Reaction of 1 with Trifluoroacetaldehyde Ethyl Hemiacetal. Trifluoroacetaldehyde ethyl hemiacetal (1.8 mL) was added to a toluene solution (10 mL) of **1** (1.63 g, 1.8 mmol) and PPh_3 (1.10 g, 4.0 mmol) by a trap-to-trap distillation. After 1 day at 0 °C, H_2 (1.5 mmol) and N_2 (1.5 mmol) were detected in the gas phase. Then hexane (40 mL) was added to the brown solution. Similar workup in the reaction of **1** with ethyl trifluoroacetate gave brown crystals (350 mg, 20%). **5**: mp = 135 °C dec; $\mu_{eff} = 2.6\ \mu_B$. Anal. Calcd: see above. Found: C, 70.5; H, 5.3; P, 9.2; Co, 5.9.

Reaction of 5 with Dry HCl. Dry HCl (0.8 mmol) was introduced to the ether solution of **5** (243 mg, 0.246 mmol) to give trifluoroacetaldehyde ethyl hemiacetal (0.22 mmol, 90%).

Reaction of 2 with Phenyl Propionate. Phenyl propionate (3.5 mmol) was added to **2** (164 mg, 0.19 mmol) in a Schlenk flask. After evacuation of gas in the flask, the mixture was stirred at 0 °C for 5 h and gradually warmed to room temperature. After 1 day, CH_4 (0.013 mmol) and $C_2H_5COCH_3$ (0.13 mmol) were liberated, and a brown solution containing a yellow precipitate was obtained. Hexane (40 mL) was added to the mixture, and the precipitate was separated by filtration, washed with hexane, and dried in vacuo (52 mg, 32%). **3**: IR ν(C–O) 1280 cm^{-1}. The reactions of 2,2,2-trifluoroethyl carboxylates and carboxylic anhydrides were carried out analogously.

X-ray Measurement. The cell dimensions and space-group symmetries were preliminarily checked by Weissenberg photographs by using Ni Kα radiation. The systematic absences suggested the space group $P2_1/c$. Determination of cell constants and collection of intensity data were carried out on a Riganku AFC-5 diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.7107 Å). Unit cell constants were determined by least squares refinement of 25 reflections. Intensity data were collected by an ω-2θ scan mode up to 2θ = 50° with the scan rate of 16°/min at 50/KV, 170 mA. The scan range was (1.0 + 0.45 tan θ)°. Standard *LP* corrections were applied, but corrections for the absorption effect were neglected (μ(Mo Kα) = 4.9 cm^{-1}). The number of independent reflections used for the structure refinement $F_o > 3\sigma F_o$ is 2966.

Determination and Refinement of the Structure. The structure of the compound was solved by the heavy-atom method. All the non-hydrogen atoms were refined anisotropically. Subsequent difference Fourier maps did not reveal the positions of hydrogen atoms because the thermal vibration of the molecule was fairly large. The largest peak in a final difference map was ca. 1.0 eA^{-3} around the Co atom. The final anisotropic thermal parameters and the listing of observed and calculated structure factors are available as supplementary materials. All the atomic scattering factors were taken from Cromer and Waber.[23] The anomalous dispersidon coefficients of Cromer and Liberman were used for Co atom.[24] Block-diagonal least-squares refinement to minimized function $w(F_o - kF_c)^2$ was employed. The weight w was taken as $(\sigma + aF_o + bF_o^2)^{-1}$, where σ is the standard deviation for each reflection, and the values of a and b used were 0.2 and 0.009, respectively. All the computations were carried out on a HITAC computer at the Hiroshima University Information Processing Center. The computer programs used were UNICS program with a slight modification.[25] An ORTEP drawing was carried out by the XTL system on a Syntex diffractometer.[26]

Supplementary Material Available: Selected intermolecular short contacts (Table XIII), selected least-squares planes and dihedral angles (Table IX), F_o and F_c tables (Table X), anisotropic temperature factors (Table XI), mean-square displacement tensor of atoms (Table XII), atomic parameters for the hydrogen atoms (Table XIII), and the unit cell packing diagram in **3** (28 pages). Ordering information is given on any current masthead page.

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(24) Cromer, D. T.; Waber, J. T. "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, p 72.

(25) Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970,** *53,* 1891.

(26) Ashida, T. In "The Universal Crystallographic Computation Program System"; Sakurai, T., Ed.; The Crystallographis Society of Japan: Tokyo, 1979.

Fixation and Activation of Carbon Dioxide on Aluminum Porphyrin. Catalytic Formation of Carbamic Ester from Carbon Dioxide, Amine, and Epoxide

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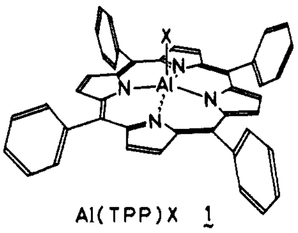
Abstract: Carbon dioxide is trapped by (5,10,15,20-tetraphenylporphinato)aluminum acetate in the presence of a secondary amine in the form of an aluminum carbamate on the opposite side to the acetate group with respect to the porphyrin plane. Carbon dioxide thus trapped by aluminum porphyrin is activated enough to undergo a catalytic reaction involving secondary amine and epoxide to afford dialkylcarbamic ester under atmospheric pressure at room temperature.

Carbon dioxide is one of the most ubiquitous carbon resources, but its activation is essential for chemical fixation and utilization because of the inertness under ordinary conditions. Although there are a number of studies as to the activation of carbon dioxide, the examples of the catalytic fixation so far reported are rather limited.[1]



Al(TPP)X **1**

We have investigated the fixation of carbon dioxide catalyzed by metalloporphyrins and reported previously that aluminum porphyrin having an axial aluminum alkoxide group (**1**, X = OR) in the presence of 1-methylimidazole catalyzes the reaction between carbon dioxide and epoxide to form cyclic carbonate, involving the insertion of carbon dioxide into the aluminum alkoxide bond.[2] Our related studies revealed that (*N*-methyl-5,10,15,20-tetraphenylporphinato)zinc ethyl (Zn(NMTPP)Et (**2**)) reacts with a mixture of carbon dioxide and secondary amine to

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(1) Kolomnikov, I. S.; Grigoryan, M. Kh. *Russ. Chem. Rev.* **1978,** *47* (4), 334 (Translated from *Usp. Khim.* **1978,** *47,* 603). Eisenberg, R.; Hendriksen, D. E. *Adv. Catal.* **1979,** *28,* 141. Inoue, S.; Yamazaki, N. "Organic and Bio-organic Chemistry of Carbon Dioxide"; Kodansha: Tokyo, 1981. Palmer, D. A.; Eldik, R. V. *Chem. Rev.* **1983,** *83,* 651.

(2) Takeda, N.; Inoue, S. *Bull. Chem. Soc. Jpn.* **1978,** *51,* 3564. Aida, T.; Inoue, S. *J. Am. Chem. Soc.* **1983,** *105,* 1304.

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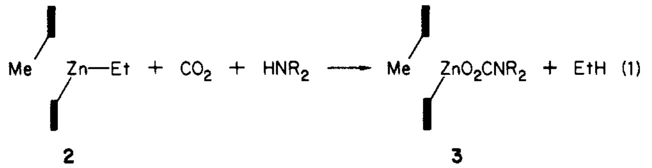
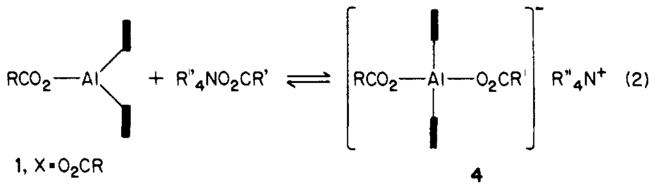
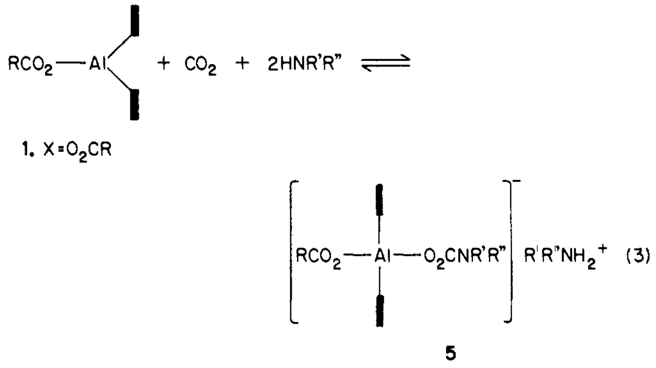
give the corresponding (porphinato)zinc dialkylcarbamate (Zn(NMTPP)O_2CNR_2 (**3**))[3] (eq 1).



More recently, a hexa-coordinate aluminum porphyrin complex (**4**) was found to form by mixing (5,10,15,20-tetraphenylporphinato)aluminum carboxylate (Al(TPP)O_2CR (**1**), X = O_2CR) and tetraalkylammonium carboxylate[4] (eq 2).



As the development of these studies, we describe in the present paper a novel, unusual type of activation and catalytic fixation of carbon dioxide under mild conditions with aluminum porphyrin having an axial aluminum carboxylate group (**1**, X = O_2CR). In the presence of a secondary amine, carbon dioxide was found to be trapped in the form of an aluminum carbamate on the opposite side to the carboxylate group with respect to the porphyrin plane (eq 3).



Although the "insertion" of carbon dioxide into the transition metal (Ti, Zr, V, Nb, Ta, and W)–nitrogen bond to form metal carbamate, actually proceeding via the substitution of the metal–nitrogen bond by carbamic acid, was reported,[5] the results described in this article presents a different, novel type of formation of metal carbamate by the coordination of carbamate group to the metal (Al).

Carbon dioxide thus trapped in the form of a novel aluminum porphyrin was found to be activated enough to undergo a catalytic reaction involving amine and epoxide under mild conditions. Upon mixing Al(TPP)O_2CCH_3 (**1**, X = O_2CCH_3) with a large excess of dialkylamine, carbon dioxide, and epoxide, the catalytic formation of a carbamic ester was observed.

Results and Discussion

Formation of Hexa-Coordinate Aluminum Porphyrin from (Porphinato)aluminum Carboxylate, Carbon Dioxide, and Dialkylamine. When carbon dioxide enriched in ^{13}C was bubbled under atmospheric pressure into a $CDCl_3$ solution of Al(TPP)O_2CCH_3[6] (**1**, X = O_2CCH_3) at room temperature in the presence of 2 molar equiv of diethylamine. the mixture exhibited the ^{13}C NMR spectrum as shown in Figure 1. The resonances due to methyl and carbonyl carbons of the acetate group are observed at δ 17 (g) and 170 (a), respectively.[7] The appearance of a strong resonance at δ 152 (c) should be noted. Since the resonance of the carbonyl carbon of Zn(NMTPP)O_2CNEt_2 (**3**, R = Et) is observed at δ 157,[3] the resonance c is assigned to the carbonyl carbon of a carbamate group bound to the aluminum atom. On the other hand, the mixture of carbon dioxide and diethylamine exhibited the resonance due to the carbonyl carbon of diethylammonium diethylcarbamate at δ 161. Resonance b (δ 160) is due to the formation of diethylammonium diethylcarbamate from carbon dioxide enriched in ^{13}C and a slight excess of diethylamine present in the system. The resonances e (δ 41), f (δ 38) and h (δ 12), i (δ 12) are assigned to the methylene and methyl carbons of the diethylamino group, respectively.[8]

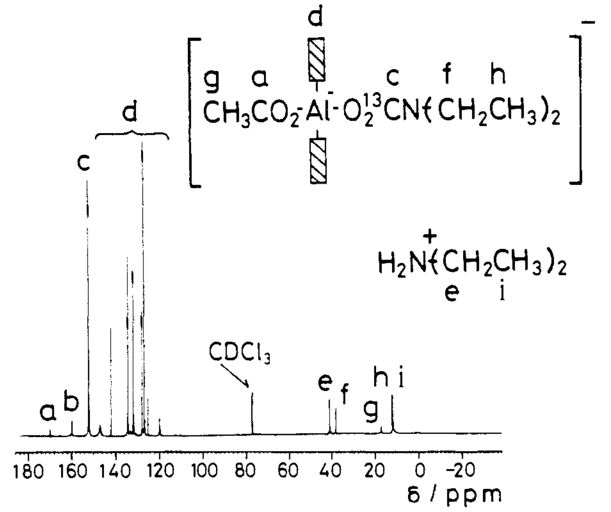


Figure 1. ^{13}C NMR spectrum of the mixture of Al(TPP)O_2CCH_3 (**1**, X = O_2CCH_3) and diethylamine (1:2) in $CDCl_3$ after bubbling $^{13}CO_2$ at room temperature.

In the mixture of Al(TPP)O_2CCH_3 (**1**, X = O_2CCH_3), dialkylamine and carbon dioxide, remarkable upfield shifts in the ^1H NMR spectrum were observed for the signals corresponding to dialkylamino group when compared with the mixture of carbon dioxide and dialkylamine, i.e., dialkylammonium dialkylcarbamate. This indicates that the dialkylamino group in the resulting product is in the proximity of the porphyrin ring. An example for the Al(TPP)O_2CCH_3–*N*-methylbenzylamine–carbon dioxide system is shown in Figure 2B. When compared with the mixture of *N*-methylbenzylamine and carbon dioxide (Figure 2C), the signals due to protons of methyl, methylene, *o*-phenyl, *m*-phenyl, and *p*-phenyl of the *N*-methylbenzyl group shifted from δ 2.9 (b″) and δ 2.4 (b‴) to δ -0.4 (b′), from δ 4.5 (c″) and δ 3.8 (c‴) to δ 0.6 (c′), and from δ 7.3 (e″) to δ 5.5 (e′), δ 6.7 (f′), and δ 6.9 (g′), respectively.[9] A broad signal at δ 2.9 (Figure 2B, d′) is considered to be due to *N-H* of dialkylammonium ion. This is largely upfield shifted from the resonance of *N-H* of $(PhCH_2(CH_3)NCO_2{\cdot}H_2N(CH_3)CH_2Ph)$ at δ 9.6 (Figure 2C, d″), by the effect of the porphyrin ring current. The signal for the acetate group of Al(TPP)O_2CCH_3 also exhibited an upfield shift from δ -1.4 (Figure 2A, a) to -2.3 (Figure 2B, a′), indicating that the acetate group is bound to aluminum atom of a hexa-coordinate aluminum porphyrin.[10,11]

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(3) Inoue, S.; Nukui, M.; Kojima, F. *Chem. Lett.* **1984**, 619.

(4) Aida, T.; Inoue, S. *J. Am. Chem. Soc.* **1985**, *107*, 1358.

(5) Chisholm, M. H.; Extine, M. W. *J. Am. Chem. Soc.* **1977**, *99*, 792.

(6) Yasuda, T.; Aida, T.; Inoue, S. *J. Macromol. Sci. Chem.* **1984**, *A21*, 1035.

(7) For Al(TPP)O_2CCH_3, the resonances of methyl and carbonyl carbons of the acetate group are at δ 20 and 168, respectively.

(8) For the mixture of carbon dioxide and diethylamine: $H_2N^+(CH_2CH_3)_2$ δ 41, $(CH_3CH_2)_2NCO_2^-$ δ 40, $(CH_3CH_2)_2NCO_2^-$ δ 13, and $H_2N^+(CH_2CH_3)_2$ δ 12.

(9) For *N*-methylbenzylamine: N-CH_3 δ 2.6, N-CH_2-Ph δ 3.7, N-*H* δ 1.3, and N-CH_2-*Ph* δ 7.3. For the mixture of Al(TPP)O_2CCH_3 and *N*-methylbenzylamine: -O_2CCH_3 δ -1.8, N-CH_3 δ 0.0, N-CH_2-Ph δ 1.0, N-*H* δ -1.6, N-CH_2-*Ph*(*o*) δ 6.2, and N-CH_2-*Ph*(*m*,*p*) δ 7.0.

(10) For Al(TPP)O_2CCH_3-$Et_4N^+CH_3CO_2^-$ (**4**, R = R′ = CH_3, R″ = Et), δ -2.0; in $CDCl_3$ at room temperature.[4]

Table I. Reaction of Carbon Dioxide (CO_2), Diethylamine ($(C_2H_5)_2NH$), and Epoxide ($CH(R_1)CH(R_2)O$) with $(TPP)AlO_2CCH_3$ (**1**, X = O_2CCH_3) in $CHCl_3$[a]

run	epoxide		P_{CO_2},[b]	temp,[c]		yield,[d] %	
no.	R_1	R_2	atm	°C	time, h	$(C_2H_5)_2NCO_2CH(R_2)CH(R_1)OH$ (**6**)	$(C_2H_5)_2NCH(R_2)CH(R_1)OH$ (**7**)
1	CH_3	H	1	r.t.	1	6	29
2	CH_3	H	1	r.t.	204	34	38
3	CH_3	H	50	70	1	6	8
4	C_2H_5	H	1	r.t.	168	12	82
5	C_6H_5	H	1	r.t.	168	15	75
6	CH_2OCH_3	H	1	r.t.	168	6	86
7	CH_3 (cis)	CH_3	1	r.t.	168	8	60

[a] $[Epoxide]_0/[(C_2H_5)_2NH]_0/[(TPP)AlO_2CCH_3]_0$ = 100/100/1. [b] Pressure of carbon dioxide. [c] r.t. = about 20 °C. [d] By ^1H NMR.

Table II. Reaction of Carbon Dioxide (CO_2), Dialkylamine (R_1R_2NH), and 1,2-Epoxypropane ($CH(CH_3)CH_2O$) with $(TPP)AlO_2CCH_3$ (**1**, X = O_2CCH_3) in Pyridine[a]

run	dialkylamine		P_{CO_2},[b]	temp,		yield,[c] %	
no.	R_1	R_2	atm	°C	time, h	$R_1R_2NCO_2CH_2CH(CH_3)OH$ (**6**)	$R_1R_2NCH_2CH(CH_3)OH$ (**7**)
1	C_2H_5	C_2H_5	1	r.t.[d]	72	35	48
2	C_2H_5	C_2H_5	50	40	6	18	3
3	C_2H_5	C_2H_5	50	50	6	23	7
4	C_2H_5	C_2H_5	50	60	1	29	15
5	C_2H_5	C_2H_5	50	60	6	47	9
6	C_2H_5	C_2H_5	50	80	6	41	22
7	$-(CH_2-)_5$		50	60	6	31	
8	$CH(CH_3)_2$	$CH(CH_3)_2$	50	60	6	46[e]	34[e]

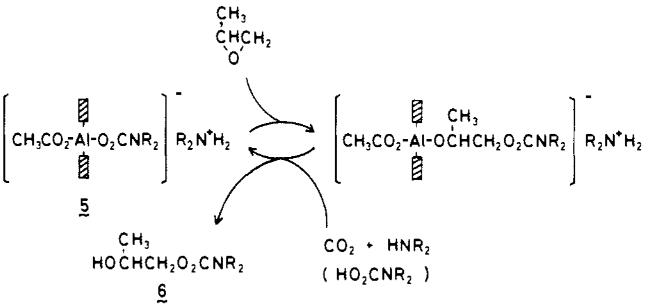
[a] $[1,2\text{-Epoxypropane}]_0/[R_1R_2NH]_0/[(TPP)AlO_2CCH_3]_0$ = 100/100/1. [b] Pressure of carbon dioxide. [c] By gas chromatography. [d] About 20 °C. [e] By ^1H NMR.

In Figure 2B, it is of particular interest to note that the ratios of the intensity of the signals a′ (3 H), b′ (6 H), c′ (4 H), d′ (2 H), e′ (4 H), f′ (4 H), and g′ (2 H) to that of the proton at pyrrole-β (j′, 8 H) indicate the existence of two *N*-methylbenzylamino groups in the proximity of the porphyrin. This corresponds to the formation of a novel hexa-coordinate aluminum porphyrin (**5**) carrying both a carboxylate group and a carbamate group as axial ligands, with a paired dialkylammonium group close to the porphyrin ring (eq 3). When the molar ratio of *N*-methylbenzylamine to $Al(TPP)O_2CCH_3$ (**1**, X = O_2CCH_3) increased, a single NMR signal observed respectively for each kind of proton of *N*-methylbenzylamino group (Figure 2B) showed a downfield shift toward that in a simple mixture of carbon dioxide and *N*-methylbenzylamine (Figure 2C). Thus, there is considered to exist a rapid equilibrium in eq 3.

The infrared spectrum of the $Al(TPP)O_2CCH_3$–diethylamine system upon introduction of carbon dioxide exhibited a new absorption band at 1560 cm^{-1}, with disappearance of the absorption at 1650 cm^{-1} due to the acetate group of $Al(TPP)O_2CCH_3$. Since the absorptions due to the carbonyl stretching vibrations of $Zn(NMTPP)O_2CNEt_2$ (**3**, R = Et) and of the mixture of carbon dioxide and diethylamine are observed at 1560 and 1650 cm^{-1}, respectively, the new absorption at 1560 cm^{-1} is considered assignable to the carbonyl stretching vibrations of acetate and diethylcarbamate groups bound to the aluminum atom.

Thus, the above observations strongly indicate that dialkylcarbamate, formed from carbon dioxide and dialkylamine, coordinates to the aluminum atom of $Al(TPP)O_2CCH_3$ (**1**, X = O_2CCH_3) from the opposite side to the acetate group with respect to the porphyrin plane to form a hexa-coordinate complex **5**. This complex (**5**) is not very stable; when nitrogen was bubbled at room temperature to flash the dissolved carbon dioxide out of the reaction mixture containing **5**, the infrared spectrum showed a decrease in the intensity of the absorption at 1560 cm^{-1}.

Scheme I



Catalytic Formation of Carbamic Ester from Carbon Dioxide, Amine, and Epoxide. When an epoxide was added to a mixture of dialkylamine, carbon dioxide, and a small amount of $Al(TPP)O_2CCH_3$ (**1**, X = O_2CCH_3), catalytic formation of dialkylcarbamic ester was observed under mild conditions. For example, in the reaction with 100 molar equiv of 1,2-epoxypropane and diethylamine with respect to $Al(TPP)O_2CCH_3$ in chloroform under atmospheric pressure at room temperature for 1 h, the turnover as to the formation of 2-hydroxypropyl diethylcarbamate (**6**, R = Et) was six (Table I, run 1). The formation of 1-(diethylamino)-2-propanol (Table I, **7**, $R_1 = CH_3$, R_2 = H), a product from the amine and the epoxide, was also observed (29 equiv with respect to $Al(TPP)O_2CCH_3$). However, the formation of 1-methyl-2-hydroxyethyl diethylcarbamate, the isomer of **6**, and 4-methyl-1,3-dioxolan-2-one, the product from the epoxide and carbon dioxide, was not detected. In the absence of $Al(TPP)O_2CCH_3$ (**1**, X = O_2CCH_3), neither the carbamic ester nor the amino alcohol were formed under the same conditions.[12] In the reaction for 8 days, the turnover as to the formation of the carbamic ester increased to 34 (Table I, run 2).

Thus, carbamic ester was catalytically formed from carbon dioxide, dialkylamine, and epoxide by $Al(TPP)O_2CCH_3$ (**1**, X = O_2CCH_3). The catalytic formation of 2-hydroxypropyl diethylcarbamate (**6**, R = Et) is considered to proceed by the in-

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(11) Similar spectral changes ascribable to the formation of a hexa-coordinate aluminum porphyrin (4) were observed for the mixture of $Al(TPP)O_2CCH_3$, acetic acid, and *N*-methylbenzylamine: δ −0.8 (N–C*H*₃), δ 0.3 (N–C*H*₂–Ph), δ 4.7, 6.4, 6.8 (N–CH₂–*Ph*), δ 5.5 (N–*H*), and δ −2.5 (O₂CC*H*₃), in $CDCl_3$ at room temperature.

(12) See also: Yoshida, Y.; Inoue, S. *J. Chem. Soc., Perkin Trans. 1* **1979**, 3146.

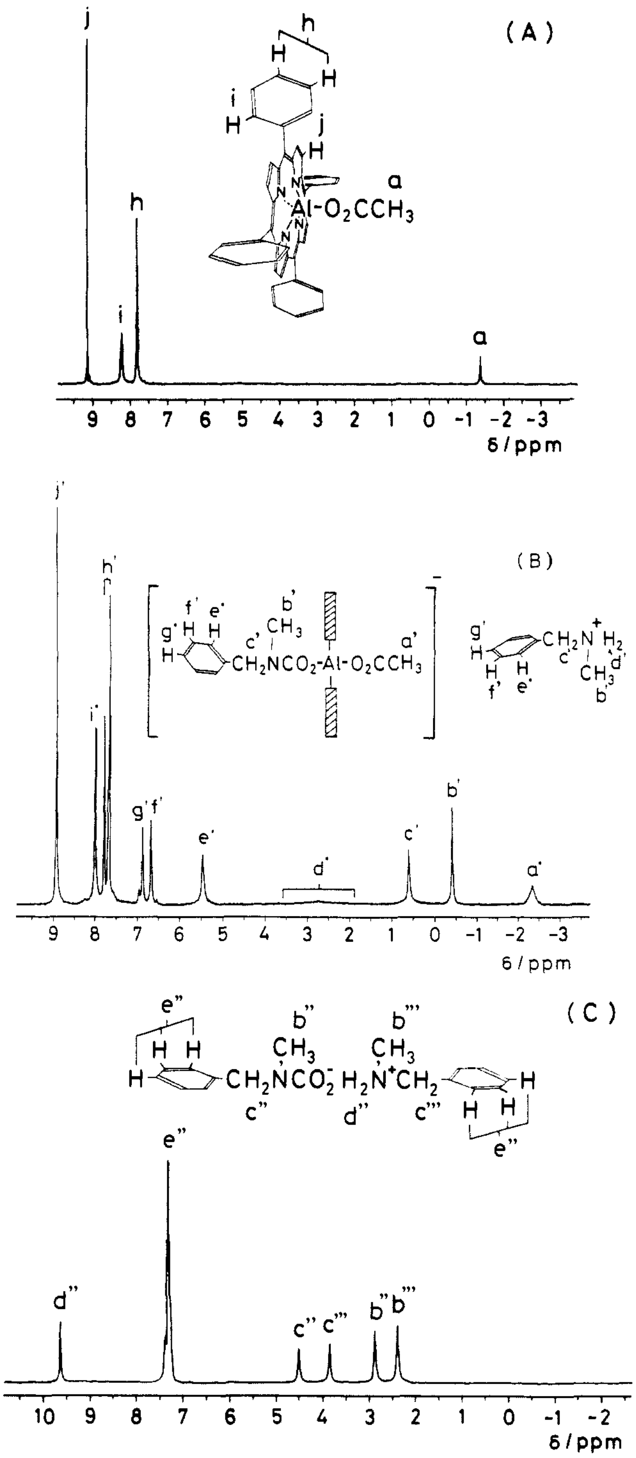

Figure 2. ^{1}H NMR spectra of (A) Al(TPP)O_2CCH_3 (**1**, X = O_2CCH_3), (B) the mixture of Al(TPP)O_2CCH_3 and *N*-methylbenzylamine (1:2) after bubbling carbon dioxide at room temperature, and (C) *N*-methylbenzylamine after bubbling carbon dioxide at room temperature, in $CDCl_3$.

sertion of epoxide to the (porphinato)aluminum carbamate **5** to form an aluminum alkoxide, followed by the substitution by diethylcarbamic acid (from carbon dioxide and diethylamine) to give the product **6**, regenerating the aluminum carbamate **5** (Scheme I). In the presence of a large excess of diethylamine and carbon dioxide, substitution of Et_2NCO_2–Al for CH_3CO_2–Al of **5** possibly occurs to give an aluminum porphyrin containing two carbamate groups bound to the aluminum atom.

The reaction under a pressure of carbon dioxide (50 atm) at 70 °C for 1 h did not increase the formation of the carbamic ester, while the amount of amino alcohol decreased to 8 equiv with respect to Al(TPP)O_2CCH_3 (Table I, run 3). Better results were obtained when pyridine was used as solvent in place of chloroform (Table II). For example, in the reaction under atmospheric pressure of carbon dioxide at room temperature, the turnover as to the formation of the carbamic ester of 35 was attained after 3 days (Table II, run 1). The reaction at higher temperature under a pressure of carbon dioxide was found very much effective for the synthesis of the carbamic ester. An example is the reaction in pyridine at 60 °C under 50 atm of pressure of carbon dioxide (Table II, run 4); the turnover for the carbamic ester reached to 29 even after 1 h, while that for the amino alcohol was low (15). In the reaction for 6 h (Table II, run 5), the turnover for the carbamic ester increased to 47, while the amount of the amino alcohol did not increase (9).

Carbamic ester could be obtained also from other dialkylamines such as piperidine and diisopropylamine (Table II, runs 7 and 8); the turnovers as to the formation of the corresponding carbamic esters were 31 and 47, respectively, in the reaction in pyridine under 50 atm pressure of carbon dioxide at 60 °C for 6 h. The reaction of carbon dioxide, diethylamine, and epoxides other than 1,2-epoxypropane such as 1,2-epoxybutane, phenylepoxyethane, 1,2-epoxy-3-methoxypropane, and *cis*-2,3-epoxybutane, carried out in chloroform under atmospheric pressure at room temperature for 1 week (Table I, runs 4–7), was found to give the corresponding carbamic esters, the turnover ranging from 6 to 15.

Experimental Section

Materials. 5,10,15,20-Tetraphenylporphine ($TPPH_2$) was prepared by the reaction between pyrrole and benzaldehyde in refluxing propionic acid and purified by recrystallization from chloroform–methanol.[13] Triethylaluminum was purified by distillation under reduced pressure in a nitrogen atmosphere. Commercial acetic acid and carbon dioxide were used without further purification. Dialkylamines and epoxides were distilled over a mixture of calcium hydride and potassium hydroxide in a nitrogen atmosphere. Chloroform and dichloromethane were washed successively with sulfuric acid, water, aqueous sodium bicarbonate, and water and then dried and distilled over calcium hydride in a nitrogen atmosphere. Pyridine was distilled over a mixture of calcium hydride and potassium hydroxide in a nitrogen atmosphere.

Preparation of Al(TPP)O_2CCH_3.[6] $TPPH_2$ (2 mmol) was placed in a Pyrex flask (200 mL) equipped with a three-way cock and a magnetic stirrer and was purged by dry nitrogen. Dichloromethane (40 mL) was introduced to dissolve $TPPH_2$. Triethylaluminum (2 mmol) was added to this solution, and the mixture was stirred for more than 2 h at room temperature. After the quantitative formation of Al(TPP)Et (**1**, X = Et),[14] a slight excess of acetic acid (2.4 mmol) was added. The mixture was stirred overnight, and evaporated under reduced pressure at about 110 °C to remove the excess of acetic acid and the solvent. Chloroform (40 mL) was added to dissolve the residue, and the mixture was evaporated to remove completely the residual acetic acid, if any, to leave Al(TPP)O_2CCH_3.

Reaction of Carbon Dioxide, Dialkylamine, and Epoxide. To the solution of Al(TPP)O_2CCH_3 (**1**, X = O_2CCH_3) in chloroform (0.5 mmol, 0.05 M) in a Pyrex flask (100 mL) equipped with a three-way cock and a magnetic stirrer was added dialkylamine (50 mmol). Carbon dioxide was bubbled into the mixture for 5 min, and epoxide (50 mmol) was added. A balloon (ca. 2000 mL) filled up with carbon dioxide was fitted through a three-way cock, and the reaction mixture was stirred at room temperature. After a definite time, the reaction mixture was evaporated under reduced pressure at room temperature to remove unreacted carbon dioxide, epoxide, dialkylamine, and solvent. The residue was dissolved in $CDCl_3$ for NMR spectral analysis of the product. In the reaction under the pressure of carbon dioxide, the solution of Al(TPP)O_2CCH_3 (**1**, X = O_2CCH_3) (0.5 mmol, 0.1 M) in chloroform or pyridine was introduced into an autoclave (100 mL) flushed with nitrogen. Dialkylamine (50 mmol) was added, carbon dioxide was bubbled into the mixture for 5 min, epoxide (50 mmol) was added, a pressure of carbon dioxide (50 atm) was applied, and the mixture was stirred magnetically at a prescribed temperature. After a definite time, the reaction mixture was evaporated under reduced pressure at room temperature, and the residue was subjected to spectroscopic and gas chromatographic analyses of the product. As the standard sample for gas chromatography, a mixture of 2-hydroxypropyl dialkylcarbamate (**6**) and 1-methyl-2-hydroxyethyl dialkylcarbamate was prepared by refluxing 4-methyl-

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1,3-dioxolan-2-one and dialkylamine at 60 °C for 22 h,[12,15] followed by distillation under reduced pressure.

Measurements. ^{1}H and ^{13}C NMR spectra were measured on a JEOL JNM-GX 400 FT NMR spectrometer. Infrared spectra were measured with a Hitachi 260-30 infrared spectrophotometer. Gas chromatography was carried out on an Ohkura Gas Chromatograph Model-103 equipped with a glass capillary column of 30 m × 0.28 mm; adsorber, silicone SF-96.

Registry No. TPPH$_2$, 917-23-7; **1** (X = Et), 63256-30-4; **1** (X = O$_2$CCH$_3$), 85709-47-3; **4** (R = R′ = Me; R″ = Et), 99547-43-0; **6** (R$_1$ = Me; R$_2$ = H), 37499-12-0; **6** (R$_1$ = Et; R$_2$ = H), 99532-93-1; **6** (R$_1$ = Ph; R$_2$ = H), 99532-94-2; **6** (R$_1$ = CH$_2$OMe; R$_2$ = H), 99532-95-3; **6** (R$_1$ = R$_2$ = Me), 99532-96-4; **6** (R = *i*-Pr), 99532-98-6; 6 (R = (–CH$_2$–)$_5$), 99532-99-7; 7 (R$_1$ = Me; R$_2$ = H), 4402-32-8; **7** (R$_1$ = Et; R$_2$ = H), 2683-58-1; 7 (R$_1$ = Ph; R$_2$ = H), 4249-64-3; 7 (R$_1$ = CH$_2$OMe; R$_2$ = H), 3141-80-8; 7 (R$_1$ = R$_2$ = Me), 99532-97-5; **7** (R = *i*-Pr), 2109-63-9; AlEt$_3$, 97-93-8; $\overline{\mathrm{CH(Me)CH_2O}}$, 75-56-9; $\overline{\mathrm{CH(Et)\text{-}CH_2O}}$, 106-88-7; $\overline{\mathrm{CH(Ph)CH_2O}}$, 96-09-3; CH(CH$_2$OMe)CH$_2$O, 930-37-0; (*cis*)-$\overline{\mathrm{CH(Me)CH(Me)O}}$, 1758-33-4; HNEt$_2$, 109-89-7; HN(Pr-*i*)$_2$, 108-18-9; CO$_2$, 124-38-9; NHMe(CH$_2$Ph), 103-67-3; piperidine, 110-89-4.

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Dynamics of Spin-State Interconversion and Cooperativity for Ferric Spin-Crossover Complexes in the Solid State. 5.[1] Variable-Temperature Spectroscopic, Magnetic, and Single-Crystal X-ray Structural Characterizations of the Spin-State and Order–Disorder Transformations of a Schiff Base Complex

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Abstract: Two types of solid-state structural dynamics are exhibited by [Fe(3-OEt-SalAPA)$_2$]ClO$_4$·C$_6$H$_6$, where 3-OEt-SalAPA is the monoanion of the Schiff base condensate of 3-ethoxysalicylaldehyde and *N*-(3-aminopropyl)aziridine. Variable-temperature magnetic susceptibility and EPR data show that the compound undergoes a gradual, but complete, spin-crossover transformation for which there are equal populations of high- and low-spin complexes at 205 K. Only a single quadrupole-split doublet is seen in the Mössbauer spectrum at all temperatures from 111 to 306 K. Thus, this complex is interconverting between low- and high-spin states at a rate faster than the inverse of the Mössbauer time scale. No hysteresis is seen in any of the spectroscopic or magnetic measurements. A multiple-temperature structural investigation has provided an independent characterization of the spin transformation. This characterization is in complete accord with the magnetic data but reveals a second structural transformation whose presence is not reflected in the spectroscopic or magnetic data. This second transformation, at about 180 K, is an order–disorder transformation which results in a change of space group from $C2/c$ at high temperature to $P2_1/c$ at low temperature. The abrupt nature of this transformation, the observed hysteresis ($\Delta T = 15$ K), and the observation of two phases in the hysteresis region are characteristic of a first-order transition. The order–disorder transformation involves a dynamic interconversion of two crystallographically distinct sites. Preservation of the local environments at the two iron sites accounts for the insensitivity of the spin-equilibrium thermodynamics to the transformation. Although the X-ray investigation provides no direct evidence of the rate of interconversion between the two environments, the possible influence of this dynamic process on the rate of spin-state interconversion is discussed.

Solid-state spin-crossover transformations have been of recent interest because they provide a means for investigating just how an intramolecular process (the spin-state interconversion) is coupled to the intermolecular interactions intrinsic to a condensed phase. To date, research in this area[5–8] has centered to a greater extent on the solid-state factors that influence the thermodynamics at the spin-crossover transformation and to a lesser extent on the factors that influence spin-state interconversion rates. In fact, very little is known about the role of intermolecular interactions in inhibiting or enhancing these rates in the solid state. Within the past few years, several ferric spin-crossover solids have been discovered which may provide new insights into this problem.

In two of the preceding papers[9,10] in this series the magnetic and spectroscopic properties of the new ferric N$_4$O$_2$ spin-crossover

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