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The Role of Hydrogen Bond and Crystal Solvent in the Solid-state (β-α) Photoisomerization of Novel 2-(*N*-phenylcarbamoyl)ethyl Cobaloxime Complexes [1]

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The Role of Hydrogen Bond and Crystal Solvent in the Solid-state (β-α) Photoisomerization of Novel 2-(*N*-phenylcarbamoyl)ethyl Cobaloxime Complexes [1]

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The 2-(phenylcarbamoyl)ethyl group bonded to the cobalt atom in cobaloxime complexes was isomerized on exposure to visible light in the solid-state. The three complexes with different amines as axial base ligands were prepared and their crystal structures were determined by X-ray analysis. The reaction rates in the solid-state were mainly affected by the hydrogen bonds of the reactive group with the neighboring molecules and the occupation of crystal solvent molecules around the reactive group.

Keywords: Solid-state reaction; Cobaloxime complex; Hydrogen bond; Reaction rate; Crystal solvent; (β-α) photoisomerization

INTRODUCTION

Since the X-ray-triggered crystalline-state racemization of (*R*)-1-cyanoethyl[(*S*)-1-phenylethylamine]bis(dimethylglyoximato)cobalt(III) was unexpectedly found [2] without degradation of the single crystal form, such crystalline-state racemization reactions of the chiral 1-cyanoethyl group in the cobaloxime complexes with a variety of axial ligands have been reported and their reaction rates are successfully explained in terms of the reaction cavity, which was defined as a void space around the reactive group and was limited by a concave surface of the spheres of the surrounding atoms around the reactive group in the crystal [3,4]. Recently, visible light-triggered solid-state racemizations were found to occur and were extensively investigated for cobaloximes coordinated with a variety of reactive groups including chiral 1-cyanoethyl, 1-methoxycarbonyl, 1,2-dimethoxycarbonylethyl, 1,2-diethyoxycarbonylethyl and 1,2-diallyloxycarbonylethyl groups [6–8]. A quantitative relationship between the reaction rate and the size of the reaction cavity has been proposed [8]. This reaction made it easy to

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*Address for correspondence: Department of Chemistry, Toho University School of Medicine, Omorinishi, Ota-ku, Tokyo 143-8540, Japan. Tel.: +81-3-3762-4151 Ext. 2555, Fax: +81-2-5493-5430, e-mail: yohgo@med.toho-u.ac.jp compare reaction rates among several different types of complexes and also correlate widely their reaction rates with the size of their cavities and other rate-controlling factors such as hydrogen bonding and mobile solvent included [4–8].

Moreover, the solid-state photoisomerization of various 2-cyanoethyl cobaloximes [5–9] and 2-(*N*-substituted carbamoyl)ethyl cobaloximes [10] were reported. In the previous paper, the crystal structures of the 2-carbamoylethyl and 2-methylcarbamoylethyl cobaloxime complexes were analyzed by X-rays [11].

In this paper, the crystal structures of three 2-(phenylcarbamoyl)ethyl cobaloxime complexes are analyzed and a relation between the reaction rate and crystal structure will be examined in the five complexes including the 2-carbamoyl and 2-methylcarbamoyl complexes reported previously.

RESULTS

Crystal Structure and Molecular Structure

The three 2-phenylcarbamoyl complexes, bis(dimethylglyoximato) [2-(phenylcarbamoyl)ethyl] [(*R*)-2-phenylglycinol]cobalt(III) (**a**), bis(dimethylglyoximato) [(*R*)-1-methylpropylamine] [2-(phenylcarbamoyl)ethyl]cobalt(III) (**b**), and bis(dimethylglyoximato)[(*S*)-phenylalaninol] [2-(phenylcarbamoyl)ethyl]cobalt(III) (**c**) and the previous two complexes, (2-carbamoylethyl)-bis(dimethylglyoximato)[(*R*)-1-(1-naphthyl)ethylamine] cobalt(III) (**d**) [11], bis(dimethylglyoximato) [2-(methylcarbamoyl)ethyl] [methyl(*S*)-phenylalaninate]cobalt(III) (**e**) [11] are shown in Figure 1. The crystal data and experimental details of the three crystals are summarized in Table I. The torsion angles of CO1–C9–C10–C11, C10–C11–N5–C12, and C9–C10–C11–N5, which show the conformation of the carbamoyl group, are summarized in Table II. The carbamoyl group in each molecule has *trans* conformation around the C9–C10 bond. This means the carbamoyl group is nearly perpendicular to the cobaloxime plane. Table III shows the intramolecular and intermolecular hydrogen bonds in five complex crystals.

Bis(dimethylglyoximato) [2-(phenylcarbamoyl)ethyl] [(*R*)-2-phenylglycinol] Cobalt(III): Crystal a

The crystal structure viewed along the a axis and the molecular structure [15] are shown in Figures 2 and 3, respectively. The N5 atom of the 2-(phenylcarbamoyl)ethyl group is hydrogen bonded with the O3 atom of the cobaloxime moiety of the neighboring molecule at $(x, y, z-1)$. The O6 atom of the (*R*)-2-phenylglycinol group is hydrogen bonded with the O1 atom of the neighboring cobaloxime plane at $(x, y, z+1)$. The N6 atom of the amino group is hydrogen bonded with the O6 atom of the (*R*)-2-phenylglycinol moiety of the neighboring molecule at $(-x+1.5, -y+2, z-0.5)$.

Bis(dimethylglyoximato) [(*R*)-1-methylpropylamine] [2-(phenylcarbamoyl)ethyl] Cobalt(III): Crystal b

The crystal structure viewed along the b axis and the molecular structure are shown in Figures 4 and 5, respectively. The crystal has two crystallographically independent molecules, A and B. There are four H_2O molecules as crystal solvents in a unit cell. The hydrogen bonds involving crystal solvents and 2-phenylcarbamoyl groups make a three-dimensional network. [N6A···O5B, N5A···O101, N6B···O5A$(x, y, z+1)$, N5B···O102$(x, y-1, z)$, O101···O3A, O101···N3A, O102···O3B$(x, y+1, z)$, O102···O1B, O104···O5B].

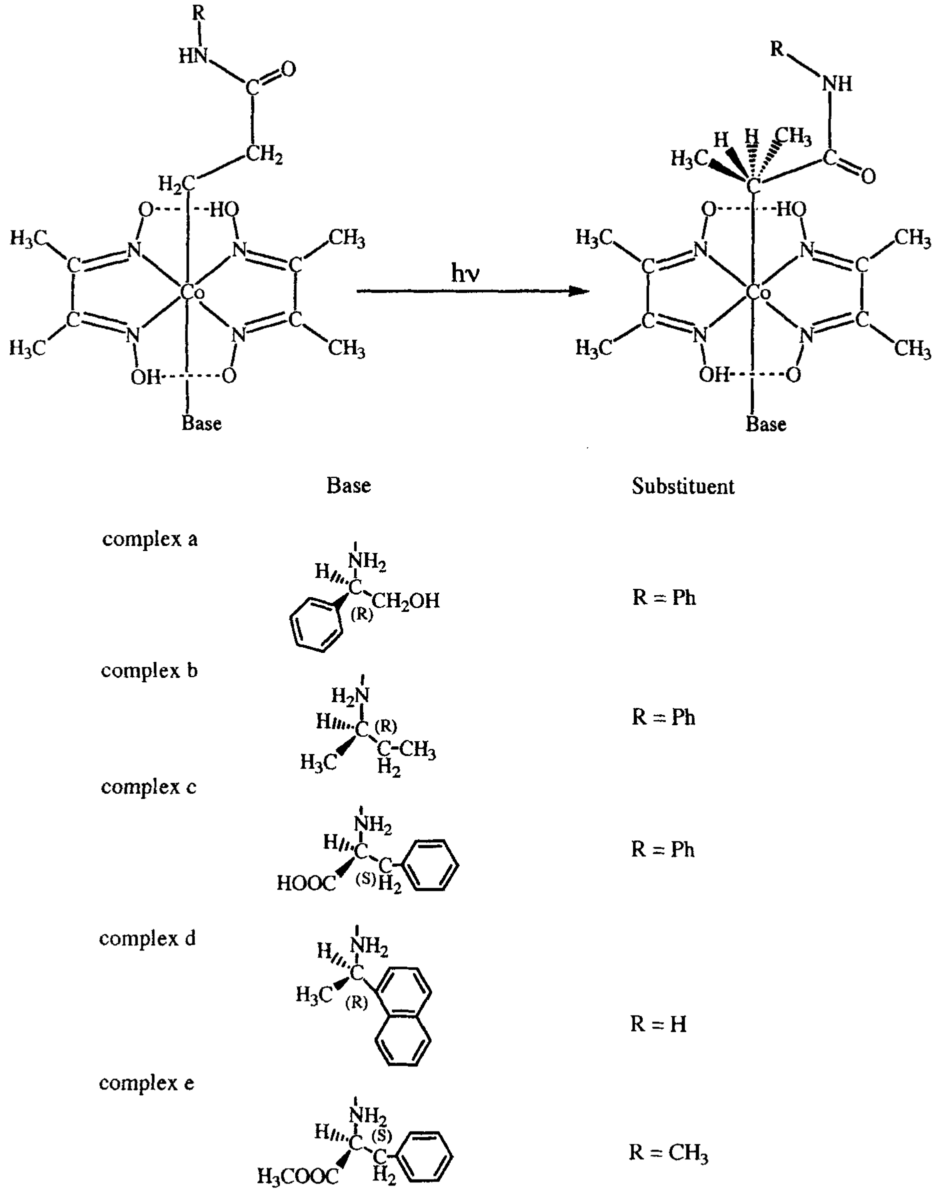

FIGURE 1 Solid-state photoisomerization of *N*-substituted(carbamoyl)ethyl cobaloxime complexes.

Bis(dimethylglyoximato) [(*S*)-phenylalaninol] [2-(phenylcarbamoyl)ethyl] Cobalt(III): Crystal c

Figures 6 and 7 show the crystal structure viewed along the *a* axis and the molecular structure, respectively. The O6 atom of the 2-(phenylcarbamoyl)ethyl group is hydrogen bonded with the O2 atom of the cobaloxime moiety of the neighboring molecule at $(-x, y+1, -z)$. The N6 atom of the amino group makes intramolecular hydrogen bond with the O6 atom. The N5 atom of the 2-(phenylcarbamoyl) ethyl group is hydrogen bonded with the O6

TABLE I Crystal data and details of refinement

	Complex **a**	Complex **b**	Complex **c**	Complex **d**	Complex **e**
a/Å	10.628(3)	15.186(2)	10.006(3)	7.852(3)	11.097(4)
b/Å	33.002(3)	9.861(2)	13.107(3)	15.962(5)	10.914(3)
c/Å	7.755(3)	18.463(3)	11.314(2)	11.951(4)	11.178(4)
$\alpha/°$	90.00	90.00	90.00	90.00	90.00
$\beta/°$	90.00	91.63(1)	109.382(3)	105.48(3)	91.50(3)
$\gamma/°$	90.00	90.00	90.00	90.00	90.00
V/Å^3	2719.9(13)	2755.8(8)	1399.8(5)	1443.6(9)	1353.3(7)
Space Group	$P2_12_12_1$	$P2_1$	$P2_1$	$P2_1$	$P2_1$
Z	4	4	2	2	2
No. of parameters	346	608	366	356	382
No. of reflections used in refinement	3549	6711	6412	3442	3291
S	1.15	0.905	1.00	1.12	1.07
$(\Delta/\sigma)_{\max}$	0.02	< 0.001	0.001	< 0.001	< 0.001
$(\Delta\rho)_{\min}/e\text{Å}^{-3}$	2.528	0.773	0.265	1.052	1.396
$(\Delta\rho)_{\max}/e\text{Å}^{-3}$	−1.674	−0.305	−0.213	−0.393	−0.294
R	0.071	0.060	0.041	0.054	0.046
wR	0.183	0.138	0.088	0.121	0.132
Crystal dimensions/mm^3	0.3 × 0.3 × 0.2	0.5 × 0.1 × 0.08	0.2 × 0.1 × 0.1	0.5 × 0.5 × 0.1	0.5 × 0.5 × 0.5
Scan technique	ω	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$
Scan range	$\sin\theta/\lambda \leq 0.65$ Å^{-1}	$\sin\theta/\lambda \leq 0.65$ Å^{-1}	$\sin\theta/\lambda \leq 0.65$ Å^{-1}	$\sin\theta/\lambda \leq 0.65$ Å^{-1}	$\sin\theta/\lambda \leq 0.65$ Å^{-1}
	$0 \leq h \leq 13$	$0 \leq h \leq 19$	$0 \leq h \leq 12$	$0 \leq h \leq 10$	$0 \leq h \leq 14$
	$0 \leq k \leq 42$	$0 \leq k \leq 12$	$-17 \leq k \leq 17$	$0 \leq k \leq 20$	$0 \leq k \leq 14$
	$0 \leq l \leq 13$	$-24 \leq l \leq 23$	$-14 \leq l \leq 13$	$-15 \leq l \leq 14$	$-14 \leq l \leq 14$
Weighting scheme $[P = (Fo^2 + 2Fc^2)/3]$	$1/[\sigma2(Fo^2 + (0.1945P)^2]$	$1/[\sigma2(Fo^2 + (0.0780P)^2]$	$1/[\sigma2(Fo^2 + (0.0398P)^2]$	$1/[\sigma2(Fo^2 + (0.0887P)^2]$	$1/[\sigma2(Fo^2) + (0.1018P)^2 + 0.093P]$

TABLE II Selected torsion angles

Complex		CO(1)−C(9)−C(10)−C(11)	C(10)−C(11)−N(5)−C(12)	C(9)−C(10)−C(11)−N(5)
a		172.1(7)	−179.3(8)	−128.6(9)
b	A	−170.7(7)	−173.1(9)	83.1(13)
	B	177.1(8)	−179.9(9)	−86.0(12)
c		−172.0(3)	172.3(4)	123.6(4)
d		−179.6(4)	−179.8*	−163.4(6)
e	A	−173.8(8)	−167.1(17)	75.0(17)
	B	174.9(10)	−172.7(15)	109(2)

* The torsion angle of C10−C11−N5−H05A is used for the complex **d** instead of the torsion angle of C10−C11−N5−C12.

atom of the (*S*)-phenylalaninol group of the neighboring molecule at $(-x, y-1/2, -z)$.

(2-Carbamoylethyl)bis(dimethylglyoximato)[(*R*)-1-(1-naphthyl)ethylamine] Cobalt(III): Crystal d and Bis(dimethylglyoximato)[2-(methylcarbamoyl)ethyl][methyl(*S*)-phenylalaninate] Cobalt(III): Crystal e

The crystal structure and the molecular structure of **d** and **e** are shown in Figures 8–11 [11].

Photochemical Reaction in Solid-state

Powdered samples of the five complexes **a–e** were suspended in nujol and were irradiated with a solar simulator (flux density: 100 mW/cm^2) at a preset interval. After each irradiation, the axial bases were displaced with an achiral ligand such as methyldiphenylphosphine or dimethylphenylphosphine to give the corresponding phosphine-coordinated complexes. The ratio of the produced 1-*N*-substituted carbamoyl group to the original 2-*N*-substituted

TABLE III Intermolecular and intramolecular hydrogen bonding

Complex	D–H···A	d(D–H)	d(H···A)	d(D···A)	< (DHA)	Symmetry transformation
a	O(6)–H(006)···O(1)#1	0.82	2.25	2.802(8)	124.7	#1 $x, y, z+1$
	N(6)–H(06A)···O(6)	0.9	2.32	2.821(9)	114.7	
	N(6)–H(06B)···O(6)#2	0.9	2.46	3.274(9)	151.3	#2 $-x+3/2, -y+2, z-1/2$
	N(5)–H(05)···O(3)#3	0.86	2.15	3.010(9)	175.7	#3 $x, y, z-1$
b	N(6A)–H(06B)···O(05B)	0.9	2.52	3.075(11)	120.6	
	N(5A)–H(05A)···O(101)	0.86	2.02	2.874(13)	175.7	
	N(6B)–H(06D)···O(5A)#1	0.9	2.29	3.105(12)	150.8	#1 $x, y, z+1$
	N(5B)–H(05B)···O(102)#2	0.86	2.03	2.884(10)	171.2	#2 $x, y-1, z$
	O(101)–H(111)···O(3A)	0.99	2.12	2.851(10)	129.3	
	O(101)–H(111)···N(3A)	0.99	2.46	3.336(11)	147.7	
	O(102)–H(121)···O(3B)#3	0.98	1.92	2.859(10)	162.1	#3 $x, y+1, z$
	O(102)–H(121)···N(3B)#3	0.98	2.56	3.303(11)	133	#3 $x, y+1, z$
	O(102)–H(122)···O(1B)	0.99	1.91	2.854(9)	160.3	
	O(104)–H(142)···O(05B)	0.99	2.04	2.832(10)	135.9	
c	O(6)–H(006)···O(2)#1	0.82	2.01	2.822(3)	173.5	#1 $-x, y+1/2, -z$
	N(6)–H(06B)···O(6)	0.9	2.22	2.735(4)	115.7	
	N(5)–H(05)···O(6)#2	0.86	2.6	3.378(4)	150.9	#2 $-x, y-1/2, -z$
d	N(6)–H(06A)···O(10)#1	0.9	2.56	3.288(6)	138.6	#1 $x+1, y, z$
	N(6)–H(06B)···O(5)#2	0.9	2.09	2.993(5)	177	#2 $-x, y-1/2, -z$
	N(5)–H(05A)···O(10)#3	0.86	2.12	2.946(5)	159.9	#3 $-x-1, y+1/2, -z$
	N(5)–H(05B)···O(3)#4	0.86	2.14	2.980(6)	167	#4 $x-1, y, z$
	O(10)–H(010)···O(1)	0.82	1.88	2.703(5)	178.9	
e	NONE					

carbamoyl group was determined by HPLC using CHIRALCEL OD–H. The reaction rate constant was obtained assuming first-order kinetics [10]. The results are summarized in Table IV.

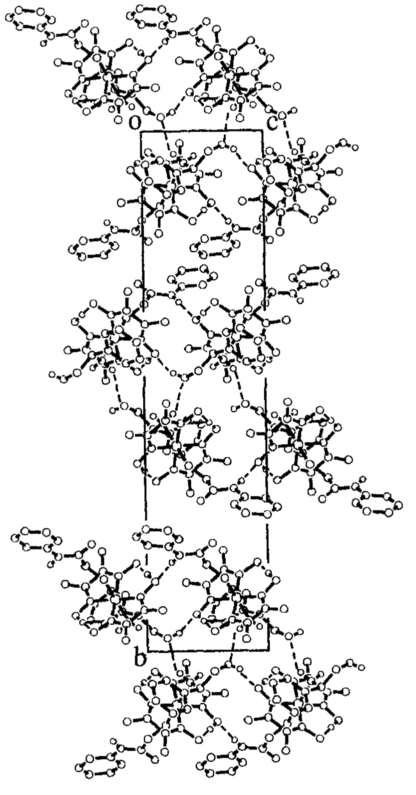

FIGURE 2 Crystal structure of complex **a** viewed along the *a* axis. Dotted lines indicate hydrogen bonds.

DISCUSSION

The reaction cavities for the *N*-substituted carbamoyl groups in the five crystals were calculated. The size of each cavity is given in Table IV, in which the rate constant, crystal solvent molecule, and hydrogen bonds involving the carbamoyl group are also listed. The rate constant of **b** is significantly greater than those of **a** and **c**, although the order of the cavity size is **a** > **b** > **c**. If the controlling factor of the reactivity in the three complexes is only the size of the reaction cavity, the reaction rate should be in the order of **a** > **b** > **c**. Similarly, the contradiction may appear when the cavities of **d** and **e** are compared. The rate constant of complex **e** is expected to be considerably higher than that of **d**

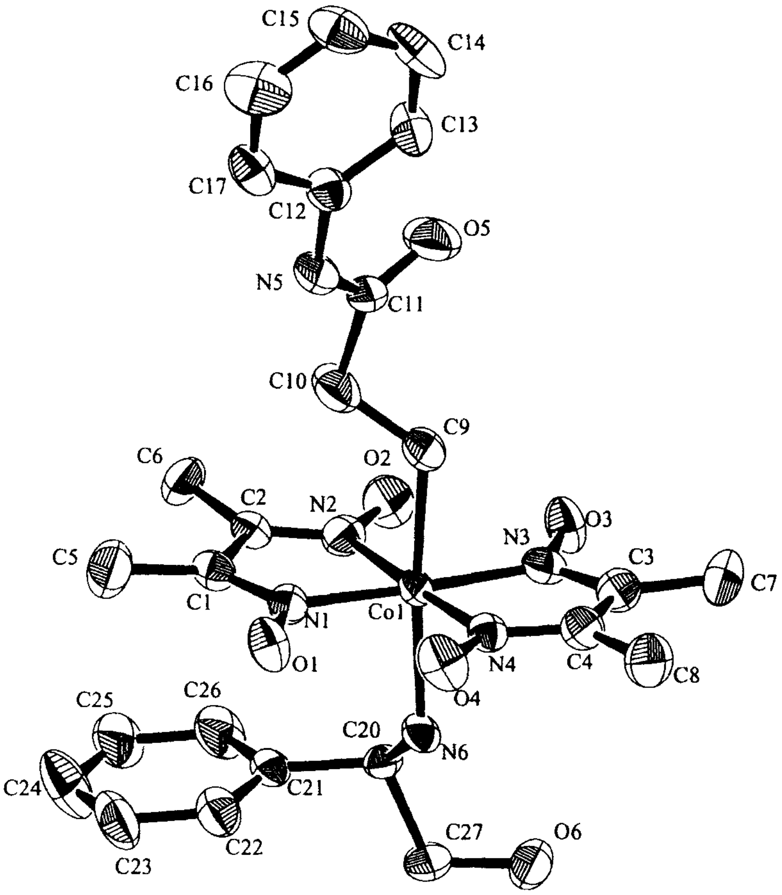

FIGURE 3 Molecular structure of complex **a** and numbering scheme of the atoms. The thermal ellipsoids show at 50% probability level.

because the carbamoyl group of the molecules make contact with each other along the 2_1 axis and such a column-like structure around the reactive groups should accelerate the reaction [12]. In spite of the advantageous factor, the rate constants of **d** and **e** are almost comparable. Some other factors, which control the reactivity, must be taken into account for the carbamoyl groups.

In the previous papers, we reported that the hydrogen bonding to the reactive groups lowered the reactivity because the reactive groups are anchored by the intermolecular hydrogen bonds and the movement of the atoms in the process of isomerization may be inhibited [8, 13]. However, if the reactive groups make hydrogen bonds with the solvent atoms, they tend to accelerate the reaction [8, 14]. In the crystals of **a** to **c**, the hydrogen bonds of the carbamoyl group in **a** [N5· · ·O3($x,y,z-1$)] and **c** [N5· · ·O6($-x,y-1/2,-z$)] should lower the reactivity, whereas the reaction rate of **b** should be accelerated since the hydrogen bonds are made with the solvent water molecules [N5A· · ·O101, N5B· · ·O102($x,y-1,z$), O104· · ·O5B]. This well explains the order of the reaction rates among the three crystals of **a** to **c**.

In the crystals of **d**, the hydrogen bond of the carbamoyl group [N5· · ·O3($x-1,y,z$)] would reduce the reaction rate whereas another hydrogen bond is made with the solvent methanol molecule [N5· · ·O10($-x-1,y+1/2,-z$)]. As a

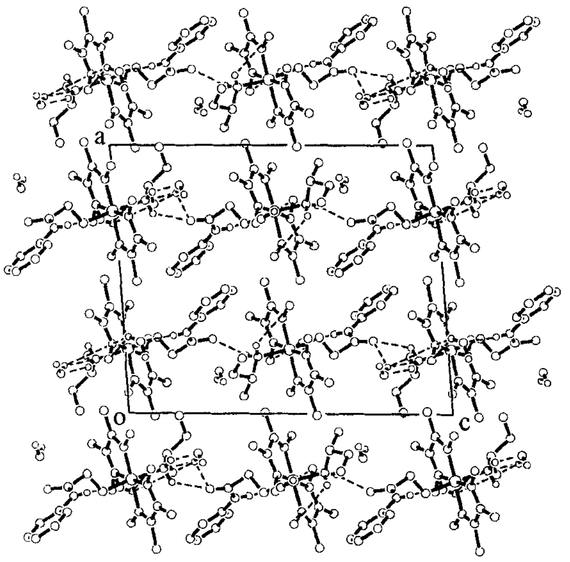

FIGURE 4 Crystal structure of complex **b** viewed along the *b* axis. Dotted lines indicate hydrogen bonds.

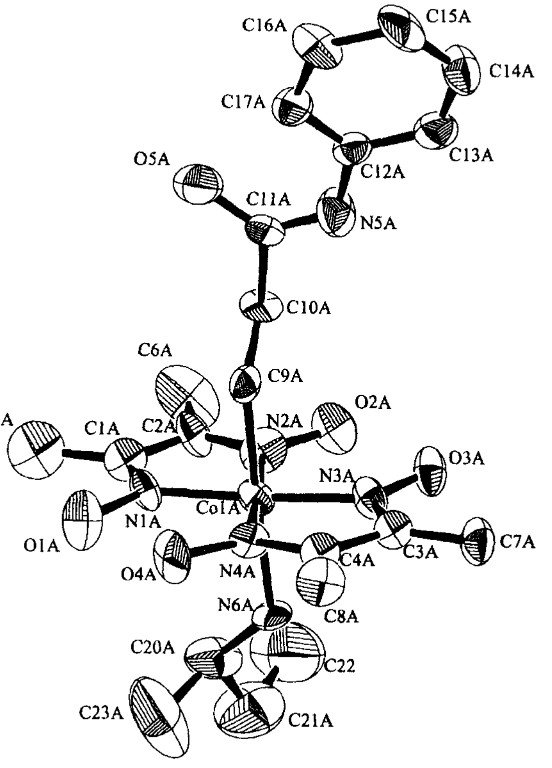

FIGURE 5 Molecular structure of complex **b** and numbering scheme of the atoms. The thermal ellipsoids show at 50% probability level.

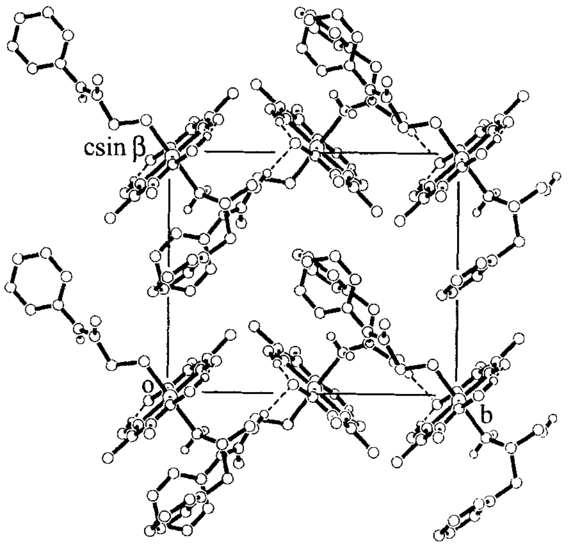

FIGURE 6 Crystal structure of complex **c** viewed along the *a* axis. Dotted lines indicate hydrogen bonds.

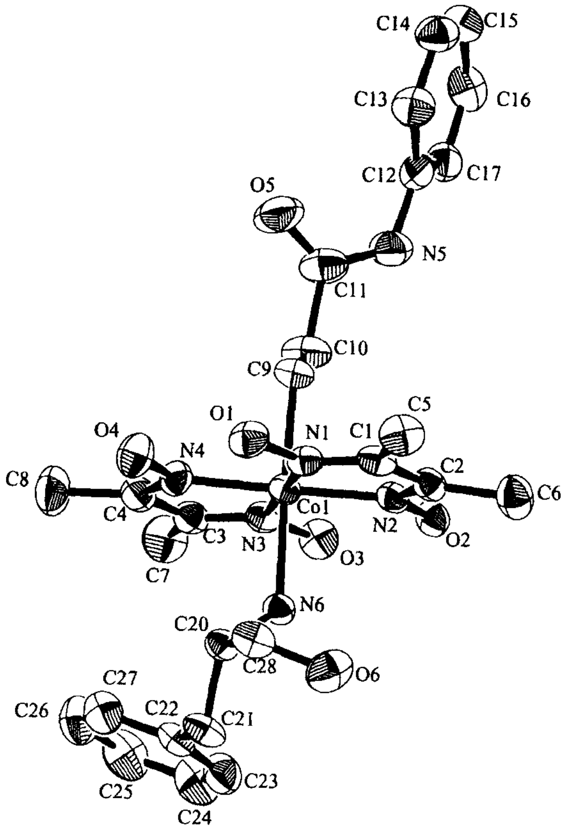

FIGURE 7 Molecular structure of complex **c** and numbering scheme of the atoms. The thermal ellipsoids show at 50% probability level.

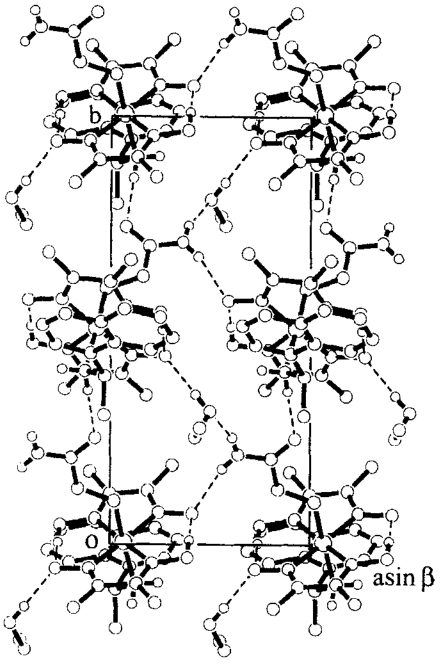

FIGURE 8 Crystal structure of complex **d** viewed along the *c* axis. Dotted lines indicate hydrogen bonds.

result, the crystal **d** may have nearly the same reaction rate as that of **e**.

The above results suggest that the reactivity is lowered or accelerated if the reactive group makes hydrogen bonds with the neighboring complexes or the crystal solvent molecules, respectively.

Crystal Structure Analysis

All data sets were collected on a Rigaku AFC-5R or on a Rigaku AFC7-S four-circle diffractometer with MoKα radiation ($\lambda = 0.71073$ Å). The diffractometer was covered with a clack sheet to shut out the room light. Three-dimensional intensity data were collected by means of a ω–2θ scan technique at $8^\circ \mathrm{min}^{-1}$ in 2θ. Absorption correction was applied. The structures were solved by direct method with the program SHELXS-86 [16] for **b**, and others with SAPI91 in TEXSAN [17]. The structure refinement was

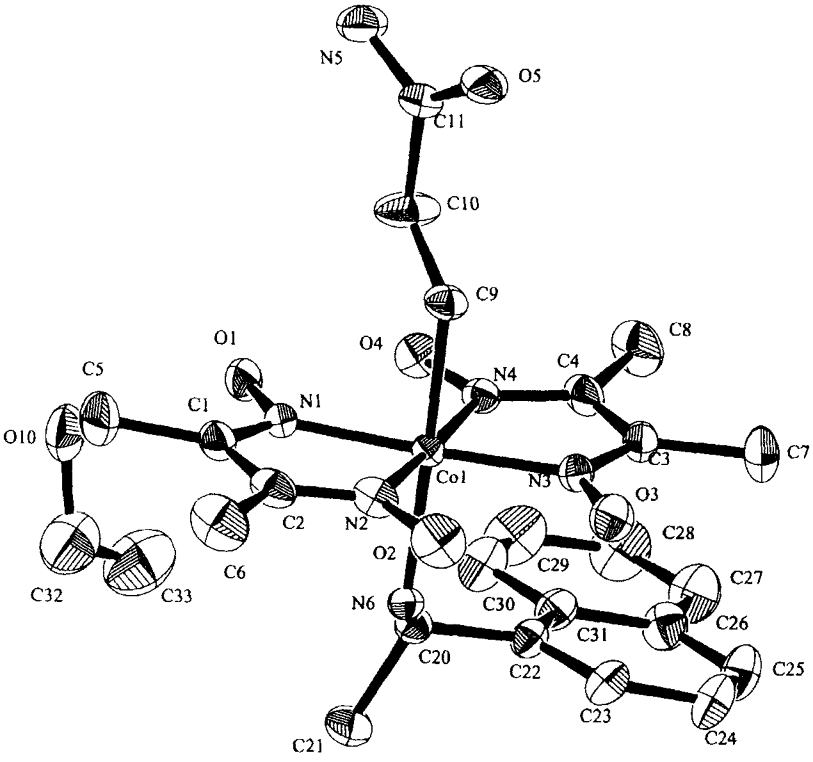

FIGURE 9 Molecular structure of complex **d** and numbering scheme of the atoms. The thermal ellipsoids show at 50% probability level.

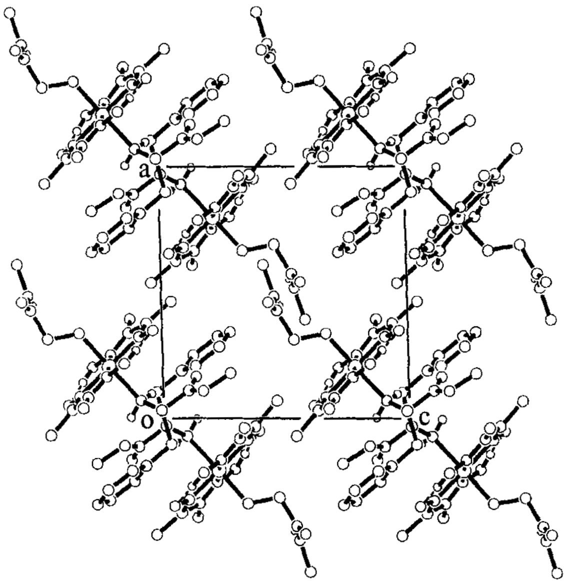

FIGURE 10 Crystal structure of complex **e** viewed along the *b* axis. Dotted lines indicate hydrogen bonds.

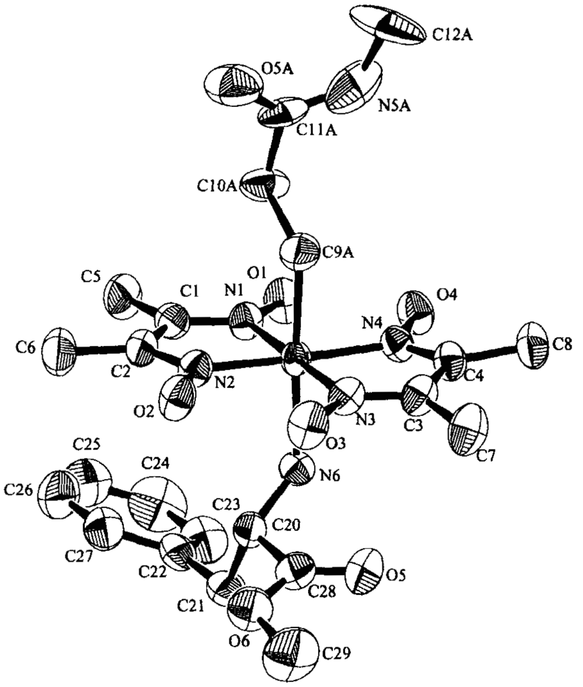

FIGURE 11 Molecular structure of complex **e** and numbering scheme of the atoms. The thermal ellipsoids show at 50% probability level.

carried out by the full-matrix least-squares with SHELXL-97 [18]. The absolute structure was determined by the Flack parameter [19]. All the hydrogen atoms were generated geometrically. The positional parameters of the H atoms were constrained to have C–H distances of 0.96 Å for

TABLE IV Rate canstants and the structures

Complex	Cavity (Å^3)	Rate constant (s^{-1})	Solvent	Hydrogen bond involving reactive group
a	53.656	$\ll 1.00 \times 10^{-5}$	none	N5···O3, 3.10(9) Å
b	53.598 51.238	9.94×10^{-5}	H_2O	N5A···O101, 2.874(13) Å N6B···O5A, 3.105(12) Å N5B···O102, 2.884(10) Å O104···O5B, 2.832(10) Å
c	50.123	$\ll 1.00 \times 10^{-5}$	none	N5···O6, 3.378(4) Å
d	12.078	3.68×10^{-5}	EtOH	N5···O10, 2.946(5) Å N5···O3, 2.980(6) Å
e	32.231	4.34×10^{-5}	none	none

primary, 0.97 Å for secondary and 0.93 for aromatic H atoms. The H-atom U values were constrained to have 1.2 times the equivalent isotropic U value of their attached atoms (1.5 for methyl groups). The atomic scattering factors were taken from International Tables for Crystallography [20]. The CIF data of the crystals were deposited with the Cambridge Crystallographic Data Center (CCDC), CCDC 144422–144424.

The preparation of the series of *N*-substituted cobaloxime complexes was basically carried out according to the literature methods with minor change [10].

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[1] This paper is dedicated to Professor Fumio Toda on the occasion of the celebration of his 67th birthday.

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