Contribution from the Departments of Chemistry Education and Chemistry,
Seoul National University, Seoul 151, Korea

Nickel(II) Complexes of Novel Ligands Containing a Tetraazabicyclononane Ring: Syntheses and Structures of [3,7-Bis(2-aminoethyl)-1,3,5,7-tetraazabicyclo[3.3.1]nonane]nickel(II) Perchlorate and (8-Methyl-1,3,6,8,10,13,15-heptaazatricyclo[13.1.1.1^{13,15}]octadecane)nickel(II) Perchlorate

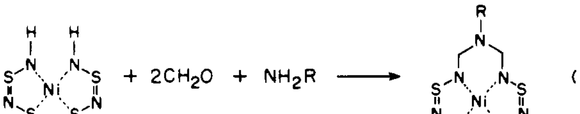
Myunghyun Paik Suh,* Whanchul Shin,* Hyunju Kim, and Chung Hoe Koo

Received October 7, 1986

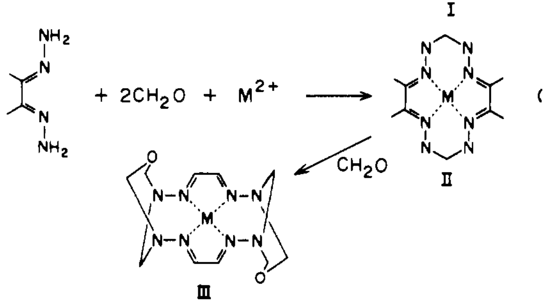
Square-planar Ni(II) complexes that contain a tetraazabicyclononane ring in the ligands were synthesized, and their X-ray crystal structures were determined. The noncyclic Ni(II) complex of 3,7-bis(2-aminoethyl)-1,3,5,7-tetraazabicyclo[3.3.1]nonane, [Ni($C_9H_{22}N_6$)](ClO_4)$_2$ (**1**), was prepared by the template condensation reaction of ethylenediamine, formaldehyde, and ammonia in the presence of Ni(II) ion. The macrocyclic Ni(II) complex of 8-methyl-1,3,6,8,10,13,15-heptaazatricyclo[13.1.1.1^{13,15}]octadecane, [Ni($C_{12}H_{27}N_7$)](ClO_4)$_2$ (**2**), was synthesized by the reaction of **1** with formaldehyde and methylamine. Complex **1** decomposes relatively rapidly while complex **2** exhibits marked stability in acidic aqueous solutions. Cyclic voltammetry indicates that the formal potentials of redox couples NiL^{2+}/NiL^{3+} and NiL^{2+}/NiL^{+} are +1.24 and −1.34 V for complex **1** and +1.32 and −1.39 V for complex **2**, respectively, vs. SCE. [Ni($C_9H_{22}N_6$)](ClO_4)$_2$ crystallizes in the orthorhombic space group *Imm*2 with a = 7.459 (1) Å, b = 9.287 (1) Å, c = 12.725 (1) Å, and Z = 2. The structure was solved by Patterson methods and refined isotropically to an R value of 0.093 for 405 observed reflections measured with Mo Kα radiation on a diffractometer. The cation has crystallographic *mm* symmetry. The Ni(II) ion coordinates four nitrogens in a square-planar arrangement with an average Ni–N distance of 1.90 Å. The structure could not be refined anisotropically due to disorder phenomena in the perchlorate anions and possibly in the whole cation. [Ni($C_{12}H_{27}N_7$)](ClO_4)$_2$ crystallizes in the monoclinic space group $P2_1/c$ with a = 15.351 (3) Å, b = 9.521 (1) Å, c = 14.065 (2) Å, β = 92.49 (2)°, and Z = 4. The structure was solved by Patterson methods and refined to an R value of 0.0493 for 2286 observed reflections measured with Mo Kα radiation on a diffractometer. The cation has a pseudo plane of symmetry that is perpendicular to the square-planar coordination plane. The Ni(II) ion is shifted 0.0034 (1) Å from the least-squares plane of four nitrogen donors with an average Ni–N distance of 1.918 ± 0.003 Å. The N–Ni–N angle, 89.1 (2)°, and the N–N bite distance, 2.691 (6) Å, of the six-membered chelate ring involving the tetraazabicyclononane ring are unusually small.

Introduction

Various complexes have been synthesized by the template condensation of amines with aldehydes or ketones in the presence of metal ions.[1-10] In particular, formaldehyde has been utilized for cyclization to link two amine moieties. For example, the polydentate complex I[5] and macrocyclic complexes II[6] and III[7] have been synthesized as indicated in eq 1 and 2.



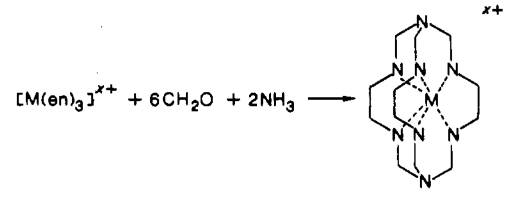
I



II

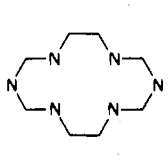
III

More recently Co(III), Pt(IV), and Ni(II) macrobicyclic complexes IV were prepared from the condensation reaction of [M(en)$_3$]$^{x+}$, formaldehyde, and ammonia.[8-10]

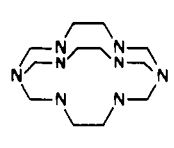


IV

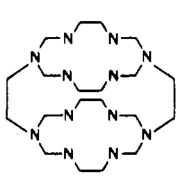
We have attempted to prepare the complexes of various ligands such as a, b, and c from the condensation reaction of ethylenediamine, formaldehyde, and ammonia by utilizing Ni(II) ion as a template.



a

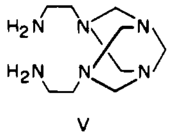


b

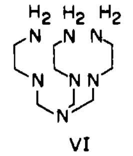


c

We have obtained, however, the Ni(II) complex of an unexpected noncyclic tetradentate ligand V as the major product, in addition to the macrobicyclic complex IV (M = Ni) and the Ni(II) complex with a noncyclic hexadentate ligand VI as the minor products from the reaction. Complex IV (M = Ni) and the Ni(II) complex of VI were already reported, and the stability of methylendiamine linkage was discussed.[10-12]



V



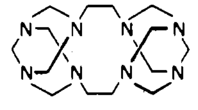
VI

---

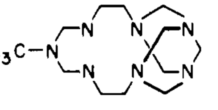
(1) Konefal, E.; Loeb, S. J.; Stephan, D. W.; Willis, C. J. *Inorg. Chem.* **1984**, *23*, 538.
(2) Martin, J. W. L.; Timmons, J. H.; Martell, A. E.; Willis, C. J. *Inorg. Chem.* **1980**, *19*, 2328.
(3) Loeb, S. J.; Richardson, J. R.; Willis, C. J. *Inorg. Chem.* **1983**, *22*, 2736.
(4) Eggleston, D. S.; Jackels, S. C. *Inorg. Chem.* **1980**, *19*, 1953.
(5) Thewalt, U.; Bugg, C. E. *Chem. Ber.* **1972**, *105*, 1614.
(6) Peng, S. M.; Gordon, G. C.; Goedken, V. L. *Inorg. Chem.* **1978**, *17*, 119.
(7) Peng, S. M.; Goedken, V. L. *Inorg. Chem.* **1978**, *17*, 820.
(8) Creaser, I. I.; Geue, R. M.; Harrowfield, J. M.; Herlt, A. J.; Sargeson, A. M.; Snow, M. R.; Springborg, J. *J. Am. Chem. Soc.* **1982**, *104*, 6016.
(9) Boucher, H. A.; Lawrance, G. A.; Lay, P. L.; Sargeson, A. M.; Bond, A. M.; Sangster, D. F.; Sullivan, J. C. *J. Am. Chem. Soc.* **1983**, *105*, 4652.
(10) Suh, M. P.; Shin, W.; Kim, D.; Kim, S. *Inorg. Chem.* **1984**, *23*, 618.

0020-1669/87/1326-1846$01.50/0

The Ni(II) complex of V, 3,7-bis(2-aminoethyl)-1,3,5,7-tetraazabicyclo[3.3.1]nonane, contains primary amine groups, and we expected that the complex could undergo further condensation reactions with formaldehyde and ammonia to yield a macrocyclic ligand VII, which contains two tetraazabicyclononane rings.



VII



VIII

However, the complexes of VII were never produced. The Ni(II) complex of V, instead, reacted with formaldehyde and methylamine to result in the Ni(II) complex of macrocycle VIII, 8-methyl-1,3,6,8,10,13,15-heptaazatricyclo[13.1.1.1^{13,15}]octadecane.

This paper is an account of the syntheses and X-ray structure determinations of the complexes $[Ni(C_9H_{22}N_6)](ClO_4)_2$ and $[Ni(C_{12}H_{27}N_7)](ClO_4)_2$, which contain ligands V and VIII, respectively.

Experimental Section

Materials. All solvents and chemicals used in synthesis were of reagent grade and were used without further purification. For electrochemical experiments, high-purity acetonitrile was obtained from Aldrich Chemical Co. and dried over 5-Å molecular sieves.

Measurements. Conductance measurements were performed by using an Industrial Instruments Model RC 216 B2 conductivity bridge in conjunction with a Beckman Model C1-BB1 conductivity cell with the cell constant of 0.10 cm^{-1}. Infrared spectra were measured with a Perkin-Elmer Model 283 spectrophotometer. Electronic absorption spectra were recorded with a Varian Tectron 635D UV/vis spectrophotometer. Proton magnetic resonance spectra were recorded with a Varian EM360 60-MHz NMR spectrometer. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN. Cyclic voltammetry was carried out with a Princeton Applied Research Corp. (PARC) 173 potentiostat coupled with a PARC 175 universal programmer and Watanabe XY recorder. The electrochemical data were obtained in acetonitrile with 0.1 M $(n\text{-}Bu)_4NClO_4$ as supporting electrolyte. The working electrode was a platinum disk, the auxiliary electrode was a coiled platinum wire, and the reference electrode was Ag/AgClO$_4$ (0.1 M in CH_3CN), which showed +0.24 V vs. SCE.

Synthesis. *Caution!* Some of the compounds containing perchlorate anions must be regarded as potentially explosive and should be handled with caution.

$[Ni(C_9H_{22}N_6)](ClO_4)_2$. To a stirred methanol (60 mL) solution of $NiCl_2 \cdot 6H_2O$ (23.8 g) were added 98% ethylenediamine (13.5 mL), 28% ammonia (13.5 mL), and 36% aqueous formaldehyde (32.4 mL), and the mixture was refluxed for 48 h until a dark brown solution resulted. The solution was filtered to remove insoluble nickel hydroxide. Excess perchloric acid was added to the filtrate to induce crystallization. The yellow crystals formed were filtered and washed with a 1:1 mixture of methanol and water. The crystals were recrystallized from hot water with a few milliliters of triethylamine added. The complex was also crystallized from the reaction mixture by adding an aqueous solution of LiClO$_4$ instead of HClO$_4$. In this case, yellow crystals mixed with pink crystals were formed. The mixture was separated by fractional crystallization from hot water. The resulting needle-shaped yellow crystals were filtered, washed with cold methanol, and dried in vacuo. The same complex was formed even when the condensation was carried out with a great excess of formaldehyde and ammonia. Crystals for X-ray crystallographic work were obtained by dissolving the yellow crystals in 1:1 methanol–water mixture followed by slow evaporation of the solvent. Yield: ≈92%. Anal. Calcd for $NiC_9H_{22}N_6Cl_2O_8$: C, 22.91; H, 4.70; N, 17.81; Ni, 12.44. Found: C, 23.35; H, 4.81; N, 17.79; Ni, 12.44.

$[Ni(C_{12}H_{27}N_7)](ClO_4)_2$. $[Ni(C_9H_{22}N_6)](ClO_4)_2$ (3.5 g) was dissolved in 1:1 methanol–water (60 mL). Into this solution were added 36% formaldehyde (3.5 mL) and 40% methylamine (2.8 mL), and the mixture was refluxed for 48 h. The reaction mixture was filtered hot, and the solution was concentrated and cooled. Then, yellow needle-shaped crystals were formed, which were filtered, washed with a methanol–water mixture, and air-dried. Crystals for X-ray studies were obtained by cooling a saturated water solution. Yield: ≈73%. Anal. Calcd for $NiC_{12}H_{27}N_7Cl_2O_8$: C, 27.35; H, 5.16; N, 18.60. Found: C, 26.79; H, 4.91; N, 18.21.

Table I. Summary of Crystal Data and Data Collection for $[Ni(C_{12}H_{27}N_7)](ClO_4)_2$

fw	527.01
a, Å	15.351 (3)
b, Å	9.521 (1)
c, Å	14.065 (2)
β, deg	92.49 (2)
V, Å^3	2053.7 (5)
space group	$P2_1/c$
Z	4
d_{measd}, g cm^{-3}	1.693
d_{calcd}, g cm^{-3}	1.705
abs coeff, cm^{-1}	12.17
cryst size, mm^3	0.30 × 0.45 × 0.15
T of data collcn, °C	18
wavelength of Mo Kα radiation, Å	0.71069
monochromator	graphite crystal
data collcn method	$2\theta/\omega$ scan
scan speed in 2θ, deg/min	2
scan range in ω, deg	$1.3 + 0.55 \tan \theta$
max 2θ, deg	50.0
no. of unique data measd	3642
no. of obsd data ($F_o > 6\sigma(F_o)$)	2286
number of variables	380
$R_F{}^a$	0.0493
$R_{wF}{}^b$	0.0543
goodness of fit^c	0.986

$^a R_F = \sum||F_o| - |F_c||/\sum|F_o|$. $^b R_{wF} = [\sum w(|F_o| - |F_c|)^2/\sum wF_o{}^2]^{1/2}$. ^{c}Error in an observation of unit weight is equal to $[\sum w(|F_o| - |F_c|)^2/(m - n)]^{1/2}$, where m = number of observations and n = number of variables in the least-squares refinement.

$[Ni(C_9H_{22}N_6)](PF_6)_2$ and $[Ni(C_{12}H_{27}N_7)](PF_6)_2$. To an acetonitrile suspension of perchlorate salts of corresponding complex ions was added excess NH_4PF_6 dissolved in acetonitrile. The complex went into the solution, and white precipitates of NH_4ClO_4 were formed. After NH_4ClO_4 was filtered off, water was added dropwise to the filtrate to induce crystallization. The crystals were filtered, washed with a 5:1 mixture of water and acetonitrile, and dried.

$[Ni(C_9H_{22}N_6)(NCS)_2]$. To an acetonitrile solution (50 mL) of $[Ni(C_9H_{22}N_6)](ClO_4)_2$ (2 g) was added excess KSCN (1.5 g) dissolved in methanol. The solution was concentrated and cooled. Blue precipitates contaminated with KClO$_4$ were isolated. The KClO$_4$ contaminant was removed from the mixture by heating a methanol suspension of the precipitate and filtering the less soluble blue crystals. The blue crystals were purified further by recrystallization from acetonitrile containing dissolved KSCN to prevent dissociation of the coordinated NCS$^-$ ligands. The needle-shaped blue crystals that formed were filtered, washed with a 1:5 mixture of acetonitrile and ether, and dried in vacuo. Anal. Calcd for $NiC_{11}H_{22}N_8S_2$: C, 33.95; H, 5.70; N, 28.79. Found: C, 33.08; H, 5.99; N, 29.16.

X-ray Diffraction Measurements. $[Ni(C_9H_{22}N_6)](ClO_4)_2$. An initial X-ray photographic examination established that the crystal system was orthorhombic. Systematic extinctions ($h + k + l = 2n$ only) indicated that the space group could be either $I2_12_12_1$, $I222$, $Immm$, or $Imm2$. The anticipated presence of the molecular symmetry in the ligand, together with the requirement of only two formula units in the unit cell, suggested the correct space group to be $Imm2$. This choice was later confirmed in the process of structure determination. The intensities of 482 independent reflections were measured by using Mo Kα radiation within the range of $2\theta < 60°$ on an automated Rigaku AFC diffractometer.[13] A total of 47 reflections were considered unobserved as defined by $F < 6\sigma(F)$. Details of crystallographic studies of this complex are similar to those described for $[Ni(C_{12}H_{27}N_7)](ClO_4)_2$ unless stated specifically. The crystal data are as follows: fw 471.9; orthorhombic; $a = 7.459$ (1), $b = 9.287$ (1), $c = 12.725$ (1) Å; $V = 881.9$ Å^3; $d_{measd} = 1.77$, $d_{calcd} = 1.73$ g cm^{-3}; $Z = 2$; space group $Imm2$; $\mu = 13.94$ cm^{-1}; $F(000) = 484$.

$[Ni(C_{12}H_{27}N_7)](ClO_4)_2$. An initial X-ray photographic examination established that the crystals were monoclinic with space group $P2_1/c$. The unit cell parameters were determined by a least-squares fit of 2θ angles for 25 reflections ($10° < 2\theta < 35°$) measured with Mo Kα radiation. The 2θ value used for each reflection was the average of the values for the Friedel pair. Details of the crystal parameters along with

---

(11) Suh, M. P.; Kim, D.; Kim, S. *Inorg. Chem.* **1985**, *24*, 3712.

(12) Shin, W.; Kim, S. S.; Suh, M. P. *Abstracts of Papers*, Meeting of the American Crystallographic Association, Aug 1982; American Crystallographic Association: San Diego, CA, 1982; p C9.

(13) Data collection and data reduction were performed by using the Rigaku-Denki AFC software system for a PDP-8 computer.

Table II. Atomic Coordinates (×10^3; ×10^2 for primed O's) and Thermal Parameters (10^2 × Å^2) for $[Ni(C_9H_{22}N_6)](ClO_4)_2$[a]

atom	*x*	*y*	*z*	U_{iso}	sof[b]
Ni	0	0	0	3.2 (4)	0.25
N(1)	162 (6)	0	−234 (3)	7 (1)	0.5
N(2)	0	142 (5)	−108 (5)	6 (1)	0.5
N(3)	0	150 (6)	101 (5)	7 (1)	0.5
C(1)	0	0	−294 (7)	9 (2)	0.25
C(2)	169 (6)	127 (5)	−170 (3)	8 (1)	1.0
C(3)	0	292 (8)	−49 (5)	8 (1)	0.5
C(4)	0	285 (8)	59 (5)	11 (1)	0.5
Cl(A)	0	0	389 (1)	5.8 (9)	0.25
O(1)	0	122 (9)	327 (6)	10	0.39
O(2)	154 (9)	0	455 (5)	10	0.39
O(1)′	0	13 (3)	43 (2)	10	0.11
O(2)′	154 (9)	0	455 (5)	10	0.11
Cl(B)	0	500	609 (1)	5.8 (9)	0.25
O(3)	154 (9)	500	679 (5)	10	0.16
O(4)	0	425 (7)	544 (5)	10	0.16

[a] Esd's in parentheses refer to the least significant digit. The coordinates without esd's were those fixed by the space group symmetry. Thermal parameters without esd's were fixed during the refinement. [b] Site occupancy factor.

Table III. Atomic Coordinates and Equivalent Thermal Parameters of Non-Hydrogen Atoms for $[Ni(C_{12}H_{27}N_7)](ClO_4)_2$[a]

atom	*x*	*y*	*z*	U_{eq}[b]	sof[c]
Ni	75568 (4)	51404 (6)	16935 (4)	48	1.0
N(1)	7105 (3)	7074 (5)	−221 (3)	31	1.0
N(3)	7855 (3)	4959 (5)	391 (3)	41	1.0
N(6)	8543 (3)	3982 (5)	2023 (3)	40	1.0
N(8)	8255 (3)	3697 (6)	3717 (4)	52	1.0
N(10)	7186 (3)	5344 (5)	2971 (3)	37	1.0
N(13)	6551 (3)	6219 (4)	1284 (3)	37	1.0
N(15)	6334 (3)	4891 (5)	−199 (3)	48	1.0
C(2)	7928 (4)	6355 (7)	−117 (5)	48	1.0
C(4)	8709 (4)	4206 (8)	348 (5)	50	1.0
C(5)	8752 (4)	3160 (7)	1158 (5)	49	1.0
C(7)	8486 (5)	3031 (7)	2868 (5)	52	1.0
C(9)	7375 (5)	4183 (8)	3680 (5)	56	1.0
C(11)	6236 (4)	5635 (7)	2899 (5)	47	1.0
C(12)	6108 (4)	6714 (6)	2142 (4)	45	1.0
C(14)	5968 (4)	5258 (6)	692 (5)	46	1.0
C(16)	6479 (5)	6163 (7)	−751 (5)	54	1.0
C(17)	6758 (4)	7482 (6)	664 (4)	44	1.0
C(18)	7129 (4)	4127 (7)	−111 (5)	47	1.0
C(19)	8880 (6)	4667 (11)	4137 (6)	76	1.0
Cl(A)	6098 (1)	1239 (1)	1519 (1)	55	1.0
Cl(B)	8906 (1)	8484 (2)	2267 (1)	55	1.0
O(1)	5810 (4)	100 (5)	2043 (5)	103	1.0
O(2)	6359 (8)	2355 (7)	2128 (6)	146	0.824
O(3)	5451 (5)	1822 (10)	921 (9)	134	0.824
O(4)	6808 (5)	852 (8)	979 (6)	111	0.824
O(5)	9423 (3)	9244 (6)	2938 (4)	90	1.0
O(6)	8815 (5)	9296 (10)	1430 (5)	98	0.831
O(7)	9309 (5)	7178 (9)	2006 (8)	113	0.831
O(8)	8069 (3)	8190 (8)	2594 (4)	74	0.831
O(2)′	556 (2)	244 (3)	170 (2)	6 (1)	0.176
O(3)′	573 (3)	86 (6)	64 (3)	13 (2)	0.176
O(4)′	688 (2)	156 (4)	143 (3)	9 (1)	0.176
O(6)′	907 (3)	844 (4)	143 (3)	9 (1)	0.169
O(7)′	917 (3)	717 (6)	263 (3)	13 (2)	0.169
O(8)′	801 (2)	925 (4)	247 (3)	9 (1)	0.169

[a] Positional parameters, ×10^4, ×10^5 for Ni, and ×10^3 for primed O's; thermal parameters, Å^2 and Å^2 × 10^2 for isotropic ones of primed *O*'s. [b] $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a^*_i a^*_j a_i a_j$. Those with esd's are isotropic thermal parameters. [c] site occupancy factor.

data collection are summarized in Table I. The intensities were collected with graphite-monochromated Mo Kα radiation. The background was counted for 12 s at either end of the scan range. Three standard reflections were monitored every 50 reflections throughout the data collection and showed random variations of ±1.1% with no significant trends. After corrections for Lorentz and polarization effects appropriate for graphite-monochromated radiation were applied, the intensity data were converted to relative structure factor amplitudes. Of the 3787 independent reflections measured within the range of $2\theta < 50°$, 3642 reflections were unique after averaging the symmetry-related reflections. When $0kl$ and $0k\bar{l}$ reflections were merged, internal consistency *R* index ($R = [\sum(N\sum w(F_{mean} - F)^2)/\sum((N-1)\sum(wF^2))]^{1/2}$, where *N* was the number of equivalent reflection pairs and *w* was the weight) was 0.0203. A total of 1356 (37.2%) reflections were considered unobserved as defined by $F_o < 6\sigma(F_o)$. No correction for the absorption and extinction effects was made.

Determinations of the X-ray Structures. $[Ni(C_9H_{22}N_6)](ClO_4)_2$. The structure was solved by Patterson and Fourier methods. On the basis of the positions of the nickel ion fixed at the origin and two chlorine atoms that were consistent with the sharpened Patterson map, a difference Fourier map revealed the structure of the ligand with *mm* symmetry that was coincident with the crystallographic symmetry. Two perchlorate anions also should have *mm* symmetry, and only two oxygen atoms for each anion were unique. For perchlorate A, the positions of two distinctive pairs were refined with site occupancy factors of 0.39 and 0.11, respectively. For perchlorate B, major sites for the two oxygen atoms could be refined with a site occupancy factor of 0.16. However, there were several prominent difference peaks that violated the *mm* symmetry restriction. Furthermore, U_{11}'s of the light atoms in the ligand became very large upon anisotropic refinement and geometrically calculated positions of the hydrogen atoms could not be refined either. Therefore, the refinement was finished isotropically at $R = 0.093$. The final atomic parameters are listed in Table II.

$[Ni(C_{12}H_{27}N_7)](ClO_4)_2$. The structure was solved by Patterson and Fourier methods. From the sharpened Patterson map, the positions of the nickel and the two chlorine atoms were determined. A total of 27 non-hydrogen atoms were identified in the difference Fourier map phased with three heavy atoms. One cycle of isotropic full-matrix least-squares refinement reduced the *R* factor to 0.145. Anisotropic refinement reduced the *R* factor to 0.102, and 20 hydrogen atoms were identified from a difference map. The positions of the remaining seven hydrogen atoms were calculated geometrically with idealized bond lengths (1.08 Å) and angles. At this stage, there was a clear indication of disorder in the perchlorate anions. Among the various disordered models tested, the rotational disorder model with the Cl–O bond as a rotational axis for each of the anions gave the best results. A common site occupancy factor was assigned to each of the three oxygen atoms in the anions. After the site occupancy factors were refined, the oxygen atoms in the major sites were refined anisotropically and those in the minor sites isotropically. The isotropic thermal parameters of the hydrogen atoms were fixed with the values of 1.2 times those of the bonded atoms. The refinement converged at $R = 0.0493$ for 2289 observed reflections. The weighted *R* was 0.0543. The function $\sum w(|F_o| - |F_c|)^2$ was minimized in the refinement. *w*, the weight of the reflection, was defined by $k/(\sigma^2(F_o) + gF_o^2)$, where $\sigma(F_o)$ was from counting statistics and *k* and *g* were optimized in the least-squares procedure ($k = 0.568$ and $g = 0.0062$). The largest parameter shift in the final refinement cycle was 0.675 esd for the anisotropic thermal parameter of O(7). The largest difference peaks of 0.87 and 0.85 e Å^{-3} appeared at the centers of the Ni–N(10) and Ni–N(3) bonds, respectively. Employment of the atomic scattering factors of various ionization states of the nickel atom, namely, Ni^0, Ni^+ or Ni^{2+}, did not affect these residual densities. The next highest difference peak (0.38 e Å^{-3}) was located in the vicinity of perchlorate A. All of the calculations were done by using the program SHELX 76[14] on a VAX 11/780 computer. Atomic scattering factors for Ni^{2+}, Cl, O, N, C, and H and the terms of the anomalous dispersion correction were taken from ref 15 as incorporated in SHELX 76. The final atomic parameters are listed in Table III. Structure factors are available as supplementary material.

Results and Discussion

Synthesis. Template condensation of ethylenediamine, formaldehyde, and ammonia in the presence of Ni(II) ion produced the Ni(II) complex of noncyclic ligand V, $[Ni(C_9H_{22}N_6)]^{2+}$. The complex of ligand a, which was expected initially, was never isolated. $[Ni(C_9H_{22}N_6)]^{2+}$ contains a 1,3,5,7-tetraazabicyclo[3.3.1]nonane ring, which resembles the structure of hexamethylenetetramine, and the nature of the condensation leading to this complex may be analogous to that producing hexamethylenetetramine from the reaction of formaldehyde and ammonia. It has been known that methylenediamine groups ($R_2NCH_2NR_2$) are unstable when they contain primary or sec-

---

(14) Sheldrick, G. M. *SHELX 76, Program for Crystal Structure Determination*; University of Cambridge: Cambridge, England, 1976.

(15) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV.

Table IV. Spectra and Conductance Data of Square-Planar Nickel(II) Complexes

complexes	IR, cm^{-1}	electronic spectra[b] λ_{max}, nm (ϵ, M^{-1} cm^{-1})	Λ_M(solvent),[a] Ω^{-1} cm^{-2} M^{-1}
$[Ni(C_9H_{22}N_6)](ClO_4)_2$	ν_{NH}; 3320, 3280	435 (83)	229 (H_2O)
	δ_{NH}; 1595		
$[Ni(C_{12}H_{27}N_7)](ClO_4)_2$	ν_{NH}; 3213	433 (80)	186 (H_2O)
$[Ni(C_9H_{22}N_6)(NCS)_2]$	ν_{NH}; 3320, 3265, 3180	568 (12)[c]	68.4 (CH_3CN)
	ν_{CN}; 2070	364 (22)	
	ν_{CS}; 790		
$[Ni([14]N_4mac)]^{2+}$ [20]		446	
$[Ni([14]macN_4Ld)]^{2+}$ [21]		450	
$[Ni([14]aneN_4)]^{2+}$ [22]		445	
$[Ni(2,3,2\text{-}tetN_4)]^{2+}$ [22]		446	
$[Ni(8,10\text{-}Me_2[13]aneN_4)](PF_6)_2$ [23]		428 (145)	
$[Ni(8,8,10\text{-}Me_3[13]aneN_4)]^{2+}$ [24]		429 (119)	
$[Ni(8,10,10\text{-}Me_3[13]7\text{-}eneN_4)](ClO_4)_2$ [25]		437 (92)	

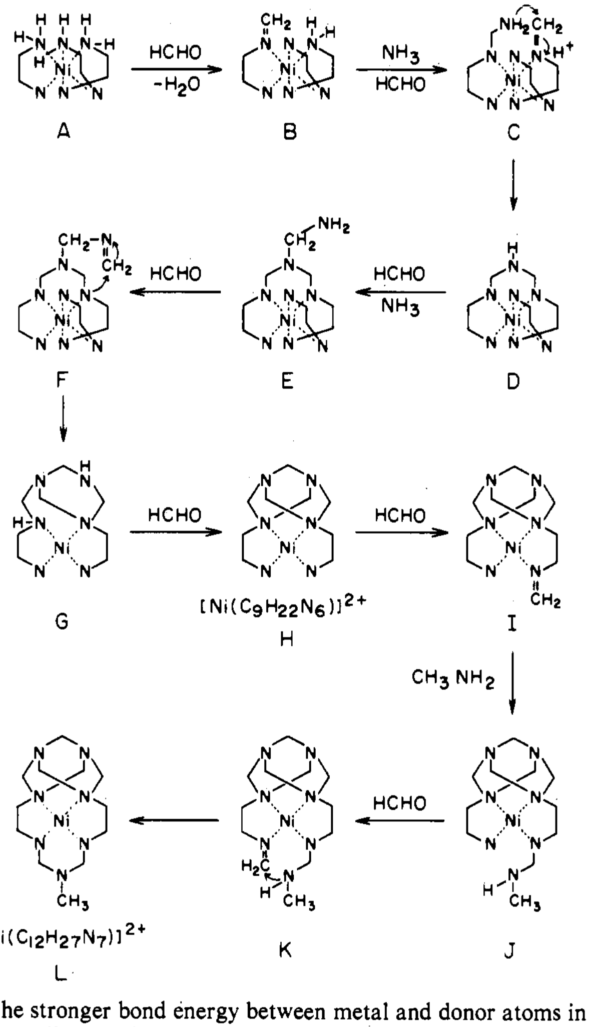
[a] At 20 °C. [b] In aqueous solutions unless otherwise indicated. [c] In CH_3CN solutions with an excess of KSCN dissolved in MeOH.

ondary amines, and only those with tertiary amines are isolable.[16] In addition, we have also reported that methylenediamine groups containing secondary nitrogens can be stabilized by the coordination of the secondary nitrogens to a metal ion.[10,11] Therefore, the formation of $[Ni(C_9H_{22}N_6)]^{2+}$ instead of $[Ni(a)]^{2+}$ is attributable to the instability of $[Ni(a)]^{2+}$ due to the presence of the uncoordinated secondary nitrogens of methylenediamine groups.

Complex $[Ni(C_9H_{22}N_6)]^{2+}$ was the major product of the condensation reaction even when a great excess of formaldehyde and ammonia was used in the synthesis. Moreover, isolated $[Ni(C_9H_{22}N_6)](ClO_4)_2$ never underwent further condensation with formaldehyde and ammonia. Thus, numerous attempts to synthesize the Ni(II) complex of VII, which contains two tetraazabicyclononane rings symmetrically, were unsuccessful. The complex instead reacted with formaldehyde and methylamine, resulting in a complex of macrocyclic ligand VIII, $[Ni(C_{12}H_{27}N_7)]^{2+}$. Complex $[Ni(C_{12}H_{27}N_7)]^{2+}$ contains methylenediamine linkages that include secondary nitrogens, all of which are coordinated to the metal ion.

The proposed synthetic routes for the complexes of $C_9H_{22}N_6$ and $C_{12}H_{27}N_7$ are shown in Scheme I. First ethylenediamine (A) which is coordinated to Ni(II) ion reacts with formaldehyde to form an imine (B). The imine is attacked by NH_3 to yield a *gem*-diamine (C), which subsequently condenses with other imine to form the first six-membered ring (D). The uncoordinated secondary nitrogen of the six-membered ring reacts with formaldehyde and ammonia, producing a *gem*-diamine (E). The *gem*-diamine (E) thus formed condenses with formaldehyde to form an imine (F), which is attacked by a coordinated secondary nitrogen resulting in a triazacyclohexane ring (G). Finally, the two secondary nitrogens of G, one uncoordinated and the other coordinated to Ni(II) ion, are linked by a methylene group by the reaction with formaldehyde, giving $[Ni(C_9H_{22}N_6)]^{2+}$ (H). The primary amines of $[Ni(C_9H_{22}N_6)]^{2+}$ (H) react with formaldehyde and methylamine by a similar reaction sequence to complete the macrocyclization, resulting in $[Ni(C_{12}H_{27}N_7)]^{2+}$.

Scheme I



Properties and Spectra. Complexes $[Ni(C_9H_{22}N_6)](ClO_4)_2$ and $[Ni(C_{12}H_{27}N_7)](ClO_4)_2$ are soluble in polar solvents such as H_2O, Me_2SO, CH_3CN, or CH_3NO_2. The noncyclic complex $[Ni(C_9H_{22}N_6)](ClO_4)_2$ is relatively unstable while the macrocyclic complex $[Ni(C_{12}H_{27}N_7)](ClO_4)_2$ is stable in acidic solutions. Spectra of an aqueous solution (2.3×10^{-3} M) of $[Ni(C_9H_{22}N_6)](ClO_4)_2$ indicated that 50% of the complex decomposed in 1 min upon the addition of $HClO_4$ (0.15 M). However, the absorbance changes of an aqueous solution (2.0×10^{-3} M) of $[Ni(C_{12}H_{27}N_7)](ClO_4)_2$ revealed that only about 40% of the complex decomposed in 20 h upon the addition of $HClO_4$ (0.15 M). The kinetic stability of macrocyclic complexes against ligand dissociation, relative to the noncyclic ligand complexes, has long been known.[17,18] This stability is partially due to the ligand rigidity and the stronger bond energy between metal and donor atoms in macrocyclic complexes. The solvation enthalpies and entropies also play important roles in determining this kinetic stability.

The infrared and the electronic absorption spectra of the complexes synthesized are summarized in Table IV. The infrared spectra of the complexes indicate that $[Ni(C_9H_{22}N_6)](ClO_4)_2$ contains primary amine groups and $[Ni(C_{12}H_{27}N_7)](ClO_4)_2$ has secondary amines. The electronic spectra exhibit maximum absorptions of $[Ni(C_9H_{22}N_6)]^{2+}$ and $[Ni(C_{12}H_{27}N_7)]^{2+}$ at 435 and 433 nm, respectively, indicating the presence of square-planar Ni(II)–N_4 chromophores.[19] It is noteworthy that the absorptions

---

(16) Barton, O.; Ollis, W. D. *Comprehensive Organic Chemistry*; Pergamon: Oxford, England, 1979; Vol 2, p 83.

(17) Kadan, T. *Helv. Chim. Acta* **1979**, *53*, 617.

(18) Cabbiness, D. K.; Margerum, D. W. *J. Am. Chem. Soc.* **1970**, *92*, 2151.

(19) Lever, A. B. P. *Inorganic Electronic Spectroscopy*; Elsevier: Armsterdam, The Netherlands, 1984; pp 534–542.

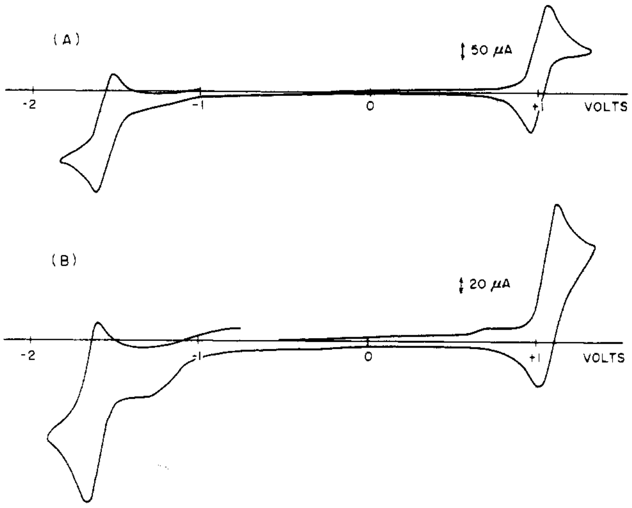


Figure 1. Cyclic voltammograms of Ni(II) complexes in acetonitrile (0.1 M TBAP) at a platinum electrode (scan rate 100 mV/s, concentration 1×10^{-3} M, T = 293 K). Potential in volts vs. Ag/AgClO$_4$ (0.1 M CH$_3$CN):[23] (A) [Ni($C_9H_{22}N_6$)](ClO$_4$)$_2$; (B) [Ni($C_{12}H_{27}N_7$)](ClO$_4$)$_2$.

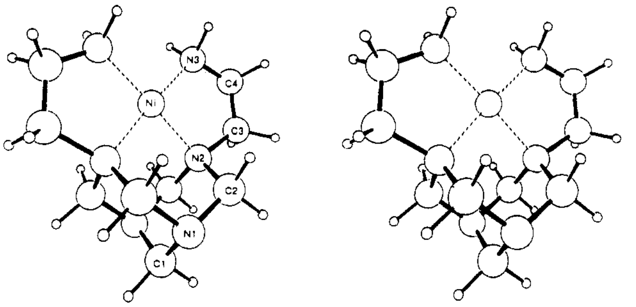


Figure 2. Stereoscopic view of the [Ni($C_9H_{22}N_6$)]$^{2+}$ cation.

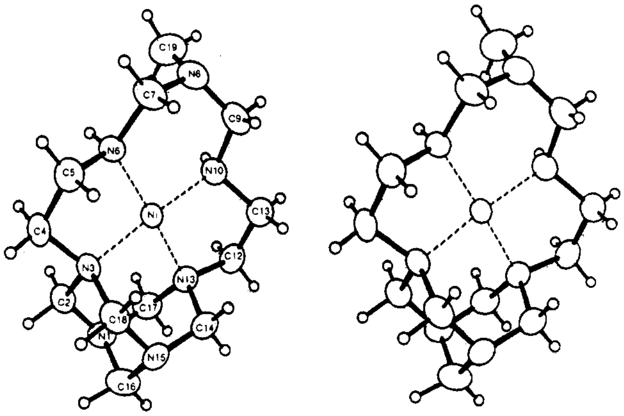


Figure 3. Stereoscopic view of the [Ni($C_{12}H_{27}N_7$)]$^{2+}$ cation.

Table V. Bond Lengths (Å) and Angles (deg) for [Ni($C_9H_{22}N_6$)](ClO$_4$)$_2$

Ni-N(2)	1.90 (3)	Ni-N(3)	1.90 (3)
N(1)-C(1)	1.43 (4)	N(1)-C(2)	1.43 (3)
N(2)-C(2)	1.50 (4)	N(2)-C(3)	1.59 (6)
C(3)-C(4)	1.36 (4)	C(4)-N(3)	1.37 (5)
N(2)-Ni-N(2)	88 (2)	N(2)-Ni-N(3)	89 (1)
N(3)-Ni-N(3)	94 (2)	Ni-N(2)-C(2)	109 (2)
Ni-N(2)-C(3)	106 (3)	Ni-N(3)-C(4)	114 (3)
N(1)-C(1)-N(1)	115 (4)	C(2)-N(1)-C(2)	113 (3)
C(1)-N(1)-C(2)	110 (2)	N(1)-C(2)-N(2)	110 (3)
C(2)-N(2)-C(2)	115 (3)	C(2)-N(2)-C(3)	110 (2)
N(2)-C(3)-C(4)	116 (5)	C(3)-C(4)-N(3)	116 (5)

of these complexes appear at relatively short wavelengths compared with those of other square-planar Ni(II) complexes containing tetraamine ligands of similar chelate ring sequence such as [Ni(2,3,2-tetN$_4$)]$^{2+}$ and [Ni([14]aneN$_4$)]$^{2+}$[20-22] but are comparable to those of Ni(II) complexes of 13-membered macrocycles[23-25] as indicated in Table IV. This means that the ligands in the present study exert extraordinarily strong ligand fields because of the squeezing effect of the bicyclononane moiety. [Ni($C_9H_{22}N_6$)](ClO$_4$)$_2$ reacted with an excess of KSCN in acetonitrile solutions forming tetragonal [Ni($C_9H_{22}N_6$)(NCS)$_2$]. The infrared spectrum of [Ni($C_9H_{22}N_6$)(NCS)$_2$] (Table IV) shows ν_{CN} at 2070 cm^{-1} and ν_{CS} at 790 cm^{-1} for NCS$^-$ ligands, indicating the coordination of NCS$^-$ ligands through the nitrogen atoms.[26,27] The isothiocyanato ligands of the complex are easily dissociated on dissolution in polar solvents such as H_2O or Me$_2$SO, resulting in the parent square-planar complex. The value of the molar conductance of the complex lies between that of a nonelectrolyte and that of a 1:1 type electrolyte,[28] because of the partial ionization of NCS$^-$ ligands from the complex in acetonitrile solutions.

The efforts to remove the nickel from [Ni($C_{12}H_{27}N_7$)](ClO$_4$)$_2$ by treating with excess NaCN as described by Barefield[29] or by protonating the nitrogens of the ligands were unsuccessful. The ligands containing the methylenediamine (N–C–N) moieties with secondary nitrogens are unstable[16] and thus seem to be decomposed when the metal ions are removed from the complexes.

Electrochemistry. In a cyclic voltammogram in acetonitrile solutions (Figure 1), a one-electron reduction and a one-electron oxidation are observed for [Ni($C_9H_{22}N_6$)](ClO$_4$)$_2$ and [Ni($C_{12}H_{27}N_7$)](ClO$_4$)$_2$. For [Ni($C_9H_{22}N_6$)]$^{2+}$, the oxidation at +1.00 and the reduction at −1.58 V vs. Ag/AgClO$_4$ (0.1 M CH$_3$CN)[30] are quasi-reversible (ΔE_p = 0.10 and 0.11 V, respectively). For [Ni($C_{12}H_{27}N_7$)]$^{2+}$, the oxidation at +1.08 is quasi-reversible (ΔE_p = 0.09 V) and the reduction at −1.63 V is reversible (ΔE_p = 0.06 V). These data indicate that both oxidation and reduction become somewhat more difficult in the macrocyclic complex [Ni($C_{12}H_{27}N_7$)]$^{2+}$ than in the noncyclic [Ni($C_9H_{22}N_6$)]$^{2+}$. This implies that the ring size fitness of the Ni(II) ion in the macrocyclic ligand $C_{12}H_{27}N_7$ would make the transition from Ni(II) to Ni(III) or Ni(I) more unfavorable than in the noncyclic ligand $C_9H_{22}N_6$.

Structures of the Complexes. [Ni($C_9H_{22}N_6$)](ClO$_4$)$_2$. A stereoview of the cation with the atomic numbering scheme is presented in Figure 2. The bond lengths and angles are listed in Table V. The cation has crystallographic *mm* symmetry. Ni and C(1) lie on the 2-fold symmetry axis where the two mirror planes intersect. N(2), C(3), C(4), and N(3) of the ethylenediamine moiety are located on the (100) mirror plane while N(1) is on the (010) mirror plane. The nickel ion has the square-planar structure, being coordinated to the four nitrogen atoms of the two ethylenediamine moieties of the ligand with an average Ni–N distance of 1.90 Å. The coordination plane coincides with the (100) mirror plane. Although all of the Ni–N distances are identical, the coordination geometry is distorted such that the separation between the nitrogen donors in the open ends of the ligand is wider than that involving the bicyclononane ring. The N(3)–Ni–N(3) angle is 94 (2)° while the N(2)–Ni–N(2) angle is 88 (2)°. The bite angle of the five-membered chelate ring is 89 (1)°. Some of the C–N bond lengths appear unreasonably short or long. However, elemental and spectroscopic analyses

---

(20) Nishida, Y.; Hayashida, K.; Oishi, N.; Kida, S. *Inorg. Chim. Acta* **1980**, *38*, 213.

(21) Hay, R. W.; Bembi, R.; Sommerville, W. *Inorg. Chim. Acta* **1982**, *59*, 147.

(22) Fabbrizzi, L. *Inorg. Chem.* **1977**, *16*, 2667.

(23) Holtman, M. S.; Cummings, S. C. *Inorg. Chem.* **1976**, *15*, 660.

(24) Curtis, N. F. *Coord. Chem. Rev.* **1968**, *3*, 3.

(25) Curtis, N. F.; House, D. A. *J. Chem. Soc. A* **1967**, 537.

(26) (a) Martin, J. W. C.; Johnston, J. H.; Curtis, N. F. *J. Chem. Soc., Dalton Trans.* **1978**, *68*. (b) Curtis, N. F.; Curtis, Y. M. *Aust. J. Chem.* **1966**, *19*, 1423.

(27) (a) Curtis, N. F.; *J. Chem. Soc., Dalton Trans.* **1974**, 347. (b) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination* Compounds, 3rd ed.; Wiley: New York, 1978; p 270.

(28) Geary, W. J. *Coord. Chem. Rev.* **1971**, *7*, 81.

(29) Barefield, E. K. *Inorg. Chem.* **1972**, *9*, 2273.

(30) A reference electrode Ag/AgClO$_4$ (0.1 M CH$_3$CN) shows +0.24 V vs. SCE. Therefore, potential measured against SCE will be 0.24 V higher than that measured against Ag/AgClO$_4$ (0.1 M CH$_3$CN).

Table VI. Bond Lengths (Å) and Angles (deg) for $[Ni(C_{12}H_{27}N_7)](ClO_4)_2$

Ni–N(3)	1.916 (4)	Ni–N(6)	1.914 (5)
Ni–N(10)	1.918 (4)	Ni–N(13)	1.922 (4)
N(1)–C(2)	1.439 (8)	N(1)–C(16)	1.472 (9)
N(1)–C(17)	1.429 (7)	N(3)–C(2)	1.515 (8)
N(3)–C(4)	1.497 (8)	N(3)–C(18)	1.516 (8)
N(6)–C(5)	1.494 (8)	N(6)–C(7)	1.499 (8)
N(8)–C(7)	1.412 (9)	N(8)–C(9)	1.426 (9)
N(8)–C(19)	1.440 (11)	N(10)–C(9)	1.509 (9)
N(10)–C(11)	1.483 (8)	N(13)–C(12)	1.488 (7)
N(13)–C(14)	1.506 (8)	N(13)–C(17)	1.527 (7)
N(15)–C(14)	1.438 (8)	N(15)–C(16)	1.461 (8)
N(15)–C(18)	1.421 (8)	C(4)–C(5)	1.511 (10)
C(11)–C(12)	1.486 (9)		
N(6)–Ni–N(3)	87.7 (2)	N(10)–Ni–N(6)	95.4 (2)
N(13)–Ni–N(3)	89.1 (2)	N(13)–Ni–N(10)	87.7 (2)
N(10)–Ni–N(3)	176.4 (2)	N(13)–Ni–N(6)	175.8 (2)
C(2)–N(3)–Ni	113.4 (4)	C(17)–N(13)–Ni	114.0 (3)
C(4)–N(3)–Ni	109.1 (4)	C(12)–N(13)–Ni	108.4 (3)
C(18)–N(3)–Ni	106.9 (4)	C(14)–N(13)–Ni	107.0 (3)
C(2)–N(3)–C(4)	108.6 (5)	C(17)–N(13)–C(12)	109.1 (4)
C(18)–N(3)–C(4)	111.0 (5)	C(14)–N(13)–C(12)	111.1 (4)
C(18)–N(3)–C(2)	107.8 (4)	C(14)–N(13)–C(17)	107.2 (4)
C(16)–N(1)–C(2)	108.7 (5)	C(16)–N(15)–C(18)	108.7 (5)
C(17)–N(1)–C(2)	113.5 (5)	C(14)–N(15)–C(18)	114.5 (5)
C(17)–N(1)–C(16)	110.0 (5)	C(14)–N(15)–C(16)	109.7 (5)
N(1)–C(2)–N(3)	112.5 (5)	N(1)–C(17)–N(13)	112.2 (4)
N(15)–C(14)–N(13)	112.6 (5)	N(15)–C(18)–N(3)	112.6 (5)
N(1)–C(16)–N(15)	109.3 (5)		
C(5)–C(4)–N(3)	107.2 (5)	C(11)–C(12)–N(13)	108.1 (5)
C(4)–C(5)–N(6)	105.4 (5)	C(12)–C(11)–N(10)	106.1 (5)
C(5)–N(6)–Ni	107.4 (3)	C(11)–N(10)–Ni	106.6 (4)
C(7)–N(6)–Ni	117.9 (4)	C(9)–N(10)–Ni	119.2 (4)
C(7)–N(6)–C(5)	110.6 (5)	C(9)–N(10)–C(11)	110.0 (5)
C(19)–N(8)–C(7)	116.5 (6)	N(8)–C(7)–N(6)	115.1 (5)
C(9)–N(8)–C(7)	112.8 (5)	N(10)–C(9)–N(8)	114.6 (6)
C(19)–N(8)–C(9)	114.9 (6)		

indicate that all of the carbon and nitrogen atoms are saturated. It is meaningless to compare the molecular dimensions of this complex with those of the relevant compounds due to the poor quality of the data mainly associated with the disorder phenomena. In addition to the disorder phenomena present in the perchlorate anions, the possibility that the whole cation might be disordered in the direction of the *a* axis may well account for the failure of the anisotropic refinement of the structure. The packing is very loose along the *a* direction such that the closest contact occurs between the two bicyclononane rings of the cations related by a unit cell translation with a separation of ca. 5 Å. This is consistent with the fact that U_{11} components of all atoms always kept increasing during the anisotropic refinement processes. A swinging motion of the whole cation with the nickel ion as a pivot center seems possible.

$\mathbf{[Ni(C_{12}H_{27}N_7)](ClO_4)_2}$. A stereoview of the cation with the atomic numbering scheme is presented in Figure 3. The bond lengths and angles are listed in Table VI. The cation possesses a pseudo plane of symmetry perpendicular to the square-planar coordination plane. The Ni, N(1), N(15), and N(8) atoms form a good plane with a maximum deviation of 0.003 (5) Å. The atoms related by a pseudo mirror plane show very similar displacements (less than 3σ) from the plane except for the C(7) and C(9) pair of atoms. C(16) and C(19) are displaced from the mirror plane by 0.025 (7) and 0.034 (9) Å, respectively. The bicyclononane ring is asymmetrically arranged with respect to the coordination plane, C(16) being displaced by 0.321 (7) Å from the plane. The Ni–N(3)–C(18) and Ni–N(13)–C(14) angles are 106.9 (4) and 107.3 (3)°, while the Ni–N(3)–C(2) and Ni–N(13)–C(17) angles are 113.4 (4) and 114.0 (3)°, respectively. N(8) is more or less close to the coordination plane with a displacement of 0.308 (5) Å, while the corresponding N(1) and N(15) atoms are displaced by 0.981 (5) and 1.391 (5) Å, respectively.

The four nitrogen donor atoms form a plane with a maximum deviation of 0.011 (5) Å, showing a slight tetrahedral distortion. The nickel ion is displaced by 0.034 (1) Å from the least-squares plane, showing a slight square-pyramidal distortion instead of the tetrahedral distortion often observed in other square-planar macrocyclic complexes.[31-34] The average Ni–N bond length is 1.918 ± 0.003 Å, which falls in the range (1.86–1.94 Å) normally observed for the square-planar Ni(II) complexes coordinating tetraaza macrocycles.[33-41] It is shorter by ~0.02 Å than those in the complexes of saturated 14-membered tetraaza macrocycles[39-41] but longer by 0.06 Å than that in the square-planar $[Ni(Me_2[13]aneN_4)](ClO_4)_2$.[42] Although N-methylation of the secondary nitrogen donors of the macrocyclic complexes resulted in the decrease of the ligand field strength that has been explained by the increase in the Ni–N distances in the N-methylated complexes,[43] no significant differences in the Ni–N distances between the secondary and tertiary amines are observed in the present study.

There are 19 N–C bonds in the ligand. The lengths of the N–C single bonds show systematic variations, ranging from 1.412 to 1.527 Å, according to the environments of the nitrogen atoms. There are five tertiary nitrogen atoms, namely, N(1), N(3), N(8), N(13), and N(15). The four bonds from N(3) and N(13) to the carbon atoms of the bicyclononane ring are longest with an average length of 1.516 ± 0.009 Å, which is significantly longer than the average N–C bond length of 1.474 ± 0.006 Å observed in hexamethylenetetramine.[44] The average length of the N(3)–C(4) and N(13)–C(12) bonds is 1.493 ± 0.006 Å. Lengthening of these N–C bonds is consistent with the fact that N(3) and N(13) are coordinated to the nickel ion. The bonds around N(1) and N(15) also show systematic variations. The four N–C bonds involving N(1) and N(15), namely, N(1)–C(2), N(1)–C(17), N(15)–C(14), and N(15)–C(18), have an average length of 1.432 ± 0.008 Å while the N(1)–C(16) and N(15)–C(16) bonds have an average value of 1.467 ± 0.008 Å. These differences in the N–C bond lengths can be correlated with the differences in the N–C–N bond angles. The average N–C–N angle for C(2), C(14), C(17), and C(18) is 112.5 ± 0.2°, while the N(1)–C(16)–N(15) angle is 109.3 (5)°. The N–C–N angles involving the four carbon atoms correspond to contribution of 27.7% s character to the N–C bonds, while that for C(16) corresponds to contribution of 24.8% s character to the N–C bonds.[45] Therefore, the decreased s character of C(16) results in the longer N–C bond lengths.

Among the N–C bonds involving the tertiary nitrogen atoms, those around N(8) are shortest with an average value of 1.426 ± 0.014 Å. Wide variations in the N–C bonds can also be correlated with the degree of the contribution of the sp^2 character to the hybridization of the nitrogen atoms, which can be represented with the displacements of the nitrogen atoms from the planes formed by the three carbon atoms bonded to the tertiary nitrogen atoms. These are 0.511 (4), 0.510 (4), 0.450 (5), 0.443

---

(31) Richardson, M. F.; Sievers, R. *J. Am. Chem. Soc.* **1972**, *94*, 4134.
(32) D'Aniellor, M. J., Jr.; Mocella, M. T.; Wagner, F.; Barefield, E. K.; Paul, I. C. *J. Am. Chem. Soc.* **1975**, *97*, 192.
(33) Ito, T.; Toriumi, K. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1981**, *B37*, 88.
(34) Sugimoto, M.; Fujita, J.; Ito, H.; Toriumi, K.; Ito, T. *Inorg. Chem.* **1983**, *22*, 955.
(35) Kilbourn, B. T.; Ryan, R. R.; Dunitz, J. D. *J. Chem. Soc. A* **1969**, 2407.
(36) Murray-Rust, R.; Murray-Rust, J. *Acta Crystallogr. Sect. B: Struct. Crystallog. Cryst. Chem.* **1979**, *B35*, 1704.
(37) Ferguson, G.; Restivo, R. J.; Hay, R. W. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1979** *B35*, 159.
(38) Curtis, N. F. In *Coordination Chemistry of Macrocyclic Compounds*; Melson, G. A., Ed.; Plenum: New York, 1979; pp 223–225 and 244–247.
(39) Curtis, N. F.; Swann, D. A.; Waters, T. N. *J. Chem. Soc., Dalton Trans.* **1973**, 1963.
(40) Krajewski, J. W.; Urbanczyk-Lipkowski, Z.; Gluzinski, P. *Bull. Acad. Pol. Sci., Ser. Sci. Chem.* **1977**, *25*, 853.
(41) Krajewski, J. W.; Urbanczyk-Lipkoskwi, Z.; Gluzinski, P. *Pol. J. Chem.* **1978**, *52*, 1513.
(42) Waters, J. M.; Whittle, K. R. *J. Inorg. Nucl. Chem.* **1972**, *34*, 155.
(43) Jubran, N. J.; Gizburg, G.; Cohen, H.; Koresh, Y.; Meyerstein, D. *Inorg. Chem.* **1985**, *24*, 251.
(44) Mak, C. W. T.; Lau, O. W. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1978**, *B34*, 1290.
(45) Huheey, J. E. *Inorganic Chemistry*, 3rd ed.; Harper International SI Edition: Cambridge, England, 1983; p 224.

(5), and 0.332 (6) Å for N(3), N(13), N(1), N(15), and N(8), respectively. N(3) and N(13) have the least contribution of sp^2 character and thus the longest N–C bonds while N(8) has the shortest N–C bonds due to increased sp^2 character. The average N–C length for the secondary N(6) and N(10) atoms is 1.496 ± 0.011 Å.

Two perchlorate anions are assumed to be rotationally disordered about the Cl(A)–O(1) and Cl(B)–O(5) bonds. The average angles of rotation are about 48 and 38° for perchlorate A and B, respectively. Two anions are located above and below the coordination plane. The Ni–Cl(A) and Ni–Cl(B) distances are 4.338 (1) and 3.299 (1) Å, respectively.

There are five six-membered and two five-membered rings in the cation. The two six-membered rings in the bicyclononane ring assume a stable chair conformation with average intracyclic torsion angles of 59 ± 5 and 58 ± 4°. The two six-membered chelate rings formed between the bicyclononane ring and the nickel ion also assume a chair conformation. However, the six-membered ring formed by Ni, N(6), C(7), N(8), C(9), and N(10) assumes a conformation intermediate between the normal and the half-chair conformations, with C(7)–N(6)–Ni–N(10) and C(9)–N(10)–Ni–N(6) torsion angles of 30.9 (4) and –29.5 (4)°, respectively. The two five-membered chelate rings formed by the ethylenediamine moieties assume an unsymmetrical gauche (or an envelope) conformation. C(4) and C(12) are 0.136 (7) and 0.093 (6) Å below the coordination plane, while C(5) and C(11) are 0.569 (7) and 0.572 (7) Å above this plane, respectively. The N(3)–C(4)–C(5)–N(6) and N(13)–C(12)–C(11)–N(10) torsion angles are –50.9 (5) and 51.2 (5)°, respectively.

The N–Ni–N bite angle in each of the five-membered chelate rings is 87.7 (2)° and the N–N bite distances are 2.654 (6) and 2.660 (6) Å, which are normally observed values in the five-membered rings of the Ni(II) macrocyclic complexes.[33,36,37,46] The N(6)–Ni–N(10) bite angle of 95.4 (2)° and the N(6)–N(10) distance of 2.836 (6) Å are also the normal values for the six-membered rings.[33,36,37] However, the N(3)–Ni–N(13) bite angle of 89.1 (2)° and the N(3)–N(13) bite distance of 2.691 (6) Å involving the bicyclononane ring are smaller than those for the six-membered ring but comparable to the values for the five-membered ring. The same trend is also observed in $[Ni(C_9H_{22}N_6)](ClO_4)_2$. The intracyclic valence angles at N(1), N(15), C(2), C(18), C(17), and C(14) are important for determining the N–N separation in the tetraazabicyclononane ring. There seems to be no chance for lengthening of this bite distance because these angles, ranging from 112.2 to 114.5°, are already larger than the normal values of 107° for $N(sp^3)$ and 109.5° for $C(sp^3)$.

The present study shows that the overall structural properties of the tetraazabicyclononane ring are similar to those of the five-membered ring in the coordination sphere. Therefore, the macrocyclic ligand in this study is more similar to a $[13]aneN_4$, which contains three five-membered rings and a six-membered ring, than to a $[14]aneN_4$, in which the five-membered and the six-membered rings are alternating. Then the properties of a ligand containing two bicyclononane rings symmetrically would resemble those of the $[12]aneN_4$ rather than those of the $[14]aneN_4$. In general, the stability of the square-planar Ni(II) macrocyclic complexes depends on the ring size of the ligand in the order $[12]aneN_4 < [13]aneN_4 < [14]aneN_4 > [15]aneN_4 > [16]aneN_4$.[47–50] Therefore, the failure in synthesizing the Ni(II) complex of VII, in which two bicyclononane rings are linked by the ethylenediamine moieties, may be explained by assuming its resemblance to the complex of a $[12]aneN_4$ having lower stability.

Acknowledgment. Financial support for this work was provided by the Korea Science and Engineering Foundation and the Basic Research Institute Program (1985), Ministry of Education, Korea.

Supplementary Material Available: Tables of anisotropic thermal parameters, atomic coordinates of the hydrogen atoms, bond lengths and angles involving the hydrogen atoms and the perchlorate ions, least-squares planes, and torsion angles for $[Ni(C_{12}H_{27}N_7)](ClO_4)_2$ (6 pages); tables of final observed and calculated structure factors for the two complexes (14 pages). Ordering information is given on any current masthead page.

---

(46) Bailey, M. F.; Maxwell, I. E. *J. Chem. Soc., Dalton, Trans.* **1972**, 938.

(47) Fabbrizzi, L.; Paoletti, P.; Clay, R. M. *Inorg. Chem.* **1978**, *17*, 1042.

(48) Fabbrizzi, L.; Licheloni, M.; Paoletti, P. *Inorg. Chem.* **1980**, *19*, 535.

(49) Anichini, A.; Fabbrizzi, L.; Paoletti, P.; Clay, R. M. *J. Chem. Soc., Dalton Trans.* **1978**, 577.

(50) Gallori, E.; Martini, E.; Micheloni, M.; Paoletti, P. *J. Chem. Soc., Dalton Trans.* **1980**, 1722.

Contribution from the School of Chemical Sciences,
University of Illinois at Urbana-Champaign, Urbana, Illinois 61801

Organosulfide Group Transfer Reactions of Transition-Metal Carbonyl Radicals: Electronic and Steric Effects[1]

Kang-Wook Lee and Theodore L. Brown*

Received October 7, 1986

Photochemical reactions of $M_2(CO)_{10}$ (M = Mn, Re) with RSSR (R = Me, Ph) or $MeSSiMe_3$ in hexane at ambient temperature yield $(\mu\text{-SR})_2M_2(CO)_8$ (70–85%) and $[M(CO)_3SR]_4$ (0–15%). The corresponding reaction of $Re_2(CO)_8L_2$ almost quantitatively yields $(\mu\text{-SR})_2Re_2(CO)_6L_2$, and the reaction of $Re_2(CO)_{10}$ and $[Me_2NC(S)S]_2$ gives $(\eta^2\text{-}S_2CNMe_2)Re(CO)_4$. The initial product for each reaction is $RSM(CO)_4L$ (L = CO, PR_3), formed by RS group transfer from RSSR to the $^{\bullet}M(CO)_4L$ radical generated by photolysis. $(\mu\text{-SR})_2M_2(CO)_8$ is in equilibrium with the 16-electron species $RSM(CO)_4$ under photochemical conditions. Laser flash photolysis kinetics studies reveal the electronic and steric effects of L ligands in the $Re(CO)_4L^{\bullet}$ radical and the steric effect of the R group in RSSR on the group transfer rate constant. The relative rate constants for reactions of $Re(CO)_4PMe_3^{\bullet}$ with various dialkyl disulfides decrease in the order methyl > *n*-butyl > *sec*-butyl > *tert*-butyl (630:280:36:1). The rate constants for group transfer for a series of $Re(CO)_4L^{\bullet}$ radicals fit a two-parameter free energy relationship wherein the electronic and the steric parameters of L are represented. The reaction is accelerated by increased electron donor capability of L and retarded by increased size of L.

Introduction

There has recently been extensive interest in the reactions of photogenerated metal carbonyl species.[2] 17-electron transition-metal carbonyl radicals, formed by photolysis of metal–metal single-bonded dimers, undergo various reactions such as recom-

---

[1] This research was supported by the National Science Foundation through Research Grant CHE 83-12331.

[2] For reviews see: (a) Brown, T. L. *Ann. N.Y. Acad. Sci.* **1980**, *333*, 80. (b) Meyer, T. J.; Caspar, J. V. *Chem. Rev.* **1985**, *85*, 187. (c) Geoffroy, G. L.; Wrighton, M. S. *Organometallic Photochemistry*; Academic: New York, 1979. (d) Kobayashi, T.; Yasufuku, K.; Iwa, J.; Yesaka, H.; Noda, H.; Ohtani, H. *Coord. Chem. Rev.* **1985**, *64*, 1.

0020-1669/87/1326-1852$01.50/0