Syntheses, Characterization, and Structures of (Monomethyl Carbonato)-Nickel(II), -Copper(II), and -Cobalt(II) Complexes with Tetraazacycloalkanes Obtained from CO_2 Uptake

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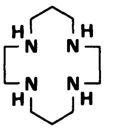
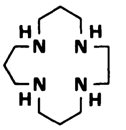
A new series of monomethyl carbonato complexes of nickel(II), cobalt(II), and copper(II) containing tetraazacycloalkanes (L) have been synthesized and characterized: $Ni(L)(O_2COCH_3)(ClO_4)$ (L=[14]aneN_4 (**1**); L=[15]aneN_4 (**2**); L=*iso*-[14]aneN_4 (**3**); L=*RSRS*-Me_4[14]aneN_4 (**4**)), [Ni(*RRSS*-Me_4[14]aneN_4)$(O_2COCH_3)_2$]·$HNEt_3ClO_4$ (**5**), Cu([14]aneN_4)$(O_2COCH_3)(ClO_4)$ (**6**), [Cu(Me_4[14]aneN_4)(O_2COCH_3)]$(ClO_4)\cdot CH_3OH$ (**7**), and Co(L)$(O_2COCH_3)(ClO_4)$ (L=[15]aneN_4 (**8**); L=Me_4[14]aneN_4 (**9**)), where [14]aneN_4=1,4,8,11-tetraazacyclotetradecane, [15]aneN_4=1,4,8,12-tetraazacyclopentadecane, *iso*-[14]aneN_4=1,4,7,11-tetraazacyclotetradecane, Me_4[14]aneN_4=1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane, *RSRS*-=1*RS*,4*SR*,8*RS*,11*SR*-, and *RRSS*-=1*RS*, 4*RS*,8*SR*,11*SR*-. These compounds have been obtained through CO_2 uptake reaction in basic methanol from the corresponding four-coordinate complex, [M(L)]$(ClO_4)_2$. X-Ray structures of three compounds, **4**, **5**, and **6**, have been determined. Compound **4** is a five-coordinate complex with the trigonal bipyramidal geometry (Type II), in which $CH_3OCO_2^-$ is coordinated in a unidentate fashion. Compound **5** is a tetragonally distorted six-coordinate complex with two unidentate $CH_3OCO_2^-$ at axial sites (Type III). Compound **6** is also a tetragonally distorted six-coordinate complex but the $CH_3OCO_2^-$ ligand bridges two neighboring [Cu([14]aneN_4)]$^{2+}$ to form a linear chain structure (Type I). All the monomethyl carbonato complexes synthesized are classified into these three types on the basis of IR and/or electronic spectral data, supplemented with the X-ray results. Efficiency of the CO_2 uptake depends strongly on the coordination structure which is controlled by a combination of metal ion and tetraazacycloalkane. Differences in reactivity among the complexes of various metal ions and factors influencing the efficiency have been discussed in connection with the zinc(II) system which undergoes the most effective CO_2 uptake of this type.

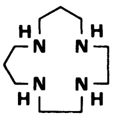
Recently we reported facile CO_2 uptake by zinc(II) complexes containing tetraazacycloalkanes (L).[1] In the system, CO_2 is taken up very easily, in certain cases spontaneously from the air, as monoalkyl carbonate ion in alcohol (ROH) under mild conditions to give Zn(L)$(O_2COR)(ClO_4)$. It is thought that square-planar coordination of a tetraazacycloalkane with an appropriate cavity size leaves the Zn^{2+} ion coordinately unsaturated and that it makes the effective uptake reaction possible. Therefore, coordination structure controlled by a combination of tetraazacycloalkane and metal ion is an important factor for such the CO_2 uptake. In this paper, we synthesized a new series of monomethyl carbonato complexes using various divalent metal ions, Co^{2+}, Ni^{2+}, and Cu^{2+}, and tetraazacycloalkanes shown below[2] in order to compare efficiency of the CO_2 uptake and to explore its factors. Aiming to investigate structural factors, single crystal X-ray analyses have been also carried out on three monomethyl carbonato complexes, [Ni(*RSRS*-Me_4[14]aneN_4)(O_2COCH_3)](ClO_4),[3] [Ni(*RRSS*-Me_4[14]aneN_4)$(O_2COCH_3)_2$]·$HNEt_3ClO_4$,[3] and Cu([14]aneN_4)$(O_2COCH_3)$$(ClO_4)$, which have different coordination geometries.



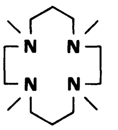
[14] ane N_4



[15] ane N_4



iso-[14] ane N_4



Me_4 [14] ane N_4

Experimental

Materials. The tetraazacycloalkanes, [14]aneN_4, [15]aneN_4, and Me_4[14]aneN_4, were purchased from Strem Chemical Inc. *Iso*-[14]aneN_4 was prepared according to the literature.[4] Starting nickel(II) complexes, [Ni(L)]$(ClO_4)_2$ (L=[14]aneN_4, [15]aneN_4, *iso*-[14]aneN_4, *RSRS*-Me_4[14]aneN_4), were prepared from the free ligands L and $Ni(ClO_4)_2\cdot 6H_2O$ in methanol and recrystallized from water or methanol. [Ni(*RRSS*-Me_4[14]aneN_4)]$(ClO_4)_2$ was prepared by *N*-methylation of the complex, [Ni([14]aneN_4)]$(ClO_4)_2$.[5] [Cu([14]aneN_4)]$(ClO_4)_2$ was obtained as follows. A methanolic solution of [14]aneN_4 was mixed with an equimolar amount of $CuCl_2$ in methanol under stirring. After a while, addition of a methanolic solution of $NaClO_4$ to this solution gave purple precipitate, which was recrystallized from hot methanol containing a small amount of 2,2-dimethoxypropane or $NaOCH_3$. On cooling, red-purple needles came out of the solution. The same procedure was applied to the synthesis of [Cu([15]aneN_4)]$(ClO_4)_2$ to give blue-violet crystals. The blue-violet complex, [Cu(Me_4[14]aneN_4)]$(ClO_4)_2$, was prepared by the reaction of $Cu(ClO_4)\cdot 6H_2O$ and Me_4[14]aneN_4 in methanol. FSO_3CH_3 was purchased from Wako Pure Chemical Industries, Ltd.

Ni(L)$(O_2COCH_3)(ClO_4)$ (1, L=[14]aneN_4; 2, L=[15]aneN_4; 3, L=*iso*-[14]aneN_4): CO_2 gas was bubbled into a methanol solution (50—100 cm^3) of Ni(L)$(ClO_4)_2$ (1 mmol)

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containing NEt_3 (1 mmol) at room temperature. After a while, a precipitate began to come out of the solution, but a stream of CO_2 was passed through the solution further for several hours. Pale pink, blue, and purple products of **1**, **2**, and **3**, were filtered and washed with methanol. Yield 89, 83, and 72% for **1**, **2**, and **3**, respectively. Found for **1**: C, 33.29; H, 6.39; N, 12.97%. Calcd for $NiClO_7N_4C_{12}H_{27}$: C, 33.25; H, 6.28; N, 12.92%. Found for **2**: C, 34.52; H, 6.16; N, 12.38%. Calcd for $NiClO_7N_4C_{13}H_{29}$: C, 34.89; H, 6.53; N, 12.52%. Found for **3**: C, 33.53; H, 6.37; N, 13.16%. Calcd for $NiClO_7N_4C_{12}H_{27}$: C, 33.25; H, 6.28; N, 12.92%.

[Ni(*RSRS*-Me$_4$[14]aneN$_4$)(O$_2$COCH$_3$)](ClO$_4$) (4) and [Ni(*RRSS*-Me$_4$[14]aneN$_4$)(O$_2$COCH$_3$)$_2$]·HNEt$_3$ClO$_4$ (5): When a stream of CO_2 was bubbled through a methanolic solution (50 cm^3) of Ni(*RSRS*-Me$_4$[14]aneN$_4$)(ClO$_4$)$_2$ (1 mmol) in the presence of an excess of NEt_3, color of the solution turned green immediately from pink-red. The solution was rotoevaporated to ca. 10 cm^3 and stood for a few days at −20 °C under CO_2 atmosphere to give green crystals of **4**. The blue complex **5** was prepared in a similar way from [Ni(*RRSS*-Me$_4$[14]aneN$_4$)](ClO$_4$)$_2$. Compound **5** was also obtained from the green methanolic solution containing [Ni(*RSRS*-Me$_4$[14]aneN$_4$)](ClO$_4$)$_2$, a large excess of NEt_3, and saturated CO_2 via configurational change of Me$_4$[14]aneN$_4$, when the solution was allowed to stand for several weeks. Found for **4**: C, 38.94; H, 6.79; N, 11.54%. Calcd for $NiClO_7N_4C_{16}H_{35}$: C, 39.25; H, 7.09; N, 11.44%. Compound **5** could not be analyzed because it decomposed rapidly in the air, but its composition is unambiguous from the X-ray analysis (vide infra).

Cu(L)(O$_2$COCH$_3$)(ClO$_4$)·*n*CH$_3$OH (6, L=[14]aneN$_4$, *n*=O; 7, L=Me$_4$[14]aneN$_4$, *n*=1): These complexes were prepared from [Cu(L)](ClO$_4$)$_2$ in the same way as described for **4**. Compounds **6** and **7** are purple and blue, respectively, and **7** was obtained as methanol solvate. Found for **6**: C, 32.61; H, 6.15; N, 12.51%. Calcd for $CuClO_7N_4C_{12}H_{27}$: C, 32.88; H, 6.21; N, 12.78%. Found for **7**: C, 38.78; H, 7.47; N, 10.64%. Calcd for $CuClO_8N_4C_{17}H_{39}$: C, 38.29; H, 7.47; N, 10.62%.

Co([15]aneN$_4$)(O$_2$COCH$_3$)(ClO$_4$) (8): A methanolic solution (50 cm^3) of [15]aneN$_4$ (5 mmol) was added to a methanolic solution (50 cm^3) of Co(ClO$_4$)$_2$·6H$_2$O (5 mmol) under a nitrogen atmosphere. Color of the solution turned red brown. After refluxing for 2 h, an excess of NEt_3 was added to the filtered solution and then CO_2 was bubbled through the solution. Pink-red crystals formed were filtered and stored under a nitrogen atmosphere to avoid air oxidation. Found: C, 34.56; H, 6.38; N, 12.28%. Calcd for $CoClO_7N_4C_{13}H_{29}$: C, 34.87; H, 6.53; N, 12.51%.

[Co(Me$_4$[14]aneN$_4$)(O$_2$COCH$_3$)](ClO$_4$) (9): A methanol solution (80 cm^3) of Me$_4$[14]aneN$_4$ (10 mmol) was added dropwise to a stirred methanol solution (50 cm^3) of Co(ClO$_4$)$_2$·6H$_2$O (10 mmol) under bubbling CO_2 at room temperature. Color of the solution became red purple and concomitantly white precipitate, presumably a salt of perchloric acid and Me$_4$[14]aneN$_4$, came out. When an excess of NEt_3 was added into the reaction mixture and CO_2 bubbling was continued, the white precipitate dissolved again and then red-purple precipitate of **9** was obtained. Yield 80%. Found: C, 39.21; H, 7.19; N, 11.43%. Calcd for $CoClO_7N_4C_{16}H_{35}$: C, 39.23; H, 7.20; N, 11.44%.

Measurements. Infrared spectra were recorded on a Jasco IR-810 or a Hitachi 295 spectrometer. Electronic spectra were measured on a Hitachi 340 spectrophotometer. Solid state spectra were taken as nujol mulls mounted between polyethylene films. ^{1}H NMR spectra were obtained on a JEOL JNM-GX400 spectrometer at 400 MHz.

Magnetic susceptibility measurements on cobalt(II) complexes were carried out at 77 K by the Hartshorn bridge method⁶⁾ (operating at 300 Hz). Tutton's salt, [Mn(OH$_2$)$_6$]-SO$_4$·(NH$_4$)$_2$SO$_4$, was used as a standard.

X-Ray diffraction data were obtained on a Rigaku AFC-5 four-circle diffractometer with use of graphite-monochromatized Mo *Kα* radiation. Diffraction data were collected at room temperature for **4** and **6** but at 168 K under a nitrogen stream for **5** because it decomposed rapidly in the air at room temperature. The low-temperature measurement was made with an attached Rigaku variable-temperature apparatus using a cold nitrogen gas stream method. The procedures used for data collection were standard and have been described previously.⁷⁾ The intensity data were corrected for Lorentz-polarization effects and for absorption.

Solution and Refinement of the Structures. The structure of **4** was solved by a standard Patterson and Fourier method, whereas the direct method was used for **5** and **6**. All the structures were refined by the block-diagonal least-squares technique. The atomic scattering factors for non-hydrogen atoms were taken from Ref. 8 and those for hydrogen from Stewart, Davidson, and Simpson.⁹⁾ The effects of anomalous dispersion for non-hydrogen atoms were corrected. The weights (w) were taken as $w=[\sigma^2_{\text{count}}+(0.015|F_o|)^2]^{-1}$. All the hydrogen atoms were located by difference syntheses. Non-hydrogen and hydrogen atoms were refined anisotropically and isotropically, respectively. Calculations of the refinements for all the compounds converged smoothly.¹⁰⁾ All the calculations were carried out on a HITAC M-200H computer at the Computer Center of the Institute for Molecular Science with the Universal Crystallographic Computation Program System UNICS III¹¹⁾ and MULTAN 78.¹²⁾

Results

Synthesis and Characterization. Table 1 lists compounds prepared in this study along with their IR data. Monomethyl carbonato complexes are obtained by bubbling CO_2 through methanolic solutions of [M(L)](ClO$_4$)$_2$ (M=Ni^{2+}, Cu^{2+}, and Co^{2+}) containing NEt_3 as a base (Eq. 1).

$$\begin{gathered}\mathrm{CH_3OH + CO_2 + NEt_3 \rightleftharpoons CH_3OCO_2^- + HNEt_3^+}\\ \mathrm{M(L)^{2+}} + n\mathrm{CH_3OCO_2^-} \longrightarrow \mathrm{M(L)(O_2COCH_3)}_n{}^{m+} \qquad (1)\\ (n=1,\ m=1 \text{ or } n=2,\ m=0).\end{gathered}$$

Addition of NEt_3 was necessary in these systems, although, in some zinc(II) systems, the CO_2 uptake reaction proceeds under base-free conditions. In the systems of the nickel(II) complexes with [14]aneN$_4$ and [15]aneN$_4$, CO_2 is taken up from the air spontaneously in the presence of an equivalent amount of NEt_3 and the monomethyl carbonato

Table 1. IR Data of $-OCO_2^-$ Group (cm^{-1})[a)]

Compound	$\nu_1(OCO_2)$[b)]	$\nu_2(OCO_2)$[b)]	$\pi(OCO_2)$[c)]	$\Delta\nu$[d)]
$Ni([14]aneN_4)(O_2COCH_3)(ClO_4)$ (**1**)	1614 vs	1306 m, 1320 s	810 w	294
$Ni([15]aneN_4)(O_2COCH_3)(ClO_4)$ (**2**)	1620 vs	1312 s	812 m	308
Ni(*iso*-[14]aneN$_4$)(O_2COCH_3)(ClO_4) (**3**)	1618 s	1316 s, 1330 m	814 w	302
[Ni(*RSRS*-Me$_4$[14]aneN$_4$)(O_2COCH_3)](ClO_4) (**4**)	1636 w, 1676 s	1310 s	816 m	366
[Ni(*RRSS*-Me$_4$[14]aneN$_4$)(O_2COCH_3)$_2$]·$HNEt_3$·ClO_4 (**5**)	1648 s, 1672 s	1306 m	815 w	366
$Cu([14]aneN_4)(O_2COCH_3)(ClO_4)$ (**6**)	1646 vs	1300 vs	816 s	346
$[Cu(Me_4[14]aneN_4)(O_2COCH_3)](ClO_4)$ (**7**)	1660 vs	1306 vs	806 s	354
$Co([15]aneN_4)(O_2COCH_3)(ClO_4)$ (**8**)	1620 vs	1316 vs	808 m	304
$[Co(Me_4[14]aneN_4)(O_2COCH_3)](ClO_4)$ (**9**)	1630 m, 1670 s	1306 vs	806 s	364

a) vs=very strong, s=strong, m=medium, and w=weak. b) Stretching. c) Out-of-plane bending. d) $\Delta\nu=\nu_1-\nu_2$.

Table 2. Electronic Spectral Data for (Monomethyl Carbonato)Nickel(II) Complexes[a)]

Compd	$\tilde{\nu}/10^3\ cm^{-1}$			
1	9.7	15.6	19.6	29.5
2	9.5 sh	12.5	17.6	27.8
3	11.5 sh	14.7	18.4	28.2
4	9.4	15.4	20.4	25.4
5	8.6	12.0	16.5	26.7

a) sh=shoulder.

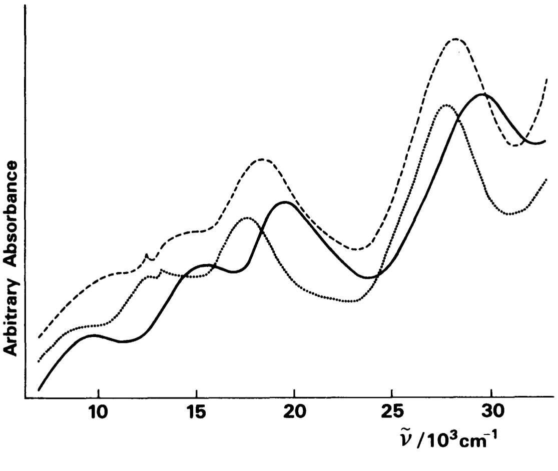


Fig. 1. Electronic absorption spectra (in methanol) of $Ni([14]aneN_4)(O_2COCH_3)(ClO_4)$ (**1**) (——), $Ni([15]aneN_4)(O_2COCH_3)(ClO_4)$ (**2**) (······), and Ni(*iso*[14]aneN$_4$)(O_2COCH_3)(ClO_4) (**3**) (----).

complexes were isolated as a single product.

In contrast with the nickel(II) systems, the reactivity of $[Cu(L)]^{2+}$ toward monomethyl carbonate ions was so weak that only the starting complex, $[Cu(L)](ClO_4)_2$, was recovered when an equimolar amount of NEt_3 was present in the solution. However, when a large excess of NEt_3 was added, (monomethyl carbonato)copper(II) complexes, **6** and **7**, were successfully isolated. But we failed to isolate a desired product from $[Cu([15]aneN_4)](ClO_4)_2$ even in the presence of a large excess of NEt_3.

As to cobalt(II) complexes, it may be worth while pointing out the following observation. The cobalt(II) complex with $[15]aneN_4$ was easily oxidized by air, so that the reaction was carried out under a nitrogen atmosphere. On the other hand, the cobalt(II) complex with $Me_4[14]aneN_4$ was extraordinarily air stable and it underwent the uptake reaction in the air smoothly.

We pointed out previously for the zinc(II) system that stretching vibrational bands (ν_1 and ν_2) of the $-OCO_2$ group reflect a coordination mode of the monomethyl carbonato ligand.[1a)] That is, in the case of unidentate $CH_3OCO_2^-$, the ν_1 band appears at higher frequencies than that of bridged $CH_3OCO_2^-$. In addition, the intensity of ν_2 is strong as compared with ν_1 in unidentate $CH_3OCO_2^-$, and vice versa in bridged $CH_3OCO_2^-$. Similar trends were also observed for the present nickel(II)- and cobalt(II)-monomethyl carbonato complexes (Table 1). The frequency difference between ν_1 and ν_2 was as much as 360 cm^{-1} in compounds **4**, **5**, and **9**, while it was at most 300 cm^{-1} in **1**—**3** and **8**. Thus, complemented with the relative band intensities, the $CH_3OCO_2^-$ ligands in complexes with $Me_4[14]aneN_4$ are assigned to unidentate coordination and those in other compounds to bridged coordination. However, it was difficult for copper(II) complexes to assign the coordination mode from IR data because they do not show a distinct tendency.

As shown in Fig. 1 and Table 2, the ligand field electronic spectrum of nickel(II) complex, **1**, **2**, **3**, or **5** consists of four bands except for a sharp peak due to spin-forbidden transition around 13000 cm^{-1}. Each spectrum shows clearly the splitting typical of tetragonal nickel(II) complexes in the lowest energy region (8000—15600 cm^{-1}).[13)] The lowest and the second lowest energy bands are assigned to $^3E_g \leftarrow {}^3B_{1g}$ and $^3B_{2g} \leftarrow {}^3B_{1g}$, respectively, which arise from the tetragonal splitting of $^3T_{2g} \leftarrow {}^3A_{2g}$ in Oh symmetry. Thus compounds **1**, **2**, **3**, and **5** have coordination geometry of the *trans*-NiO_2N_4 type. The spectral pattern of green compound **4** is quite different from others and indicates a five-coordinate structure.

Nujol mull solid state electronic spectra of (monomethyl carbonato)copper(II) complexes, **6** and **7**, show one broad absorption band at 19000 and 14300 cm^{-1}, respectively. The d-d band position is at lower energy than those of the corresponding square-planar four-coordinate complexes, $[Cu(L)]^{2+}$.[14] This indicates the occurrence of an axial interaction of the fifth or sixth ligand with the Cu^{2+} ion although coordination geometry of the copper(II) complexes is not clear from the electronic spectra.[15]

(Monomethyl carbonato)cobalt(II) complexes, **8** and **9**, are pale pink and red purple in color, respectively. Their electronic spectral patterns are quite different ($\tilde{\nu}_{max}/10^3$ cm^{-1}: 19.7 and 22.1 for **8**; 6.9, 13.5, 18.6, 19.9, and 20.7 for **9**). The spectral pattern of **8** resembles those of high spin octahedral cobalt(II) complexes, $[Co(OH_2)_6]^{2+}$ and $[Co(NH_3)_6]^{2+}$. On the other hand, the spectral pattern of **9** is very similar to that of high-spin five-coordinate complexes with the trigonal bipyramidal geometry, $[Co(tbcyclen)X]^+$ (X=Cl, NCS; tbcyclen=1,4,7,10-tetrabenzil-1,4,7,10-tetraazacyclododecane)[16] and $[Co(MSBen\text{-}N(C_2H_5)_2(NCS)_2]$ (MSBen-N$(C_2H_5)_2$=Schiff base derived from o-(methylthio)benzaldehyde and *N,N*-diethylethylenediamine)[17]. But the pattern of **9** differs clearly from that of a low-spin five coordinate complex having the trigonal bipyramidal geometry, [Co(CR)X]Y (X, Y=Cl, Br, I etc., CR=2,12-dimethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),2,11,13,15-pentaene.[18] Magnetic moments for **8** and **9** have been found to be 4.09 and 4.21 μ_B, respectively. These results indicate that compound **8** is a high spin six-coordinate complex whereas **9** is a high spin five-coordinate complex.

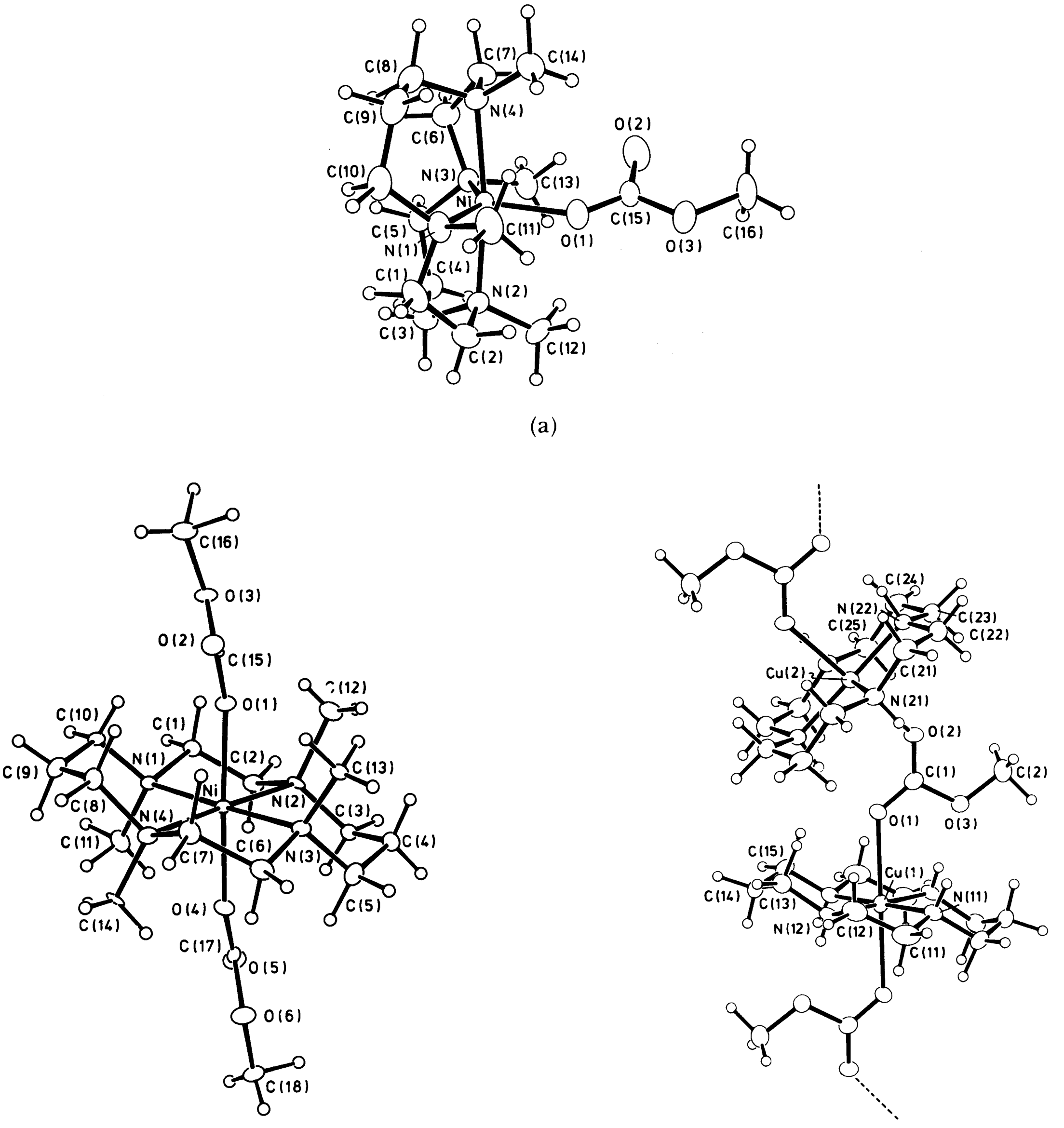
X-Ray Structure. Partinent crystallographic parameters and final *R* indices for three analyzed compounds, **4**, **5**, and **6**, are summarized in Table 3. Their positional and thermal parameters for non-hydrogen atoms are given in Tables 4-6, respectively. Figure 2 shows X-ray structures and Table 7 lists relevant bond distances and angles.

$[Ni(\textit{RSRS}\text{-}Me_4[14]aneN_4)(O_2COCH_3)](ClO_4)$ (**4**) was found to be a mononuclear five-coordinate complex with the trigonal bipyramidal geometry (Fig. 2(a)). The macrocycle is folded and the $CH_3OCO_2^-$ ligand is coordinated in a unidentate fashion. The overall structure of **4** is essentially the same as that of the corresponding zinc(II) complex, $[Zn(Me_4[14]aneN_4)(O_2COCH_3)](ClO_4)$[1b]. All the four methyl groups of the $Me_4[14]aneN_4$ ligand are disposed toward the same side as the $CH_3OCO_2^-$ ligand. A main difference between these two structures is as follows: An angle subtended at the Ni atom by two axial bonds, Ni–N(2) and Ni–N(4), is 171.2(2)°, which is much wider than the corresponding angle of the zinc complex (166.2(1)°); Apical bonds (Ni–N(2) and Ni–N(4)) are similar in length to the in-plane ones in the nickel complex, while the formers are longer by

Table 3. Crystallographic Parameters

	4	5	6
Formula	$NiClO_7N_4C_{16}H_{35}$	$NiClO_{10}N_5C_{24}H_{54}$	$CuClO_7N_4C_{12}H_{27}$
F_w	489.63	666.87	438.37
Cryst syst	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	Aa	$P2_1/n$
a/Å	11.375(1)	23.909(5)	12.303(3)
b/Å	12.415(1)	12.221(2)	15.498(3)
c/Å	8.323(1)	11.134(2)	9.649(2)
α/deg	109.082(8)	90	90
β/deg	98.74(1)	94.51(2)	94.18(2)
γ/deg	87.19(1)	90	90
V/Å^3	1097.9(2)	3243(1)	1835.0(6)
Z	2	4	4
d_c/g cm^{-3}	1.48	1.365	1.59
d_m/g cm^{-3}	1.47	—	1.57
Cryst size/mm	0.36×0.44×0.72	0.64×0.40×0.37	0.64×0.08×0.08
Scan range	$1.4+0.5\tan\theta$	$1.2+0.5\tan\theta$	$1.3+0.5\tan\theta$
μ/mm^{-1}	1.050	0.740	1.425
2θ range/deg	2—55	2—55	2—55
Unique data[a]	3771	2983	1558
No. of variables	403	587	344
R	0.052	0.048	0.042
R_w	0.075	0.063	0.052

a) $|F_o|>3\sigma(|F_o|)$.



(a)

(b)

(c)

Fig. 2. ORTEP view of the structure, (a): [Ni(*RSRS*-Me$_4$[14]aneN$_4$)(O$_2$COCH$_3$)](ClO$_4$) (**4**), (b): [Ni(*RRSS*-Me$_4$[14]aneN$_4$)(O$_2$COCH$_3$)$_2$]·HNEt$_3$ClO$_4$ (**5**), (c): Cu([14]aneN$_4$)(O$_2$COCH$_3$)(ClO$_4$) (**6**).

ca. 0.1 Å in the zinc complex. Although the in-plane coordination bond lengths are not much different between the nickel and zinc complexes, deviations of the in-plane coordination bond angles from 120° are larger in the nickel complex than in the zinc complex.

As shown in Fig. 2(b), the structure of **5** is of the *trans*-NiO$_2$N$_4$ type with the macrocycle in a plane and with two unidentate CH$_3$OCO$_2$$^-$ occupying the axial sites. This 2:1 complex (two CH$_3$OCO$_2$$^-$'s per a metal ion) is the first example among about twenty monoalkyl carbonato complexes of M(II)-tetraazacycloalkane we prepared. There is an approximate inversion center at the nickel atom, although all the atoms in the complex cation are crystallographically independent. The overall skeletal structure of the macrocycle is the same as that of the most strain-free form of the [14]aneN$_4$ ligand, five- and six-membered chelate rings being in the gauche and chair conformations, respectively. The average Ni-N distance is 2.163(9) Å and is comparable to a reported value (2.16(1) Å) for [Ni$_2$(*RRSS*-Me$_4$[14]aneN$_4$)$_2$(N$_3$)$_3$]I.[3a) But it is about 0.1 Å longer than those found in high-spin complexes without N-methyl groups, *trans*-[NiX$_2$([14]aneN$_4$)].[19) This is the outcome of the *N*-methylation of [14]aneN$_4$ which causes a decrease in the ligand field strength. Monomethyl carbonato ligands are oriented parallel to the fence of the CH$_3$ groups on the same side, avoiding mutual steric interactions (Fig. 2(b)). Angles of Ni-O(1)-C(15) and

Table 4. Atomic Parameters for [Ni(*RSRS*-Me_4[14]aneN_4)-(O_2COCH_3)](ClO_4) (**4**)[a]

Atom	*x*	*y*	*z*	B_{eq}[b]
Ni	21456(4)	24187(4)	4045(6)	2.4
Cl	6008(1)	2080(1)	-2619(2)	4.0
O(1)	888(3)	2346(3)	1789(4)	4.8
O(2)	-372(4)	3763(4)	1723(6)	6.3
O(3)	-571(3)	2609(3)	3242(5)	5.1
O(4)[c]	6556(5)	2558(5)	-879(6)	8.5
O(5)[c]	6037(7)	2843(5)	-3504(8)	13.0
O(6)[c]	6541(7)	1065(5)	-3389(8)	13.0
O(7)[c]	4823(5)	1848(6)	-2613(9)	11.7
N(1)	2599(3)	662(3)	-232(5)	3.6
N(2)	3464(3)	2633(3)	2615(4)	3.3
N(3)	2570(3)	4034(3)	255(4)	2.9
N(4)	1041(3)	2202(3)	-1996(4)	3.5
C(1)	3701(4)	623(4)	916(7)	4.5
C(2)	3659(4)	1453(4)	2698(6)	4.2
C(3)	4618(4)	3101(4)	2492(6)	4.1
C(4)	4527(4)	4271(4)	2284(6)	4.2
C(5)	3877(4)	4288(4)	579(6)	3.6
C(6)	2127(4)	3962(4)	-1543(6)	4.0
C(7)	949(4)	3368(5)	-2138(7)	4.5
C(8)	1588(5)	1416(5)	-3467(6)	4.7
C(9)	1805(5)	230(5)	-3406(7)	5.6
C(10)	2825(5)	126(4)	-2046(7)	4.5
C(11)	1670(4)	-41(4)	79(8)	4.7
C(12)	3074(5)	3328(5)	4283(6)	4.7
C(13)	1956(4)	5003(4)	1431(7)	4.4
C(14)	-200(4)	1797(5)	-2116(7)	5.0
C(15)	23(4)	2943(4)	2211(6)	3.5
C(16)	-1637(5)	3251(6)	3709(8)	6.0

a) Positional parameters are multiplied by 10^4 except for positional parameter of Ni, for which the values are multiplied by 10^5. b) $B_{eq}=4/3(\sum_i\sum_j a_i a_j \beta_{ij})$, where the a_i's are the unit-cell edges in direct space. c) Perchlorate oxygen atom.

Table 5. Atomic Parameters for [Ni(*RRSS*-Me_4[14]aneN_4)-$(O_2COCH_3)_2$]·$HNEt_3ClO_4$ (**5**)[a]

Atom	*x*	*y*	*z*	B_{eq}[b]
Ni	0	2497(1)	0	1.2
Cl	2513(2)	1260(1)	-2475(4)	3.2
O(1)	-356(2)	2732(4)	-1767(4)	1.9
O(2)	-1101(2)	3672(4)	-2527(4)	2.2
O(3)	-686(2)	2327(3)	-3603(3)	2.0
O(4)	397(2)	2312(4)	1755(4)	2.2
O(5)	1136(2)	1308(4)	2601(4)	2.5
O(6)	725(2)	2626(4)	3616(4)	2.7
O(7)[c]	2997(3)	588(5)	-2333(7)	5.9
O(8)[c]	2009(4)	687(1)	-2700(11)	12.3
O(9)[c]	2531(7)	1841(5)	-1506(10)	17.9
O(10)[c]	2630(4)	1993(7)	-3457(11)	11.1
N(1)	-58(2)	747(4)	-282(4)	1.5
N(2)	805(2)	2429(4)	-776(4)	1.4
N(3)	73(2)	4240(4)	234(4)	1.6
N(4)	-789(2)	2604(4)	823(4)	1.8
N(5)	2723(2)	-4106(5)	-2592(5)	2.5
C(1)	396(3)	582(5)	-1123(5)	1.7
C(2)	929(3)	1192(5)	-718(5)	1.8
C(3)	1271(2)	3011(5)	-68(5)	1.5
C(4)	1149(3)	4233(6)	66(6)	2.3
C(5)	641(3)	4527(6)	833(7)	3.0
C(6)	-365(3)	4450(5)	1119(6)	2.3
C(7)	-901(3)	3792(6)	717(6)	2.2
C(8)	-1218(3)	1960(5)	9(6)	2.5
C(9)	-1109(3)	732(5)	-140(6)	2.3
C(10)	-622(3)	433(5)	-861(5)	1.4
C(11)	84(3)	64(5)	826(6)	2.2
C(12)	817(3)	2793(6)	-2135(6)	2.6
C(13)	-37(3)	4978(5)	-809(5)	2.0
C(14)	-818(3)	2266(5)	2038(5)	1.7
C(15)	-732(3)	2995(5)	-2578(5)	1.5
C(16)	-1143(3)	2501(6)	-4553(6)	3.0
C(17)	760(2)	2049(5)	2558(5)	1.6
C(18)	1114(3)	2465(7)	4607(6)	3.0
C(19)	2418(3)	-3129(6)	-3154(8)	3.5
C(20)	2488(8)	-2055(6)	-2500(15)	4.9
C(21)	2677(4)	-5100(7)	-3418(8)	3.8
C(22)	2086(5)	-5503(9)	-3770(17)	10.2
C(23)	2555(4)	-4324(6)	-1312(7)	3.3
C(24)	2844(5)	-5330(9)	-851(13)	8.5

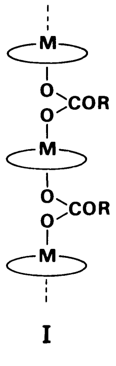
a) Positional parameters are multiplied by 10^4. b) See footnote in Table 4 for B_{eq}. c) Perchlorate oxygen atom.

Ni-O(4)-C(17) widen up to 156.4(4)° and 158.9(4)°, respectively.

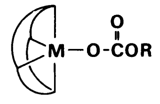
The crystal structure of Cu([14]aneN_4)(O_2COCH_3)(ClO_4) (**6**) is isostructural with Zn([14]aneN_4)(O_2COCH_3)(ClO_4). As shown in Fig. 2(c), the $CH_3OCO_2^-$ ligand bridges adjacent Cu([14]aneN_4) units, forming a linear chain along the a axis. Two independent copper atoms (Cu(1) and Cu(2)) are situated at a crystallographic inversion center. Intramolecular hydrogen bonds operate between NH of [14]aneN_4 and the O(3) atom of the $CH_3OCO_2^-$ ligand (O(3)···HN(12)=2.40(6) Å, O(3)···HN(11)=2.60(6) Å), as in the zinc complex.

Discussion

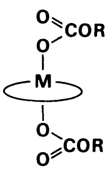
Nickel(II) Complexes. Three types of coordination structures (I—III) are found in (monomethyl carbonato)nickel(II) complexes. Type I is a linear-chain structure with the bridging monomethyl carbonato ligand. Compounds **1**, **2**, and **3** are assigned to this type from IR and electronic spectral data. The second type (II) is a mononuclear five-coordinate structure with the unidentate monomethyl carbonato ligand and is found for compound **4**. These two types have been already known in zinc(II) complexes.[1] Type III, which is a mononuclear six-coordinate complex containing two unidentate $CH_3OCO_2^-$, has been newly found for compound **5**. As to the CO_2 uptake reaction, compounds with the structural type I were the most effective in the nickel(II) complexes as well as in the zinc(II) systems.[1] CO_2 is taken up spontaneously from the air in the system of this type to form desired monomethyl carbonato complexes. In complexes



I



II



III

Table 6. Atomic Parameters for Cu([14]aneN_4)(O_2COCH_3)(ClO_4) (**6**)[a)]

Atom	*x*	*y*	*z*	B_{eq}[b)]
Cu(1)	5000	5000	0	2.8
Cu(2)	0	5000	0	2.8
Cl	2095(2)	6679(2)	-3908(2)	4.5
O(1)	2960(4)	4841(3)	-207(5)	3.5
O(2)	1374(4)	4452(3)	-1325(5)	4.1
O(3)	2952(4)	4302(3)	-2323(5)	3.9
O(4)[c)]	2245(8)	6667(9)	-2485(8)	15.3
O(5)[c)]	1129(6)	6243(6)	-4353(8)	10.1
O(6)[c)]	2143(10)	7442(7)	-4498(14)	18.2
O(7)[c)]	2948(9)	6241(10)	-4269(13)	18.3
N(11)	4898(5)	5684(4)	-1781(6)	3.4
N(12)	4812(4)	6140(4)	946(6)	3.4
N(21)	38(4)	6105(4)	-1128(6)	3.1
N(22)	-1123(4)	4592(4)	-1490(6)	3.0
C(1)	2367(6)	4542(5)	-1202(7)	3.1
C(2)	2335(7)	3941(6)	-3486(8)	5.0
C(11)	5031(7)	6606(5)	-1374(9)	4.9
C(12)	4452(7)	6765(5)	-122(9)	4.5
C(13)	4126(6)	6133(6)	2143(8)	4.8
C(14)	4506(7)	5497(6)	3283(8)	5.3
C(15)	4388(7)	4579(6)	2857(7)	4.9
C(21)	-938(6)	6094(5)	-2125(8)	4.2
C(22)	-1069(6)	5193(5)	-2670(7)	4.1
C(23)	-1080(6)	3680(5)	-1912(7)	3.8
C(24)	-1147(6)	3074(5)	-689(9)	4.3
C(25)	-156(6)	3077(5)	346(8)	4.3

a) Positional parameters are multiplied by 10^4. b) See footnote in Table 4 for B_{eq}. c) Perchlorate oxygen atom.

with Me_4[14]aneN_4, steric constraints provided by *N*-methyl groups of Me_4[14]aneN_4 prevent monomethyl carbonato ligand from bridge coordination, giving structural type II or III. The Me_4[14]aneN_4 ligand in the *RSRS*-form folds easily to afford the type II structure, whereas *RRSS*-Me_4[14]aneN_4 cannot fold to form the type III complex.

As was mentioned in the experimental section, compound **5** was produced also from the solution of **4** through the nitrogen configuration inversion of Me_4[14]aneN_4 from *RSRS*- to *RRSS*-form. The electronic spectrum of a methanol solution of **4** containing an excess of NEt_3 and saturated CO_2 was found to change with time. The absorption maximum of the original solution at 681 nm shifted gradually toward higher frequencies, that is, toward the absorption band of **5** and reached an equilibrium position. The more NEt_3 was added, the larger and faster the band shifted. Moore et al. reported that the *RSRS*- and *RRSS*-isomers of $[Ni(Me_4[14]aneN_4)]^{2+}$ are interconvertible, and that the conversion occurs at a relatively slow rate in DMSO or DMF but rapidly in the presence of a strongly coordinating amine such as propylamine.[20)] In our case, however, reverse reaction, i.e., conversion from **5** to **4** was not observed. An absorption spectrum of **5** in methanol did not change at all at least for a month. Compound **5** decomposes rapidly in the air liberating CO_2, although it is stable in a nitrogen atmosphere or in a vacuum.[21)] The instability of **5** is reflected in bond angles of Ni–O–C in the monomethyl carbonato ligands. The corresponding angle in other monomethyl carbonato[1b)] or carbonato complexes[22)] is in the range of 122—136°, which are close to 120° expected for the oxygen atom in the sp^2 hybridization. However, the angles in **5** (157.7° in average) are by far larger.

The monomethyl carbonato ligand was successfully converted into dimethyl carbonate by treating with FSO_3CH_3 in $CDCl_3$. The formation of dimethyl carbonate was easily followed by ^1H NMR. The conversion efficiency in the present nickel(II) complexes was not much different from the case of zinc(II) complexes described previously.[1a)]

Copper(II) Complexes. IR data of the (monomethyl carbonato)copper(II) complexes did not provide definite evidence for structural information. It is because an interaction of $CH_3OCO_2^-$ with $[Cu(L)]^{2+}$ is very weak. In fact, the X-ray structure of Cu([14]aneN_4)(O_2COCH_3)(ClO_4) (**6**) demonstrates clearly the weakness of the interaction. As described previously, the crystal structure of **6** is isomorphous with the Zn analogue, Zn([14]aneN_4)(O_2COCH_3)(ClO_4), which has been found to be one of the most effective system as to the efficiency of the CO_2 uptake among about 20 systems explored in a series of our studies. In the zinc structure, one of the Zn atoms takes an out-of-plane position,[1b)] but such an out-of-plane displacement has not been found in **6** in spite of the constrained coordination environment. The double of the Cu···Cu separation (12.303(3) Å) corresponds to the length of the a axis, and is slightly longer than that of the zinc complex (12.128(2) Å). These structural informations show that the Cu–O interaction is rather weak. The Cu–O distances are as large as 2.351(6) and 2.516(5) Å, while the Zn–O lengths are 2.143(3) and 2.227(3) Å. This difference is consistent with the observation that the $CH_3OCO_2^-$ uptake by the zinc complex takes place much easier. The occurrence of such a weak interaction in copper(II) complexes was observed spectrally in a methanol solution. A d-d band of $[Cu(L)]^{2+}$ shifts to lower energies as the concentration of NEt_3 increases. Such a spectral change was observed for all the copper(II) complexes studied, $[Cu(L)](ClO_4)_2$ (L=[14]aneN_4, [15]aneN_4, and Me_4[14]aneN_4). The spectral change indicates that a monoalkyl carbonato adduct exists in equilibrium with the starting $[Cu(L)]^{2+}$. The d-d band shift upon addition of a large excess of NEt_3 was as much as 2400 cm^{-1} for compound **7**, whereas it was only 800 cm^{-1} for **6**. Complemented by structural data for other Me_4[14]aneN_4 complexes, this may indicate that the coordination geometry about Cu in **7** is of the trigonal bipyramidal type. An interaction between Cu^{2+} and $CH_3OCO_2^-$ is stronger in **7** than in **6**.

Table 7. Relevant Bond Lengths(Å) and Angles(°)

$[Ni(RSRS\text{-}Me_4[14]aneN_4)(O_2COCH_3)](ClO_4)$ (**4**)

Ni	-O(1)	1.991(4)	O(1)	-C(15)	1.226(6)
Ni	-N(1)	2.126(4)	O(2)	-C(15)	1.255(7)
Ni	-N(2)	2.142(4)	O(3)	-C(15)	1.342(6)
Ni	-N(3)	2.132(4)	O(3)	-C(16)	1.450(8)
Ni	-N(4)	2.135(4)			

O(1)	-Ni	-N(1)	95.4(2)	N(2)	-Ni	-N(4)	171.7(2)
O(1)	-Ni	-N(2)	89.8(2)	N(3)	-Ni	-N(4)	85.0(2)
O(1)	-Ni	-N(3)	118.5(2)	Ni	-O(1)	-C(15)	133.4(4)
O(1)	-Ni	-N(4)	98.5(2)	C(15)	-O(3)	-C(16)	115.9(5)
N(1)	-Ni	-N(2)	85.0(2)	O(1)	-C(15)	-O(2)	127.4(5)
N(1)	-Ni	-N(3)	145.9(2)	O(1)	-C(15)	-O(3)	113.6(4)
N(1)	-Ni	-N(4)	93.7(2)	O(2)	-C(15)	-O(3)	118.9(5)
N(2)	-Ni	-N(3)	91.5(1)				

$[Ni(RRSS\text{-}Me_4[14]aneN_4)(O_2COCH_3)_2]\cdot HNEt_3\cdot ClO_4$ (**5**)

Ni	-O(1)	2.101(4)	O(2)	-C(15)	1.214(8)
Ni	-O(4)	2.117(5)	O(3)	-C(15)	1.415(7)
Ni	-N(1)	2.165(5)	O(3)	-C(16)	1.477(8)
Ni	-N(2)	2.172(5)	O(4)	-C(17)	1.239(7)
Ni	-N(3)	2.151(5)	O(5)	-C(17)	1.274(8)
Ni	-N(4)	2.165(6)	O(6)	-C(17)	1.380(8)
O(1)	-C(15)	1.265(7)	O(6)	-C(18)	1.400(8)

O(1)	-Ni	-O(4)	176.9(2)	N(2)	-Ni	-N(4)	178.0(2)
O(1)	-Ni	-N(1)	89.0(2)	N(3)	-Ni	-N(4)	87.4(2)
O(1)	-Ni	-N(2)	86.5(2)	Ni	-O(1)	-C(15)	156.4(4)
O(1)	-Ni	-N(3)	90.1(2)	C(15)	-O(3)	-C(16)	113.2(5)
O(1)	-Ni	-N(4)	94.9(2)	Ni	-O(4)	-C(17)	158.9(4)
O(4)	-Ni	-N(1)	92.7(2)	C(17)	-O(6)	-C(18)	121.3(5)
O(4)	-Ni	-N(2)	90.9(2)	O(1)	-C(15)	-O(2)	128.2(5)
O(4)	-Ni	-N(3)	88.2(2)	O(1)	-C(15)	-O(3)	109.5(5)
O(4)	-Ni	-N(4)	87.6(2)	O(2)	-C(15)	-O(3)	122.3(5)
N(1)	-Ni	-N(2)	87.3(2)	O(4)	-C(17)	-O(5)'	131.5(6)
N(1)	-Ni	-N(3)	178.2(2)	O(4)	-C(17)	-O(6)	113.4(6)
N(1)	-Ni	-N(4)	94.2(2)	O(5)	-C(17)	-O(6)	114.9(5)
N(2)	-Ni	-N(3)	91.2(2)				

$Cu([14]aneN_4)(O_2COCH_3)(ClO_4)$ (**6**)

Cu(1)	-O(1)	2.352(5)	Cu(2)	-N(22)	2.010(6)
Cu(1)	-N(11)	2.032(6)	O(1)	-C(1)	1.226(9)
Cu(1)	-N(12)	2.023(5)	O(2)	-C(1)	1.252(8)
Cu(2)	-O(2)	2.515(5)	O(3)	-C(1)	1.393(9)
Cu(2)	-N(21)	2.015(6)	O(3)	-C(2)	1.423(9)

O(1)	-Cu(1)	-N(11)	88.2(2)	Cu(1)	-O(1))	-C(1)	131.0(5)
O(1)	-Cu(1)	-N(12)	89.0(2)	Cu(2)	-O(2)	-C(1)	128.3(5)
N(11)	-Cu(1)	-N(12)	85.6(2)	C(1)	-O(3)	-C(2)	116.2(6)
O(2)	-Cu(2)	-N(21)	89.1(2)	O(1)	-C(1)	-O(2)	129.6(7)
O(2)	-Cu(2)	-N(22)	88.6(2)	O(1)	-C(1)	-O(3)	117.5(6)
N(21)	-Cu(2)	-N(22)	85.6(2)	O(2)	-C(1)	-O(3)	112.8(6)

Cobalt(II) Complexes. Cobalt(II) complexes, **8** and **9**, are classified to types I and II, respectively, from the spectral and magnetic susceptibility data. Compound **8** is easily oxidized to the tervalent state and this enables discussion on the structure of **8**. When an aqueous solution of compound **8** acidified with HCl was stirred in the air, brown solid was produced. The product was identified as the most stable isomer of *trans*-$[Co^{III}Cl_2([15]aneN_4)](ClO_4)$, in which one five-membered and three six-membered chelate rings adopt a gauche-skew-chair-chair conformational sequence.[23] Since nitrogen configurations would be retained in the process of the oxidation, the skeletal structure of $[15]aneN_4$ in compound **8** is considered to be the same. This overall conformation is different from that found for the corresponding zinc(II) complex in $[\{Zn([15]aneN_4)\}_3(O_2COCH_3)_2](ClO_4)_4$, which has the $[15]aneN_4$ ligand in a gauche-chair-skew-chair conformation.[1b] On the other hand, compound **9** was found to be very stable in the air. The trigonal bipyramidal geometry characteristic of this particular macrocycle prevents $Co(Me_4[14]aneN_4)^{2+}$ from the air oxidation. To our knowledge, compound **9** is the first example that assumes a high-spin five coordinate structure in tetraaza macrocyclic cobalt(II) complexes.

Comparison of Metal Ions from the Viewpoint of the CO_2 Uptake. Among tetraazacycloalkane complexes of various metal ions studied, the zinc complexes are the most superior in the efficiency of the CO_2 uptake as monoalkyl carbonate ion. As discussed in detail in the previous paper,[1)] coordinately unsaturated situation introduced by square-planar coordination of a tetraazacycloalkane ligand is the most important in the case of the zinc(II) systems. The uptake reaction by the nickel(II) systems was not so effective as the zinc(II) systems. A Ni^{2+} ion has $3d^8$ valence electron configuration and a square-planar four-coordinate structure is one of the stable geometries for nickel(II) complexes. That is, axial sites of starting nickel(II) complexes with tetraazacycloalkane are supposed to be not so reactive as those of the zinc(II) complexes. It is well known that nickel(II) complexes with tetraazacycloalkanes (L) exists in a coordinating solvent or in the presence of coordinating anions as an equilibrium mixture between square-planar four-coordinate species and five- or six-coordinate species (Eq. 2). Thermodynamic parameters of the equilibrium

$$[Ni(L)]^{2+} + nX \rightleftharpoons [Ni(L)X_n]^{m+} \qquad (2)$$
$$n=1 \text{ or } 2;\ m=0\text{—}2,$$

in aqueous solution ($X=H_2O$) have been reported for various tetraaza macrocycles. The position of the equilibrium depends strongly on the kind of the in-plane ligand. For example, in the case of L=[14]aneN$_4$, only 28% of the complex exists as six-coordinate species at room temperature, while, in the case of L=[15]aneN$_4$, six-coordinate species amounts to as much as 99%.[24)] A position of the equilibrium of Eq. 2 has been known to be affected by an electronic factor, that is, ligand field strength of the in-plane ligand. We tried to correlate an equilibrium constant with efficiency in the uptake of monoalkyl carbonate ion. But such a correlation was not observed in the present system. A steric factor contributes more strongly than the electronic one. In fact, the following facts are noted between [Ni(*RRSS*-Me$_4$[14]aneN$_4$)]$^{2+}$ and [Ni([14]aneN$_4$)]$^{2+}$: in aqueous solution, the former favors six-coordination over four-coordination and vice versa in the latter, while compound **5** containing the *RRSS*-Me$_4$[14]aneN$_4$ ligand is so unstable that it returns to the four-coordinate complex rapidly in the air.[21)] However, the electronic effect on the uptake reaction was indeed noted in the case where ligand field strength of the macrocyclic ligand is by far stronger and, therefore, the equilibrium of Eq. 2 is shifted far to the left. [Ni(Me$_2$[13]dienatoN$_4$)]$^+$ (Me$_2$[13]dienatoN$_4$= 11,13-dimethyl-1,4,7,10-tetraazacyclotrideca-10,12-diene)[25)] is such an example and it did not afford a monomethyl carbonato complex. One more fact that deserves a brief comment on the nickel(II) system, is that a nickel(II) complex containing linear tetramines such as 3,2,3-tet (3,2,3-tet=4,7-diazadecane-1,10-diamine) instead of tetraazacycloalkane undergoes the uptake of monomethyl carbonate ion. A zinc(II) complex having 3,2,3-tet never undergoes such a reaction. Possibly, this is due to the difference in coordination behavior between nickel(II) and zinc(II). Ni(3,2,3-tet)$^{2+}$ prefers a square-planar geometry and has coordinately unsaturated nature. On the other hand, Zn(3,2,3-tet)$^{2+}$ assumes a tetrahedrally distorted geometry which is more stable than a square planar form, and therefore it does not undergo further ligand uptake.

The uptake efficiency of the copper(II) complexes was the lowest among the metal ions studied. This originates from the inherently weak reactivity of axial sites of tetragonal copper(II) complexes. As described previously, the X-ray structure of compound **6** demonstrates clearly such a situation.

The cobalt(II) system is disadvantageous to the formation of monomethyl carbonato complexes because cobalt(II) complexes with four nitrogen donors are generally susceptible to oxidation. However, the Co([15]aneN$_4$) complex underwent the uptake reaction smoothly under oxygen-free conditions. The Co(Me$_4$[14]aneN$_4$) system is an exception. It forms a five-coordinate cobalt(II) complex with an extra unidentate ligand (X), CoX(Me$_4$[14]aneN$_4$)$^+$, which is exceptionally stable to oxidation. Cobalt(II) complexes resemble zinc(II) complexes in the point that they can take many different types of coordination geometries.[26)] It seems that the efficiency of the cobalt complexes is not much different from that of the zinc complexes under oxygen free conditions.

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3) For [Ni(Me$_4$[14]aneN$_4$)]$^{2+}$, two configurational isomers are known [a) F. Wagner, M. T. Mocella, M. J. D'Aniello, Jr., A. H. -J. Wang, E. K. Barefield, *J. Am. Chem. Soc.*, **96**, 2625 (1974); b) M. J. D'Aniello, M. T. Mocella, F. Wagner, E. K. Barefield, and I. C. Paul, *J. Am. Chem. Soc.*, **97**, 192 (1975)]. One contains the Me$_4$[14]aneN$_4$ ligand with coordinated nitrogens in the 1*RS*,4*SR*,8*RS*,11*SR*-form, the other in the 1*RS*,4*RS*,8*SR*,11*SR*-form. These ligands are abbreviated as *RSRS*-Me$_4$[14]aneN$_4$ and *RRSS*-Me$_4$[14]aneN$_4$, respectively, throughout this paper.

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21) The resulting product is orange in color indicating a four-coordinate nickel(II) complex. When this change was followed by IR spectra, bands at 1670 and 1306 cm^{-1} due to the monomethyl carbonate group disappeared gradually and a new peak appeared at 1630 cm^{-1}. This band suggested an existence of hydrogencarbonate ion. In fact, analytical data of the product was consistent with $[Ni(Me_4[14]aneN_4)](O_2COH)(ClO_4)$: Found: C, 38.10; H, 7.04; N, 11.79%. Calcd for $NiClO_7N_4C_{15}H_{33}$: C, 37.88; H, 6.99; N, 11.78%. Therefore, the decomposition of **5** is considered to be induced by the reaction with moisture, as shown below.

$$[Ni(Me_4[14]aneN_4)(O_2COCH_3)_2]\cdot HNEt_3ClO_4$$

$$\xrightarrow[H_2O]{CO_2,\ 2CH_3OH,\ NEt_3} [Ni(Me_4[14]aneN_4)](O_2COH)(ClO_4).$$

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