Bull. Chem. Soc. Jpn., **64**, *2183—2187 (1991)*

β-α Photoisomerization of Cobaloxime Complexes in the Solid State. III. Accelerated Reaction Rate by Hydrogen Bond

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(Received January 18, 1991)

The crystal structures of two cobaloxime complexes with different axial base ligands have been determined by X-ray analysis at room temperature. I: (3-Aminopyridine)(2-cyanoethyl)bis(dimethylglyoximato)cobalt(III); the cystal is monoclinic, the space group being $C2/c$, Z=8 with a=28.849(8), b=7.746(2), c=18.429(5) Å, and β=105.71(3)°. II: (Aniline)(2-cyanoethyl)bis(dimethylglyoximato)cobalt(III) aniline solvate; the crystal is monoclinic, the space group being $P2_1/c$, Z=4 with a=14.228(7), b=11.426(4), c=14.178(3) Å, and β=91.92(3)°. Both structures were refined by a full-matrix least-squares method to final R values of 0.070 and 0.074 for 3886 and 3311 observed reflections, respectively. Their photoisomerization rates in the solid state obtained from changes in the IR spectra, 3.2 and 4.2×10^{-4} s^{-1}, respectively, are significantly greater than those of the related compounds. The hydrogen bonds between the reactive 2-cyanoethyl groups and the atoms of the neighboring molecules in the two crystals should be responsible for the greater reaction rates. Taking into account the role of the hydrogen bonds, a probable isomerization mechanism is proposed.

The 2-cyanoethyl group bonded to the cobalt atom in the bis(dimethylglyoximato)cobalt(III), cobaloxime, complex was found to be isomerized to the 1-cyanoethyl group upon exposure to visible light.[1] The photoreaction, β–α isomerization, proceeds only in the solid state, and the reverse reaction has not yet been observed.

Since the reactive group is very similar to that in 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.[2] A series of cobaloxime complexes with different axial base ligands has been prepared and the relation between the reaction rate and the reaction cavity examined.

For a complex with 3-methylpyridine as an axial base ligand (3mp), two crystal forms (I and II) were obtained under the same conditions. The powdered sample of form II revealed a significantly greater rate than that of form I. The reaction cavity around the 2-cyanoethyl group of form II is greater than that of the form I, indicating that the cavity size is one factor controlling the reaction rate.[3] For a complex with pyridine used as an axial base ligand (py), two forms were also crystallized under the same conditions. Although the reaction cavity of form II was significantly smaller than that of form I, form II revealed a significantly greater reaction rate than did form I. The 2-cyanoethyl group in form II takes a nearly parallel conformation to the cobaloxime plane, whereas that of form I takes a perpendicular conformation. The 2-cyanoethyl group with a parallel conformation would be more easily transformed to the α-cyanoethyl group than that with a perpendicular conformation, since the former has a closer resemblance in shape to the 1-cyanoethyl group than does the latter. Therefore, such a topochemical factor should be the second factor controlling the reaction rate in the case of the complex (py).[4]

It was recently reported that for four complexes with 3-ethylpyridine (3ep),[5] 4-ethylpyridine (4ep),[5] 3-cyanopyridine (3cp),[6] and 4-aminopyridine (4ap)[6] the reaction rates could be well-explained in terms of the above two factors. However, the two complexes with 3-aminopyridine (3ap) and aniline (1ab) as axial base ligands revealed significantly greater reaction rates than those expected from the above two factors.

The present paper deals with the two complexes, 3ap and 1ab, and proposes a third factor.

Experimental

Crystal Structures. The complexes were synthesized by a previously reported method.[7] The crystals were obtained from hot methanol solutions. The approximate dimensions of the crystals used were 0.3×0.3×0.1 (3ap) and 0.3×0.3×0.1 mm (1ab). X-Ray measurements were performed with a Rigaku four-circle diffractometor (AFC-4). Mo $K\alpha$ radiation monochromated by graphite (λ=0.71069 Å) was used. The cell parameters were refined by least-squares on the basis of 16 and 15 independent 2θ values ($20°<2\theta<30°$) for 3ap and 1ab, respectively. Three-dimensional intensity data were collected up to 2θ=55° (3ap) and 50° (lab); the ranges of hkl were −36 to 36, 0, to 10, and 0 to 22 (3ap), and −16 to 16, 0 to 13, and 0 to 16 (1ab). The intensities were measured using an ω–2θ scan technique and a scan speed $4°(2\theta)$ min^{-1}. The background counts were accumulated for 5 s both before and after each scan. Three standard reflections were monitored for every 50 reflections, and no significant variations in the intensities were observed. The reflections for $|F_o|>3\sigma(|F_o|)$ were considered as being observed and used for structural determinations. Although corrections for the Lorentz and polarization factors were made, no correction for the absorption was applied.

The structure of 3ap was solved by the direct method with a program called MULTAN 78,[8] refined by full-matrix least-squares with the program called SHELX 76.[9] All of the hydrogen atoms were found on the difference map. The final refinement was made with the anisotropic temperature factors for non-hydrogen atoms and the isotropic ones for hydrogen atoms. The quantities minimized were $\sum w(|F_o|-|F_c|)^2$ and $w=[\sigma^2(|F_o|+0.004|F_o|^2]^{-1}$. The final R and R_w values became 0.070 and 0.084 for 3886 observed reflections. No peaks higher than 0.3 eÅ^{-3} were found on the final difference map.

Table 1. Final Atomic Coordinates ($\times10^5$ for Co, and $\times10^4$ for C, N, and O) and Equivalent Isotropic Thermal Parameters for 3ap

Atom	x	y	z	B_{eq}
Co(1)	39751(2)	17774(7)	60516(3)	2.9
N(1)	3570(1)	3720(5)	5794(2)	3.5
N(2)	3437(1)	949(5)	6328(2)	3.6
N(3)	4380(1)	−155(5)	6326(2)	3.5
N(4)	4521(1)	2652(5)	5806(2)	3.7
O(1)	3711(1)	5163(4)	5521(2)	4.8
O(2)	3429(1)	−642(5)	6644(2)	4.8
O(3)	4250(1)	−1574(4)	6629(2)	4.7
O(4)	4551(1)	4280(5)	5548(2)	5.2
C(1)	3144(2)	3591(6)	5883(3)	4.0
C(2)	3066(2)	1928(7)	6205(3)	4.2
C(3)	4805(2)	−41(6)	6206(3)	4.0
C(4)	4887(2)	1614(6)	5897(3)	3.8
C(5)	2783(3)	5038(10)	5723(4)	6.7
C(6)	2610(2)	1449(12)	6403(4)	6.6
C(7)	5159(2)	−1490(10)	6388(4)	6.0
C(8)	5342(2)	2104(10)	5713(4)	5.6
N(5)	3399(3)	4963(8)	7630(3)	7.9
C(9)	4261(2)	2560(7)	7114(3)	3.9
C(10)	4207(3)	4444(7)	7310(3)	5.4
C(11)	3748(3)	4761(7)	7480(3)	5.8
N(6)	3714(1)	828(4)	4974(2)	3.1
C(12)	3574(2)	−804(6)	4869(3)	3.4
C(13)	3403(2)	−1564(6)	4151(3)	3.8
C(14)	3379(2)	−503(7)	3533(3)	4.5
C(15)	3524(2)	1187(7)	3636(3)	4.5
C(16)	3689(2)	1815(7)	4356(3)	4.1
N(7)	3250(2)	−3206(7)	4083(3)	6.0

$B_{eq}=(8/3)\pi^2\sum_i\sum_j U_{ij}a_i^*a_j^*\boldsymbol{a}_i\cdot\boldsymbol{a}_j$.

Table 2. Final Atomic Coordinates ($\times10^5$ for Co, and $\times10^4$ for C, N, and O) Equivalent Isotropic Thermal Parameters for 1ab

Atom	x	y	z	B_{eq}
Co(1)	67767(5)	2186(6)	15038(5)	3.4
N(1)	7774(3)	1247(4)	1804(3)	4.2
N(2)	6075(3)	1602(4)	1632(3)	4.3
N(3)	5779(3)	−804(4)	1187(3)	3.9
N(4)	7483(3)	−1164(4)	1408(3)	3.8
O(1)	8676(3)	919(5)	1867(3)	5.2
O(2)	5122(3)	1646(4)	1546(3)	5.6
O(3)	−5111(3)	−447(4)	1110(3)	5.0
O(4)	8426(3)	−1197(4)	1551(3)	5.2
C(1)	7548(4)	2343(6)	1893(4)	5.0
C(2)	6542(5)	2557(5)	1801(4)	5.0
C(3)	6007(4)	−1892(5)	1029(4)	4.6
C(4)	7019(4)	−2099(5)	1151(4)	4.4
C(5)	8264(7)	3287(8)	2075(7)	7.8
C(6)	6100(7)	3730(7)	1885(7)	7.5
C(7)	5296(6)	−2815(7)	786(6)	6.9
C(8)	7495(6)	−3247(6)	1004(6)	6.2
N(5)	7257(5)	1820(7)	4466(6)	10.3
C(9)	6554(5)	−226(7)	2849(4)	5.5
C(10)	7341(6)	−96(7)	3556(5)	6.1
C(11)	7303(5)	987(7)	4083(6)	6.4
N(6)	6887(3)	639(5)	69(3)	3.6
C(12)	7563(3)	22(5)	−488(3)	3.6
C(13)	7323(5)	−960(6)	−978(4)	4.5
C(14)	7977(7)	−1558(8)	−1490(5)	6.0
C(15)	8881(6)	−1173(9)	−1487(6)	6.8
C(16)	9139(5)	−194(10)	−1000(5)	6.7
C(17)	8475(4)	422(7)	−492(4)	5.0
C(2B)[a]	10235(9)	4672(21)	934(10)	11.6
C(3B)[a]	10046(10)	5813(17)	633(13)	11.8
N(1B)[a]	10186(13)	6616(17)	1369(12)	11.8
C(1B)[a]	9826(8)	6122(20)	−299(18)	13.3

a) Occupancy factors of C(2B), C(3B), N(1B), and C(1B) are 0.5. $B_{eq}=(8/3)\pi^2\sum_i\sum_j U_{ij}a_i^*a_j^*\boldsymbol{a}_i\cdot\boldsymbol{a}_j$.

The procedure of a structure determination for the 1ab was similar to that for 3ap. An aniline molecule appeared in the difference map, which occupies an inversion center with disordered orientations. Some of the hydrogen atoms were found on the difference map. The others were calculated geometrically and refined with C–H distances constrained to 1.00 Å. The final refinement was made with the anisotropic temperature factors for non-hydrogens atoms and isotropic ones for hydrogen atoms. The weighting scheme was $w=[\sigma^2(|F_o|)+0.004|F_o|^2]^{-1}$. The final R and R_w values became 0.074 and 0.074 for 3311 reflections. No peaks higher than 0.5 e Å^{-3} were found on the final difference map. The atomic scattering factors were taken from International Tables for X-ray Crystallography.[10] The final atomic coordinates and equivalent isotropic temperature factors for non-hydrogen atoms are given in Tables 1 and 2. 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 kept in the office of Chemical Society of Japan. Computations were carried out on M-280H and M-680H computers at the Computer Centre of the University of Tokyo.

β-α Isomerization. KBr disks which contained 1% of the 2-cyanoethyl complex were exposed to a 500 W Xe lamp. The IR spectra of the KBr disk were measured at intervals of 5 min and 10 min for 3ap and 1ab, respectively. The absorption assigned to the stretching vibration mode of the cyano group, ν_{CN} in 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. Since the change during the early stages, within 40 min, was represented by first-order kinetics, the rate constant was obtained by least-squares fitting.

Results

The crystal structures of 3ap and 1ab are shown in Figs. 1 and 2, respectively. For 3ap, N(5) in the cyanoethyl group is hydrogen-bonded to N(7) of the amino group in the neighboring molecule at (x,$-y$, 0.5+z)[N(5)···N(7) 3.135(10) Å]. The molecules are connected along the c axis as a ribbon by hydrogen bonds. For 1ab, a unit cell contains two free aniline molecules, which occupy the inversion centers. The N(5) atom in the cyanoethyl group is hydrogen-bonded to N(6) of the amino group of the neighboring molecule at (x, 0.5$-y$, 0.5+z) [N(5)···N(6) 3.076(10) Å], and O(3) is hydrogen-bonded to N(6) of the adjacent molecule at (1$-x$, $-y$, $-z$). The molecules form a ribbon comprising two rows along the c axis. Free aniline mole-

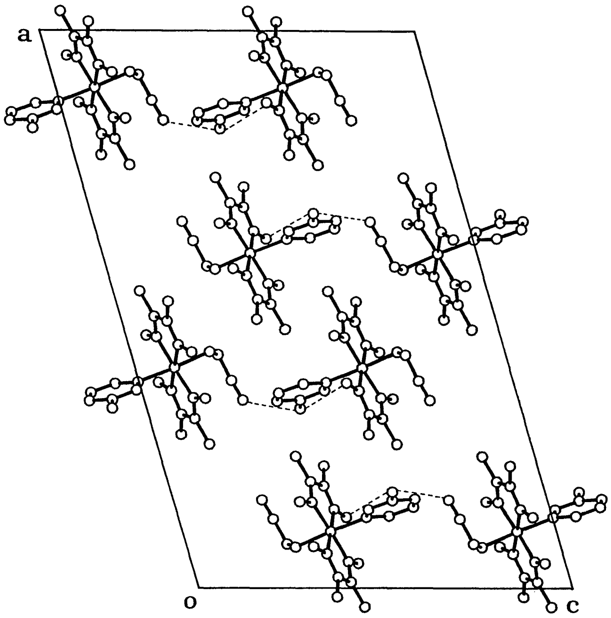

Fig. 1. Crystal structure of 3ap viewed along the *b* axis. Broken lines indicate the hydrogen bonds.

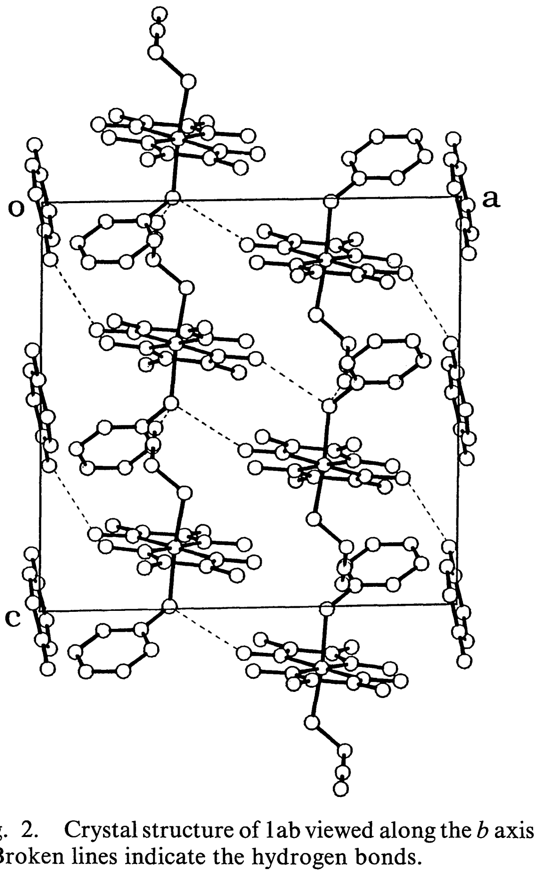

Fig. 2. Crystal structure of 1ab viewed along the *b* axis. Broken lines indicate the hydrogen bonds.

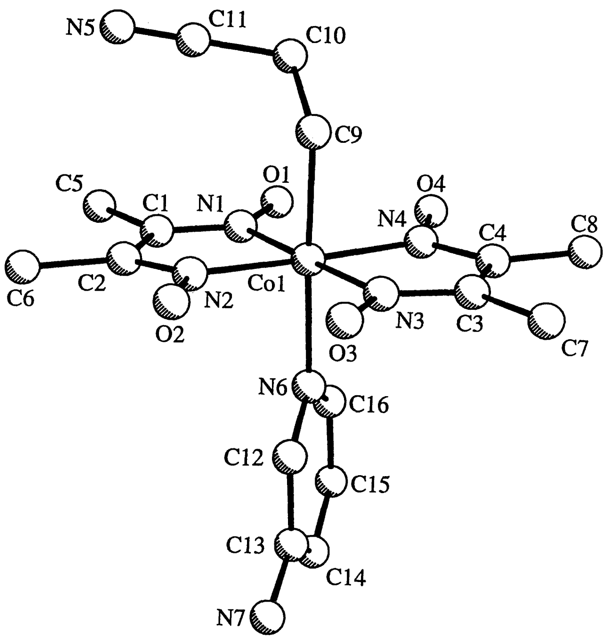

Fig. 3. Molecular structure of 3ap.

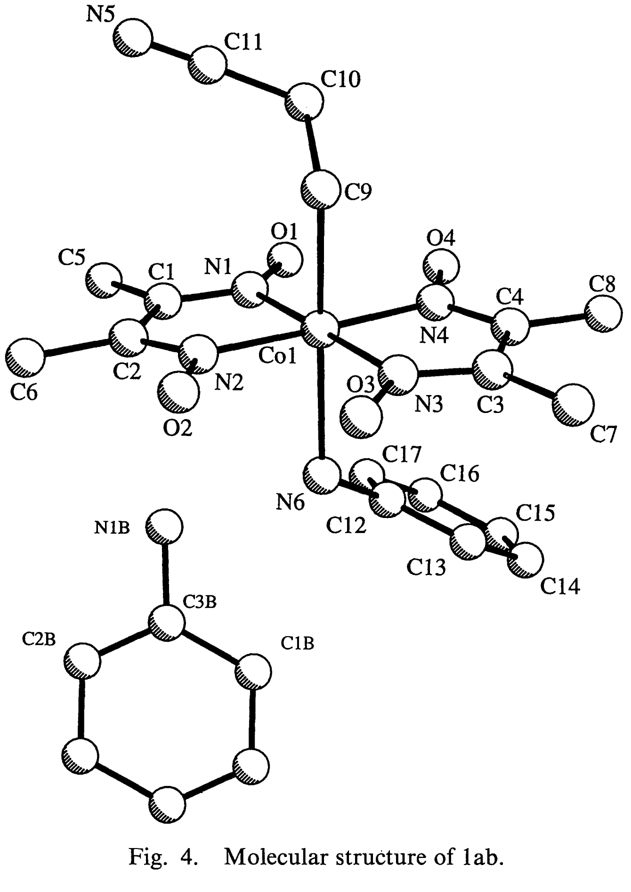

Fig. 4. Molecular structure of 1ab.

cules are hydrogen-bonded to the O(1) of the neighboring cobaloxime molecule, forming walls between the ribbons.

The molecular structures of 3ap and 1ab are shown in Figs. 3 and 4, respectively. The selected bond distances and angles of 3ap and 1ab are shown in Tables 3. Torsional angles of Co(1)–C(9)–C(10)–C(11) in 3ap and 1ab are +84.7(6)° and +96.9(4)°, respectively. This means the 2-cyanoethyl groups in both complexes are approximately parallel to their cobaloxime planes. The

Table 3. Selected Bond Distances (l/Å) and Bond Angles (ϕ/°)

	3ap	1ab
Co(1)-N(1)	1.885(4)	1.882(5)
Co(1)-N(2)	1.874(4)	1.880(5)
Co(1)-N(3)	1.882(4)	1.879(5)
Co(1)-N(4)	1.880(4)	1.881(5)
Co(1)-C(9)	2.001(5)	2.009(8)
Co(1)-N(6)	2.059(4)	2.102(6)
N(1)-Co(1)-N(2)	80.7(2)	81.5(2)
N(1)-Co(1)-N(3)	179.1(2)	178.6(2)
N(1)-Co(1)-N(4)	98.9(2)	98.4(2)
N(1)-Co(1)-C(9)	93.9(2)	91.1(3)
N(1)-Co(1)-N(6)	90.1(2)	87.6(2)
N(2)-Co(1)-N(3)	98.9(2)	98.1(2)
N(2)-Co(1)-N(4)	178.0(2)	179.3(2)
N(2)-Co(1)-C(9)	89.5(2)	94.9(3)
N(2)-Co(1)-N(6)	91.5(2)	89.8(2)
N(3)-Co(1)-N(4)	81.4(2)	82.1(2)
N(3)-Co(1)-C(9)	85.2(2)	87.6(3)
N(3)-Co(1)-N(6)	90.8(2)	93.7(2)
N(4)-Co(1)-C(9)	88.6(2)	85.9(3)
N(4)-Co(1)-N(6)	90.5(2)	89.5(2)
C(9)-Co(1)-N(6)	176.0(2)	174.9(3)

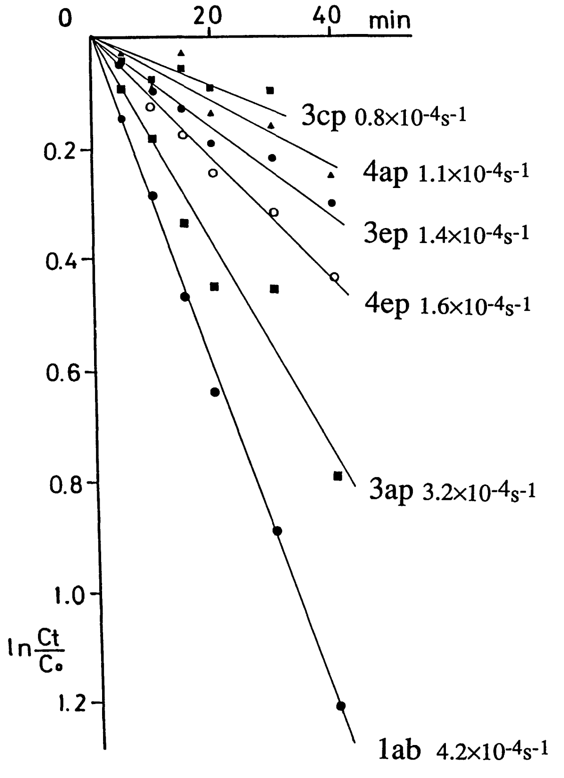

Fig. 5. Reaction rate for β-α isomerization for 3ep, 4ep, 3cp, 4ap, 3ap, and 1ab. Solid lines are obtained by least-squares fitting, assuming the first-order kinetics.

molecular structure of 3ap is similar to those of the other cobaloxime complexes with pyridine derivatives; pyridine,[4] 3-methylpyridine,[3] 3-ethylpyridine, and 4-ethylpyridine.[5] For 1ab, the Co(1)–N(6)–C(12) angle is 119.3(4)°. Approximately the same angle was observed in bis(aniline)bis(dimethylglyoximato)cobalt(III)chloride,[11] 119.5(7)°. Such expanded angles would be caused by short contacts between the aniline and cobaloxime moieties. The shortest distances between the nitrogen atom of the cobaloxime moieties and the benzene ring of aniline ligand are 3.016(7) Å and 2.920(8) Å for 1ab and the bis(aniline) complex.

Table 4. Cavity Size (V/Å^3) and Rate Constant (k/s^{-1}, ×10^4)

	V	k	Conformation
3cp	12.24	0.8	Perpendicular
4ap	14.99	1.1	Perpendicular
3ep	13.12	1.4	Parallel
4ep	14.00	1.6	Parallel
3ap	10.06	3.2	Parallel
1ab	14.97	4.2	Parallel

The rate of isomerization during the early stages follows first-order kinetics (Fig. 5), in which the rates of 3-cyanopyridine (3cp), 4-aminopyridine (4ap), 3-ethylpyridine (3ep), 4-ethylpyridine (4ep), 3-aminopyridine (3ap), aniline (1ab) are given. The 3ap and 1ab crystals have significantly greater values than do the other four crystals.

Discussion

Table 4 gives the cavity size,[12] the rate constant during the early stages and the conformation of the 2-cyanoethyl group for six complex crystals: 3ep, 4ep, 3cp, 4ap, 3ap, and 1ab. The crystals with a parallel conformation have greater rate constants than do those with the perpendicular type. The second topochemical factor observed in the two crystal forms of the pyridine complex[4] plays an important role, even if the crystals have different base ligands. Moreover, in the two crystals with a perpendicular conformation, 3cp and 4ap, the crystal with a greater cavity has a greater rate constant. The first cavity factor observed in the two crystal forms of 3mp[3] controls the reaction rate when the reactive group takes the perpendicular conformation. For crystals with a parallel conformation, however, the first factor has no effect on the reaction rate. Although the cavity of 3ap is smaller than those of 3ep and 4ep, the rate constant of 3ap is greater than those of 3ep and 4ep. This fact indicates that the third factor should be taken into account.

It appears that solvent molecules may cause the greater reaction rate, since the 1ab crystal has another aniline as a crystalline solvent. However, the 3ap crystal, which has a greater reaction rate too, has no solvent and the 3cp has a water molecule used as a solvent in spite of the smallest reaction rate. This suggests that the solvation may have no significant effect on the reaction rate.

Only in the 3ap and 1ab crystals, the nitrogen atoms of the 2-cyanoethyl groups have hydrogen bonds with the

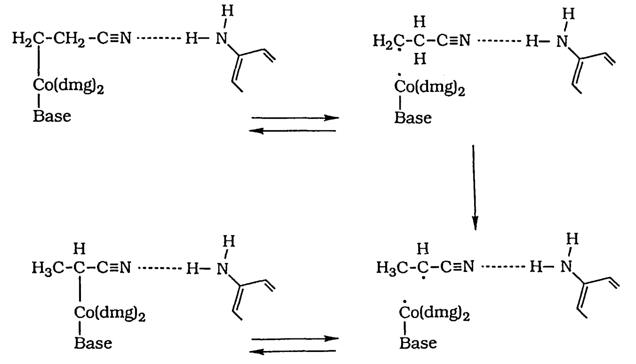

Fig. 6. Mechanism of β-α isomerization. The hydrogen bonds are indicated by broken lines.

amino groups of the neighboring molecules. Although hydrogen bonds are also observed in the 3cp crystal, they connect the solvent water molecules with the neighboring cobaloxime moieties; the nitrogen atom of the 2-cyanoethyl group does not take part in the hydrogen bonding.

A probable mechanism of the β-α photoisomerization associated with the hydrogen bond is shown in Fig. 6. When the Co-C bond is cleaved by visible light, the 2-cyanoethyl radical is produced. Such a homolyitic Co-C bond cleavage of the cobaloxime complexes has been extensively reported.[13,14] Since the produced radicals may be unstable, and cannot move so easily in the crystalline lattice, most part of the radicals would return to the original 2-cyanoethyl group. However, a small parts of the radicals may be transformed to the 1-cyanoethyl radicals by virtue of lattice vibration; the rate-determining step is probably the 2→1 radical transformation in this photoisomerization.

If the nitrogen atom of the 2-cyanoethyl group is hydrogen bonded to the amino group in a neighboring molecule, the produced 2-cyanoethyl radical may be stabilized and the prolonged lifetime of the 2-cyanoethyl radical would cause an increased extent of the 2→1 radical transformation. The four crystals with a parallel-type conformation, therefore, can be divided into two classes depending on whether or not the reactive group has a hydrogen bond with the neighboring molecule. The first factor, the cavity factor, controls the reaction rate in both classes.

In conclusion, the reaction rate is well explained by three factors in the solid state β-α photoisomerization of cobaloxime complexes; the size of the cavity, the conformation of the reactive group and the hydrogen bond with the reactive group. Although the structure in which the 2-cyanoethyl group with a perpendicular conformation is hydrogen-bonded to the neighboring molecule has not yet been observed, the third factor seems to be most important among the three factors, considering the significantly greater reaction rate of 3ap and 1ab crystals. As a matter of course, the second factor is more important than the first. Table 4 indicates that the reaction rate is affected by the first factor only if the second and third factors are equivalent.

This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture.

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