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Tetraaza Macrocyclic Metal Complexes Containing a Medium-Sized Chelate Ring. 2. X-ray Structural Studies of *trans*-Dichloro(1,4,7,10-tetraazacyclotetradecane)nickel(II) Hydrate, (1,4,7,10-Tetraazacyclopentadecane)nickel(II) Perchlorate, and *trans*-Dichloro(1,4,7,10-tetraazacyclohexadecane)nickel(II)

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Molecular structures of the three title tetraaza macrocyclic nickel(II) complexes, *trans*-$[NiCl_2(C_{10}H_{24}N_4)]\cdot H_2O$ (**1**), $[Ni(C_{11}H_{26}N_4)](ClO_4)_2$ (**2**), and *trans*-$[NiCl_2(C_{12}H_{28}N_4)]$ (**3**), have been determined by single-crystal X-ray analyses. Crystal data are as follows: for **1**, monoclinic, space group $P2_1/n$, $a = 12.102$ (1) Å, $b = 16.803$ (2) Å, $c = 7.672$ (2) Å, $\beta = 96.54$ (1)°, $V = 1549.9$ (3) Å^3, $Z = 4$; for **2**, orthorhombic, space group $P2_1nb$, $a = 14.357$ (2) Å, $b = 16.109$ (1) Å, $c = 8.248$ (1) Å, $V = 1907.9$ (4) Å^3, $Z = 4$; for **3**, monoclinic, space group $C2/c$, $a = 16.747$ (5) Å, $b = 10.390$ (2) Å, $c = 11.708$ (5) Å, $\beta = 126.16$ (1)°, $V = 1644.6$ (9) Å^3, $Z = 4$. The seven-membered ring of **1** adopts a skew(h) conformation with a mean Ni–N distance of 2.07 (3) Å. The eight-membered ring of the four-coordinate complex **2** takes an intermediate structure between the crown and boat–boat forms with a mean Ni–N distance of 1.909 (8) Å. The nine-membered ring of **3** takes a structure very similar to that of the most strain-free cyclononane conformer, the twist–chair–boat form, with a Ni–N distance of 2.236 (1) Å. Considerable ring strain has been noted in structural parameters of the eight- and nine-membered chelate rings. In the *trans*-dichloro complexes **1** and **3**, the mean Ni–Cl distance of **1** (2.548 (8) Å) is considerably longer than that of **3** (2.426 (1) Å), while the mean Ni–N distance of **1** (2.07 (2) Å) is shorter than that of **3** (2.16 (11) Å).

Introduction

It has been reported that a medium-sized metal chelate ring composed of an 8–11-membered ring is not formed easily owing to severe ring strain as involved in medium-sized cycloalkanes.[4] In a previous paper, we prepared a series of tetraaza macrocyclic nickel(II) complexes composed of three five-membered rings and one seven-, eight-, or nine-membered ring.[5] In this study, we have carried out single-crystal X-ray analyses on some of these compounds in order to investigate structures and chelate ring strain of the medium-sized chelate rings. Suitable single crystals for the X-ray study were obtained with the three title compounds: *trans*-dichloro(1,4,7,10-tetraazacyclotetradecane)nickel(II) hydrate (**1**), *trans*-$[NiCl_2(N_47)]\cdot H_2O$; (1,4,7,10-tetraazacyclopentadecane)nickel(II) perchlorate (**2**), $[Ni(N_48)](ClO_4)_2$; *trans*-dichloro(1,4,7,10-tetraazacyclohexadecane)nickel(II) (**3**), *trans*-$[NiCl_2(N_49)]$. Compounds **1** and **3** are six-coordinate high-spin complexes, whereas compound **2** is a square-planar low-spin complex.

Experimental Section

Preparation of the Compounds. The preparation of the compounds has been described elsewhere.[5] Blue-violet prismatic crystals of **1** were grown slowly from an acetonitrile–chloroform mixed solution (4:6 (v/v)). The elemental analysis showed that the compound is a monohydrate. Orange block crystals of **2** were obtained by recrystallization from water. Emerald green polyhedral crystals of **3** were grown slowly from an acetonitrile–chloroform mixed solution (4:6 (v/v)).

Collection and Reduction of X-ray Diffraction Data. For each crystal, diffraction data were obtained on a Rigaku AFC-5 four-circle diffractometer controlled by a FACOM U-100 computer and the Rigaku FOS program system, with use of graphite-monochromatized Mo Kα radiation (λ = 0.71073 Å). Diffraction data were measured at 172 K for complex **1**, at 293 K for **2**, and at 171 K for **3**. The low-temperature measurements were made with an attached Rigaku variable-temperature apparatus based on a cold nitrogen gas stream method. The temperature was measured after the data collection with a thermocouple mounted at the same position of the crystal. The fluctuation in temperature at 170 K was less than 1 K. The data for compound **2** were obtained at room temperature roughly thermostated at 293 K, because the crystals fractured at ca. 250 K as evidenced by splitting of the Bragg peaks.

For each crystal, lattice parameters and their standard deviations were obtained from a least-squares fit of 50 2θ values with $26° < 2\theta < 31°$. No hysteresis in the lattice parameters was observed for complexes **1** and **3**.

For all the data sets, the θ–2θ scan mode was used at a scan rate of 3° min^{-1} to record the intensities. Scan widths ($\Delta\theta$) were calculated from the formula $\Delta\theta = (A + 0.5 \tan \theta)°$, where the values of A were 1.3 for complexes **1** and **3** and 1.1 for **2**. The intensity measurments were automatically repeated until $\sigma_c(|F_o|)/|F_o|$ became less than 0.05, where $\sigma_c(|F_o|)$ denotes a standard deviation calculated from counting statistics. The maximum number of iterations was 3.

The intensities of 3 standard reflections were monitored for each crystal at 50-reflection intervals. Fluctuations for the F_o values were less than 4% during the data collection. The intensity data were corrected for Lorentz-polarization effects. Absorption corrections were applied with a numerical integration procedure with a Gaussian grid (6 × 6 × 6). Pertinent crystallographic parameters for the three compounds are summarized in Table I.

Solution and Refinement of the Structures. All the structures were solved and refined by standard Patterson, Fourier, and block-diagonal least-squares techniques. The atomic scattering factors for non-hydrogen atoms were taken from ref 6 and those for hydrogen from Stewart, Davidson, and Simpson.[7] The effects of anomalous dispersion for non-hydrogen atoms were corrected in structure factor calculations. Reliability factors are defined as $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, where F_o and F_c are the observed and calculated structure factors, respectively. The weights (w) were taken as $w = [\sigma_c^2 + (0.015|F_o|)^2]^{-1}$.

In each case, the positions of the nickel and some of the ligand atoms were determined from three-dimensional Patterson functions. Successive Fourier syntheses permitted location of the remaining non-

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Table I. Crystallographic Parameters

	trans-$[NiCl_2(N_47)]\cdot H_2O$[a]	$[Ni(N_48)](ClO_4)$[b]	*trans*-$[NiCl_2(N_49)]$[c]
formula	$NiCl_2N_4C_{10}H_{24}\cdot H_2O$	$NiN_4C_{11}H_{26}Cl_2O_8$	$NiCl_2N_4C_{12}H_{28}$
fw	347.95	471.96	357.98
cryst syst	monoclinic	orthorhombic	monoclinic
space group	$P2_1/n$	$P2_1nb$	$C2/c$
a, Å	12.102 (1)	14.357 (2)	16.747 (5)
b, Å	16.803 (2)	16.109 (1)	10.390 (2)
c, Å	7.672 (2)	8.248 (1)	11.708 (5)
β, deg	96.54 (1)	90	126.16 (1)
V, Å^3	1549.9 (3)	1907.9 (4)	1644.6 (9)
Z	4	4	4
d_c, g cm^{-3}	1.49	1.64	1.45
d_m, g cm^{-3}	1.46 (at 24 °C)	1.63	1.42 (at 16 °C)
cryst size, mm	0.40 × 0.33 × 0.33	0.48 × 0.44 × 0.22	0.40 × 0.44 × 0.26
scan range	1.3 + 0.5 tan θ	1.1 + 0.5 tan θ	1.3 + 0.5 tan θ
μ, mm^{-1}	1.59	1.34	1.49
2θ range, deg	2–60	2–65	2–65
no. of data	5053	3907	3695
$\|F_o\| > 3\sigma(\|F_o\|)$	3770	2068	3088
no. of variables	268	340	148
R	0.049	0.048	0.028
R_w	0.075	0.057	0.038

[a] Diffraction data were measured at 172 K. Unit cell parameters at 293 K are $a = 12.181$ (1) Å, $b = 16.874$ (2) Å, $c = 7.764$ (1) Å, $\beta = 96.64$ (1)°, $V = 1585.1$ (3) Å^3, and $d_{calcd} = 1.46$ g cm^{-3}. [b] Data at 293 K. [c] Diffraction data were measured at 171 K. Unit cell parameters at 293 K are $a = 16.857$ (4) Å, $b = 10.437$ (2) Å, $c = 11.752$ (4) Å, $\beta = 125.89$ (2)°, $V = 1675.2$ (8) Å^3, and $d_{calcd} = 1.42$ g cm^{-3}.

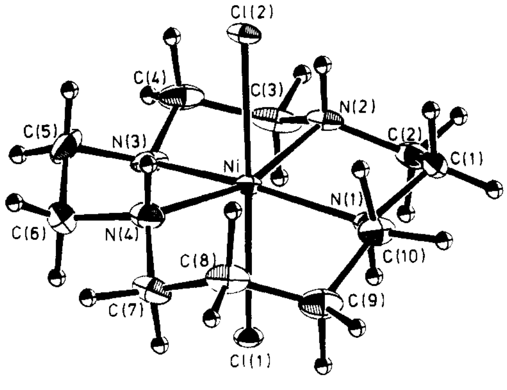

Figure 1. Perspective view of the structure of *trans*-$[NiCl_2(N_47)]$, showing the atom numbering scheme. Thermal ellipsoids are depicted at the 30% probability level.

hydrogen atoms. For complex **2**, systematic absences (*hk*0 for *k* odd and *h*0*l* for *h* + *l* odd) are consistent with space groups *Pmnb* and $P2_1nb$. The latter was indicated by the distribution of peaks in the Patterson map and confirmed by the successful structure refinement. In the case of complex **3**, the unit cell size, the space group, and the Patterson map suggested that the nickel should lie on a twofold axis that is perpendicular to the Ni–Cl bond. Anisotropic temperature factors were introduced for all non-hydrogen atoms. Further difference syntheses permitted location of all the hydrogen atoms, and their positional and isotropic thermal parameters were refined. The final *R* indices are listed in Table I. A final difference Fourier map for each crystal was featureless. Positional parameters for non-hydrogen atoms in compounds **1**–**3** are given in Tables II–IV, respectively.

All the 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.[8]

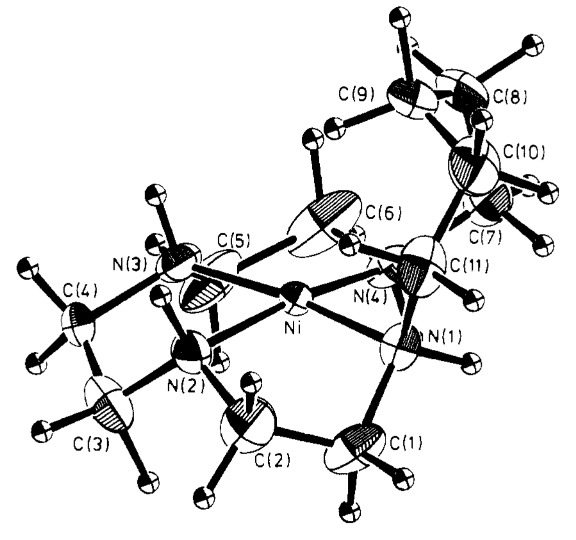

Figure 2. Perspective view of the structure of $[Ni(N_48)]^{2+}$, showing the atom numbering scheme. Thermal ellipsoids are depicted at the 30% probability level.

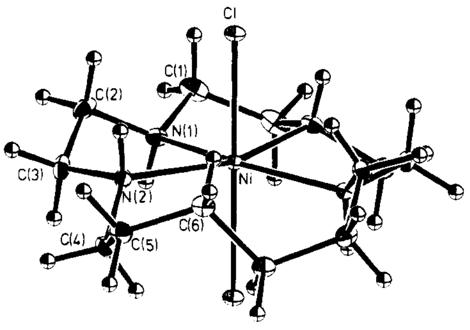

Figure 3. Perspective view of the structure of *trans*-$[NiCl_2(N_49)]$, showing the atom numbering scheme. Thermal ellipsoids are depicted at the 30% probability level.

Results and Discussion

Figures 1–3 show perspective views of complexes **1**–**3**, respectively. Tables V–VII list relevant bond distances and angles. Deviations of atoms included in a first coordination sphere from the N_4 best plane are given in Table VIII.

***trans*-$[NiCl_2(N_47)]\cdot H_2O$ (1).** As shown in Figure 1, the geometry about the Ni in this compound is of a *trans*-$NiCl_2N_4$ type, in contrast with the case for $[Ni(NCS)_2(N_47)]$, which has been found to have a cis-type structure with the macrocycle folded.[9] Three five-membered rings of the trien moiety ($-HN(CH_2)_2NH(CH_2)_2NH(CH_2)_2NH-$) adopt a stable gauche conformation and the seven-membered ring takes a skew(h)[10] conformation (Figure 4b). The structure of the skew(h) is similar to that of cycloheptane in a twist–chair form, which is the most strain free among various cycloheptane conformers.[11] The skew(h) seven-membered chelate ring has also been found for tris(1,4-butanediamine)cobalt(III) bromide.[12] A seven-membered diamine chelate ring found in the crystal of (2,4,4,11,11,13-hexamethyl-1,5,10,14-tetraazacyclooctadeca-1,13-diene)copper(II) perchlorate, [Cu(*cis*-[18]dieneN$_4$)](ClO$_4$)$_2$, has a crescent-shaped structure,[13] and

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Table II. Atomic Parameters for *trans*-[$NiCl_2(N_47)$]·H_2O[a]

atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ni	24 741 (3)	8 806 (2)	−2 077 (5)	161 (2)	314 (2)	218 (2)	−39 (1)	24 (1)	−1 (1)
Cl(1)	42 813 (6)	8 372 (5)	−15 953 (10)	183 (3)	431 (4)	302 (4)	−6 (3)	89 (3)	56 (3)
Cl(2)	6 792 (6)	9 832 (5)	12 397 (11)	212 (3)	390 (4)	415 (4)	−78 (3)	138 (3)	−77 (3)
O	58 602 (24)	23 574 (20)	−19 701 (47)	430 (16)	659 (21)	918 (26)	−68 (15)	94 (17)	245 (19)
N(1)	33 254 (20)	2 183 (16)	17 615 (33)	192 (11)	381 (15)	285 (12)	−19 (10)	76 (9)	51 (11)
N(2)	18 342 (21)	−2 010 (18)	−10 927 (36)	219 (12)	472 (17)	349 (14)	−111 (11)	128 (10)	−137 (12)
N(3)	18 393 (21)	12 645 (21)	−26 733 (35)	167 (12)	743 (22)	255 (13)	−17 (13)	13 (9)	34 (14)
N(4)	26 263 (23)	20 922 (20)	4 086 (43)	317 (15)	443 (17)	494 (18)	−49 (13)	144 (13)	−42 (14)
C(1)	27 772 (27)	−5 730 (21)	16 795 (50)	317 (16)	307 (17)	560 (22)	11 (14)	175 (15)	118 (16)
C(2)	25 277 (28)	−8 179 (21)	−2 339 (57)	349 (19)	303 (18)	722 (28)	−71 (14)	210 (19)	−137 (17)
C(3)	16 297 (31)	−1 506 (29)	−30 301 (49)	366 (19)	927 (34)	354 (18)	−332 (21)	173 (15)	−295 (20)
C(4)	10 932 (29)	6 487 (31)	−34 818 (47)	265 (16)	995 (36)	294 (17)	−140 (20)	−10 (13)	−61 (20)
C(5)	14 468 (33)	21 002 (30)	−25 181 (56)	391 (20)	877 (35)	504 (23)	310 (21)	114 (18)	375 (23)
C(6)	23 716 (34)	25 539 (25)	−13 016 (65)	438 (21)	435 (22)	735 (30)	−2 (18)	155 (20)	205 (21)
C(7)	35 913 (32)	24 173 (25)	14 414 (57)	402 (20)	498 (23)	561 (24)	−162 (17)	192 (18)	−76 (19)
C(8)	37 290 (32)	20 717 (29)	33 294 (55)	369 (19)	724 (30)	468 (22)	−110 (20)	104 (17)	−135 (21)
C(9)	42 802 (32)	12 628 (29)	36 447 (52)	379 (20)	788 (32)	384 (20)	−98 (20)	48 (16)	−102 (20)
C(10)	35 255 (28)	5 470 (27)	35 175 (41)	313 (16)	756 (28)	201 (14)	−20 (18)	27 (12)	47 (16)

[a] Positional and thermal parameters are multiplied by 10^5 and 10^4, respectively.

Table III. Atomic Parameters for [$Ni(N_48)$]$(ClO_4)_2$[a]

atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ni	0	1754 (1)	−80 (1)	320 (2)	441 (3)	302 (2)	45 (4)	−4 (4)	20 (3)
Cl(1)	−2251 (1)	111 (1)	3505 (2)	581 (9)	653 (9)	394 (7)	−28 (9)	−22 (8)	69 (7)
Cl(2)	76 (2)	2678 (1)	5378 (2)	804 (13)	671 (9)	301 (6)	−88 (12)	27 (10)	50 (6)
O(1)	−2673 (6)	829 (4)	2774 (9)	1503 (76)	936 (44)	972 (50)	472 (44)	126 (50)	157 (40)
O(2)	−2052 (9)	184 (7)	5136 (8)	1743 (100)	2151 (102)	445 (34)	−875 (88)	−259 (45)	101 (43)
O(3)	−1449 (7)	−26 (5)	2622 (11)	1365 (72)	2194 (89)	1108 (62)	1029 (68)	704 (57)	916 (65)
O(4)	−2867 (7)	−554 (5)	3374 (10)	1662 (83)	1518 (61)	1076 (58)	−741 (62)	−747 (61)	338 (54)
O(5)	858 (6)	2286 (6)	6068 (10)	1067 (63)	2218 (92)	846 (53)	231 (68)	−252 (49)	−199 (59)
O(6)	434 (9)	3247 (4)	4300 (9)	2788 (137)	864 (46)	733 (45)	−506 (63)	299 (67)	206 (34)
O(7)	−427 (7)	2071 (4)	4502 (9)	1681 (84)	922 (40)	814 (42)	−398 (52)	−445 (52)	87 (37)
O(8)	−424 (8)	3025 (8)	6658 (9)	1281 (70)	3567 (127)	569 (41)	618 (88)	134 (48)	−434 (68)
N(1)	444 (4)	797 (3)	−1197 (7)	471 (30)	464 (27)	513 (31)	−53 (25)	91 (27)	−16 (24)
N(2)	−1190 (4)	1185 (4)	−124 (7)	396 (28)	774 (39)	497 (32)	−35 (28)	19 (27)	106 (30)
N(3)	−606 (5)	2663 (4)	942 (6)	760 (44)	798 (40)	308 (25)	317 (36)	28 (28)	10 (27)
N(4)	1063 (5)	2452 (4)	−303 (6)	642 (39)	603 (33)	368 (27)	−189 (31)	86 (25)	−66 (24)
C(1)	−323 (7)	549 (5)	−2307 (9)	1078 (75)	621 (38)	529 (39)	−368 (45)	83 (44)	−226 (33)
C(2)	−1146 (7)	466 (6)	−1324 (12)	739 (59)	972 (61)	780 (62)	−272 (53)	78 (51)	−145 (54)
C(3)	−1868 (6)	1830 (6)	−462 (13)	431 (43)	1052 (71)	935 (66)	84 (46)	−75 (45)	128 (54)
C(4)	−1689 (6)	2479 (8)	707 (11)	507 (47)	1926 (107)	514 (45)	613 (62)	−30 (40)	−143 (61)
C(5)	−235 (10)	3398 (5)	386 (10)	1648 (138)	575 (42)	630 (46)	260 (61)	464 (62)	−40 (33)
C(6)	860 (10)	3249 (5)	542 (13)	1756 (126)	826 (63)	685 (53)	−841 (76)	348 (70)	−260 (46)
C(7)	2007 (7)	2114 (7)	96 (10)	564 (52)	1187 (71)	665 (51)	−356 (53)	95 (42)	−197 (49)
C(8)	2043 (7)	1710 (7)	1821 (12)	568 (53)	1543 (90)	734 (57)	96 (58)	−320 (47)	−240 (57)
C(9)	1417 (6)	984 (6)	2119 (10)	605 (52)	1294 (72)	530 (44)	184 (54)	−145 (40)	136 (51)
C(10)	1516 (7)	265 (5)	949 (13)	828 (64)	800 (56)	918 (69)	340 (51)	64 (54)	256 (50)
C(11)	702 (7)	92 (5)	−118 (11)	855 (64)	484 (38)	862 (58)	190 (41)	239 (53)	140 (38)

[a] Positional and thermal parameters are multiplied by 10^4.

Table IV. Atomic Parameters for *trans*-[$NiCl_2(N_49)$][a]

atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ni	0	14 195 (2)	25 000	148 (1)	136 (1)	126 (1)	0	75 (1)	0
Cl	10 811 (2)	15 576 (2)	50 622 (3)	206 (1)	239 (1)	130 (1)	4 (1)	77 (1)	7 (1)
N(1)	−7 353 (7)	−1 100 (9)	26 629 (9)	255 (4)	189 (4)	173 (4)	−42 (3)	121 (3)	0 (3)
N(2)	−11 815 (6)	25 097 (9)	24 253 (9)	165 (4)	219 (4)	162 (3)	12 (3)	97 (3)	31 (3)
C(1)	−5 452 (12)	−13 069 (11)	21 982 (15)	550 (8)	163 (4)	341 (6)	−85 (5)	306 (7)	−46 (4)
C(2)	−17 674 (9)	2 567 (12)	19 871 (13)	208 (5)	313 (5)	233 (5)	−96 (4)	90 (4)	41 (4)
C(3)	−17 316 (9)	15 319 (12)	26 382 (14)	181 (5)	327 (6)	291 (6)	22 (4)	157 (4)	96 (4)
C(4)	−9 907 (9)	36 640 (11)	33 035 (12)	238 (5)	281 (5)	204 (5)	60 (4)	149 (4)	5 (4)
C(5)	−11 597 (8)	49 168 (11)	25 155 (12)	252 (5)	238 (5)	249 (5)	73 (4)	139 (4)	−17 (4)
C(6)	−5 565 (8)	50 246 (10)	19 274 (12)	263 (5)	175 (4)	230 (5)	19 (4)	131 (4)	15 (3)

[a] Positional and thermal parameters are multiplied by 10^5 and 10^4, respectively.

that found in the trans analogue, [Cu(*trans*-[18]dieneN_4)]$(ClO_4)_2$,[13] resembles cycloheptane in a boat form.[11]

Although the Ni–N(4) distance (2.093 (3) Å) associated with the seven-membered ring is slightly longer, all other Ni–N distances are within the normal range expected for a high-spin nickel(II) complex with four nitrogen donors in a square plane.[14] In terms of the Ni–N distance, complex **1** is much less strained than the complexes having the eight- or nine-

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Table V. Bond Distances (Å) and Angles (deg) for *trans*-[$NiCl_2(N_47)$]·H_2O

Ni-Cl(1)	2.540 (1)	N(3)-C(4)	1.464 (5)
Ni-Cl(2)	2.556 (1)	N(3)-C(5)	1.491 (6)
Ni-N(1)	2.056 (3)	N(4)-C(6)	1.525 (6)
Ni-N(2)	2.060 (3)	N(4)-C(7)	1.442 (5)
Ni-N(3)	2.062 (3)	C(1)-C(2)	1.521 (6)
Ni-N(4)	2.093 (3)	C(3)-C(4)	1.515 (7)
N(1)-C(1)	1.484 (4)	C(5)-C(6)	1.571 (6)
N(2)-C(2)	1.445 (5)	C(7)-C(8)	1.552 (6)
N(2)-C(3)	1.481 (5)	C(8)-C(9)	1.521 (7)

Cl(1)-Ni-Cl(2)	177.6 (1)	Ni-N(2)-C(3)	107.1 (2)
Cl(1)-Ni-N(1)	84.8 (1)	C(2)-N(2)-C(3)	121.4 (3)
Cl(1)-Ni-N(2)	98.4 (1)	Ni-N(3)-C(4)	108.4 (2)
Cl(1)-Ni-N(3)	82.7 (1)	Ni-N(3)-C(5)	108.1 (2)
Cl(1)-Ni-N(4)	93.7 (1)	C(4)-N(3)-C(5)	120.8 (3)
Cl(2)-Ni-N(1)	95.6 (1)	Ni-N(4)-C(6)	107.2 (2)
Cl(2)-Ni-N(2)	84.1 (1)	Ni-N(4)-C(7)	122.5 (2)
Cl(2)-Ni-N(3)	97.5 (1)	C(6)-N(4)-C(7)	110.6 (3)
Cl(2)-Ni-N(4)	83.9 (1)	N(1)-C(1)-C(2)	108.8 (3)
N(1)-Ni-N(2)	84.4 (1)	N(2)-C(2)-C(1)	106.7 (3)
N(1)-Ni-N(3)	161.1 (1)	N(2)-C(3)-C(4)	107.4 (3)
N(1)-Ni-N(4)	109.7 (1)	N(3)-C(4)-C(3)	107.6 (3)
N(2)-Ni-N(3)	83.5 (1)	N(3)-C(5)-C(6)	107.0 (3)
N(2)-Ni-N(4)	162.3 (1)	N(4)-C(6)-C(5)	109.0 (3)
N(3)-Ni-N(4)	85.2 (1)	N(4)-C(7)-C(8)	111.4 (3)
Ni-N(1)-C(1)	105.6 (2)	C(7)-C(8)-C(9)	118.8 (4)
Ni-N(2)-C(2)	107.8 (2)		

Table VI. Bond Distances (Å) and Angles (deg) within [$Ni(N_48)$]$^{2+}$

Ni-N(1)	1.906 (5)	N(4)-C(6)	1.491 (11)
Ni-N(2)	1.939 (6)	N(4)-C(7)	1.498 (12)
Ni-N(3)	1.900 (6)	C(1)-C(2)	1.439 (14)
Ni-N(4)	1.904 (7)	C(3)-C(4)	1.445 (15)
N(1)-C(1)	1.487 (11)	C(5)-C(6)	1.596 (20)
N(1)-C(11)	1.490 (10)	C(7)-C(8)	1.565 (13)
N(2)-C(2)	1.525 (12)	C(8)-C(9)	1.495 (14)
N(2)-C(3)	1.452 (11)	C(9)-C(10)	1.514 (13)
N(3)-C(4)	1.595 (11)	C(10)-C(11)	1.489 (15)
N(3)-C(5)	1.377 (11)		

N(1)-Ni-N(2)	84.4 (3)	Ni-N(4)-C(6)	107.9 (6)
N(1)-Ni-N(3)	172.3 (3)	Ni-N(4)-C(7)	119.3 (5)
N(1)-Ni-N(4)	99.3 (2)	C(6)-N(4)-C(7)	112.8 (8)
N(2)-Ni-N(3)	88.2 (3)	N(1)-C(1)-C(2)	106.6 (6)
N(2)-Ni-N(4)	169.5 (3)	N(2)-C(2)-C(1)	109.2 (7)
N(3)-Ni-N(4)	87.5 (3)	N(2)-C(3)-C(4)	105.7 (8)
Ni-N(1)-C(1)	105.5 (5)	N(3)-C(4)-C(3)	112.9 (7)
Ni-N(1)-C(11)	114.3 (5)	N(3)-C(5)-C(6)	103.1 (7)
C(1)-N(1)-C(11)	110.3 (6)	N(4)-C(6)-C(5)	106.5 (8)
Ni-N(2)-C(2)	109.6 (5)	N(4)-C(7)-C(8)	112.4 (7)
Ni-N(2)-C(3)	104.8 (5)	C(7)-C(8)-C(9)	117.1 (8)
C(2)-N(2)-C(3)	116.5 (7)	C(8)-C(9)-C(10)	115.9 (8)
Ni-N(3)-C(4)	104.4 (5)	C(9)-C(10)-C(11)	116.5 (8)
Ni-N(3)-C(5)	109.7 (6)	N(1)-C(11)-C(10)	113.9 (7)
C(4)-N(3)-C(5)	119.8 (8)		

Table VII. Bond Distances (Å) and Angles (deg) for *trans*-[$NiCl_2(N_49)$]

Ni-Cl	2.426 (1)	N(2)-C(4)	1.486 (1)
Ni-N(1)	2.087 (1)	C(1)-C(1′)	1.520 (2)
Ni-N(2)	2.236 (1)	C(2)-C(3)	1.512 (2)
N(1)-C(1)	1.465 (1)	C(4)-C(5)	1.522 (1)
N(1)-C(2)	1.464 (1)	C(5)-C(6)	1.526 (2)
N(2)-C(3)	1.487 (2)	C(6)-C(6′)	1.523 (1)

Cl-Ni-N(1)	88.97 (3)	Ni-N(2)-C(3)	105.58 (7)
Cl-Ni-Cl	173.22 (1)	C(3)-N(2)-C(4)	109.67 (12)
Cl-Ni-N(1′)	96.20 (3)	Ni-N(2)-C(4)	123.88 (7)
N(1)-Ni-N(2)	80.39 (4)	N(1)-C(1)-C(1′)	106.97 (10)
N(1)-Ni-N(1′)	80.81 (5)	N(1)-C(2)-C(3)	105.82 (9)
N(1)-Ni-N(2′)	159.76 (4)	N(2)-C(3)-C(2)	110.97 (15)
N(2)-Ni-N(2′)	119.14 (4)	N(2)-C(4)-C(5)	112.55 (12)
Ni-N(1)-C(1)	110.06 (12)	C(4)-C(5)-C(6)	113.59 (12)
C(1)-N(1)-C(2)	117.77 (10)	C(5)-C(6)-C(6′)	113.24 (11)
Ni-N(1)-C(2)	108.93 (8)		

Table VIII. Deviations of Atoms (Å) from the Calculated N_4 Best Plane[a]

[$NiCl_2(N_47)$]		[$Ni(N_48)$](ClO_4)$_2$		[$NiCl_2(N_49)$]	
Ni	−0.007 (2)	Ni	0.105 (3)	Ni	0.000 (1)
N(1)	0.148 (4)	N(1)	0.043 (8)	N(1)	0.146 (1)
N(2)	−0.226 (4)	N(2)	−0.054 (9)	N(2)	−0.082 (1)
N(3)	0.307 (4)	N(3)	0.063 (9)	N(1′)	−0.146 (1)
N(4)	−0.213 (4)	N(4)	−0.057 (9)	N(2′)	0.082 (1)

[a] Estimated standard deviations were calculated by Ito's method.[26]

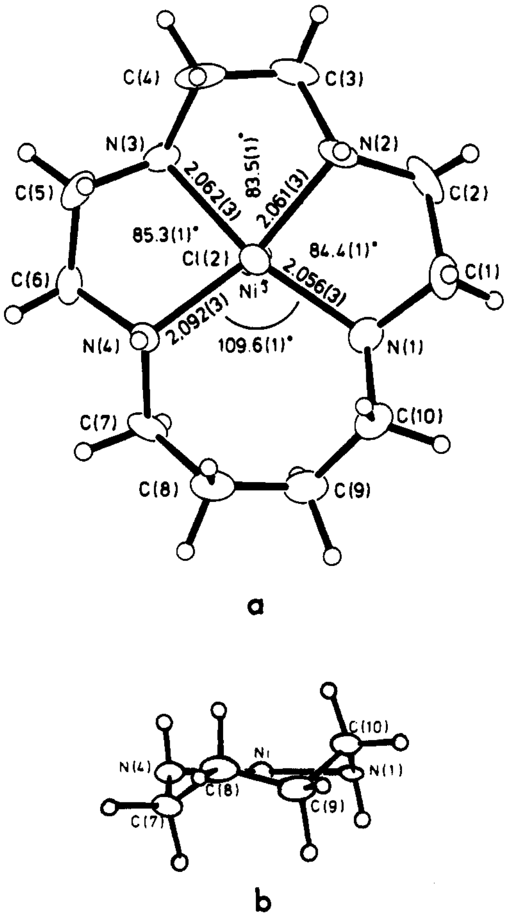

Figure 4. (a) Structure of *trans*-[$NiCl_2(N_47)$] as viewed along the normal to the NiN_4 plane. (b) Structure of the seven-membered ring in *trans*-[$NiCl_2(N_47)$].

membered chelate ring (see below). Bite angles of three five-membered rings range from 83.5 (1) to 85.3 (1)° and are normal.[15] However, the bite angle of the seven-membered ring is widened to 109.6 (1)°. This value is by far larger than those reported for other seven-membered diamine chelate rings (89.2 (2)° for the tris(1,4-butanediamine)cobalt(III) ion;[12] 88 and 89° for bis(L-ornithianato)palladium(II);[16] 90° for the *trans*-dichlorobis(1,4-butanediamine)cobalt(III) ion[17]) and is indicative of strain in this complex. Within the seven-membered ring, close hydrogen–hydrogen contacts are observed between 1,3-diaxial positions: H[C(10)]···H[C(8)], 2.22 (5) Å; H[C(8)]···H[N(4)], 2.24 (6) Å; H[N(1)]···H[C(9)], 2.25 (5) Å.

Deviations of the four nitrogen atoms from the N_4 best plane (Table VIII) indicate that the geometry of the four nitrogens

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(15) For example: Saito, Y. "Inorganic Molecular Dissymmetry"; Springer-Verlag: Berlin, 1979; Vol. 4, Chapter IV.

(16) Nakayama, Y.; Matsumoto, K.; Ooi, S.; Kuroya, H. *J. Chem. Soc., Chem. Commun.* **1973**, 170.

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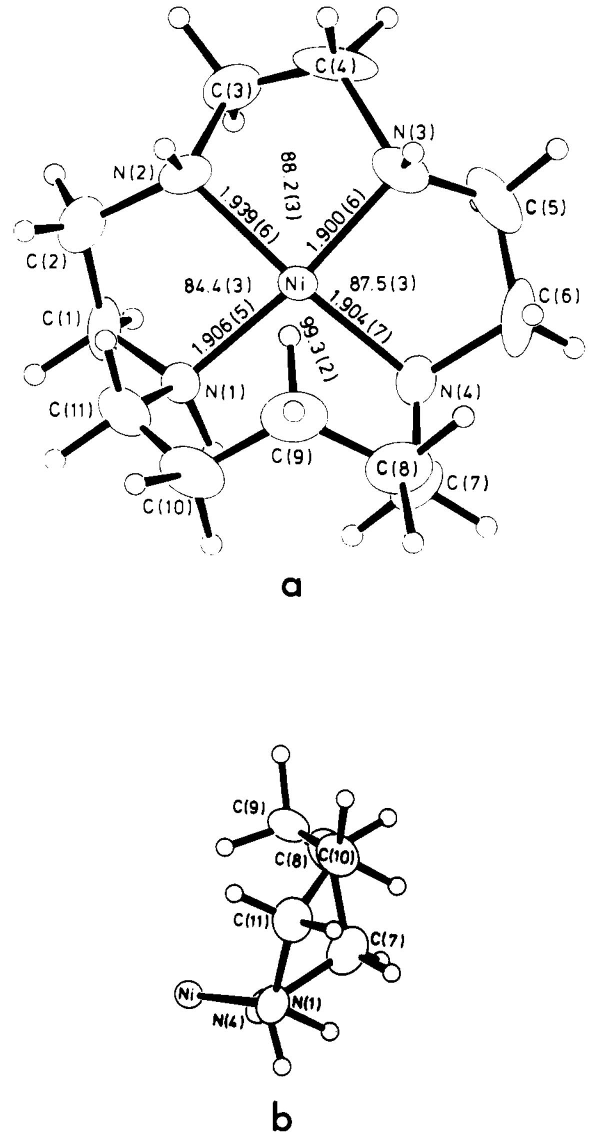

Figure 5. (a) Structure of $[Ni(N_48)]^{2+}$ as viewed along the normal to the NiN_4 plane. (b) Structure of the eight-membered ring in $[Ni(N_48)]^{2+}$.

about the Ni is tetrahedrally distorted. The Ni–N(1)–N(4) and Ni–N(2)–N(3) planes intersect with a dihedral angle of 17.3°. This distortion may arise from the hole size provided by this ligand, which would be slightly small to accomodate a high-spin Ni(II) ion in a planar fashion.[9] The angles about the carbon atoms in the trien moiety are within the normal tetrahedral angle. On the other hand, those in the seven-membered ring are considerably widened. This trend has been commonly observed in structures of other seven-membered diamine chelate rings.[12,16,17]

The Ni–Cl distances (2.540 (1) and 2.556 (1) Å) are considerably longer than those reported so far for a *trans*-$NiCl_4N_4$-type complex.[18,19] This feature is discussed later.

Water of crystallization is hydrogen bonded to Cl(1) and the N(4)–H group of an adjacent complex, forming a one-dimensional chain of complexes.

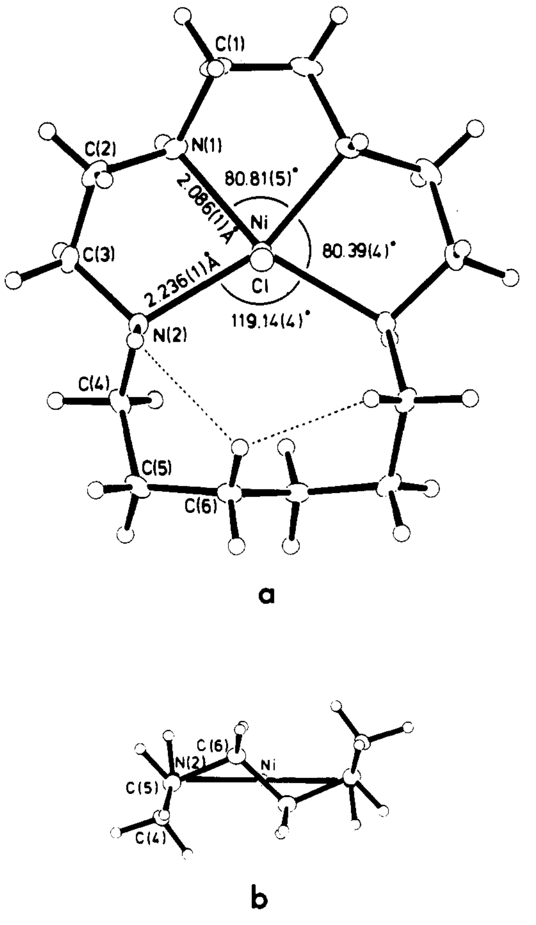

Figure 6. (a) Structure of *trans*-$[NiCl_2(N_49)]$ as viewed along the normal to the NiN_4 plane. (b) Structure of the nine-membered ring in *trans*-$[NiCl_2(N_49)]$.

$[Ni(N_48)](ClO_4)_2$ (2). As is shown in Figure 2, the Ni in this complex is surrounded by a square-planar array of four nitrogen atoms. No axial interactions with perchlorate oxygens are observed in the crystal structure. In a structure of a reported tetraaza macrocyclic nickel(II) complex in which a nickel(II) ion is surrounded by a square-planar array of secondary amine nitrogens, all of the four NH protons are disposed either above or below the NiN_4 plane.[20] However, the N(1)H proton is oriented in an equatorial direction with respect to the NiN_4 plane. This indicates that the skeletal structure of the macrocyclic ligand in **2** is extremely distorted. The ^{13}C NMR spectrum of **2** in solution shows that carbon atoms are pairwise equivalent,[5] and thus the complex has a symmetrical structure on an NMR time scale. However, the geometry about the Ni found in the crystal is highly unsymmetrical as is evident from the Ni–N distances and the N–Ni–N angles (see Table VI). A similar unsymmetrical eight-membered chelate ring with oxygen and nitrogen donor atoms has been found for a copper(II) complex of 1,4,10,13-tetraoxa-7,16-diazacyclooctadecane-7,16-diacetic acid, where the coordination bond lengths are highly unsymmetrical (Cu–O, 2.638 (1) Å, and Cu–N, 2.046 (1) Å).[21] All carbon atoms within the eight-membered ring in **2** are disposed on the same side of the NiN_4 plane. As a result, chelate rings associated with the trien moiety cannot adopt a stable gauche–gauche–gauche conformation and the central five-membered ring is in the nearly eclipsed form. If a conformation of the eight-membered ring of **2** is inferred by analogy with the cyclooctane structure,[11] it is intermediate between boat–boat and crown (see Figure 5b). This form is quite

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(18) Bosnich, B.; Mason, R.; Pauling, P. J.; Robertson, G. B.; Tobe, M. L. *J. Chem. Soc., Chem. Commun.* **1965**, 97.

(19) Ito, T.; Toriumi, K. *Acta Crystallogr., Sect. B* **1981**, *B37*, 88.

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different from that of the most strain-free cyclooctane (twist-chair-chair).

As shown in Figure 2, one of the hydrogen atoms bonded to C(9) is located near the axial coordination site with the Ni···H[C(9)] distance of 2.31 (6) Å. A number of strained bond lengths and angles are noted not only within the eight-membered ring but also in the trien ring moiety (see Table VI).

***trans*-[$NiCl_2(N_49)$] (3).** As is seen in Figures 3 and 6a, this complex has a crystallographic twofold axis through the Ni, the midpoint of the C(6)-C(6′) bond in the nine-membered ring, and the midpoint of the C(1)-C(1′) bond in the central five-membered ring. Three five-membered rings associated with the trien moiety adopt a stable gauche conformation. The structure of the nine-membered ring is very similar to that of cyclononane in the most strain-free, twist-boat-chair conformation[22] (see Figure 6b). The nine-membered ring has the corner carbon atoms (C(5), C(5′)) as seen in large cycloalkanes (see Figure 6a). The structural parameters about the Ni are indicative of a large amount of strain in the complex. Bite angles of the three five-membered rings are narrowed to 80.39 (4) -80.81 (5)°, while that of the nine-membered ring is opened out to 119.14 (4)°. The Ni-N(2) distance associated with the nine-membered ring is lengthened to 2.236 (1) Å, while the Ni-N(1) distance associated with only five-membered rings is within the normal range (2.086 (1) Å).

Deviations of the four nitrogen atoms from the N_4 best plane (Table VIII) show that the square-planar array of the nitrogens about the Ni is more planar than that of the N_47 analogue. The dihedral angle between the Ni-N(1)-N(1′) and Ni-N(2)-N(2′) planes is 8.6°. A large angle distortion is noted at the Ni-N(2)-C(4) angle (123.88 (7)°) within the nine-membered ring. Angle strain of carbon atoms within the nine-membered ring is not so significant (112.6 (1)-113.6 (1)°).

In crystal structures of cyclononane derivatives, strong transannular hydrogen-hydrogen interactions have been noted.[23,24] Likewise, close hydrogen-hydrogen contacts are observed in the nine-membered chelate ring: H[C(6)]··· H[N(2)], 2.31 (3) Å; H[C(6)]···H[C(4′)], 2.22 (3) Å. They are depicted as dashed lines in Figure 6a.

The Ni-Cl distance of 2.426 (1) Å is significantly shorter than those in *trans*-[$NiCl_2(N_47)$] (**1**).

Correlation between the Ni-Cl and Ni-N Distances—An Electronically Controlled Cis Effect. The Ni-Cl distances of complexes **1** and **3** are 2.548 (8) (average) and 2.426 (1) Å, respectively, and are significantly different from each other. It seems that the Ni-Cl distance becomes longer as the mean Ni-N distance decreases (see Table V and VII). The spatial orientation of the macrocyclic ligand in these complexes indicates no obvious intramolecular steric interaction against chloride ion coordination. The nature of this phenomenon must be electronic in origin. Busch et al. reported a correlation, which they called a cis effect, between ligand field parameters Dq^z (axial) and Dq^{xy} (in plane) in the electronic spectra of *trans*-diacido(tetraaza macrocycle)nickel(II) complexes: the Dq^z value decreases linearly as the Dq^{xy} value increases.[25] The correlation observed for the Ni-Cl and Ni-N distances should be of the same nature as the cis effect. A similar trend is observed for the Ni-Cl (2.492 Å) and Ni-N (2.058 (8) Å) distances of *trans*-dichloro(1,4,8,11-tetraazacyclotetradecane)nickel(II).[18]

It is most reasonable to consider the correlation found for Ni-Cl and Ni-N distance of *trans*-dichloro(tetraaza macrocycle)nickel(II) complexes to be a result of the electronically controlled cis effect.

Registry No. 1, 84194-09-2; **2**, 84194-12-7; **3**, 84194-18-3.

Supplementary Material Available: Tables of hydrogen atomic coordinates and structure factors and stereoscopic views of the crystal structures of complexes **1-3** (50 pages). Ordering information is given on any current masthead page.

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Rhodium Nitro Complexes as Oxygen-Transfer Agents: Oxidation of Olefins

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In acetonitrile, dicationic rhodium nitrosyl complexes [$(bpy)(CH_3CN)_3RhNO]^{2+}(PF_6^-)_2$ (**5**) and [$(CH_3CN)_4RhNO]^{2+}(BF_4^-)_2$ (**9**) are oxidized by molecular oxygen to the corresponding nitro complexes **7** and **10**. Complex **7** oxidizes ethylene or terminal olefins to acetaldehyde or alkanones only in the presence of $(PhCN)_2PdCl_2$ (an olefin activator). In nitromethane, the acetonitrile ligand in complex **10** is displaced by olefins and an oxygen atom from the nitro ligand in **10** is transferred to the coordinated olefin in the absence of a cocatalyst with the formation of acetaldehyde from ethylene and 2-alkanones from terminal olefins. In contrast to the dicationic complexes, the neutral complex $(CH_3CN)_2Rh(NO)Cl_2$ (**13**) does not form the corresponding nitro complex when exposed to molecular oxygen. A plausible explanation is offered for this seemingly contradictory behavior of the dicationic and the corresponding neutral rhodium nitrosyl complexes.

Introduction

In previous reports, we described the roles played by py(saloph)$CoNO_2$ (**1**) and py(TPP)$CoNO_2$ (**2**) (Table I) in the selective oxidation of organic substrates.[1] For a bimetallic system consisting of the above coordinatively saturated nitro complexes as oxygen-transfer agents and palladium(II) species as olefin activators, we have demonstrated the oxidation of ethylene to acetaldehyde and higher terminal olefins to 2-alkanones.[1b,d] The most important extension of this system was recently achieved by the replacement of palladium(II) by thallium(III). In this modified bimetallic system, the oxidation of olefins leads to epoxides rather than ketones.[2] Olefins are

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