and Mix-II, were formed between two cobaloxime complexes that have the 2-cyanoethyl and 2-cyanopropyl groups as axial ligands. Although the 2-cyanopropyl group has a *trans* conformation, whereas the 2-cyanoethyl groups take *cis* conformations in their component crystals, the 2-cyanopropyl groups in the two mixed crystals take *cis* conformations that are adopted by the *cis* conformation of the partner 2-cyanoethyl group. Thus, conformational mimicry was observed in spite of the 1:1 molar ratio.

In the Mix-I and Mix-II crystals, photoisomerization was observed from the 2-cyanoethyl and 2-cyanopropyl groups to the 1-cyanoethyl and 1-cyanopropyl groups, respectively, with retention of the single-crystal form. When Mix-I was irradiated for 40 h, about 36% of the reactant molecules reacted to give the products, and the isomerization rates of the 2-cyanoethyl and 2-cyanopropyl groups were approximately the same. The conformations of the produced 1-cyanopropyl groups in Mix-I and Mix-II were influenced by the shapes of the reaction cavities in the mixed crystals.

The isomerization rates of the component crystals and the two mixed crystals on exposure to a xenon lamp were measured in the solid state. The reaction-rate constants were estimated assuming first-order kinetics. The rate constant of the component crystal with the 2-cyanopropyl group was significantly smaller than the rate constants of the component crystals with the 2-cyanoethyl groups. Such different rate constants were caused by the different conformations in the 2-cyanopropyl (*trans*) and the 2-cyanoethyl (*cis*) groups. Since the 2-cyanopropyl groups take *cis* conformations in the two mixed crystals because of the partner's conformation, the isomerization rates of 2-cyanopropyl were drastically increased. This shows that the conformational mimicry has a great influence on the photoreactivity of the cobaloxime complexes. The different rate constants of the two mixed crystals can be explained on the basis of the size of the reaction cavities. Further research related to the cooperative reactivity in other mixed crystals is in progress.

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References

Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435–436.

Braga, D., Cojazzi, G., Paolucci, D. & Grepioni, F. (2001). *Chem. Commun.* **9**, 803–804.

Ding, Y., Simonyan, M., Yonehara, Y., Uruichi, M. & Yakushi, K. (2001). *J. Mater. Chem.* **11**, 1469–1475.

Hasegawa, M., Endo, Y., Aoyama, M. & Saigo, K. (1989). *Bull. Chem. Soc. Jpn*, **62**, 1556–1560.

Hasegawa, M., Maekawa, Y., Kato, S. & Saigo, K. (1987). *Chem. Lett.* pp. 907–910.

Jones, W., Theocharis, C. R., Thomas, J. M. & Desiraju, G.R. (1983). *J. Chem. Soc. Chem. Commun.* pp. 1443–1444.

Molecular Structure Corporation & Rigaku Corporation (2000). *TEXSAN*. Version 1.11. MSC, 9009 New Trails Drive, The Woodlands, TX 77381–5209, USA/Rigaku, 3–9-12, Akishima, Tokyo, Japan.

Nakanishi, H., Jones, W. & Parkinson, G. M. (1979). *Acta Cryst.* B**35**, 3103–3106.

Ohashi, Y., Sekine, A., Shimizu, E., Hori, K. & Uchida, A. (1990). *Mol. Cryst. Liq. Cryst.* **186**, 37–44.

Ohashi, Y., Yanagi, K., Kurihara, T., Sasada, Y. & Ohgo, O. (1981). *J. Am. Chem. Soc.* **103**, 5805–5812.

Ohgo, Y. & Takeuchi, S. (1985). *J. Chem. Soc. Chem. Commun.* pp. 21–23.

Sacconi, L., Ciampolini, M. & Speroni, G. P. (1965). *J. Am. Chem. Soc.* **87**, 3102–3106.

Schrauzer, G. N. & Windgassen, R. J. (1967). *J. Am. Chem. Soc.* **89**, 1999–2007.

Sekine, A. (1992). PhD thesis, Tokyo Institute of Technology, Tokyo, Japan.

Sekine, A. & Ohashi, Y. (1996). *J. Mol. Struct.* **374**, 269–275.

Sekine, A., Ohashi, Y., Shimizu, E. & Hori, K. (1991). *Acta Cryst.* C**47**, 53–56.

Sheldrick, G. M. (1997). *SHELXL97. Program for the Refinement of Crystal Structure.* University of Gottingen, Germany.

Siemens (1995). *SMART* and *SAINT. Area-Detector Control and Integration Software.* Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Theocharis, C. R., Desiraju, G. R. & Jones, W. (1984). *J. Am. Chem. Soc.* **106**, 3606–3609.

Uchida, A., Danno, M., Sasada, Y. & Ohashi, Y. (1987). *Acta Cryst.* B**43**, 528–532.

Uchida, A., Ohashi, Y. & Ohgo, Y. (1991). *Acta Cryst.* C**47**, 1177–1180.

Uchida, A., Ohashi, Y. & Sasada, Y. (1986). *Nature* (*London*), **320**, 51–52.

Vithana, C., Uekusa, H., Sekine, A. & Ohashi, Y. (2002). *Acta Cryst.* B**58**, 227–231.

Weiss, R. G., Ramamurthy, V. & Hammond, G. S. (1993). *Acc. Chem. Res.* **26**, 530–536.

Yoshiike, M. (1998). Master's thesis, Tokyo Institute of Technology, Japan.