tris(ethylenediamine)nickel(II) salts in methanol to give the novel type of nickel(II) complexes containing two *N*-glycosides derived from the reaction of an amino sugar and a diamine.

Previously we predicted that an *N*-glycoside from an aldose and a diamine coordinates to the nickel ion through the oxygen atom of he hydroxyl group on C-2 of the sugar moiety and through the two N atoms of the diamine.[3] Though the sugars are amino sugars and they have an amino group on C-2 instead of a hydroxyl group, the coordination behavior of *N*-glycosides derived from amino sugars is expected to be similar to that of glycosylamines from aldohexoses. Thus, the present work could confirm our previous structural prediction for nickel(II) complexes of aldoses.[3]

The present crystal structure and circular dichroism studies of the related complexes indicate that the gauche conformation of the sugar chelate ring and the absolute configuration around the secondary nitrogen atom will depend on the orientation of the amino group on C-2 of the sugar moiety and they make significant contributions to the circular dichroism. Thus the results obtained in this work suggest that the CD pattern of the first d–d transition offers a potentially useful tool in assigning the coordination geometry of amino sugars.

The complexes obtained exhibit a high degree of hydrolytic stability in contrast to the instability of the analogous complexes derived from monosaccharides.[3] This fact is noteworthy in connection with the medical usefulness of amino sugars.

Recently much attention has been attracted to nickel-containing hydrogenases.[25] Accordingly, elucidation of the fundamental coordination behavior of sugars or amino sugars to nickel should provide useful information to aid in the interpretation of reaction mechanisms of metal-containing enzymes.

Acknowledgment. The authors wish to thank Prof. Kozo Sone and Prof. Yutaka Fukuda of Ochanomizu Women University for obtaining magnetic data and Prof. Junnosuke Fujita of Nagoya University and Prof. Osamu Yamauchi of Kanazawa University for their helpful discussions. Acknowledgement is made to the donors of the Asahi Glass Foundation for Industrial Technology, administered by Asahi Glass Kogyo Co., Ltd. This work was partially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education of Japan (No. 56540355).

Registry No. en, 107-15-3; [Ni(D-*N*-gl-en)$_2$]Cl$_2$, 94595-50-3; [Ni(D-*N*-gal-en)$_2$]Cl$_2$, 94499-89-5; [Ni(D-*N*-man-en)$_2$]Cl$_2$, 94595-99-0; [Ni(D-*N*-gl-en)$_2$]Br$_2$·4H$_2$O, 94595-51-4; tris(ethylenediamine)nickel(II) dichloride, 13408-70-3; D-glucosamine, 3416-24-8; D-galactosamine, 7535-00-4; D-galactosamine hydrochloride, 1772-03-8.

Supplementary Material Available: A listing of the anisotropic thermal parameters (Table IIb), a stereoscopic view of the unit cell, and a table of structure factor amplitudes (22 pages). Ordering information is given on any current masthead page.

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(24) Watabe, M.; Zama, M.; Yoshikawa, S. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 1354–1357.

(25) Xavier, A. V.; Teixeira, M.; Moura, K.; Moura, J. J. G.; Legall. J. 1st International Conference on Bioinorganic Chemistry, Florence, Italy, June 1983; Abstracts, pp 13–14.

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Facile CO_2 Uptake by Zinc(II)–Tetraazacycloalkane Complexes. 1. Syntheses, Characterizations, and Chemical Properties of (Monoalkyl carbonato)(tetraazacycloalkane)zinc(II) Complexes

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Zn(II)–tetraazacycloalkane complexes take up CO_2 in alcohol very easily and reversibly at room temperature to fix it into resulting complexes as monoalkyl carbonate. A series of Zn(II)–monoalkyl carbonato complexes, $\mathrm{Zn(L)(O_2COR)(ClO_4)}$ (L = $[14]\mathrm{aneN_4}$, $[15]\mathrm{aneN_4}$, $\mathrm{Me_2}[14]\mathrm{aneN_4}$, $\mathrm{Me_4}[14]\mathrm{aneN_4}$; R = CH_3, Et) and $[\mathrm{Zn(L)}]_3(\mathrm{O_2COR})_2(\mathrm{ClO_4})_4$ (L = $[15]\mathrm{aneN_4}$; R = *n*-Bu), have been obtained from the reactions with CO_2 and characterized by IR and NMR spectroscopies. Generally, addition of a base such as NaOR or NEt_3 facilitates the uptake reaction of CO_2. In systems of methanol solution of the $[14]\mathrm{aneN_4}$ or $[15]\mathrm{aneN_4}$ complex, the reaction proceeds spontaneously in a neutral solution below ca. 10 °C, CO_2 being taken up from the air. The monoalkyl carbonato complex ($\mathrm{Zn\text{–}O_2COR}$) exists in organic solvents such as chloroform and dichloromethane in equilibrium with its decarboxylated Zn–OR complex. The equilibrium involves reversible desorption and absorption of CO_2. A decrease in temperature makes the equilibrium shift toward the increase in the amount of the $\mathrm{Zn\text{–}O_2COR}$ complex. For the $[15]\mathrm{aneN_4}$ system, the equilibrium constant ($K = [\mathrm{Zn([15]aneN_4)\text{–}O_2COCH_3}]/[\mathrm{Zn([15]aneN_4)\text{–}OCH_3}][\mathrm{CO_2}]$) is found to be $K_{20.2\,°\mathrm{C}} = 5.8\ \mathrm{M^{-1}}$. The monoalkyl carbonato ligand has been converted into dialkyl carbonate by treatment with FSO_3R (R = CH_3, Et). Various factors influencing the efficient CO_2 uptake have been discussed.

Introduction

Coordination of CO_2 to a transition-metal complex and reactions of the resulting complex have been of interest in connection with the utilization of CO_2.[1] Besides direct coordination of CO_2 to transition metals with its intact form,[2] many insertion reactions of CO_2 into an M–X bond (X = H, C, O, N) have been reported.[3] Most cases of X = O are various metal alkoxides. Chisholm et al. proposed an alcohol-catalyzed chain mechanism for apparent CO_2 insertion into a Mo–O bond of $\mathrm{Mo_2(OR)_6}$ in solution.[3d]

$$\mathrm{ROH + CO_2 \rightleftharpoons ROCOOH}$$

$$\mathrm{M\text{–}OR + ROCOOH \rightarrow M\text{–}O_2COR + ROH} \qquad (1)$$

They also reported that reaction of dialkylamide complexes of

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(1) (a) Eisenberg, R.; Hendriksen, D. E. *Adv. Catal.* **1979**, *28*, 79. (b) Inoue, S.; Yamazaki, N., Eds. "Organic and Bioorganic Chemistry of Carbon Dioxide"; Kodansha: Tokyo, 1981.

(2) For example: (a) Calabrese, J. C.; Herskovitz, T.; Kinney, J. B. *J. Am. Chem. Soc.* **1983**, *105*, 5914. (b) Gambarotta, S.; Arena, F.; Floriani, C.; Zanazzi, P. F. *Ibid.* **1982**, *104*, 5082. (c) Aresta, M.; Nobile, C. F. *J. Chem. Soc., Chem. Commun.* **1975**, 636.

(3) See ref 1a, and references cited therein. The examples of CO_2 insertion into the M–O bond are: (a) Goodsel, A. J.; Blyholder, G. *J. Am. Chem. Soc.* **1972**, *94*, 6725. (b) Hidai, M.; Hikita, T.; Uchida, Y. *Chem. Lett.* **1972**, 521. (c) Tsuda, T.; Sanada, S.; Ueda, K.; Saegusa, T. *Inorg. Chem.* **1976**, *15*, 2329. (d) Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Reichert, W. W. *J. Am. Chem. Soc.* **1978**, *100*, 1727. (e) Aida, T.; Inoue, S. *Ibid.* **1983**, *105*, 1304.

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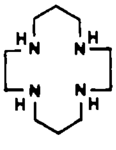
tungsten with CO_2 was not CO_2 insertion but proceeded through similar ligand exchange to give the $R_2NCO_2^-$ complex.[4] If reaction sites on a metal complex are designed in much more sophisticated way, similar uptake reactions of CO_2 will be possible in more efficient manner. We have found a new system of Zn(II) complexes containing tetraazacycloalkanes ([14]aneN_4 = 1,4,8,11-tetraazacyclotetradecane, [15]aneN_4 = 1,4,8,12-tetraazacyclopentadecane, Me_2[14]aneN_4 = 5,12-dimethyl-1,4,8,11-tetraazacyclotetradecane, Me_4[14]aneN_4 = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane), which take up CO_2 in alcohol as monoalkyl carbonate. Particularly fascinating characteristics of the present system are that the CO_2 uptake reactions proceed under very mild conditions and even in the presence of water (up to ca. 20% (v/v)) and that, in certain cases, CO_2 is taken up spontaneously from the air. In this paper, we report the syntheses and the characterizations of the monoalkyl carbonato complexes and their chemical properties. X-ray structural studies have been also carried out for the three monomethyl carbonato complexes, Zn([14]aneN_4)(O_2COCH_3)(ClO_4), [[Zn([15]aneN_4)]$_3$(O_2COCH_3)$_2$](ClO_4)$_4$, and [Zn(Me_4[14]aneN_4)(O_2COCH_3)](ClO_4), in order to investigate structural factors that cause the effective CO_2 fixation. The results will be reported in a subsequent paper.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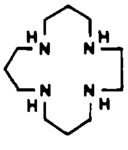
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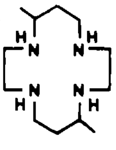
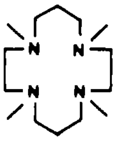

Me_2[14]aneN_4


Me_4[14]aneN_4

Experimental Section

Materials. The tetraazacycloalkanes, [14]aneN_4, [15]aneN_4, and Me_4[14]aneN_4, were purchased from Strem Chemical Inc. Me_2[14]aneN_4 was prepared according to the literature.[5] Commercial CO_2 was used without further purification for the syntheses of the compounds. But, in the preparation of NMR sample solutions, CO_2 passed through the columns of molecular sieves and $CaSO_4$ was used. $^{13}CO_2$ (90 atom % ^{13}C) and $^{13}CH_3OH$ (90 atom % ^{13}C) were purchased from Prochem. FSO_3CH_3 and FSO_3Et were purchased from Wako Pure Chemical Industries, Ltd., and Aldrich Chemical Co., respectively.

Preparations. Zn(L)(ClO_4)$_2$ (L = [14]aneN_4, [15]aneN_4, Me_2[14]aneN_4,[5] Me_4[14]aneN_4[6]). A methanolic solution of L was added to a methanolic solution containing an equimolar amount of $Zn(ClO_4)_2 \cdot 6H_2O$ with stirring at 50–60 °C. After 1 h, the solution was filtered and concentrated under the reduced pressure to yield a white precipitate. It was recrystallized from methanol to give colorless crystals. The results of elemental analyses were consistent with Zn(L)(ClO_4)$_2$ for all the compounds. IR (Nujol mull, cm^{-1}): L = [14]aneN_4, 3260 (NH), 1120 (ClO_4^-), 1040 (ClO_4^-), 626 (ClO_4^-), 616 (ClO_4^-); L = [15]aneN_4, 3270 (NH), 3230 (NH), 1100 (ClO_4^-), 622 (ClO_4^-); L = Me_2[14]aneN_4, 3260 (NH), 1120 (ClO_4^-), 1060 (ClO_4^-), 628 (ClO_4^-), 618 (ClO_4^-); L = Me_4[14]aneN_4, 1100 (ClO_4^-), 626 (ClO_4^-).

Zn([14]aneN_4)(O_2COR)(ClO_4) (1a, R = CH_3; 1b, R = Et). A methanol solution (50 mL) of [14]aneN_4 (2.0 g, 10 mmol) was added dropwise to a stirred methanol solution (30 mL) of $Zn(ClO_4)_2 \cdot 6H_2O$ (1.32 g, 10 mmol) under bubbling CO_2 at room temperature. The reaction with CO_2 was continued for several hours, and a resulting white solid was filtered. Recrystallization from methanol–acetonitrile under CO_2 atomosphere at 5 to −20 °C gave colorless needle crystals of **1a**, yield 56%. The same compound **1a** was also obtained without bubbling CO_2 from a methanol–water mixed solution (ca. 4:1 (v/v)) of Zn([14]aneN_4)(ClO_4)$_2$ by leaving it for several days in the air at ca. 5 °C.[7] Compound **1b** was prepared from an ethanol solution by a method similar to that for **1a** but addtion of a small amount of sodium or NEt_3 was required. Colorless needles were obtained by recrystallization from ethanol–acetonitrile; yield 55%. Anal. Calcd for $ZnClO_7N_4C_{12}H_{27}$ (**1a**): C, 32.74; H, 6.18; N, 12.73. Found: C, 32.43; H, 6.03; N, 12.57. Anal. Calcd for $ZnClO_7N_4C_{13}H_{29}$ (**1b**): C, 34.38; H, 6.44; N, 12.33. Found: C, 34.09; H, 6.25; N, 12.56.

Zn([15]aneN_4)(O_2COR)(ClO_4) (2a, R = CH_3; 2b, R = Et) and [Zn([15]aneN_4)]$_3$(O_2CO-*n*-Bu)$_2$(ClO_4)$_4$ (2c). These complexes were prepared by a method similar to that for **1a** by using [15]aneN_4 and corresponding alcohols. Recrystallizations of **2a** and **2b** were carried out under CO_2 atomosphere from methanol and ethanol, respectively. In the case of **2c**, a 1:1 complex formulated as Zn([15]aneN_4)(O_2CO-*n*-Bu)(ClO_4) was not obtained at all even in the presence of excess of NEt_3. Recrystallization of the crude product from 1-butanol–acetonitrile under CO_2 atomosphere gave crystals of a 3:2 complex, [Zn([15]aneN_4)]$_3$(O_2CO-*n*-Bu)$_2$(ClO_4)$_4$; yield 52, 81, and 80% for **2a**, **2b**, and **2c**, respectively. Anal. Calcd for $ZnClO_7N_4C_{13}H_{29}$ (**2a**): C, 34.37; H, 6.44; N, 12.33. Found: C, 34.09; H, 6.59; N, 12.20. Anal. Calcd for $ZnClO_7N_4C_{14}H_{31}$ (**2b**): C, 35.91; H, 6.67; N, 11.96. Found: C, 35.79; H, 6.72; N, 12.01. Anal. Calcd for $Zn_3Cl_4O_{22}N_{12}C_{43}H_{96}$ (**2c**): C, 35.10; H, 6.58; N, 11.42. Found: C, 35.05; H, 6.66; N, 11.39.

Zn(Me_2[14]aneN_4)(O_2COCH_3)(ClO_4) (3) and Zn(Me_4[14]aneN_4)(O_2COR)(ClO_4) (4a, R = CH_3; 4b, R = Et). These complexes were prepared through a reaction in the presence of NEt_3 or NaOR in a similar way. The crude product was recrystallized at 5 to −20 °C under CO_2 atomosphere from methanol for **3** and **4a** and from ethanol for **4b**; yield 49, 72, and 38% for **3**, **4a**, and **4b**, respectively. Anal. Calcd for $ZnClO_7N_4C_{14}H_{31}$ (**3**): C, 35.91; H, 6.67; N, 11.96. Found: C, 35.80; H, 6.79; N, 12.22. Anal. Calcd for $ZnClO_7N_4C_{16}H_{35}$ (**4a**): C, 38.72; H, 7.11; N, 11.29. Found: C, 38.66; H, 6.90; N, 11.23. Anal. Calcd for $ZnClO_7N_4C_{16}H_{35}$ (**4b**): C, 40.01; H, 7.31; N, 10.98. Found: C, 39.46; H, 7.07; N, 11.23.

Zn([15]aneN_4)($O_2{}^{13}COCH_3$)(ClO_4). $^{13}CO_2$ (ca. 9 mmol) was condensed into a reaction vessel containing a methanol solution (30 mL) of Zn([15]aneN_4)(ClO_4)$_2$ (0.5 mmol) and $NaOCH_3$ (0.5 mmol) by using standard vacuum line techniques. After the solution was stirred for a while at room temperature, it was cooled down to −20 °C. White crystals came out of the solution; yield 31%.

Zn([15]aneN_4)($O_2CO^{13}CH_3$)(ClO_4). Zn([15]aneN_4)(ClO_4)$_2$ (0.2 mmol) and sodium (0.2 mmol) were added to $^{13}CH_3OH$ (1 mL). The resulting suspension was kept at 40–50 °C for several hours under CO_2 atomosphere. It was cooled down to −20 °C, and then a white precipitate was filtered; yield 60%.

Measurements. Infrared spectra were recorded on a Jasco IR-810 or a Hitachi 295. NMR spectra were obtained on a JEOL FX-100 at 100 MHz or a JEOL JNM-GX400 at 400 MHz for ^1H NMR and on a JEOL FX-100 at 25 MHz or a JEOL JNM-GX400 at 100 MHz for ^{13}C NMR. Mass spectra were measured on a Hitachi M-80.

The variable-temperature ^1H and ^{13}C NMR spectral measurements were carried out in order to obtain thermodynamic parameters for the equilibrium of eq 2. Degassed $CDCl_3$ was vacuum distilled into the NMR tube that contained 15 mg of solid Zn([15]aneN_4)(O_2COCH_3)(ClO_4). After the pressure was adjusted to 1 atm at room temperature, the NMR tube was sealed off. The sample solution was prepared at the concentration of 4.6×10^{-2} M. The concentrations of the Zn–O_2COCH_3 and Zn–OCH_3 complexes at each temperature were evaluated from an integrated intensity ratio of the methyl protons of each on ^1H NMR. The concentration ratio between ZnO_2COCH_3 and CO_2 in solution was estimated via the ^{13}C NMR from the intensities of carbonato carbon and CO_2, assuming that the relaxation times of these species are not appreciably different. For this experiment, the isotopically labeled compound, Zn([15]aneN_4)($O_2{}^{13}COCH_3$)(ClO_4), was used.

Results

Syntheses of Monoalkyl Carbonato Complexes through Reaction with CO_2. A series of Zn(II)–tetraazacycloalkane complexes, Zn(L)(ClO_4)$_2$, take up CO_2 in alcohol at room temperature to give the monoalkyl carbonato complexes, Zn(L)(O_2COR)(ClO_4). Reaction routes are shown in Scheme I. The monoalkyl carbonato complex is obtained by bubbling CO_2 through an alcoholic solution containing equimolar amounts of $Zn(ClO_4)_2 \cdot 6H_2O$ and L. When a stream of CO_2 is not bubbled, the reaction gives only Zn(L)(ClO_4)$_2$. But the resulting Zn(L)(ClO_4)$_2$ also reacts with CO_2 in alcohol to give Zn(L)(O_2COR)(ClO_4). Generally, addition of a small amount of base such as NaOR or NEt_3 facilitates markedly the CO_2 fixation. As shown in Scheme I, the reaction with CO_2 is reversible. When an alcoholic solution of monoalkyl carbonato complex is purged with a stream of N_2 or is allowed to warm to ca. 50 °C, the starting complex, Zn(L)(ClO_4)$_2$, is recovered.

Efficiency of the CO_2 uptake differs strongly depending on the kinds of macrocyclic ligands and alcohols and/or the amount of base added. Among the tetraazacycloalkanes studied, the complexes with [14]aneN_4 and [15]aneN_4 take up CO_2 most effi-

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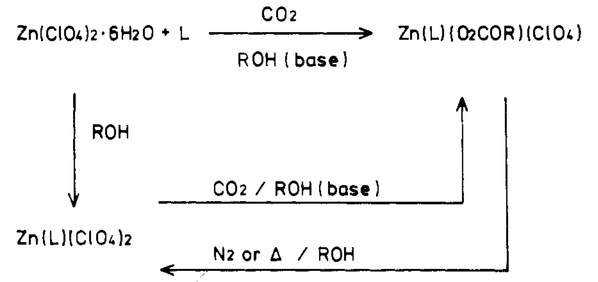
[4] Chisholm, M. H.; Extine, M.W. *J. Am. Chem. Soc.* **1977**, *99*, 792.

[5] Hay, R. W.; Piplani, D. P. *J. Chem. Soc., Dalton Trans.* **1977**, 1956.

[6] Barefield, E. K.; Wagner, F. *Inorg. Chem.* **1973**, *12*, 2435.

[7] A crystal specimen thus obtained was subjected to the X-ray analysis in the subsequent paper.

Scheme I



$Zn(L)(O_2COR)(ClO_4)$

1a: L = [14]aneN_4, R = CH_3 1b: L = [14]aneN_4, R = Et
2a: L = [15]aneN_4, R = CH_3 2b: L = [15]aneN_4, R = Et
3: L = Me_2[14]aneN_4, R = CH_3
4a: L = Me_4[14]aneN_4, R = CH_3 4b: L = Me_4[14]aneN_4, R = Et

$[Zn(L)]_3(O_2COR)_2(ClO_4)_4$
2c: L = [15]aneN_4, R = n-Bu

Table I. IR Data (cm^{-1}) Associated with the $-OCO_2^-$ Group

compd	ν_1[a]	ν_2[a]	π[b]	$\Delta\nu$[c]
$Zn([14]aneN_4)(O_2COCH_3)(ClO_4)$ (1a)	1638	1316	816	322
$Zn([14]aneN_4)(O_2COEt)(ClO_4)$ (1b)	1634	1306	814	328
$Zn([15]aneN_4)(O_2COCH_3)(ClO_4)$ (2a)	1635	1310	806	325
$Zn([15]aneN_4)(O_2{}^{13}COCH_3)(ClO_4)$	1590	1294	790	296
$Zn([15]aneN_4)(O_2COEt)(ClO_4)$ (2b)	1628	1304	810	324
$[Zn([15]aneN_4)]_3(O_2CO\text{-}n\text{-}Bu)_2(ClO_4)_4$ (2c)	1636	1308	810	328
$Zn(Me_2[14]aneN_4)(O_2COCH_3)(ClO_4)$ (3)	1628	1312	810	316
$Zn(Me_4[14]aneN_4)(O_2COCH_3)(ClO_4)$ (4a)	1676	1310	808	366
$Zn(Me_4[14]aneN_4)(O_2COEt)(ClO_4)$ (4b)	1660	1300	806	360

[a] Stretching. [b] Out-of plane bending. [c] $\Delta\nu = \nu_1 - \nu_2$.

ciently. In the case of the systems containing these particular macrocycles, the monoalkyl carbonato complexes were obtained even from the reaction in the absence of base. Furthermore, complexes **1a** and **2a** were also isolated from base-free methanolic solution by the slow reaction without bubbling CO_2 below 10 °C, CO_2 being taken up spontaneously from the air. In other systems, however, addition of base was necessary to isolate the monoalkyl carbonato complexes in a pure form. The reaction with CO_2 under base-free conditions afforded in most cases a mixture of the desired complex and the starting material, $Zn(L)(ClO_4)_2$. In the systems with Me_2[14]aneN_4 and Me_4[14]aneN_4, the monoalkylcarbonato complexes were not obtained at all from the base-free reactions.

As we go from CH_3OH to EtOH and to n-BuOH, the reactivity of $Zn(L)(ClO_4)_2$ with CO_2 was lowered. In the case of R = n-Bu, a 1:1 complex formulated as $Zn(L)(O_2CO\text{-}n\text{-}Bu)(ClO_4)$ was not produced. Instead, a 3:2 complex $[Zn(L)]_3(O_2CO\text{-}n\text{-}Bu)_2(ClO_4)_4$, was obtained as a single product. The composition ratio of 3:2 is identical with that of $[[Zn([15]aneN_4)]_3(O_2COCH_3)_2](ClO_4)_4$, the structure of which has been established by the X-ray analysis.[8]

IR Spectra. All the monoalkyl carbonato complexes showed three IR bands characteristic of an OCO_2 group (Table I). Two strong absorptions due to stretching vibration (ν) and a medium or weak out-of-plane bent band (π) appeared around 1650, 1310, and 810 cm^{-1}, respectively, as in monoalkyl carbonato complexes of other metal ions.[3a-c] Isotopical shifts observed for the ^{13}C-labeled compound, $Zn([15]aneN_4)(O_2{}^{13}COCH_3)(ClO_4)$, supported the band assignments given in Table I. But, a stretching band expected at about 1000 cm^{-1} could not be assigned owing to the overlap with very strong ClO_4^- absorption.

^1H and ^{13}C NMR Spectra. Table II lists relevant ^1H and ^{13}C NMR spectral data. It was found from NMR spectral studies that, in a $CDCl_3$ and CD_2Cl_2 solution, the monomethyl carbonato complex ($Zn-O_2COR$) undergoes partial decarboxylation to give an equilibrium mixture of the parent $Zn-O_2COR$ complex and its decarboxylated Zn–OR complex.

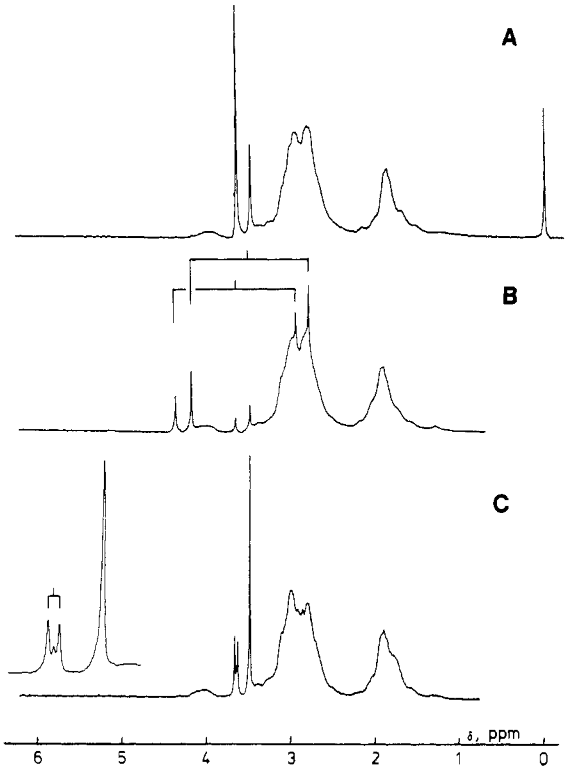


Figure 1. ^1H NMR spectra of $Zn([15]aneN_4)(O_2COCH_3)(ClO_4)$ (A) and its ^{13}C-labeled derivatives, $Zn([15]aneN_4)(O_2CO^{13}CH_3)(ClO_4)$ (B) and $Zn([15]aneN_4)(O_2{}^{13}COCH_3)(ClO_4)$ (C) in $CDCl_3$. The inset in spectrum C shows an expanded spectrum of the region δ 3.4–3.8.

As a typical example, ^1H NMR spectra of **2a** and its ^{13}C-labeled derivatives in $CDCl_3$ are shown in Figure 1. The spectrum of the unlabeled compound (Figure 1A) shows two sharp singlets at 3.48 and 3.65 ppm in addition to three broad bands due to the macrocyclic ligand (CCH_2C, δ 1.7–2.1; NCH_2, δ 2.6–3.4; NH, δ 4.0). Both of the singlets turn into a doublet respectively in the spectrum of the isotopically labeled compound derived from $^{13}CH_3OH$, $Zn([15]aneN_4)(O_2CO^{13}CH_3)(ClO_4)$, (δ 3.48 ($^1J_{^{13}CH}$ = 141 Hz), 3.65 ($^1J_{^{13}CH}$ = 145 Hz)) (Figure 1B). On the other hand, in a spectrum of $Zn([15]aneN_4)(O_2{}^{13}COCH_3)(ClO_4)$ derived from $^{13}CO_2$, only the signal at 3.65 ppm was observed as a doublet ($^3J_{^{13}CH}$ = 3.7 Hz), while the singlet at 3.48 ppm remained unchanged (Figure 1C). The value of $^3J_{^{13}CH}$ is close to that reported for $Mo_2(OCH_2CMe_3)_4(O_2{}^{13}COCH_2CMe_3)_2$ ($^3J_{^{13}CH}$ = 3 Hz).[3d] The results indicate that both singlets of the unlabeled compound originate from CH_3 protons of monomethyl carbonato ligand and that the monomethyl carbonato complex ($Zn-O_2COCH_3$, δ 3.65) coexists with its decarboxylated complex ($Zn-OCH_3$, δ 3.48) in equilibrium. ^{13}C NMR spectral data of **2a** in $CDCl_3$ also support the coexistence of the $Zn-O_2COCH_3$ and $Zn-OCH_3$ complexes, as evidenced by unequivocal assignments of key signals (for $Zn-O_2COCH_3$, CH_3 δ 53.7, O_2CO δ 160.6; for $Zn-OCH_3$, δ 50.8; for free CO_2, δ 124.9).[9] NMR spectral data for other complexes in $CDCl_3$ are interpreted in a similar way by assuming the occurrence of such equilibria (Table II).

^{13}C resonances due to carbonate carbons of the $Zn-O_2COR$ complexes were observed around 160 ppm (Table II). Only the Me_4[14]aneN_4 complexes, **4a** and **4b**, showed the signal at slightly higher field (average 158.6 ppm) than other complexes. This fact reflects a difference in the coordination mode of $ROCO_2^-$ as discussed later.

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(8) Kato, M.; Ito, T. *Inorg. Chem.*, following paper in this issue.

(9) The signal assignments were made, with the aid of isotopically labeled derivatives, by selective proton decoupling and off-resonance decoupling experiments.

Table II. ^{1}H and ^{13}C NMR Spectral Data (δ)[a]

	^{1}H		^{13}C			
compd	OR	O_2COR	OR	O_2COR	O_2COR	macrocycle
1a[b]						28.7, 48.4, 50.7, 24.9, 28.2, 46.9, 47.1, 49.7, 51.3
1b[c]	1.27 (t)	1.25 (t)				28.7, 48.4, 50.7, 24.9, 28.2, 46.9, 47.1, 49.7, 51.3
	3.73 (q)	4.01 (q)				
2a	3.48 (s)	3.65 (s)	50.8	53.7	160.6	25.1, 28.1, 28.2, 47.1, 48.4, 50.1, 51.4, 52.3, 52.4, 53.6, 54.4
2b	1.29 (t)	1.24 (t)	18.5	15.0	160.3	25.1, 28.0, 28.1, 47.2, 48.4, 49.9, 51.5, 52.4, 52.5, 53.6, 54.9
	3.72 (q)	4.04 (q)	58.5	62.2		
2c	0.94 (t)		13.9		160.5	25.0, 27.9, 28.0, 47.3, 47.9, 48.3, 49.6, 50.3, 51.5, 52.5, 52.6, 53.0, 53.5
	1.39 (sext)		18.9	19.2		
	1.56 (quint)		34.9	31.5		
	3.66 (t)	3.98 (t)	62.8	66.5		
3	3.48 (s)	3.62 (s)	50.8	53.5	160.5	21.1, 35.9, 45.5, 47.9, 49.5, 56.2
4a	3.50 (s)	3.62 (s)	50.8	53.6	158.8	21.4, 44.5, 56.8, 60.2
4b	1.24 (t)		18.5	15.0	158.4	21.4, 44.6, 56.8, 60.3
	3.72 (q)	4.01 (q)	58.5	62.0		

[a] In $CDCl_3$ solution except for ^{1}H and ^{13}C NMR spectra of 1a and ^{13}C NMR spectra of 1b. [b] Data in D_2O. Because of the low solubility, spectra in $CDCl_3$ were not obtained. [c] ^{13}C NMR data were obtained on D_2O solution.

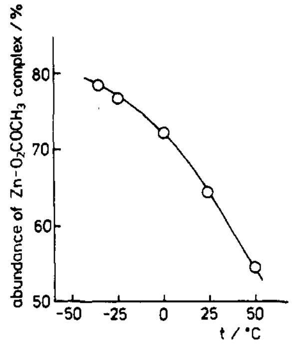


Figure 2. Relative abundance of the $Zn\text{-}O_2COCH_3$ complex in the equilibrium of eq 2 at various temperatures.

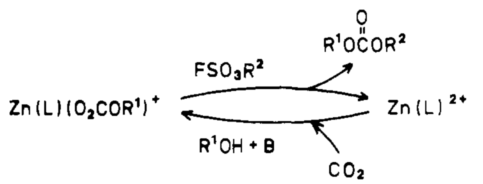
The ^{13}C NMR spectral pattern of a macrocyclic ligand moiety was very sensitive to the temperature. At room temperature, it shows generally a spectral pattern such that a single species exists in solution. For example, the [15]aneN_4 ligand in **2a** shows 11 peaks at room temperature corresponding to all inequivalent methylene carbons. The signals are definitely broader than the resonance lines due to the monomethyl carbonate or the methoxy group. As temperature is lowered down to −50 °C, the spectrum of the portion of [15]aneN_4 ligand becomes increasingly complicated.[10] The situation was similar for other compounds. In D_2O solution, monoalkyl carbonato complexes were hydrolyzed completely to give alcohol, CO_2, and possibly a carbonato complex of $[Zn(L)]^{2+}$, and so on. The hydrolysis occurred also in organic solvents such as acetonitrile and dimethyl sulfoxide by the presence of a trace amount of water.

Reversible Absorption and Desorption of CO_2. The equilibrium of eq 2 was studied on a $CDCl_3$ solution of **2a** in a sealed NMR tube by monitoring signal intensities of the $Zn\text{-}O_2COCH_3$ singlet at δ 3.65 and the $Zn\text{-}OCH_3$ singlet at δ 3.48 as a function of temperature. Figure 2 shows the relative abundance of the

$$Zn(L)\text{-}O_2COR \rightleftharpoons Zn(L)\text{-}OR + CO_2 \qquad (2)$$

$Zn\text{-}O_2COCH_3$ complex present in the solution at various temperatures. A decrease in temperature makes the equilibrium shift to increase the amount of the $Zn\text{-}O_2COCH_3$ complex. The spectral changes were completely reversible in the range of −40 to +60 °C. Thus, CO_2 is absorbed and desorbed reversibly. The equilibrium constants ($K = [Zn(L)\text{-}O_2COR]/[Zn(L)\text{-}OR][CO_2]$) were determined to be $K_{60.4 °C} = 2.2$, $K_{40.3 °C} = 3.0$, $K_{20.3 °C} = 5.8$, $K_{0.4 °C} = 12$, $K_{-19.7 °C} = 34$, and $K_{-40.3 °C} = 49\ M^{-1}$ under the experimental conditions (see Experimental Section). A plot of ln K vs. $1/T$ gave the straight line relationship in the temperature range of −20 to +40 °C. This yielded values of ΔH and ΔS of −27 kJ mol^{-1} and −76 J K^{-1} mol^{-1}, respectively.

Scheme II



Conversion of the Coordinated $ROCO_2^-$ Ligand into Dialkyl Carbonate. The monoalkyl carbonato ligand, $R^1OCO_2^-$, of the Zn complexes was successfully converted into dialkyl carbonate, R^1OCOR^2, by treating with FSO_3R^2 (Scheme II). The alkylation of $R^1OCO_2^-$ was pursued with ^{1}H NMR. When a small excess of FSO_3CH_3 was added to a $CDCl_3$ solution of **2a**, the methyl proton singlet of $Zn\text{-}O_2COCH_3$ at δ 3.65 decreased gradually and a new singlet appeared at δ 3.80, the chemical shift of which was exactly the same as that of authentic dimethyl carbonate. After 24 h, the signal at δ 3.65 disappeared completely and the peak at δ 3.80 became much stronger, while the signal at δ 3.48 still remained. The alkylation involves a side reaction to produce a small amount of $(CH_3)_2O$ (3.31 ppm). The yield of dimethyl carbonate was about 50% based on the initial concentration of the monomethyl carbonato complex. The apparent yield could be raised under such conditions that the equilibrium of eq 2 shifts to the left, that is, by the reaction under CO_2 atomosphere at low temperature. On addition of pentane to the solution after completion of the methylation, a precipitate of Zn(II) complex with [15]aneN_4 came out of the solution. The filtrate was subjected to GC–mass spectral analysis. A parent peak position at m/e 90 and its fragmentation pattern were consistent with those of authentic dimethyl carbonate. The recovered white solid reacted again with CO_2 in methanol to give **2a** as shown in Scheme II. In a similar way, methyl ethyl carbonate (δ 1.31 (t), 3.78 (s), 4.21 (q)) was obtained either by the reaction of **2a** with FSO_3Et or by the reaction of **2b** with FSO_3CH_3.

Discussion

The CO_2-uptake reactions by the present macrocyclic Zn(II) complexes are so facile that, in certain cases, CO_2 is taken up spontaneously from the air in neutral solution. However, addition of base was necessary to make the preparation of the monoalkyl carbonato complexes more efficient. As to the effect of base, there was no difference between NaOR and NEt_3, the former of which has coordinating anion whereas the latter is difficult to coordinate to the metal ion. Therefore, the base (B) is considered to play

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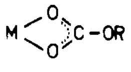
[10] The reasons that cause the temperature-dependent ^{13}C NMR spectra are uncertain, but the following explanations may be conceivable: (i) The macrocyclic ligands in the equilibrated species are magnetically equivalent at room temperature because of weak interactions between Zn and $CH_3OCO_2^-$ or CH_3O^-. (ii) A temperature-dependent conformational change is occurring (cf.: Alcock, N. W.; Herron, N.; Moor, P. *J. Chem. Soc., Dalton Trans.* **1972**, 1282).

the role of raising the concentration of monoalkyl carbonate in solution according to eq 3. All the observed data suggest that

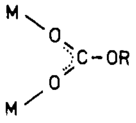
$$ROH + CO_2 + B \rightleftharpoons ROCO_2^- + BH^+ \qquad (3)$$

the monoalkyl carbonato complexes are formed by the direct reaction of ZnL^{2+} with $ROCO_2^-$, which has been produced from CO_2 in an alcoholic solution. The CO_2-uptake reactions effected by the present Zn^{2+} complexes seem to be of the same type as the system of Chishom et al.[3d]

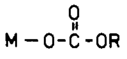
Efficiency of the CO_2 uptake depends strongly on the system. Possible coordination geometries about the central metal and a choice of ligand are important factors. IR spectral data suggest that there are two types of $ROCO_2^-$ coordination modes. When two CO stretching bands, ν_1 and ν_2 in Table I, are compared for the series of monoalkyl carbonato complexes, spectral patterns of the Me_4[14]aneN_4 complexes have a different trend from those of other compounds. The ν_1 bands at 1676 cm^{-1} for **4a** and at 1660 cm^{-1} for **4b** are at higher frequencies than those of other complexes ($\sim$1630 cm^{-1}). Furthermore, the ν_1 band is weaker than the ν_2 band for **4a** and **4b**, while the intensity relationship is reversed for other compounds. It has been pointed out for carbonato complexes that the degree of the separation between these two CO stretching bands differes depending on a coordination mode of CO_3^{2-}.[11] A similar discussion has been made for the coordination mode of CH_3COO^- in various acetato complexes: the separation between the two stretching bands is much larger in unidentate coordination and is smaller in bidentate coordination than in free ion; in binuclear complexes with bridged $CH_3CO_2^-$, the two ν(CO) are close to respective values of free ion.[11] The differences ($\Delta\nu$) between ν_1 and ν_2 for the present monoalkylcarbonato complexes are compared in Table I. As to the value of $\Delta\nu$, a small but clear distinction can be noted between complexes **1a**–**3** and complexes **4a** and **4b**. The free $CH_3OCO_2^-$ ion shows ν_1 at 1640 cm^{-1} and ν_2 at 1310 cm^{-1}, and thus $\Delta\nu$ amounts to 330 cm^{-1}.[12] The $\Delta\nu$'s for **1a**–**3** are close to the free-ion value, whereas those of **4a** and **4b** are definitely larger than 330 cm^{-1}. This suggests strongly that $ROCO_2^-$ in **4a** and **4b** acts as a unidentate ligand (structure III), while $ROCO_2^-$ in other compounds is involved in bridging or bidentate coordination (structures I or II).



I



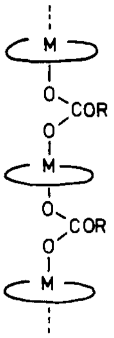
II



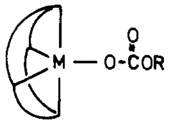
III

The difference in the coordination modes of $ROCO_2^-$ was also evident in the chemical shifts of the carbonate carbon atoms in the ^{13}C NMR spectra (Table II). The resonances of carbonate carbons of the Me_4[14]aneN_4 complexes (unidentate coordination) are upper field by ca. 2 ppm from those of other complexes with two equivalent CO bonds.

The results obtained from the IR and NMR spectral data concerning the coordination mode have been confirmed by the X-ray structural analyses of **1a**, **2a**, and **4a**.[8] The [14]aneN_4, [15]aneN_4, and Me_2[14]aneN_4 complexes assume structure IV, that is, a linear-chain structure formed by bridge coordination of the monoalkyl carbonato ligand. On the other hand, the Me_4[14]aneN_4 complexes belong to structural type V, which is a mononuclear structure with unidentate monoalkyl carbonato ligand.



IV



V

The roles played by the tetraazacycloalkanes and Zn^{2+} are essentially important. Coordination of tetraazacycloalkane leaves the Zn^{2+} coordinately unsaturated. That is, it gives rise to reactive vacant sites at Zn^{2+} in the octahedral or trigonal-bipyramidal geometry, where the uptake reaction of $ROCO_2^-$ takes place. The macrocycle with an appropriate cavity size must bring about such circumstances. In other words, it is important to design the parent ligand such that the Zn(II) complex cannot assume a stable tetrahedral geometry. In fact, neither an analogous Zn(II) complex containing a similar tetraazacycloalkane with a larger cavity size ([16]aneN_4) nor Zn(II) complexes containing flexible linear tetraamines such a 1,4,7,10-tetraazadecane or 1,5,8,12-tetraazadodecane gave the desired monoalkyl carbonato complexes under the same conditions. Possibly, a natural cavity size of [16]aneN_4 is somewhat larger than necessary to surround Zn^{2+} in a planar fashion, and thereby the resulting Zn([16]aneN_4) complex has coordination geometry with tetrahedral character. In order to investigate the role of the metal ion, we have tried similar CO_2-uptake reactions by Ni(II) and Cu(II) complexes with the same macrocyclic ligands. The Ni(II) system gave analogous monoalkyl carbonato complexes,[13] while Cu^{2+} did not work at all. There is no doubt that this stems from a difference in the reactivity of axial position between the square-planar four-coordinate Ni(II) and Cu(II) complexes. In the reaction of the Ni(II) complex, addition of base was necessary even for the [14]aneN_4 or [15]aneN_4 system and the efficiency was significantly lower than for the Zn(II) complexes. This is apparently because square-planar coordination for Ni^{2+} is more stable than for Zn^{2+}. On the other hand, the square-planar geometry resulting from coordination of tetraazacycloalkanes is very rare for Zn^{2+}. The Zn^{2+} under such circumstances must be very reactive and should tend to take up additional ligands to form a five- or six-coordinate complex. Such situations would be the driving force for the effective CO_2-uptake by the present complexes.

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(11) Nakamoto, K. "Infrared and Raman Spectra of Inorganic and Coordination Compounds"; Wiley: New York, 1978.

(12) The spectrum of free $CH_3OCO_2^-$ was obtained on CO_2-saturated methanol containing NEt_3.

(13) Details will be reported elsewhere.