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A Cis-Folded Macrocyclic Nickel(II) Complex: Molecular Structure and Thermal Reaction of *cis*-Diaqua(1,4,7,11-tetraazacyclotetradecane)nickel(II) Chloride

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The single-crystal X-ray structure and thermal behavior of *cis*-$[Ni(isocyclam)(H_2O)_2]Cl_2\cdot 2H_2O$ (isocyclam = 1,4,7,11-tetraazacyclotetradecane) are reported. The complex crystallizes in the monoclinic space group $P2_1/c$. The unit cell parameters of the complex, $NiCl_2C_{10}N_4O_4H_{32}$ (fw = 402.01), are a = 12.55 (1) Å, b = 8.11 (1) Å, c = 18.22 (1) Å, β = 98.48 (6)°, and Z = 4. The complex has a distorted octahedral geometry with two coordinated water molecules in cis positions and the isocyclam ligand coordinated in a folded fashion. The elongation in the bond distances and the deviation from a regular octahedron in the bond angles around the Ni(II) center are more pronounced than those in the corresponding *cis*-$[Ni(cyclam)(H_2O)_2]Cl_2\cdot 2H_2O$ (cyclam = 1,4,8,11-tetraazacyclotetradecane). The isocyclam complex undergoes thermal deaquation–anation in the solid state to produce *cis*-$[NiCl_2(isocyclam)]$. The *cis*-dichloro complex, when further heated, undergoes isomerization to the trans form with a change in configuration from folded to coplanar chelation of the isocyclam. The isomerization is exothermic and irreversible. In contrast, *cis*-$[NiCl_2(cyclam)]$ obtained by heating the corresponding diaqua complex, *cis*-$[Ni(cyclam)(H_2O)_2]Cl_2\cdot 2H_2O$, exhibits no thermal isomerization in the solid state.

Introduction

Many synthetic studies of metal complexes with tetraazacycloalkanes indicated that (1) the complexes commonly exhibit tetragonal stereochemistry[4–8] and (2) as the hole size of the macrocyclic ligands becomes smaller, coplanar chelation becomes more difficult.[9–11] The empirical force field calculation for free macrocyclic 12–16-membered ligands revealed that cyclam (1,4,8,11-tetraazacyclotetradecane, [14]aneN_4) exhibited the least strain with the best planarity, stabilizing the low-spin nickel(II) ion.[12,13] On the other hand, [15]aneN_4 (1,4,8,12-tetraazacyclopentadecane) and [16]aneN_4 (1,5,9,13-tetraazacyclohexadecane) have cavity sizes sufficiently large to chelate the high-spin nickel(II) ion in a coplanar fashion, forming the trans-octahedral complexes.[14,15]

Only a few studies on the complexes with isocyclam (1,4,7,11-tetraazacyclotetradecane), which has a cavity comparable to that of cyclam, have been done. Fabbrizzi et al. first reported that isocyclam reacts with the nickel(II) ion to produce both low-spin square planar and high-spin pseudooctahedral complexes.[16–18] In addition, Boeyens determined the structure of $[Ni(isocyclam)](ClO_4)_2$,[19] in which the nearly square planar coordination of isocyclam was observed.

As previously stated, many tetragonal Ni(II) complexes with 14–16-membered ligands have been synthesized, but only a few cis-folded Ni(II) complexes are known.[20–22] Recently, the tetragonal $[Ni(cyclam)]^{2+}$ ion was shown to react with bidentate chelating agents such as en (ethylenediamine), gly$^-$ (glycinate ion), and ox^{2-} (oxalate ion) to form the mixed chelates $[Ni(L)(cyclam)]^{n+}$ (n = 2, 1, and 0 for L = en, gly$^-$, and ox^{2-}, respectively), in which the cyclam is obliged to adopt a folded configuration.[23] In addition, Billo et al.[24] showed that *cis*-$[Ni(cyclam)(H_2O)_2]Cl_2\cdot 2H_2O$ has the *RRRR* nitrogen configuration and longer Ni–N bond distances (2.09–2.11 Å) when compared with those of coplanar complexes. The complex has been found to undergo cis-to-trans isomerization in solution over a wide pH range.[25,26]

We recently reported the preparation of new cis chromium(III) complexes with 14–16-membered ligands.[27] In this study, we present the preparation and the X-ray structure of *cis*-$[Ni(isocyclam)(H_2O)_2]Cl_2\cdot 2H_2O$. We also describe the solid-phase thermal cis-to-trans isomerization of the dichloro complex obtained by thermal deaquation–anation of the diaqua complex.

Experimental Section

Materials. Isocyclam (1,4,7,11-tetraazacyclotetradecane) was prepared by the known method with a slight modification.[16,28] The *cis*-diaqua complex was prepared as follows: *cis*-$[Ni(en)(isocyclam)]Cl_2\cdot 4H_2O$[25] was dissolved in water, and the pH of the solution was adjusted

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Table I. Crystal Data for *cis*-[Ni(isocyclam)$(H_2O)_2$]$Cl_2 \cdot 2H_2O$

cryst dimens/mm^3	0.2 × 0.2 × 0.3
temp/°C	23.0
λ/Å	0.710 73
formula	$NiC_{10}H_{32}N_4O_4Cl_2$
fw	402.0
cryst syst	monoclinic
space group	$P2_1/c$ (No. 14)
a/Å	12.55 (1)
b/Å	8.11 (1)
c/Å	18.22 (1)
β/deg	98.48 (6)
V/Å^3	1833.3
Z	4
D_c/g cm^{-3}	1.456
D_m/g cm^{-3}	1.465
index ranges	$0 \leq h \leq 16, 0 \leq k \leq 11,$ $-24 \leq l \leq 24$
no. of data	4728
no. of unique data[a]	2512
no. of params	191
R	0.0535
R_w[b]	0.0457
μ/cm^{-1}	13.64
2θ limits/deg	3–55

[a] $F_o > 3\sigma(F_o)$. [b] $w = 1/(\sigma(F))^2$.

Table II. Atomic Coordinates (×10^4) and Thermal Parameters of Non-Hydrogen Atoms with Their Estimated Standard Deviations in Parentheses

atom	x	y	z	B/Å^2
Ni	7399 (1)	1840 (1)	1286 (1)	2.28 (2)
Cl1	6339 (2)	−3154 (3)	1514 (1)	3.89 (6)
Cl2	8508 (2)	−1347 (3)	−619 (1)	5.11 (8)
O1	8580 (4)	219 (6)	1911 (3)	3.30 (16)
O2	7040 (4)	−257 (6)	560 (2)	3.03 (16)
O3[a]	12263 (5)	3295 (7)	2086 (3)	5.54 (20)
O4[a]	10209 (4)	3763 (7)	3996 (3)	4.77 (20)
N1	6272 (5)	1140 (7)	1999 (3)	3.21 (19)
N2	7839 (5)	3613 (7)	2106 (3)	3.50 (20)
N3	8737 (5)	2879 (8)	843 (3)	4.10 (21)
N4	6259 (4)	3165 (8)	551 (3)	2.87 (17)
C1	6414 (7)	2302 (11)	2642 (4)	4.89 (31)
C2	7539 (7)	2965 (11)	2804 (4)	4.71 (28)
C3	5959 (7)	4033 (10)	2118 (5)	5.32 (30)
C4	9157 (7)	4301 (10)	1328 (5)	4.96 (30)
C5	8606 (7)	3244 (11)	52 (4)	5.17 (30)
C6	7621 (7)	4272 (11)	−203 (4)	4.61 (30)
C7	6562 (6)	3357 (10)	−196 (4)	4.22 (27)
C8	5152 (6)	2499 (9)	461 (4)	3.86 (26)
C9	4692 (6)	2381 (9)	1175 (4)	4.11 (27)
C10	5117 (6)	963 (10)	1672 (4)	4.18 (28)

[a] Lattice water.

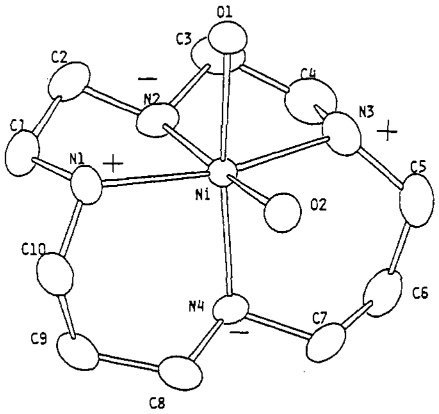

Figure 1. ORTEP drawing of the *cis*-[Ni(isocyclam)$(H_2O)_2$]$^{2+}$ cation. Hydrogen atoms are not shown; probability ellipsoids are 50%.

to ca. 3 with 0.5 mol dm^{-3} hydrochloric acid. The resulting dark brown solution was concentrated in a vacuum desiccator to produce blue *cis*-[Ni(isocyclam)$(H_2O)_2$]$Cl_2 \cdot 2H_2O$. Anal. Found: C, 29.66; H, 8.14; N, 13.91. Calcd for $NiC_{10}H_{32}N_4O_4Cl_2$: C, 29.88; H, 8.02; N, 13.94.

An attempt to prepare the *cis*-diaqua complexes of [15]aneN_4 and [16]aneN_4 from the corresponding cis en complexes always failed. *cis*-[Ni(en)([15]aneN_4)]$Br_2 \cdot 3H_2O$[25] immediately gave the *trans*-diaqua species in acidic conditions. In the case of [16]aneN_4, no *cis*-[Ni(en)-([16]aneN_4)]$^{2+}$ formation was observed even in solution.

X-ray Crystallography. Single crystals were obtained as blue blocks by recrystallization from a mixture of methanol/acetone (1:1). The unit-cell parameters and intensities were measured on a Rigaku AFC-5R automated four-circle diffractometer using graphite-monochromatized Mo Kα (λ = 0.710 73 Å) radiation at room temperature. The 2θ–ω scan mode at a rate of 6° min^{-1} was employed to record the intensities. The intensity data were corrected for Lorentz-polarization and absorption effects. The structure was solved by the heavy-atom method and refined by the block-diagonal least-squares method. The scattering factors and anomalous dispersion coefficients were taken from the literature.[29,30] Calculations were performed with the UNICS III[31,32] programs on a FACOM 760/10 computer at the Kanazawa University Information Processing Center. The crystal data of *cis*-[Ni(isocyclam)$(H_2O)_2$]-$Cl_2 \cdot 2H_2O$ are tabulated in Table I. The final atomic coordinates and thermal parameters of the non-hydrogen atoms with their estimated standard deviations are given in Table II.

Measurements. TG, DTA, and DSC measurements were carried out with a Seiko TA station SSC 5000 system under a constantly flowing nitrogen stream (0.2 dm^3 min^{-1} for TG and DTA; 0.03 dm^3 min^{-1} for DSC). Finely powdered samples (10–20 mg) were used for the measurements. Solid-phase visible and near-IR electronic spectra were recorded by a diffuse reflectance method with a Hitachi U-3400 spectrophotometer. Spectral measurements at elevated temperatures were carried out using a hand-made temperature-controlled cell. The cell was set on the spectrophotometer, and the temperature was regulated by a REX-C72 temperature controller equipped with a Cu–constantan thermocouple.

Results and Discussion

Description of the *cis*-[Ni(isocyclam)$(H_2O)_2$]$Cl_2 \cdot 2H_2O$ Structure. Figure 1 shows the perspective view of the *cis*-[Ni(isocyclam)$(H_2O)_2$]$^{2+}$ cation. The two coordinated water molecules occupy the cis positions of the Ni(II)–N_4O_2 octahedron. Isocyclam is coordinated to the Ni(II) ion in a folded fashion such that two 5-membered chelate rings form one pseudoplane and two 6-membered chelate rings form another plane. The complex cation possesses a molecular mirror plane through N4–N2–O1–O2 with respect to the ligand conformation. The configuration of the four nitrogen atoms in the complex is + − + −,[33] which corresponds to that in the *RRRR* (*trans*-V) diastereomer of [Ni(cyclam)]$^{2+}$. Such a configuration is also observed in *cis*-[Ni(cyclam)$(H_2O)_2$]$Cl_2 \cdot 2H_2O$.[24]

The selected bond distances and angles are listed in Table III. The four Ni–N bonds can be classified into two groups. One is the Ni–N2 and Ni–N4 bonds, which bisect the pseudoplanes consisting of two 5-membered chelate rings and two 6-membered rings, respectively. The other is the Ni–N1 and Ni–N3 bonds, along which the isocyclam is folded. The bond distances of the former (2.086 and 2.101 Å) correspond to those of the high-spin octahedral complexes,[34,35] while the bond distances of the latter (2.130 and 2.133 Å) are longer than those of the former. The elongation in the Ni–N bond distances is not detected in *cis*-[Ni(cyclam)$(H_2O)_2$]$Cl_2 \cdot 2H_2O$,[24] in which the four Ni–N bond

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(33) When the cis-folded isocyclam is converted into the flattened form with no changes in the configuration, the plus sign indicates that the hydrogen atom of the NH group is above the plane which consists of four nitrogens, while the minus sign indicates that it is below.

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Table III. Bond Distances (Å) and Angles (deg) for *cis*-[Ni(isocyclam)$(H_2O)_2$]$Cl_2 \cdot 2H_2O$

	Distances		
Ni–O1	2.176 (5)	Ni–O2	2.161 (5)
Ni–N1	2.130 (6)	Ni–N2	2.086 (6)
Ni–N3	2.133 (6)	Ni–N4	2.101 (6)
N1–C1	1.495 (10)	N1–C10	1.487 (10)
N2–C2	1.475 (10)	N2–C3	1.440 (10)
N3–C4	1.499 (10)	N3–C5	1.451 (10)
N4–C7	1.470 (9)	N4–C8	1.477 (9)
C1–C2	1.498 (12)	C3–C4	1.511 (13)
C5–C6	1.512 (12)	C6–C7	1.524 (12)
C8–C9	1.500 (11)	C9–C10	1.513 (11)
	Angles		
O1–Ni–O2	84.7 (2)	O1–Ni–N1	89.1 (2)
O1–Ni–N2	87.4 (2)	O1–Ni–N3	85.6 (2)
O1–Ni–N4	171.5 (2)	O2–Ni–N1	93.8 (2)
O2–Ni–N2	171.5 (2)	O2–Ni–N3	100.7 (2)
O2–Ni–N4	87.2 (2)	N1–Ni–N2	83.1 (2)
N1–Ni–N3	164.1 (2)	N1–Ni–N4	94.3 (2)
N2–Ni–N3	81.7 (3)	N2–Ni–N4	100.9 (2)
N3–Ni–N4	93.2 (2)		
Ni–N1–C1	107.2 (5)	Ni–N1–C10	118.6 (5)
C1–N1–C10	112.0 (6)	Ni–N2–C2	107.4 (5)
Ni–N2–C3	109.5 (5)	C2–N2–C3	116.1 (6)
Ni–N3–C4	108.4 (5)	Ni–N3–C5	118.5 (5)
C4–N3–C5	113.8 (6)	Ni–N4–C7	113.5 (5)
Ni–N4–C8	115.1 (4)	C7–N4–C8	107.8 (5)
N1–C1–C2	112.7 (7)	N2–C2–C1	108.1 (6)
N2–C3–C4	108.4 (6)	N3–C4–C3	110.8 (7)
N3–C5–C6	112.5 (7)	C5–C6–C7	113.7 (7)
N4–C7–C6	114.0 (6)	N4–C8–C9	113.9 (6)
C8–C9–C10	114.9 (7)	N1–C10–C9	113.7 (6)

distances are in the range 2.09–2.11 Å. The two Ni–O distances (Ni–O1 = 2.176 Å and Ni–O2 = 2.161 Å) of the isocyclam complex are also slightly longer than those (2.130 and 2.140 Å) of the cyclam complex. Such elongation of the bond distances in the isocyclam complex compared with the cyclam complex is consistent with the fact that the unsymmetrical macrocycles exhibit weaker metal–donor atom interactions than the symmetrical homolog.[16]

The bond angles N2–Ni–N4, N1–Ni–N3, and O1–Ni–O2 are 100.9, 164.1, and 84.7°, respectively, which deviate from the ideal octahedral angles. The N2–Ni–N4 and O1–Ni–O2 angles are comparable to the corresponding angles of *cis*-[Ni(cyclam)$(H_2O)_2$]$Cl_2 \cdot 2H_2O$,[24] while the axial N1–Ni–N3 angle is much more reduced than that (174.4°) of the cyclam complex. The pronounced reduction in the axial bond angle may arise from the relative arrangement of the 5- and 6-membered chelate rings (5,5,6,6) in the isocyclam complex. A similar reduction is observed in the low-spin nickel(II) complex [Ni(isocyclam)]$(ClO_4)_2$.[19] This low-spin complex with the + – + + nitrogen configuration of isocyclam has axial bond angles of 148.3 and 175.7° for N1–Ni–N3 and N2–Ni–N4,[36] respectively. Thus, the isocyclam molecule is considerably folded along the N2–Ni–N4 axis. There is a significant difference in the folding of the isocyclam ligand between [Ni(isocyclam)]$(ClO_4)_2$ and *cis*-[Ni(isocyclam)$(H_2O)_2$]$Cl_2 \cdot 2H_2O$: the isocyclam in the former is folded symmetrically with a pair of 5- and 6-membered chelate rings in a pseudoplane, while in the latter the isocyclam is folded to form two nonequivalent pseudoplanes consisting of two 5-membered chelate rings and of two 6-membered rings.

Thermal Reaction. Figure 2 shows the TG, DTA, and DSC curves of *cis*-[Ni(isocyclam)$(H_2O)_2$]$Cl_2 \cdot 2H_2O$ along with those of *cis*-[Ni(cyclam)$(H_2O)_2$]$Cl_2 \cdot 2H_2O$. The abrupt weight loss in the TG curve of the isocyclam complex at 30–50 °C and the corresponding endothermic DTA peak are due to the liberation of 4 mol of water (2 mol of coordinated water plus 2 mol of lattice water), which is responsible for the first-step color change (blue → bright blue). After the dehydration, a small but clear exothermic peak appears at about 150 °C in the DTA and DSC curves, while the TG curve remains unchanged and an irreversible color change (bright blue → violet) takes place. The enthalpy change estimated from DSC was –3.26 kJ mol⁻¹ for the exothermic reaction.

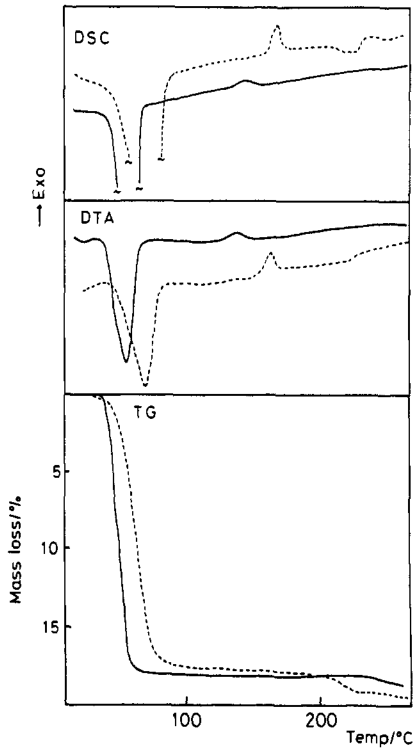

Figure 2. TG–DTA and DSC curves of *cis*-[Ni(isocyclam)$(H_2O)_2$]$Cl_2 \cdot 2H_2O$ (—) and *cis*-[Ni(cyclam)$(H_2O)_2$]$Cl_2 \cdot 2H_2O$ (- - -).

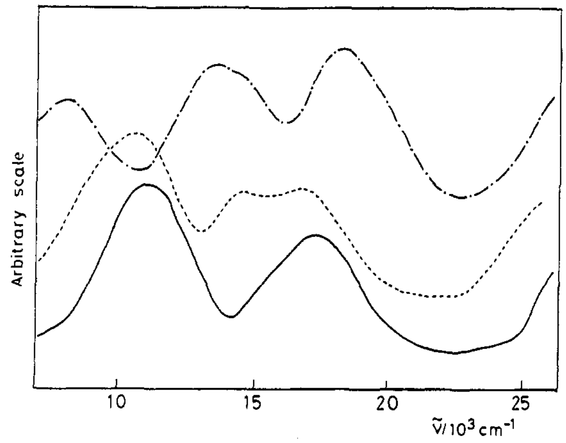

Figure 3. Electronic spectra of *cis*-[Ni(isocyclam)$(H_2O)_2$]$Cl_2 \cdot 2H_2O$ (—) and of the products obtained by heating the cis complex at 70 °C (- - -) and at 160 °C (· – ·).

Figure 3 depicts the electronic spectra of *cis*-[Ni(isocyclam)$(H_2O)_2$]$Cl_2 \cdot 2H_2O$ and those of the products obtained by heating the cis complex at 70 and 160 °C. The bright blue product at 70 °C gives a spectral pattern similar to that of the original cis-complex.[37] Therefore, the bright blue product can be identified as *cis*-[$NiCl_2$(isocyclam)], suggesting that the thermal reaction at this stage is a simple deaquation–anation with retention of the original cis geometry. In contrast, the spectrum of the violet product at 160 °C shows three d–d bands (8010, 13 290, and

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(36) The numbering of N atoms is the same as that of *cis*-[Ni(isocyclam)$(H_2O)_2$]$Cl_2 \cdot 2H_2O$.

(37) The band (17 300 cm⁻¹) of the original complex, which is due to the overlapping of $^3B_1 \rightarrow {}^3A_2(F)$, $\rightarrow {}^3B_1(F)$, and $\rightarrow {}^3B_2(F)$ transitions in a C_{2v} system, is split into two bands (14 740 and 16 670 cm⁻¹) at 70 °C.

18 270 cm^{-1}), being identical with that of *trans*-[NiCl$_2$(isocyclam)] prepared from solution. The exothermic reaction at about 150 °C is, therefore, attributable to cis-to-trans isomerization. The overall reaction of the complex can be formulated as follows: *cis*-[Ni(isocyclam)(H_2O)$_2$]Cl_2·2H_2O → *cis*-[NiCl$_2$(isocyclam)] → *trans*-[NiCl$_2$(isocyclam)].

As seen from Figure 2, the dehydration step of *cis*-[Ni(cyclam)(H_2O)$_2$]Cl_2·2H_2O proceeds at 25–80 °C to yield the blue anhydrous product *cis*-[NiCl$_2$(cyclam)]. After the dehydration, exothermic DTA and DSC peaks appear with no weight loss. The color of the sample remained unchanged before and after the reaction. The electronic spectral patterns at 90 °C (after the dehydration) and at 190 °C (after the exothermic reaction) were essentially the same as that of *cis*-[Ni(cyclam)(H_2O)$_2$]Cl_2·2H_2O (not shown). This suggests that products obtained at both 90 and 190 °C take the cis configuration and the dehydration step corresponds to the change from the *cis*-diaqua to *cis*-dichloro octahedral complex. Unfortunately, the origin of the exothermic reaction is not clear at present.

It is not easy to explain the mechanism of the thermal cis-to-trans isomerization of *cis*-[NiCl$_2$(isocyclam)] and the significant differences in thermal reactions between the isocyclam and cyclam complexes. However, as shown in the structures of *cis*-[Ni(isocyclam)(H_2O)$_2$]Cl_2·2H_2O and [Ni(isocyclam)](ClO_4)$_2$,[19] the complexes experience some large distortions in both the cis-folded (+ − + −) and coplanar (+ − + +) configurations. A similar distortion can be expected for *cis*-[NiCl$_2$(isocyclam)]. The distortion may contribute to the thermal cis-to-trans isomerization of *cis*-[NiCl$_2$(isocyclam)].

Supplementary Material Available: Tables S1–S4, giving positional parameters for all atoms and anisotropic thermal parameters, Tables S6–S9, listing intramolecular bond distances and angles, interatomic distances in the crystal, and intramolecular torsion angles, Table S10, giving least-squares planes and deviations therefrom, and Figure S1, showing two stereoviews of the full cell (20 pages); Table S5, listing observed and calculated structure factors (14 pages). Ordering information is given on any current masthead page.