β–α Photoisomerization of Cobaloxime Complexes in the Solid State. 5.[1] Reaction Rate Reduced by a Hydrogen Bond

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The crystal structures of three cobaloxime complexes with different axial base ligands have been analyzed by X-ray analysis at room temperature. I: (2-Cyanoethyl)bis(dimethylglyoximato)((*S*)-phenylalaninol)cobalt(III); the crystal is orthorhombic, the space group being $P2_12_12_1$, $Z=4$ with $a=9.416(3)$, $b=27.184(3)$, $c=9.184(3)$ Å. II: (2-Cyanoethyl)-bis(dimethylglyoximato)((*S*)-phenyl-alanine methyl ester)cobalt(III); the crystal is monoclinic, the space group being $P2_1$, $Z=4$ with $a=14.376(2)$, $b=11.988(2)$, $c=14.874(1)$ Å, and $\beta=101.05(1)°$. III: (2-Cyanoethyl)bis(dimethylglyoximato)-(methyldiphenylphosphine)cobalt(III); the crystal is monoclinic, the space group being $P2_1/n$, $Z=4$ with $a=11.558(4)$, $b=15.542(3)$, $c=14.393(5)$ Å, and $\beta=91.02(4)°$. The structures were refined by the full-matrix least-squares method to final R values of 0.041, 0.052, and 0.044 for 2340, 3287, and 4400 observed reflections, respectively. The photoisomerization rates of I, II, and III in the solid state were obtained from the changes in the IR spectra. The rate of I was insignificantly small, but the rates of II and III were calculated to be 0.1×10^{-4} and 1.9×10^{-4} s^{-1}, respectively, assuming first-order kinetics. The 2-cyanoethyl groups in the three complex crystals take perpendicular conformations to their cobaloxime planes. The 2-cyanoethyl group of I makes a hydrogen bond with the N–H group of the neighboring molecule. The non-reactivity of I may be brought about by the hydrogen bond.

The 2-cyanoethyl group bonded to the cobalt atom in the bis(dimethylglyoximato)cobalt(III), cobaloxime, complex was found to be isomerized to a 1-cyanoethyl group on exposure to visible light.[2] The photoreaction, β–α isomerization, proceeds only in the solid state, and the reverse reaction has not been observed. Since the 2-cyanoethyl group is very similar to the 1-cyanoethyl group in the crystalline-state racemization, we expected that the reaction rate would be well explained by the reaction cavity for the reactive group, as observed in the crystalline-state reaction.[3] In our previous paper,[4] we proposed that the rate of the isomerization is controlled by three factors: the size of the cavity, the conformation of the 2-cyanoethyl group, and the hydrogen bond of the 2-cyanoethyl group with the neighboring molecule. For the complex with triphenylphosphine as an axial base ligand, four crystal forms were found and different reaction rates were observed.[1] The analyzed structures had the 2-cyanoethyl groups taking the perpendicular conformation in all the four forms. The reaction rates are quantitatively dependent on the cavity volumes of the 2-cyanoethyl groups in the four forms. Similar results were observed for the complex with 3-methylpyridine as an axial base ligand.[5]

For the complex with pyridine as an axial base ligand, two crystal forms were obtained; one has the 2-cyanoethyl group with parallel conformation, the other has a perpendicular conformation. The 2-cyanoethyl group with parallel conformation is more easily transformed to a 1-cyanoethyl group than that with the perpendicular conformation.[6] This is well explained from the topochemical point of view. For the complexes with 3-aminopyridine and aniline as axial base ligands, the 2-cyanoethyl groups take parallel conformations and make hydrogen bonds with the neighboring molecules.[4] The reaction rates of these crystals are significantly greater than those of the other complex crystals with parallel conformations, although the reaction cavities are smaller than those without hydrogen bonds. This suggested that the hydrogen bond accelerates the reaction rate since it would stabilize the radical formed by the Co–C bond cleavage. However, it remained unsolved whether the hydrogen bond in the perpendicular conformation may accelerate or reduce the reaction rate, since the cyano group must move to a greater extent in the perpendicular conformation than in the parallel conformation and the hydrogen bond may restrict the movement. After many trials we found a complex crystal with a perpendicular 2-cyanoethyl group, which makes a hydrogen bond with the neighboring molecule. This paper reports the effects of the hydrogen bond on photoisomerization.

Experimental

Crystal Structure Analyses. The complexes were synthesized by the method reported previously.[7] The crystal data and the experimental details are summarized in Table 1. The structures were solved by the direct method with the program MITHRIL,[8] and refined by the full-matrix least-squares with the program

Table 1. Experimental Details

	(I)	(II)	(III)
Crystal data			
Chemical formula	$[Co(C_4H_7N_2O_2)_2(C_3H_4N)(C_9H_{13}NO)]$	$[Co(C_4H_7N_2O_2)_2(C_3H_4N)(C_{10}H_{13}NO_2)]$	$[Co(C_4H_7N_2O_2)_2(C_3H_4N)\{P(C_6H_5)_2CH_3\}]$
Chemical formula weight	494.44	522.45	543.44
Cell Setting	Orthorhombic	Monoclinic	Monoclinic
Space group	$P2_12_12_1$	$P2_1$	$P2_1/n$
a/Å	9.416(3)	14.376(2)	11.558(4)
b/Å	27.184(3)	11.988(2)	15.542(3)
c/Å	9.184(3)	14.874(1)	14.393(5)
β/°	—	101.05(1)	91.02(4)
V/Å^3	2350(1)	2515.8(5)	2585(1)
Z	4	4	4
D_x/Mg m^{-3}	1.397	1.379	1.396
$F(000)$	1040	1096	1136
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
Wavelength/Å	0.71069	0.71069	0.71069
No. of reflections for cell parameters	25	18	24
θ range/°	10—15	10—15	10—15
μ/mm^{-1}	0.772	0.729	0.765
Temperature/K	296	296	296
Crystal form	Prismatic	Prismatic	Prismatic
Crystal size/mm	0.5 × 0.25 × 0.2	0.45 × 0.3 × 0.3	0.5 × 0.5 × 0.5
Crystal color	Yellow	Orange	Orange
Data collection			
Diffractometer	AFC-7S	AFC-5R	AFC-4
Data collection method	ω	$\omega/2\theta$	$\omega/2\theta$
Scan rate /° min^{-1}	4	32	8
Absorption correction	ψscan	ψscan	None
T_{min}	0.8993	0.9006	—
T_{max}	1.0000	1.0000	—
No. of measured reflections	3073	6068	4896
No. of independent reflections	3073	6068	4741
No. of observed reflections	2340	3287	4400
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
θ_{max}/°	27.5	27.5	27.5
Range of h,k,l	$0 \rightarrow 12$	$0 \rightarrow 18$	$-14 \rightarrow 14$
	$0 \rightarrow 35$	$0 \rightarrow 15$	$0 \rightarrow 20$
	$0 \rightarrow 11$	$-19 \rightarrow 18$	$0 \rightarrow 18$
No. of standard reflections	3	3	3
Frequency of standard reflections	Every 100 reflections	Every 100 reflections	Every 100 reflections
Intensity decay/%	0	−0.44	−1.20
Refinement			
Refinement on	F^2	F^2	F^2
$R[F^2 > 2\sigma(F^2)]$	0.041	0.052	0.044
$wR(F^2)$	0.085	0.107	0.103
S	1.004	1.042	0.932
No. of reflections used in refinement	3073	6066	4741
No. of parameters used	294	624	329
H-atom treatment	Calculated	Calculated	Calculated
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0347P)^2+1.2359P]$, where $P=(F_o^2+2F_c^2)/3$	$w=1/[\sigma^2(F_o^2)+(0.0543P)^2+0.3284P]$, where $P=(F_o^2+2F_c^2)/3$	$w=1/[\sigma^2(F_o^2)+(0.0621P)^2+1.7256P]$, where $P=(F_o^2+2F_c^2)/3$
$(\Delta/\sigma)_{max}$	−0.008	0.090	0.001
$\Delta\rho_{max}$/e Å^{-3}	0.336	0.391	0.291
$\Delta\rho_{min}$/e Å^{-3}	−0.335	−0.391	−0.308
Extinction correction	None	None	None

SHELXL93.[9] In the process of the refinement, the 2-cyanoethyl group of the B molecule in II had a disordered structure. In the refinement of III, the 2-cyanoethyl group was found to have three conformations around the Co–C bond. The bond distances of the disordered 2-cyanoethyl groups were fixed to have ideal values[3] in the refinement cycles. Non-hydrogen atoms other than the disordered atoms were refined anisotropically. The disordered atoms were refined isotropically. All the hydrogen atoms were calculated geometrically by a riding model except those of the hydroxy groups in cobaloxime planes. The atomic scattering factors were taken from International Tables for Crystallography.[10] The final atomic coordinates and equivalent isotropic temperature factors for non-hydrogen atoms are given in Tables 2, 3, and 4. Lists of the anisotropic temperature factors for non-hydrogen atoms, atomic coordinates, and temperature factors for hydrogen atoms, all the bond distances and angles, as well as the observed and calculated structure factors are deposited as Document No. 69064 in the Office of the Editor of Bull. Chem. Soc. Jpn.

***β–α* Isomerization.** KBr disks that contained 1% of the 2-cyanoethyl complex were exposed to a 400 W Xe lamp. The IR spectra of the KBr disk were measured at intervals of 5 or 10 min. The absorption assigned to the stretching vibration mode of the cyano group, ν_{CN} in the 2-cyanoethyl complex, was at 2250 cm^{-1}. The peak decreased with the irradiation time and ν_{CN} of the 1-cyanoethyl complex appeared at 2200 cm^{-1}, and increased.

Results

The crystal structure of I viewed along the *a* axis and the ORTEP drawing[11] of the molecular structure with the numbering atoms are shown in Figs. 1 and 2, respectively. The N(5) atom of the 2-cyanoethyl group is hydrogen bonded with N(6) of the amino group of the neighboring molecule at $(x, y, -1+z)$ [N(5)···N(6) 3.212(6) Å]. The O(5) atom of the hydroxy group of phenylalaninol (2-amino-3-phenyl-1-propanol) is hydrogen bonded with O(1) of the cobaloxime moiety of the neighboring molecule at $(1.5-x, 2-y, 0.5+z)$ [O(5)···O(1) 2.808(4) Å]. These hydrogen bonds connect the molecules along the *c* axis.

Table 2. Fractional Atomic Coordinates and Equivalent Isotropic Displacement Parameters (Å^2) for I

Atom	*x*	*y*	*z*	U_{eq}[a)]
Co1	0.90908(6)	0.90158(2)	0.01321(6)	0.03189
N1	0.9455(4)	0.96892(12)	0.0511(4)	0.0333
N2	1.0981(4)	0.89564(13)	0.0767(4)	0.0386
N3	0.8764(4)	0.83446(12)	−0.0296(4)	0.0403
N4	0.7187(4)	0.90578(13)	−0.0492(4)	0.0396
O1	0.8459(3)	1.00395(10)	0.0318(4)	0.0429
O2	1.1697(4)	0.85239(12)	0.0799(4)	0.0550
O3	0.9783(4)	0.80043(11)	−0.0222(4)	0.0564
O4	0.6423(3)	0.94877(11)	−0.0473(4)	0.0510
C1	1.0685(5)	0.9786(2)	0.1100(5)	0.0376
C2	1.1588(5)	0.9355(2)	0.1242(5)	0.0420
C3	0.7503(6)	0.8230(2)	−0.0784(5)	0.0434
C4	0.6555(6)	0.8656(2)	−0.0844(6)	0.0455
C5	1.1089(6)	1.0290(2)	0.1594(6)	0.0533
C6	1.3056(5)	0.9361(2)	0.1871(7)	0.061
C7	0.7093(7)	0.7722(2)	−0.1257(7)	0.070
C8	0.5023(6)	0.8614(2)	−0.1248(8)	0.073
C9	0.9798(5)	0.9091(2)	−0.1913(5)	0.0443
C10	0.9311(6)	0.9538(2)	−0.2739(5)	0.0500
C11	0.9907(6)	0.9530(2)	−0.4218(6)	0.0439
N5	1.0388(5)	0.9495(2)	−0.5335(5)	0.0617
N6	0.8366(4)	0.89945(13)	0.2269(4)	0.0366
C12	0.7752(5)	0.85521(15)	0.3007(5)	0.0368
C13	0.8962(5)	0.8196(2)	0.3418(6)	0.0458
C14	0.8473(5)	0.7691(2)	0.3864(6)	0.0412
C15	0.8853(7)	0.7492(2)	0.5179(8)	0.070
C16	0.8425(8)	0.7014(2)	0.5556(8)	0.091
C17	0.7629(7)	0.6740(2)	0.4608(9)	0.076
C18	0.7258(8)	0.6936(2)	0.3296(8)	0.077
C19	0.7678(6)	0.7406(2)	0.2943(7)	0.0599
C20	0.6908(5)	0.8708(2)	0.4337(6)	0.0472
O5	0.5884(4)	0.90653(13)	0.3950(4)	0.0610

a) $U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \boldsymbol{a}_i \cdot \boldsymbol{a}_j$.

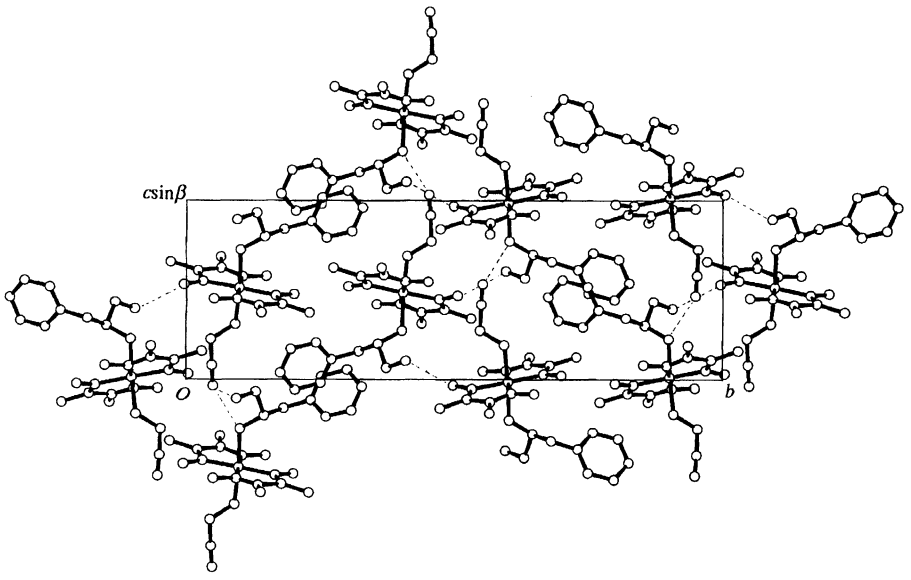


Fig. 1. Crystal structure of I viewed along the *a* axis. Intermolecular hydrogen bonds are indicated by dashed lines.

Table 3. Fractional Atomic Coordinates and Equivalent Isotropic Displacement Parameters (Å^2) for II

Atom	x	y	z	U_{eq}[a)]	Atom	x	y	z	U_{eq}[a)]
Co1A	0.61156(6)	0.36213(15)	0.36718(6)	0.0406	N3B	0.2049(5)	0.2139(6)	0.1400(4)	0.049
N1A	0.4914(4)	0.3028(6)	0.3714(4)	0.046	N4B	0.0487(5)	0.3007(7)	0.1279(5)	0.057
N2A	0.6449(5)	0.2108(6)	0.3739(5)	0.052	O1B	0.0430(5)	0.5492(6)	0.1122(5)	0.074
N3A	0.7312(4)	0.4223(6)	0.3626(4)	0.050	O2B	0.3695(3)	0.3685(7)	0.1423(3)	0.0580
N4A	0.5786(5)	0.5152(6)	0.3640(4)	0.047	O3B	0.2954(5)	0.1800(6)	0.1442(4)	0.063
O1A	0.4150(3)	0.3662(7)	0.3728(3)	0.0551	O4B	−0.0302(3)	0.3631(8)	0.1177(4)	0.080
O2A	0.7350(5)	0.1748(6)	0.3794(4)	0.067	C1B	0.2011(7)	0.5874(7)	0.1225(5)	0.050
O3A	0.8084(3)	0.3579(8)	0.3646(4)	0.069	C2B	0.2945(7)	0.5360(8)	0.1328(6)	0.049
O4A	0.4922(5)	0.5525(5)	0.3680(5)	0.063	C3B	0.1383(8)	0.1414(8)	0.1430(6)	0.060
C1A	0.4867(7)	0.1947(9)	0.3703(5)	0.045	C4B	0.0458(8)	0.1920(9)	0.1335(7)	0.063
C2A	0.5772(6)	0.1393(7)	0.3749(6)	0.051	C5B	0.1843(8)	0.7120(9)	0.1159(7)	0.080
C3A	0.7370(7)	0.5293(9)	0.3545(6)	0.058	C6B	0.3846(5)	0.6000(7)	0.1381(6)	0.060
C4A	0.6473(7)	0.5835(8)	0.3571(6)	0.057	C7B	0.1545(8)	0.0189(9)	0.1545(8)	0.086
C5A	0.3957(6)	0.1344(9)	0.3715(7)	0.076	C8B	−0.0441(7)	0.1321(9)	0.1333(7)	0.090
C6A	0.5939(8)	0.0165(8)	0.3852(7)	0.077	C9B[b)]	0.1660(6)	0.3594(10)	−0.0033(4)	0.051(2)
C7A	0.8266(6)	0.5882(9)	0.3440(7)	0.084	C10B[b)]	0.0775(6)	0.3131(9)	−0.0619(6)	0.065(3)
C8A	0.6318(8)	0.7092(8)	0.3484(8)	0.089	C11B[b)]	0.0821(8)	0.3181(10)	−0.1592(6)	0.076(4)
C9A	0.6422(6)	0.3721(9)	0.5036(4)	0.068	N5B[b)]	0.0924(9)	0.3259(10)	−0.2307(7)	0.099(4)
C10A	0.6128(8)	0.2874(9)	0.5614(5)	0.089	C9C[b)]	0.1183(21)	0.3489(39)	−0.0014(8)	0.038(10)
C11A	0.6319(6)	0.3173(8)	0.6588(6)	0.066	C10C[b)]	0.1909(23)	0.3690(56)	−0.0598(18)	0.060(12)
N5A	0.6459(6)	0.3457(8)	0.7325(5)	0.089	C11C[b)]	0.1567(29)	0.3600(53)	−0.1595(19)	0.056(12)
N6A	0.5755(4)	0.3460(6)	0.2261(3)	0.049	N5C[b)]	0.1360(28)	0.3455(38)	−0.2342(19)	0.053(11)
C12A	0.6489(6)	0.3398(7)	0.1688(5)	0.053	N6B	0.1933(3)	0.3656(7)	0.2750(3)	0.0512
C13A	0.6145(7)	0.2702(9)	0.0815(6)	0.074	C12B	0.1263(6)	0.4206(7)	0.3250(5)	0.056
C14A	0.5938(7)	0.1529(9)	0.1004(6)	0.067	C13B	0.1281(6)	0.3628(11)	0.4195(5)	0.080
C15A	0.6645(8)	0.0739(12)	0.1289(8)	0.094	C14B	0.0918(6)	0.2440(8)	0.4087(6)	0.061
C16A	0.6442(11)	−0.0367(12)	0.1474(9)	0.112	C15B	0.1521(7)	0.1547(10)	0.4206(7)	0.082
C17A	0.5518(11)	−0.0682(12)	0.1378(8)	0.107	C16B	0.1158(10)	0.0457(10)	0.4081(8)	0.090
C18A	0.4820(9)	0.0055(13)	0.1107(8)	0.100	C17B	0.0243(8)	0.0290(10)	0.3893(8)	0.086
C19A	0.5008(8)	0.1166(10)	0.0905(7)	0.084	C18B	−0.0362(8)	0.1142(10)	0.3786(10)	0.111
C20A	0.6719(7)	0.4589(9)	0.1412(6)	0.065	C19B	−0.0043(8)	0.2213(10)	0.3881(10)	0.108
O5A	0.6214(5)	0.5361(6)	0.1443(5)	0.077	C20B	0.1540(7)	0.5408(8)	0.3413(6)	0.063
O6A	0.7511(5)	0.4595(7)	0.1113(5)	0.087	O5B	0.2313(5)	0.5762(6)	0.3450(5)	0.088
C21A	0.7801(8)	0.5653(11)	0.0813(8)	0.116	O6B	0.0804(5)	0.5993(6)	0.3581(5)	0.089
Co1B	0.16956(6)	0.3653	0.13222(6)	0.0449	C21B	0.0994(9)	0.7170(9)	0.3841(9)	0.109
N1B	0.1341(5)	0.5169(6)	0.1213(5)	0.051					
N2B	0.2849(4)	0.4289(6)	0.1362(4)	0.046					

a) $U_{eq}=(1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\boldsymbol{a}_i\cdot\boldsymbol{a}_j$. The U_{eq} with esd in parentheses indicates this atom was refined with isotropic temperature factor. b) Occupancy factors of C9B, C10B, C11B and N5B are 0.83, and those of C9C, C10C, C11C and N5C are 0.17.

The crystal structure of II viewed along the *b* axis is shown in Fig. 3. There are two crystallographically independent molecules, A and B, in an asymmetric unit. The N(6A) atom of the amino group is hydrogen bonded with O(2B) of the cobaloxime moiety of the neighboring molecule at (x, y, z) [N(6A)···O(2B) 2.996(7) Å]. The N(6B) atom of the amino group is hydrogen bonded with O(1A) of the cobaloxime moiety of the neighboring molecule at (x, y, z) [N(6B)···O(1A) 3.239(6) Å]. The molecular structures of A and B with the numbering atoms are shown in Fig. 4. The 2-cyanoethyl group of the B molecule takes an disordered structure. Figures 5 and 6 show the crystal structure of III viewed along the *a* axis and the molecular structure, respectively. The 2-cyanoethyl group has three different conformations around the Co–C bond and faces to each around the inversion center. There are no unusually short contacts between the molecules.

The selected bond distances and angles of I, II, and III are listed in Table 5. Torsion angles of Co(1)–C(9)–C(10)–C(11) are −179.0(4)° in I, −172.7(7)° in IIA, −177.4(8)°, −179.0(44)° in B and C parts of IIB, −178.4(10)°, −173.8(14)°, and −175.9(4)° in A, B, and C parts of III,

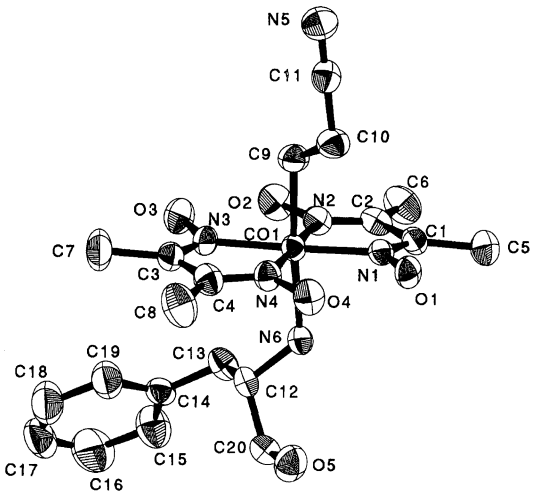


Fig. 2. Molecular structure of I showing 50% probability displacement ellipsoids.

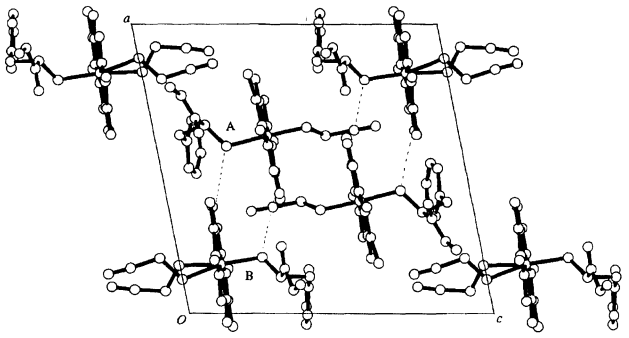
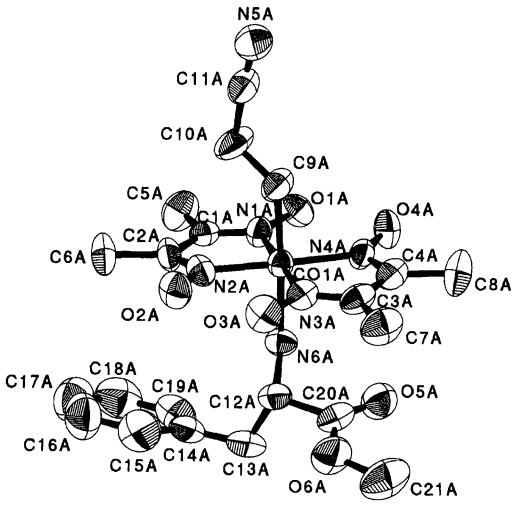
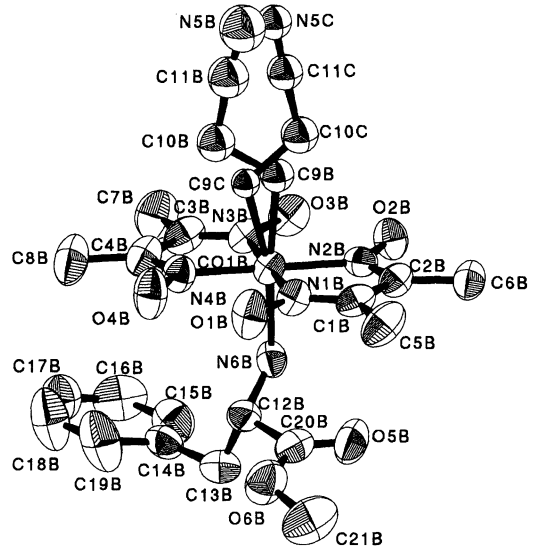


Fig. 3. Crystal structure of II viewed along the *b* axis. Intermolecular hydrogen bonds are indicated by dashed lines.



Molecule A

(a)



Molecule B

(b)

Fig. 4. Molecular structure of II showing 50% probability displacement ellipsoids. (a) molecule A and (b) molecule B.

Table 4. Fractional Atomic Coordinates and Equivalent Isotropic Displacement Parameters (Å^2) for III

Atom	*x*	*y*	*z*	U_{eq} [a)]
Co1	0.75408(3)	0.25150(2)	0.08242(2)	0.03137
N1	0.6341(2)	0.21586(14)	0.15988(15)	0.0363
N2	0.6278(2)	0.27748(15)	0.00266(15)	0.0382
N3	0.8756(2)	0.2822(2)	0.00278(15)	0.0404
N4	0.8796(2)	0.22497(14)	0.16173(15)	0.0365
O1	0.6540(2)	0.18191(13)	0.24484(13)	0.0489
O2	0.6413(2)	0.30877(15)	−0.08392(13)	0.0539
O3	0.8560(2)	0.30968(15)	−0.08528(13)	0.0537
O4	0.8662(2)	0.19304(14)	0.24786(13)	0.0497
C1	0.5292(2)	0.2276(2)	0.1291(2)	0.0412
C2	0.5256(2)	0.2640(2)	0.0350(2)	0.0408
C3	0.9797(2)	0.2745(2)	0.0357(2)	0.0420
C4	0.9826(2)	0.2417(2)	0.1311(2)	0.0419
C5	0.4227(3)	0.2077(3)	0.1821(3)	0.0656
C6	0.4157(3)	0.2833(2)	−0.0169(3)	0.0614
C7	1.0857(3)	0.2966(2)	−0.0170(3)	0.0616
C8	1.0911(3)	0.2310(2)	0.1869(3)	0.0626
C9	0.7537(2)	0.1332(2)	0.0248(2)	0.0446(6)
C10A[b)]	0.7904(18)	0.0609(8)	0.0814(9)	0.047(4)
C11A[b)]	0.7821(20)	−0.0216(8)	0.0298(9)	0.033(3)
N5A[b)]	0.7704(20)	−0.0841(9)	−0.0099(10)	0.036(3)
C10B[b)]	0.7127(23)	0.0577(8)	0.0787(12)	0.064(7)
C11B[b)]	0.7337(26)	−0.0210(12)	0.0248(15)	0.053(6)
N5B[b)]	0.7372(22)	−0.0800(15)	−0.0179(17)	0.057(8)
C10C[b)]	0.8348(7)	0.0649(3)	0.0646(4)	0.045(2)
C11C[b)]	0.8184(8)	−0.0178(5)	0.0202(5)	0.053(2)
N5C[b)]	0.8046(8)	−0.0810(5)	−0.0167(6)	0.071(3)
P1	0.74963(6)	0.39432(4)	0.13281(5)	0.0357
C12	0.6201(2)	0.4257(2)	0.1954(2)	0.0400
C13	0.5882(3)	0.3808(2)	0.2742(2)	0.0533
C14	0.4877(3)	0.4010(3)	0.3199(3)	0.0723
C15	0.4175(3)	0.4657(3)	0.2875(3)	0.0814
C16	0.4460(4)	0.5092(3)	0.2091(3)	0.0820
C17	0.5468(3)	0.4902(2)	0.1634(2)	0.0640
C18	0.8736(2)	0.4270(2)	0.2041(2)	0.0436
C19	0.8831(3)	0.4037(3)	0.2958(3)	0.0740
C20	0.9791(4)	0.4250(3)	0.3485(3)	0.0908
C21	1.0691(4)	0.4687(3)	0.3108(3)	0.0839
C22	1.0625(4)	0.4902(3)	0.2201(4)	0.0907
C23	0.9661(3)	0.4704(3)	0.1662(3)	0.0704
C24	0.7524(3)	0.4684(2)	0.0346(2)	0.0533

a) $U_{eq}=(1/3)\sum_i\sum_j U_{ij}a_i^* a_j^* \boldsymbol{a}_i\cdot\boldsymbol{a}_j$. The U_{eq} with esd in parentheses indicates this atom was refined with isotropic temperature factor.
b) Occupancy factors of C10A, C11A, and N5A are 0.26, and those of C10B, C11B, and N5B are 0.16, and those of C10C, C11C, and N5C are 0.57.

showing that all the molecules take trans conformations. This means the 2-cyanoethyl groups in these complexes take approximately perpendicular conformations to their cobaloxime planes.

The reaction cavity for each 2-cyanoethyl group was calculated in the way reported previously.[12] For the 2-cyanoethyl group of I the cavity is limited by the plane normal to and bisecting the N···H hydrogen bond. For the 2-cyanoethyl group of III the cavity volume was estimated to be a half of the combined cavity for the two 2-cyanoethyl groups facing

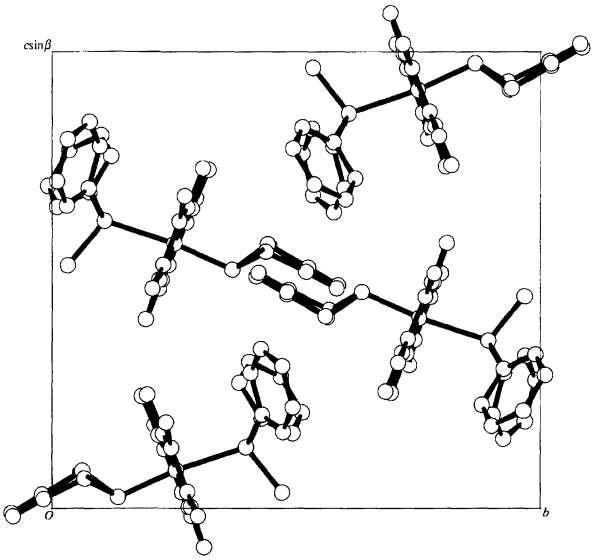


Fig. 5. Crystal structure of III viewed along the *a* axis.

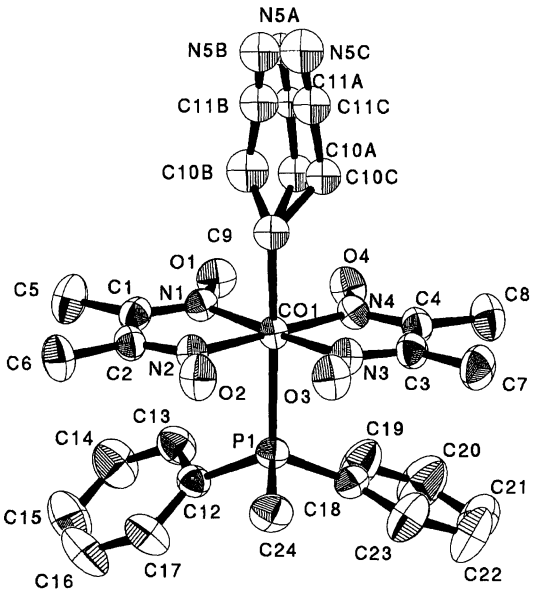


Fig. 6. Molecular structure of III showing 50% probability displacement ellipsoids.

around an inversion center.

The photoisomerization of I is insignificantly small, but the rates of the isomerization of II and III are large and appear to follow first order kinetics at the early stages. Figure 7 shows the decrease of peak height of the IR spectra of III. The rate constant was estimated to be 1.9×10^{-4} s^{-1} within 30 min, since the plots after 30 min may be explained by another rate as shown by the dashed line. The rate constant of II was also calculated to be 0.1×10^{-4} s^{-1}. To compare the rate constants with those in our previous work,[4] these values were adjusted to meet the rate constant of the standard crystal obtained in the same conditions with that in our previous work.

Discussion

Table 6 gives the cavity size, the rate constant, and the con-

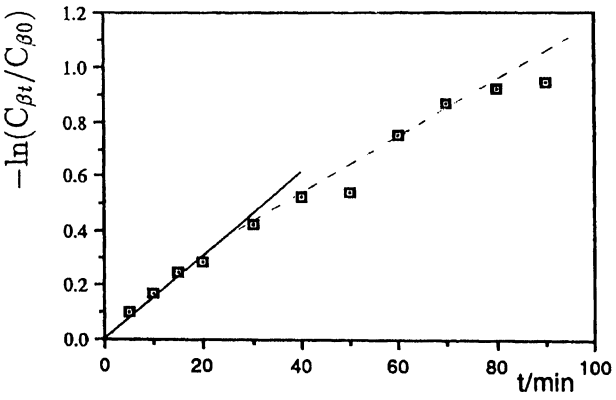


Fig. 7. Reaction rate for β–α isomerization for III. A solid line is obtained by least-squares fitting, assuming the first-order kinetics. A dashed line shows reduced rate after 30 min.

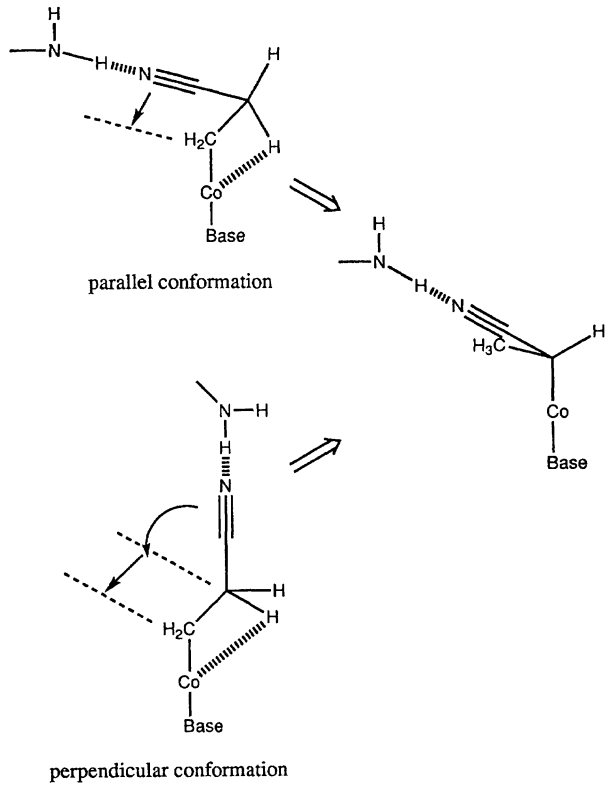


Fig. 8. A schematic drawing of the reaction process of the 2-cyanoethyl groups with parallel and perpendicular conformations on β–α photoisomerization of cobaloxime complex in the solid state.

formation of the 2-cyanoethyl group for ten complex crystals with different axial base ligands including these three crystals: aniline (1ab),[4] piperidine (pip),[13] 3-aminopyridine (3ap),[4] 4-aminopyridine (4ap),[14] 3-cyanopyridine (3cp),[14] 3-ethylpyridine (3ep),[15] and 4-ethylpyridine (4ep).[15] The crystals with parallel conformation, 1ab and 3ap, in which the nitrogen atoms of the 2-cyanoethyl groups are hydrogen bonded with the amino groups of the neighboring molecules, have greater rate constants than those of the crystals without the hydrogen bonds with the 2-cyanoethyl groups. The

Table 5. Selected Bond Distances (Å) and Bond Angles (°)

I				II		III	
Co1–N1	1.895(3)	Co1A–N1A	1.881(6)	Co1B–N1B	1.887(7)	Co1–N1	1.879(2)
Co1–N2	1.880(4)	Co1A–N2A	1.874(7)	Co1B–N2B	1.874(6)	Co1–N2	1.884(2)
Co1–N3	1.892(3)	Co1A–N3A	1.878(6)	Co1B–N3B	1.881(7)	Co1–N3	1.890(2)
Co1–N4	1.885(4)	Co1A–N4A	1.893(7)	Co1B–N4B	1.892(7)	Co1–N4	1.876(2)
Co1–C9	2.003(4)	Co1A–C9A	1.996(6)	Co1B–C9B	2.008(6)	Co1–C9	2.017(3)
				Co1B–C9C	1.992(10)		
Co1–N6	2.079(3)	Co1A–N6A	2.072(5)	Co1B–N6B	2.086(5)	Co1–P1	2.336(1)
N1–Co1–N2	81.7(2)	N1A–Co1A–N2A	81.9(3)	N1B–Co1B–N2B	80.9(3)	N1–Co1–N2	81.5(1)
N1–Co1–N3	178.2(2)	N1A–Co1A–N3A	179.6(3)	N1B–Co1B–N3B	178.6(3)	N1–Co1–N3	177.4(1)
N1–Co1–N4	99.7(2)	N1A–Co1A–N4A	98.1(3)	N1B–Co1B–N4B	99.2(3)	N1–Co1–N4	98.4(1)
N2–Co1–N3	97.8(2)	N2A–Co1A–N3A	98.4(3)	N2B–Co1B–N3B	98.3(3)	N2–Co1–N3	98.8(1)
N2–Co1–N4	178.5(2)	N2A–Co1A–N4A	178.4(3)	N2B–Co1B–N4B	179.8(2)	N2–Co1–N4	179.7(1)
N3–Co1–N4	80.8(2)	N3A–Co1A–N4A	81.6(3)	N3B–Co1B–N4B	81.0(3)	N3–Co1–N4	81.3(1)
N1–Co1–C9	90.8(2)	N1A–Co1A–C9A	90.8(3)	N1B–Co1B–C9B	89.6(4)	N1–Co1–C9	88.8(1)
				N1B–Co1B–C9C	88.1(14)		
N2–Co1–C9	89.2(2)	N2A–Co1A–C9A	90.0(4)	N2B–Co1B–C9B	83.8(3)	N2–Co1–C9	87.1(1)
				N2B–Co1B–C9C	103.5(10)		
N3–Co1–C9	87.5(2)	N3A–Co1A–C9A	89.4(3)	N3B–Co1B–C9B	89.0(4)	N3–Co1–C9	88.7(1)
				N3B–Co1B–C9C	90.6(14)		
N4–Co1–C9	91.4(2)	N4A–Co1A–C9A	88.4(4)	N4B–Co1B–C9B	96.0(3)	N4–Co1–C9	92.6(1)
				N4B–Co1B–C9C	76.3(10)		
N1–Co1–N6	85.0(1)	N1A–Co1A–N6A	86.9(2)	N1B–Co1B–N6B	94.3(3)	N1–Co1–P1	94.3(1)
N2–Co1–N6	90.9(2)	N2A–Co1A–N6A	88.6(3)	N2B–Co1B–N6B	89.8(2)	N2–Co1–P1	88.0(1)
N3–Co1–N6	96.7(2)	N3A–Co1A–N6A	93.0(2)	N3B–Co1B–N6B	87.1(3)	N3–Co1–P1	88.2(1)
N4–Co1–N6	88.7(2)	N4A–Co1A–N6A	93.0(3)	N4B–Co1B–N6B	90.3(3)	N4–Co1–P1	92.4(1)
C9–Co1–N6	175.8(2)	C9A–Co1A–N6A	177.4(3)	C9B–Co1B–N6B	172.0(3)	C9–Co1–P1	173.7(1)
				C9C–Co1B–N6B	166.7(10)		

2-cyanoethyl group of I is also hydrogen-bonded with the neighboring molecule but it takes a perpendicular conformation to its cobaloxime plane. The volume of the cavity, 11.2 Å^3 is significantly greater than that of pip (10.3 Å^3) and is nearly the same as the averaged value of II, 11.6 Å^3. This clearly suggests that the intermolecular hydrogen bond of the 2-cyanoethyl group with the neighboring molecule does not accelerate the reaction rate when the reactive group takes the perpendicular conformation. This is distinct from the reactivity of the 2-cyanoethyl group with parallel conformation, for which the intermolecular hydrogen bond accelerates the reaction rate, as shown in the crystals of 3ap and 1ab in Table 6.

When the crystal is irradiated with visible light, the Co–C bond would be cleaved and the 2-cyanoethyl radical would be produced. The radical may be easily transformed to the 1-cyanoethyl radical and stabilized if the nitrogen atom of the cyano group is hydrogen bonded with the neighboring molecule as assumed in the crystals with parallel conformation. However, the 1-cyanoethyl radical produced with a perpendicular conformation must move to a greater distance than that produced from the 2-cyanoethyl group with parallel conformation, which is schematically shown in Fig. 8. This suggests that the hydrogen bond in the perpendicular conformation should prevent the isomerization. The non-reactivity of I is probably brought about the intermolecular hydrogen bond.

The average cavity size of II, 11.6 Å^3 and the rate constant, 0.1×10^{-4} s^{-1} are between the corresponding ones of pip and 3cp, respectively. This suggests the correlation between the cavity size and the rate constant holds good for the crystal of II. On the other hand, the rate constant of III is somewhat large considering from its cavity size, since the rate constant of 4ap with a greater cavity than that of III is much smaller than the rate constant of III.

In the crystal of III, the two 2-cyanoethyl groups face each other around an inversion center. The cooperative motion of the two groups will accelerate the reaction rate as observed in the crystalline-state racemization of the chiral 1-(methoxycarbonyl)ethyl group.[16]

Table 6. Cavity Size (V/Å^3) and Rate Constant (k/s^{-1},$\times10^4$)[a]

	V	k	Conformation	Intermolecular hydrogen bond
pip	10.3	—	Perpendicular	Absence
I	11.2	≅ 0	Perpendicular	Presence
II	10.0 13.2	0.1	Both	Absence
	Average 11.6		Perpendicular	
3cp	12.2	0.8	Perpendicular	Absence
4ap	15.0	1.1	Perpendicular	Absence
3ep	13.1	1.4	Parallel	Absence
4ep	14.0	1.6	Parallel	Absence
III	13.9	1.9	Perpendicular	Absence
3ap	10.1	3.2	Parallel	Presence
1ab	15.0	4.2	Parallel	Presence

a) pip: piperidine, 3cp: 3-cyanopyridine, 4ap: 4-aminopyridine, 3ep: 3-ethylpyridine, 4ep: 4-ethylpyridine, 3ap: 3-aminopyridine, 1ab: aniline.

In conclusion, it has been clarified that the reaction rate is well explained by three factors in the solid state β–α photoisomerization of cobaloxime complexes not only for the parallel conformation but also for the perpendicular conformation; the size of the cavity, the conformation of the reactive group, and the hydrogen bond with the reactive group. However, the third factor, the hydrogen bond of the reactive group, accelerates the reaction rate for the parallel conformation but reduces the reaction rate for the perpendicular conformation.

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