June, 1985] Bull. Chem. Soc. Jpn., 58, 1755—1760 (1985)

Dialkylcarbamato Complexes of Ni(II), Zn(II), and Cd(II)-Tetraazacycloalkanes Obtained from CO_2-Uptake, and X-Ray Structure of (Diethylcarbamato)((7*RS*,14*RS*)-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane)nickel(II) Perchlorate

Haruko Ito† and Tasuku Ito*
Department of Applied Molecular Science, Institute for Molecular Science,
Okazaki National Research Institutes, Okazaki 444
(Received January 23, 1985)

Nickel(II), zinc(II), and cadmium(II) complexes of certain tetraazacycloalkanes (L), $[M(L)](ClO_4)_2$, take up CO_2 as $R_2NCO_2^-$ to give carbamato complexes, $[M(O_2CNR_2)(L)]^+$, where L=(7*RS*,14*RS*)-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (L^1) for $M=Ni^{2+}$, and L=1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane (L^2) for $M=Ni^{2+}$, Zn^{2+}, and Cd^{2+}. The resulting complexes have been characterized by means of IR, and NMR or electronic spectroscopy. X-Ray analysis of $[Ni(O_2CN(C_2H_5)_2)(L^1)]ClO_4$ (monoclinic $C2/c$, $a=15.842(3)$, $b=13.675(3)$, $c=13.753(2)$ Å, $\beta=109.94(1)°$) shows that it is a discrete six-coordinate complex with *cis*-NiO_2N_4 geometry, and the carbamato ligand is bidentate. Desired carbamato complexes were hardly obtained with $[M(L)]^{2+}$ containing tetraaza macrocyclic ligand which favors square-planar coordination. All the data indicate that carbamate ions chelate the metals, and thus use of tetraazacycloalkanes which fold readily is essential for this type of CO_2 uptake.

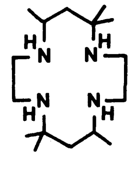
Considerable attention has been paid to the reaction of CO_2 with transition metal complexes in connection with the fixation and utilization of CO_2. We found that zinc(II)[1] and nickel(II)[2] complexes having certain tetraazacycloalkanes (L) take up CO_2 in basic alcohol solution as monoalkyl carbonate to give $[M(O_2COR)(L)]^+$. The reaction increases the coordination number of metal ion from four to five or six, as described below,

$$[M(L)]^{2+} + CO_2 + ROH + B \longrightarrow [M(O_2COR)(L)]^+ + HB^+$$

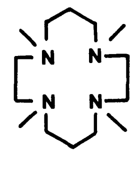
where B is base such as triethylamine or alkoxide. The starting complex, $[M(L)]^{2+}$, is of the square-planar type. In case of coordination of $ROCO_2^-$, geometry of $[M(L)]^{2+}$ changes to an octahedral or a trigonal bipyramidal type, giving rise to reactive vacant sites. Such a coordinately unsaturated nature of the $[M(L)]^{2+}$ complex is an important factor for the facile up-take reaction of the $ROCO_2^-$ ligand.

In the present study, similar reactions of certain nickel(II), zinc(II), and cadmium(II)-tetraazacycloalkane, in which CO_2 is taken up as carbamate ligand, $R_2NCO_2^-$, have been studied. The formation of free carbamate ion by the reaction of CO_2 with dialkylamine has been well characterized.[3] The tetraazacycloalkane ligand (L) used are (7*RS*,14*RS*)-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (L^1) or 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane (L^2). They are known to fold readily to afford five or six-coordinate complexes.

Carbamato complexes reported so far are obtained either by CO_2 insertion to metal-imido bond[3—5] or by ligand-exchange reaction with the carbamato ligand which has been produced in solution.[6—11] In this sence, the present reactions are of a unique type.



L^1



L^2

Experimental

Materials. α-$[Ni(L^1)](ClO_4)_2$,[12] $[Ni(O_2COCH_3)(L^2)](ClO_4)$,[2] $[Zn(O_2COH)(L^2)](ClO_4)$,[13] $[Zn(O_2COCH_3)(L^2)](ClO_4)$,[1] $[Cd(O_2COH)(L^2)](ClO_4)$,[13] and $[Cd(O_2COCH_3)(L^2)](ClO_4)$[13] were prepared according to the literature. The macrocyclic ligand L^2 was purchased from Strem Chemicals, Inc.

$[Ni(O_2CN(C_2H_5)_2)(L^1)](ClO_4)$ (1). CO_2 was bubbled through a suspended mixture of acetonitrile (10 cm³) and 1.08 g (2 mmol) of α-$[Ni(L^1)](ClO_4)_2$ for a few minutes. The violet solids of α-$[Ni(L^1)(CH_3CN)_2](ClO_4)_2$ were immediately dissolved upon addition of 0.29 g (4 mmol) of diethylamine to give blue violet solution. Continuous bubbling of CO_2 resulted in the formation of violet crystals. The mixture was kept in a freezer (−10 °C) overnight. Violet crystals (0.85 g) were recrystallized from acetonitrile. Yield: 76%.

$[Ni(O_2CNR_2)(L^1)](ClO_4)$, $R=CH_3$ (2), n-C_3H_7 (3), and n-C_4H_9 (4). These complexes were prepared in a similar way, except that chloroform was used as solvent in the case of dimethylamine.

$[Ni(O_2CN(C_2H_5)_2)(L^2)](ClO_4)$ (5). CO_2 was bubbled through chloroform solution containing 0.48 g (1 mmol) of $[Ni(O_2COCH_3)(L^2)](ClO_4)$ and 0.15 g (2 mmol) of diethylamine. The color of the solution changed from green to emerald green. CO_2 was bubbled for a minute, and diethyl ether (5 cm³) was added. Keeping the solution at −10 °C overnight, emerald green solids (0.47 g) were obtained and recrystallized from $CHCl_3$–ether. Yield 88%.

$[Ni(O_2CN(CH_3)_2)(L^2)](ClO_4)$ (6). This compound was prepared in the same way as **5** with use of dimethylamine.

$[Zn(O_2CNR_2)(L^2)](ClO_4)$, $R=CH_3$ (7), and C_2H_5 (8).

---

† Present address: Department of Chemistry, Aichi Kyoiku University, Kariya 448.

These were obtained either from $[Zn(O_2COCH_3)(L^2)](ClO_4)$ or $[Zn(O_2COH)(L^2)](ClO_4)$ in a similar way. To 3 cm³ of chloroform solution containing 0.50 g of $[Zn(O_2COCH_3)(L^2)](ClO_4)$ (1 mmol), 0.073 g (1 m mol) of diethylamine was added. After 15 min, 10 cm³ of diethylether was added and a white precipitate (0.38 g) of $[Zn(O_2CN(C_2H_5)_2)(L^2)](ClO_4)$ was obtained. Yield 70%.

$[Cd(O_2CNR_2)(L^2)](ClO_4)$, $R=CH_3$ (9), and C_2H_5 (10). These complexes were also prepared either from $[Cd(O_2COCH_3)(L^2)](ClO_4)$ or $[Cd(O_2COH)(L^2)](ClO_4)$ in a way similar to those for the corresponding zinc(II) complexes.

Elemental analyses of all the complexes prepared in this study were consistent with $[M(O_2CNR_2)(L)](ClO_4)$.

Measurements. The electronic and infrared spectra were recorded on a Hitachi 340 spectrophotometer and on a Jasco IR-810 infrared spectrophotometer, respectively. ^1H and ^{13}C NMR spectra were obtained on a Jeol FX-100 at 100 MHz and a Jeol GX-400 at 100 MHz, respectively. About 0.1 mmole of the sample was dissolved in 0.7 cm^{-3} of $CDCl_3$ for each NMR measurement.

X-Ray Analysis. A single crystal of $[Ni(O_2CN(C_2H_5)_2)(L^1)](ClO_4)$ with approximate dimensions 0.34×0.20×0.20 mm was used for X-ray study. Diffraction data were obtained on a Rigaku AFC-5 diffractometer with graphite monochromatized Mo$K\alpha$ radiation. Intensities were corrected for Lorentz and polarization factors. Crystal data are: monoclinic, C2/c, $a=15.842(3)$, $b=13.675(3)$, $c=13.753(2)$ Å, $\beta=109.94(1)°$, $V=2800.7(9)$ Å³, $Z=4$, $D_m=1.33$, $D_x=1.33$ g cm^{-3}, μ(Mo$K\alpha$)=0.83 mm^{-1}. The structure was solved by the heavy atom method and refined by block-diagonal least-squares method. The weighting scheme, $w=[\sigma_{\text{count}}{}^2+(0.015|F_o|)^2]^{-1}$, was employed. All the hydrogen atoms except for methyl hydrogens of carbamate ion were located by the difference Fourier syntheses. Hydrogens for the methyl groups were located at calculated positions. In the final refinement, all the hydrogen atoms were included with the isotropic temperature factors. The final R indicies were $R=0.048$ and $R_w=0.055$ for 2193 independent reflections with $|F_o|>3\sigma(F_o)$.[14]

Calculations were carried out on the HITAC M-200H computer at the Computer Center of the Institute for Molecular Science with the Universal Crystallographic Computation Program System, UNICS III.[15]

Results and Discussion

Synthesis. There are two routes, (A) and (B) for the preparation of the carbamato complexes, $[M(O_2CNR_2)(L)]^+$.

$$\text{(A)}\quad [M(L)]^{2+} + CO_2 + 2R_2NH \longrightarrow [M(O_2CNR_2)(L)]^+ + NH_2R_2{}^+,$$

$$\text{(B)}\quad [M(O_2CX)(L)]^+ + R_2NH \longrightarrow [M(O_2CNR_2)(L)]^+ + HX,$$

where $X=CH_3O^-$ or OH^-. The complexes, $[Ni(O_2CNR_2)(L^1)](ClO_4)$, were obtained easily through route (A). The reaction proceeds *via* the following mechanism.

$$2NHR_2 + CO_2 \rightleftharpoons (NH_2R_2)(O_2CNR_2),$$

$$\alpha\text{-}[Ni(L^1)](ClO_4)_2 + (NH_2R_2)(O_2CNR_2) \longrightarrow [Ni(O_2CNR_2)(L^1)](ClO_4) + NH_2R_2ClO_4.$$

In the case of L^2 complexes, carbamato complexes were obtained easily and cleanly *via* route (B) from corresponding hydrogencarbonato or monomethyl carbonato complexes. The formation may occur *via* the following scheme.

$$[M(O_2CX)(L^2)]^+ \rightleftharpoons [M(L^2)]^{2+} + CO_2 + X^-,$$

$$[M(L^2)]^{2+} + CO_2 + X^- + NHR_2 \longrightarrow [M(O_2CNR_2)(L^2)]^+ + HX.$$

As to the preparation of $[Ni(O_2CNR_2)(L^1)]^+$, it may be worthwhile to point out the following facts. The complex, $[Ni(L^1)]^{2+}$, is known to exist as three isomeric α-, β-, and γ-forms.[12,16] Of these three isomers, only the α-isomer reacts readily with a bidentate ligand such as oxalate,[12] acetylacetonate,[16] acetate,[17] or tartrate[18] to form *cis*-type six-coordinate complexes with the macrocyclic ligand folded. Thermodynamically most stable isomer is of the β-type, and the α-isomer isomerizes in neutral or at much faster rate in basic media to the β-isomer. Therefore, it is necessary to add dialkylamine after CO_2 is bubbled thoroughly into the solution containing α-$[Ni(L^1)](ClO_4)_2$, when the carbamato complex is synthesized through route (A). Desired carbamato complexes were hardly obtained in the case of β-$[Ni(L^1)](ClO_4)_2$, $[Ni(\textit{meso}\text{-}Me_6[14]aneN_4)](ClO_4)_2$, or $[Ni([14]aneN_4)](ClO_4)_2$, where the macrocyclic ligands take the conformation that can not fold (*meso*-$Me_6[14]aneN_4$=(7*SR*,14*RS*)-form of L^1 and $[14]aneN_4$=1,4,8,11-tetraazacyclotetradecane).

Infrared Spectra. Infrared spectra of nickel(II) and cadmium(II) complexes show strong ν_{CN} bands in the range of 1500—1520 cm^{-1}, while the corresponding absorptions of the zinc(II) complexes appear around 1580—1585 cm^{-1} (Tables 1 and 2). These frequency values of nickel(II) and cadmium(II) complexes are similar to the value of structurally determined compound **1**. Therefore, the carbamato ligands coordinate to the metals in bidente fashion. However, the values of zinc(II) complexes are somewhat higher than those of nickel(II) and cadmium(II) complexes, although they are in the normal range of bidentate carbamato ligands.[4] Rather high frequency values of zinc(II) complexes might be indicative of unsymmetric chelation of carbamate ion, since the frequency values are close to the value (ν_{CO}=1592 cm^{-1}) of $[Cd(O_2COH)(L^2)](ClO_4)$ in which two Cd–O bonds are nonequivalent and bond lengths differ by 0.152 Å.[13] Nonequivalent Zn–O bonds have also been found in six-coordinate $[Zn(O_2NC(CH_3)_2)(L^2)](ClO_4)$.[19]

Electronic Spectra of Nickel(II) Complexes. The electronic absorption spectra of nickel(II) complexes consist of three d-d bands corresponding to six-coordinate nickel(II) (Table 1). The absorption peaks of $[Ni(O_2CNR_2)(L^1)](ClO_4)$ are very close to those observed for NiL^1 complexes with *cis*-NiN_4O_2 chromophore, $[\{Ni(L^1)\}_2(d\text{-tart})(H_2O)](ClO_4)_2$,[18] and $[Ni(H_2O)_2(L^1)]Cl_2$.[20] The absorption spectra of $[Ni(O_2CNR_2)(L^2)](ClO_4)$ are quite similar to that of structurally

TABLE 1. INFRARED (IR) AND ELECTRONIC ABSORPTION (AB) SPECTRAL DATA OF $[Ni(O_2NR_2)(L)](ClO_4)$

Compounds	IR[a] $\nu_{CN,CO}/cm^{-1}$		AB[b] $\nu_{max}(\varepsilon)$	$\nu_{max}(\varepsilon)$	$\nu_{max}(\varepsilon)$
$[Ni(O_2CN(CH_3)_2)L^1](ClO_4)$	1540^m	1520	10.4(16)	17.4(20)	27.3(28)
$[Ni(O_2CN(C_2H_5)_2)L^1](ClO_4)$	1540^m	1520	10.4(17)	17.4(20)	27.3(29)
$[Ni(O_2CN(n\text{-}C_3H_7)_2)L^1](ClO_4)$	1525	1510	10.4(17)	17.4(20)	27.3(29)
$[Ni(O_2CN(n\text{-}C_4H_9)_2)L^1](ClO_4)$	1530^{sh}	1510	10.4(16)	17.4(28)	27.3(28)
$[Ni(O_2CN(CH_3)_2)L^2](ClO_4)$	1550	1515	9.52(15)	15.7(27)	25.7(52)
$[Ni(O_2CN(C_2H_5)_2)L^2](ClO_4)$	1530^m	1520	9.39(13)	15.8(34)	25.7(48)

a) Symbols m, and sh stand for medium absorption and shoulder band, respectively. b) in $CHCl_3$. ν_{max} and ε are given in $10^3\,cm^{-1}$ and in $M^{-1}\,cm^{-1}$, respectively ($1\,M=1\,mol\,dm^{-3}$).

TABLE 2. INFRARED,[a] ^1H AND ^{13}C NMR DATA[b] OF $[Zn(O_2CNR_2)(L^2)](ClO_4)$ AND $[Cd(O_2CNR_2)(L^2)](ClO_4)$.

Compounds	ν_{CN}/cm^{-1} [c]		^1H NMR[d] $\text{-C}\underline{\text{H}}_3$	$\text{-C}\underline{\text{H}}_2\text{-}$	^{13}C NMR[e] $\text{-}\underline{\text{C}}\text{H}_3$	$\text{-}\underline{\text{C}}\text{H}_2\text{-}$	$\text{C-}\underline{\text{C}}\text{-C}$	$\text{N-}\underline{\text{C}}\text{H}_3$	$\text{N-}\underline{\text{C}}\text{H}_2\text{-}$	$\text{N-}\underline{\text{C}}\text{H}_2\text{-}$
$[Zn(O_2CN(CH_3)_2)L^2](ClO_4)$	1608^m	1583	2.89^s		37.0		21.5	44.8	56.8	60.3^b
$[Zn(O_2CN(C_2H_5)_2)L^2](ClO_4)$	1610^m	1585	1.08^t	3.28^q	14.5	41.5	21.5	44.9	56.9	60.4^b
$[Cd(O_2CN(CH_3)_2)L^2](ClO_4)$	1525^{sh}	1515	2.90^s		37.5		22.3	44.5	57.0	61.2^b
$[Cd(O_2CN(C_2H_5)_2)L^2](ClO_4)$	1515^{sh}	1510	1.07^t	3.27^q	14.3	42.2	22.3	44.5	57.0	61.2^b

a) Nujol mull. b) In $CDCl_3$, TMS internal standard. c) Symbols m, and sh stand for medium absorption, and shoulder band, respectively. d) Alkyl groups in the carbamato ligand. e) b: broad.

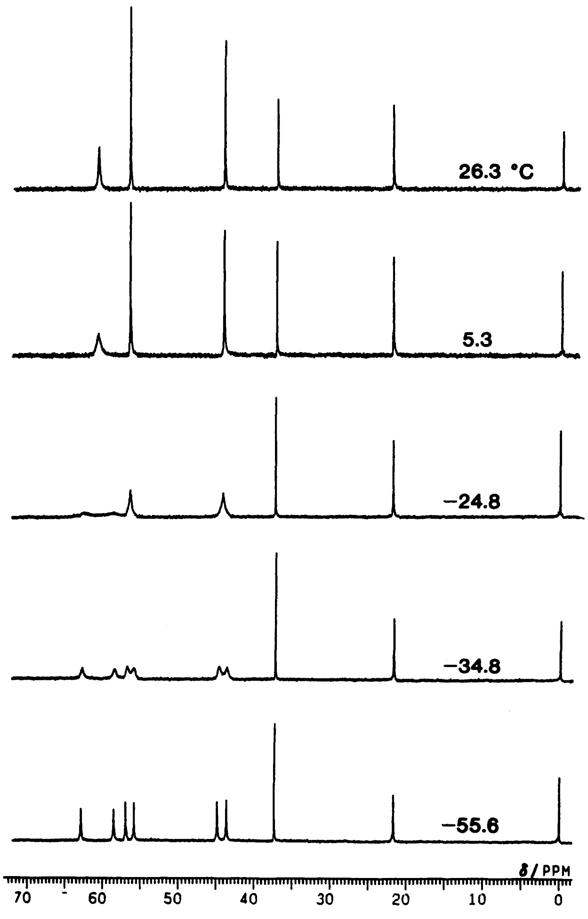
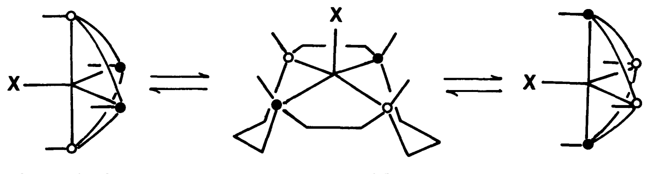


Fig. 1. The temperature depencence of ^{13}C NMR spectra of $[Cd(O_2CN(CH_3)_2)(L^2)](ClO_4)$ in $CDCl_3$. TMS is used as an internal standard.

characterized $[Ni(O_2NCH(CH_3))(L^2)](ClO_4)$, the coordination geometry of which is of the *cis*-NiN_4O_2 type.[19] The X-ray analysis of the latter complex revealed that the *N*-methyl orientation is of the three-up-one-down type in terms of Bosnich's notation.[21] The same *N*-methyl orientation may be assigned to the present $[Ni(O_2CNR_2)(L^2)]^+$ complexes from the following observations as well as the absorption data. Both $[Ni(O_2CNR_2)(L^2)](ClO_4)$ and $[Ni(O_2NCH(CH_3))(L^2)](ClO_4)$ show a single ligand field band at 502 nm in dilute perchloric acid solution, where they decompose to square-planar four coordinate species, $[Ni(L^2)]^{2+}$. On the other hand, the ligand field absorption of the complex, $[Ni(L^2)](ClO_4)_2$, prepared from nickel(II) perchlorate and L^2 (the four-up form),[22] and of the complex prepared from *N*-methylation of the two-up-two-down form of $[Ni([14]aneN_4)]^{2+}$,[23] occurs at 514 and 493 nm, respectively, in the same solvent.

NMR Spectra. ^1H and ^{13}C NMR spectral data for $[Zn(O_2CNR_2)(L^2)](ClO_4)$ and $[Cd(O_2CNR_2)(L^2)](ClO_4)$ are given in Table 2. Spectral patterns, chemical shifts, and relative intensity relations are consistent, in all respects, with $[M(O_2CNR_2)(L^2)]^+$. In all the compounds studied, two alkyl groups of the carbamato ligand are pairwise equivalent. Interestingly, the ligand L^2 shows only four sharp signals in ^{13}C NMR spectra at room temperature, that is, one-forth of the ligand is magnetically independent on ^{13}C NMR time scale. When the temperature is lowered, a sharp singlet due to the central carbon of the six-membered chelate ring and signals of the carbamato ligand remained unchanged even at 217 K but the remaining three absorptions of L^2 broaden and finally each splits into two signals. Figure 1 shows such an example for $[Cd(O_2CN(CH_3)_2)(L^2)](ClO_4)$. The spectral pattern at 217



trigonal bipyramidal square pyramidal trigonal bipyramidal

K indicates that the complex adopts C_2 symmetry. A very similar temperature dependence was also observed for $[Zn(O_2CN(CH_3)_2)(L^2)](ClO_4)$ in $CDCl_3$. This observation can be interpreted by the dynamic process shown above, as characterized well for $[ZnX(L^2)]^+$, where X is Cl^- or NCS^-,[24] and $[Cd(L^2)](NO_3)_2$.[25] The activation parameters of the dynamic processes were obtained by full line-shape analyses with use of DNMR3 program.[26] The results were $\Delta H^{\neq}=34\pm3$ and 33 ± 4 kJ mol^{-1}, and $\Delta S^{\neq}=-63\pm13$ and -61 ± 20 J deg^{-1} mol^{-1}, for zinc(II) and cadmium(II) complex respectively. The similarity of the activation parameters of both zinc(II) and cadmium(II) supports the same dynamic process.[25]

Although the infrared data indicate the formation of six-coordinate complex with the chelated carbamato ligand, the occurrence of the dynamic process suggests that the coordination geometry about the metal can be taken as the trigonal bipyramidal type. The two donor oxygens of the carbamato ligand occupy an apex of the trigonal bipyramid as shown below. In fact, X-ray structural analyses of $[Zn(O_2NC(CH_3)_2)(L^2)](ClO_4)$,[19] $[Cd(O_2COH)(L^2)](ClO_4)$,[13] and $[Cd(NO_3)(L^3)]_2[Cd(NO_3)_4]$,[27] where L^3 denotes 1,5,9,13-tetramethyl-1,5,9,13-tetraazacyclohexadecane, revealed that their coordination geometries are very similar to the structure shown above and are described better as pseudo trigonal bipyramidal. At the low temperature, the dynamic process is frozen and the complex is considered to have the trigonal bipyramidal geometry with C_2 symmetry, where the carbamato ligand chelates the metal symmetrically through two oxygen atoms.[28] In the NMR studies of the L^2 complexes of zinc(II) and cadmium(II), there were no indications for the presence of the three-up-one-down form found for the

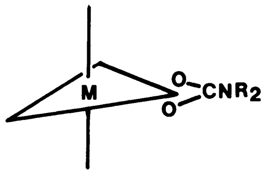


Table 3. Atomic coordinates (×10^4) and thier standard deviations

Atom	x	y	z
Ni†1	0	2288(0)	2500
Cl†1	0	−1302(1)	2500
N(L)†1	0	5067(3)	2500
C(L)†1	0	4080(3)	2500
O(L)	517(2)	3612(2)	3279(2)
C1(L)	563(3)	5606(3)	3380(4)
C2(L)	139(7)	5914(7)	4110(5)
N(1)	−901(2)	1340(2)	1447(2)
N(4)	748(2)	2205(2)	1487(2)
C(2)	−682(3)	1439(3)	493(3)
C(3)	322(3)	1397(4)	761(3)
C(5)	1756(3)	2204(4)	1898(3)
C(6)	2075(3)	1412(3)	2730(3)
C(7)	1870(3)	1515(3)	3730(3)
C1(M)	2076(3)	3197(4)	2318(4)
C2(M)	2139(4)	1992(5)	1031(5)
C3(M)	2489(3)	825(4)	4542(4)
OP(1)†1,3	−744(6)	−998(7)	1672(7)
OP(2)†1,3	375(8)	−2078(6)	2088(7)
OP(3)†1,3	−548(7)	−678(8)	2929(8)
OP(4)†2,3	−68(12)	−601(10)	3239(10)
OP(5)†2,3	−679(11)	−1818(11)	1814(12)

†1 Occupancy factor is 0.5. †2 Occupancy factor is 0.25. †3 Perchlorate oxgens (OP) were found to be in disorder, and were located at five major positions. The occupancy factors were tentatively determined so that their thermal parameters became nealy equal.

Table 4. Bond lengths (l/Å) and bond angles (ϕ/°) within the complex cation and their estimated standard deviations

Ni	-O(L)		2.121(2)	N(4)	-C(3)		1.488(5)
Ni	-N(1)		2.099(3)	N(4)	-C(5)		1.501(5)
Ni	-N(4)		2.117(3)	C(2)	-C(3)		1.507(7)
O(L)	-C(L)		1.276(3)	C(5)	-C(6)		1.530(6)
C(L)	-N(L)		1.351(6)	C(6)	-C(7)		1.523(7)
N(L)	-C1(L)		1.438(5)	C(5)	-C1(M)		1.495(7)
C1(L)	-C2(L)		1.449(11)	C(5)	-C2(M)		1.539(9)
N(1)	-C(2)		1.472(6)	C(7)	-C3(M)		1.534(6)
N(1)	-C(7′)		1.489(5)				
O(L)	-Ni	-O(L′)	62.8(1)	C(2)	-N(1)	-C(7′)	112.5(3)
O(L)	-Ni	-N(1)	158.5(1)	Ni	-N(4)	-C(3)	104.7(3)
O(L)	-Ni	-N(4)	99.9(1)	Ni	-N(4)	-C(5)	120.9(2)
O(L)	-Ni	-N(1′)	97.1(1)	C(3)	-N(4)	-C(5)	115.7(3)
O(L)	-Ni	-N(4′)	85.4(1)	N(1)	-C(2)	-C(3)	109.2(3)
N(1)	-Ni	-N(1′)	103.7(1)	N(4)	-C(3)	-C(2)	109.6(4)
N(1)	-Ni	-N(4)	85.1(1)	N(4)	-C(5)	-C(6)	108.7(4)
N(1)	-Ni	-N(4′)	91.1(1)	N(4)	-C(5)	-C1(M)	108.8(4)
N(4)	-Ni	-N(4′)	173.9(1)	N(4)	-C(5)	-C2(M)	111.0(3)
Ni	-O(L)	-C(L)	88.7(2)	C(6)	-C(5)	-C1(M)	111.8(3)
O(L)	-C(L)	-O(L′)	119.9(4)	C(6)	-C(5)	-C2(M)	109.2(4)
O(L)	-C(L)	-N(L)	120.1(2)	C1(M)	-C(5)	-C2(M)	107.4(4)
C(L)	-N(L)	-C1(L)	120.8(2)	C(5)	-C(6)	-C(7)	119.4(4)
C1(L)	-N(L)	-C1(L′)	118.4(4)	C(6)	-C(7)	-C3(M)	108.7(4)
N(L)	-C1(L)	-C2(L)	115.6(5)	C(6)	-C(7)	-N(1′)	111.3(3)
Ni	-N(1)	-C(2)	104.3(2)	C3(M)	-C(7)	-N(1′)	112.8(4)
Ni	-N(1)	-C(7′)	115.7(2)				

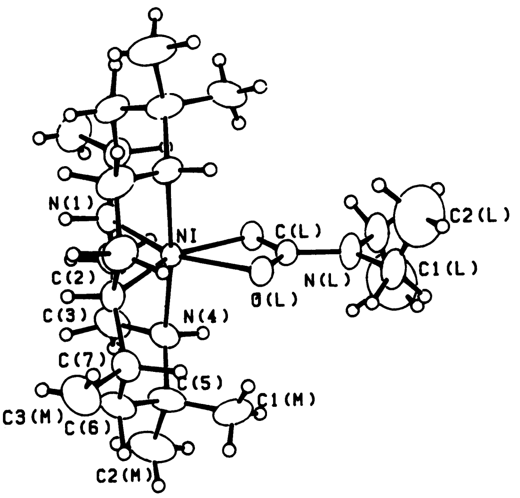


Fig. 2. ORTEP view of $[Ni(O_2CN(C_2H_5)_2)L^1]^+$ along with the atom numbering scheme.

corresponding nickel(II) complexes.

X-Ray Structure. The crystal structure of $[Ni(O_2CN(C_2H_5)_2)(L^1)](ClO_4)$ has been determined by X-ray analysis. Atomic parameters and relevant bond lengths and angles are given in Tables 3 and 4, respectively. Figure 2 shows an ORTEP view of the complex cation along with the atom numbering scheme.

Three types of coordination bonding modes are known for carbamato ligand:$^{4-11)}$ (1) unidentate, (2) bidentate chelate, and (3) bridging. The present X-ray analysis revealed that the carbamato ligand adopts the type (2) structure.

The complex has crystallographic C_2 symmetry, the C_2-axis passing through Ni, C(L) and N(L) atoms. The metal-donor atom set, NiN_4O_2, is a distorted octahedron as is seen from the bond angles about Ni (Table 4). The Ni–N distances within NiN_2O_2 plane are slightly shorter than those of the axial Ni–N bonds. The C(L)–N(L) bond is shortened to 1.351(6) Å evidently through the influence of the $-CO_2^-$ group and has partial double bond character. The bond angles around C(L) and N(L) are approximately 120°, and the NiO_2CNC_2 moiety is planar within experimental error.

As has often been found for other carbamato complexes, methyl groups of the carbamato ligand have large thermal parameters due to the disordered orientation of the ethyl groups.$^{8)}$ Short distances, N(L)–Cl(L)= 1.44(1) and Cl(L)–C2(L)=1.45(1) Å arise likely from such a situation.

All the present results including IR, NMR, electronic spectral and X-ray data indicate that the carbamato complexes obtained in this study have coordination geometry of *cis*-MO_2N_4 type. The desired carbamato complexes $[M(O_2CNR_2)(L)]^+$ were obtained with the tetraazacycloalkanes such as L^1 and L^2 which are known to fold readily, whereas tetraaza macrocyclic ligands which favor square-planar coordination did not work nicely. From these results, it is concluded that use of macrocyclic ligands of the former type is essential for the $R_2NCO_2^-$ uptake reaction by $[M(L)]^{2+}$ complexs. It is in contrast to the case of monoalkyl carbonato complex, $[M(O_2COR)(L)]^+$, formed similarly upon CO_2 uptake in basic alcohol.$^{1,2)}$

For the formation of $[M(O_2CNR_2)(L)]^+$ as well as $[M(O_2COR)(L)]^+$ unsaturated coordination of the starting complex $[M(L)]^{2+}$ is very important. Nickel(II), zinc(II) and cadmium(II) fulfill the required coordination behavior and work nicely.

The present study was supported by Grant-in-Aid for Scientific Research No. 58470039 from the Ministry of Education, Science and Culture.

References

1) M. Kato and T. Ito, *Inorg. Chem.*, **24**, 504 (1985).

2) M. Kato and T. Ito, Presented at 34th Meeting on Coordination Chemistry, Nagaoka, Oct. 1984, 3A05.

3) For example, A. Jensen, M. B. Jensen, and C. Faurholt, *Acta Chem. Scand.*, **8**, 1129 (1954); G. Astarita, G. Marrucci, and F. Gioia, *Chem. Eng. Sci.*, **19**, 95 (1964).

4) M. H. Chisholm and M. W. Extine, *J. Am. Chem. Soc.*, **99**, 782 (1977).

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

6) M. H. Chisholm, F. A. Cotton, M. W. Extine, and D. C. Rideout, *Inorg. Chem.*, **17**, 3536 (1978).

7) T. V. Ashworth, M. Nolte, and E. Singleton, *J. Organomet. Chem.*, **121**, C57 (1976).

8) F. Calderazzo, G. Dell'Amico, R. Netti, and M. Pasquali, *Inorg. Chem.*, **17**, 471 (1978); F. Calderazzo, G. Dell'Amico, M. Pasquali, and G. Perego, *ibid.*, **17**, 474 (1978).

9) F. Ozawa, T. Ito, and A. Yamamoto, *Chem. Lett.*, **1979**, 735.

10) T. Yamamoto, M. Kubota, and A. Yamamoto, *Bull. Chem. Soc. Jpn.*, **53**, 680 (1980).

11) D. B. Dell'Amico and F. Calderazzo, *J. Chem. Soc., Dalton Trans.*, **1984**, 647.

12) L. G. Warner and D. H. Busch, *J. Am. Chem. Soc.*, **91**, 4092 (1969).

13) H. Ito and T. Ito, to be published elsewhere.

14) Tables of hydrogen atomic coordinates, anisotropic thermal parameters, and observed and calculated structure factors are kept in the office of the Chemical Society of Japan (Document No. 8527).

15) T. Sakurai and K. Kobayashi, *Rikagaku Kenkyusho Hokoku*, **55**, 69 (1979).

16) N. F. Curtis, D. A. Swann, and T. N. Waters, *J. Chem. Soc., Dalton Trans.*, **1973**, 1963.

17) P. O. Whimp, M. F. Bailey, and N. F. Curtis, *J. Chem. Soc., A*, **1970**, 1956.

18) H. Ito, J. Fujita, K. Toriumi, and T. Ito, *Bull. Chem. Soc. Jpn.*, **54**, 2988 (1981).

19) H. Ito and T. Ito, presented at 34th Meeting on Coordination Chemistry, Nagaoka, Oct. 1984, 1PA10.

20) H. Ito, M. Sugimono, and T. Ito, *Bull. Chem. Soc. Jpn.*, **55**, 1971 (1982).

21) B. Bosnich, M. L. Tobe, and G. A. Webb, *Inorg. Chem.*, **4**, 1100 (1965).

22) E. K. Barefield and F. Wagner, *Inorg. Chem.*, **12**, 2435

(1973).

23) F. Wagner, M. T. Mocella, M. J. D'Aniello, Jr., A. H. J. Wang, and E. K. Barefield, *J. Am. Chem. Soc.*, **96**, 2625 (1974).

24) N. W. Alcock, N. Herron, and P. Moore, *J. Chem. Soc. Dalton, Trans.*, **1978**, 1282.

25) N. W. Alcock, E. H. Curson, N. Herron, and P. Moore, *J. Chem. Soc. Dalton Trans.*, **1979**, 1987.

26) B. Binsch, *Top. Stereochem.*, **3**, 97 (1968).

27) E. Farkas, I. Sovago, T. Kiss, and A. Gergely, *J. Chem. Soc. Dalton Trans.*, **1984**, 611.

28) Even at the low temperature, there is a possibility such that the carbamato ligand is coordinated in a unidentate fashion through one oxygen atom and bonded and non-bonded oxygen atoms exchange rapidly.[4]