disordered about two mirror related sites. The disorder of the third solvent molecule is more complex; the chlorine atoms lie on either side of a mirror plane and are disordered over two sites. The carbon atoms of this molecule are disordered over several sites and were not located.

In the full-matrix least-squares refinement the coordinates of the C atoms of the disordered solvent molecules were positioned from difference maps, and the C and N atom of the SCN^- anion were derived from geometrical considerations and were not refined. Isotropic refinement was followed by anisotropic refinement, and after inclusion of hydrogen atoms (from geometry considerations), the refinement converged with $R = 0.049$ (see Table III), and a maximum shift/error ratio of 0.04.

As a check that the space group had been correctly chosen, coordinates were derived for the complete structure in the alternative noncentrosymmetric space group $Pn2_1a$ and a new refinement process was begun. No significant improvement in parameter values or R was noted, and in spite of a damped refinement, several cation temperature factors that had behaved reasonably on the *Pnma* refinement moved to nonsensible values. It was concluded that the true space group is *Pnma* with the cation **3a** lying on a mirror plane.

The final difference synthesis in *Pnma* had maxima of 1.1 e $Å^{-3}$ in the volume element of the dichloroethane molecule, which was severely disordered, and no other chemically significant features. In the refinement, weights were based on counting statistics ($w = 1/\sigma(F)^2$) and scattering factors were taken from ref 33. All calculations were performed on a PDP11/73 computer using the SDP system of programs.[34] Final fractional coordinates for non-hydrogen atoms are in Table V. Lists of anisotropic thermal parameters, all bond lengths and angles, calculated hydrogen coordinates, and observed and calculated structure amplitudes are available as supplementary material.

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Registry No. $[\mathbf{1a}][CF_3CO_2]_2$, 89189-80-0; $[\mathbf{1b}][PF_6]_2$, 99642-80-5; $[\mathbf{2b}][PF_6]\cdot 2(CH_3)_2CO$, 104438-46-2; $[\mathbf{3a}][SCN]$, 104421-85-4; $[\mathbf{3a}][SCN]\cdot 3C_2H_4Cl_2$, 104421-88-7; SCN^-, 302-04-5.

Supplementary Material Available: Listings of anisotropic displacement parameters (Table VI), calculated hydrogen atom positions (Table VII), and PCC bond angles (Table VIII) for $\{Pt_3(SCN)(\mu_3\text{-}CO)(\mu\text{-}dppm)_3\}[PF_6]\cdot 2(CH_3)_2CO$ and general temperature factor expressions (Table X), bond distances (Table XI), bond angles (Table XII), and calculated hydrogen atom positions (Table XIII) for $[Pd_3(\mu_3\text{-}S)(CN)(\mu\text{-}dppm)_3][SCN]\cdot 3C_2H_4Cl_2$ (13 pages); listings of final $|F_o|$ and $|F_c|$ values for $[Pt_3(SCN)(\mu_3\text{-}CO)(\mu\text{-}dppm)_3][PF_6]\cdot 2(CH_3)_2CO$ (Table IX) and $[Pd_3(\mu_3\text{-}S)(CN)(\mu\text{-}dppm)_3][SCN]\cdot 3C_2H_4Cl_2$ (Table XIV) (64 pages). Ordering information is given on any current masthead page.

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Thermodynamic and Structural Studies of Configurational Isomers of $[Ni(cyclam)]^{2+}$

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Single-crystal X-ray structures of two new complexes of nickel(II)–cyclam are reported: *cis*-$[Ni(C_{10}H_{24}N_4)(OH_2)_2]Cl_2\cdot 2H_2O$ (298 K; triclinic, space group $P\bar{1}$, $a = 13.625$ (3) Å, $b = 8.0091$ (8) Å, $c = 9.187$ (1) Å, $\alpha = 101.31$ (1)°, $\beta = 92.86$ (2)°, $\gamma = 107.76$ (1)°, $\rho_{calcd} = 1.437$ g cm^{-3} for $Z = 2$ and $M_r = 402.07$, $R = 0.028$, $R_w = 0.031$) and $[Ni(C_{10}H_{24}N_4)]ZnCl_4$ (173 K; orthorhombic, space group $P4_122$, $a = 9.879$ (1) Å, $c = 18.289$ (3) Å, $\rho_{calcd} = 1.70$ g cm^{-3} for $Z = 4$ and $M_r = 466.26$, $R = 0.062$, $R_w = 0.066$). Both complexes have the *RRRR* set of nitrogen configurations. Ni–N distances average 2.10 Å in the six-coordinate complex and 1.9 Å in the four-coordinate complex. Thermodynamic parameters for the interconversion of these two isomers and the more stable *RRSS* isomer in aqueous solution have been obtained by microcalorimetric measurements of the heats of dissolution of the solid complexes and from the temperature dependence of the high-spin–low-spin equilibrium, determined spectrophotometrically. The enthalpy change for the reaction *RRRR*-planar(aq) → *RRSS*-planar(aq) is surprisingly small, −0.4 kcal mol^{-1}.

Introduction

The importance of nitrogen configurational isomers in the chemistry of metal complexes of tetraaza macrocyclic ligands is becoming more and more obvious. The involvement of configurational isomers has recently been postulated in mechanistic schemes of formation,[2] substitution,[3] and isomerization.[4] Except in the case of complexes of inert metal ions such as Co(III)[5] the observation of such species is difficult. For the more labile metal ions, extensive ligand N- or C-substitution makes isomerization more sluggish and has permitted the isolation of thermodynamically unstable configurational isomers.[6,7] Using this approach, Barefield and co-workers[8] isolated complexes of Ni(II) with the saturated tetraaza macrocycle tetramethylcyclam (1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane) in both the trans-III[9] or *RRSS*[10] and the trans-I or *RSRS* geometries (Figure 1). Recently Moore and co-workers[4] showed that the two isomers equilibrate readily in donor solvents, presumably via an intermediate trans-II (*RSRR*) isomer. The *RSRR* isomer has been detected by NMR.[4,11]

The minimum-energy form of the nickel(II) complex of the unsubstituted cyclam ligand also has the *RRSS* (trans-III) geometry.[12] Recently one of us published a convenient synthesis[13] of *cis*-$[Ni(cyclam)(H_2O)_2]^{2+}$, which contains a folded form of the ligand, and measured the rate of folded-to-planar isomerization over the pH range 1–10. In solutions of high perchlorate concentration the violet octahedral folded complex can be converted to a yellow planar low-spin complex,[14] α-$[Ni(cyclam)](ClO_4)_2$,

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(1) (a) Georgia Institute of Technology. (b) ISSECC (CNR). (c) Boston College. (d) Università di Firenze.

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(9) The original synthesis and consideration of the stereochemistry of metal complexes of cyclam was given by: Bosnich, B.; Poon, C. K.; Tobe, M. L. *Inorg. Chem.* **1965**, *4*, 1102. The five possible diastereomeric forms of the metal complex were designated as I–V with cis or trans forms to be indicated as such. The use of Cahn–Prelog–Ingold designation of nitrogen configurations as *RRRR* is not meant to indicate that only one enantiomer is present but rather to indicate the relative stereochemistries of the nitrogen atoms in this diastereomer.

(10) Note that this isomer has sometimes been referred to as the *RSSR* isomer. However, the nitrogen configurations should be designated according to their number in the compound 1,4,8,11-tetraazacyclotetradecane. This would result in the designation *RRSS* (or *SSRR* for the other enantiomer).

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Table I. Crystal Data for $[Ni(C_{10}H_{24}N_4)(H_2O)_2]Cl_2{\cdot}2H_2O$ and $[Ni(C_{10}H_{24}N_4)]ZnCl_4$

	$[Ni(C_{10}H_{24}N_4)(H_2O)_2]Cl_2{\cdot}2H_2O$	$[Ni(C_{10}H_{24}N_4)]ZnCl_4$	
mol wt	402.07	466.26	
dimens, mm	1.10 × 0.35 × 0.11	0.37 × 0.14 × 0.14	
space group	$P\bar{1}$	$P4_122$	
temp of data, collection, K	298	298	173
cell constants			
a, Å	13.625 (3)	9.961 (4)	9.879 (1)
b, Å	8.0091 (8)		
c, Å	9.187 (1)	18.370 (5)	18.289 (3)
α, deg	101.31 (1)		
β, deg	92.86 (2)		
γ, deg	107.76 (1)		
cell vol, Å^3	929.7 (3)	1823 (1)	1784.8 (5)
no. of reflcns used to determine cell constants; 2θ limits, deg	15; 16.97–27.86	15; 10.59–22.07	15; 17.43–33.23
Z	2	4	4
ρ_{calcd}, g cm^{-3}	1.437	1.70	
ρ_{exptl}, g cm^{-3}	1.44^a	1.69^b	

^{a} By flotation in carbon tetrachloride/*n*-hexane. ^{b} By flotation in 1,2-dibromoethane/hexane.

Table II. Data Collection and Refinement Details for *cis*-$[Ni(C_{10}H_{24}N_4)(H_2O)_2]Cl_2{\cdot}2H_2O$ and $[Ni(C_{10}H_{24}N_4)]ZnCl_4$

	$[Ni(C_{10}H_{24}N_4)(H_2O)_2]Cl_2{\cdot}2H_2O$	$[Ni(C_{10}H_{24}N_4)]ZnCl_4$	
diffractometer	Syntex $P2_1$		
monochromator (Bragg 2θ angle, deg)	graphite (12.2)		
radiation, Å	Mo K$\bar{\alpha}$, 0.710 69		
takeoff angle, deg	6.75		
no. of stds (monitoring freq/no. of reflcns)	$3^b/97$		
bkgd/scan time ratio (TR)^a	1.0		
scan method	θ–2θ	ω	
scan speed, min/max, deg min^{-1}	2.0/29.3	3.91/29.3	
scan width, deg	2.0	1.0	
2θ limits of data, deg	$4 < 2\theta < 50$	$4 < 2\theta < 50$	
temperature, K	298	298	173
h,k,l	$-h,-k,0$ to h,k,l	$\pm h,+k,+l$	$k \geq h$
no. of data	3499	1622	1581
no. of data used in final refinement ($F > 3\sigma_F$)	3057	1395	1518
no. of data/no. of variables	13.7	14.8	16.1
ν, cm$^{-1\,c}$	13.1	29.8	
$R = [\sum\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert]/[\sum\lvert F_o\rvert]$	0.028	0.079	0.062
$R_w = [\sum(\lvert F_o\rvert - \lvert F_c\rvert)w^{1/2}]/[\sum(\lvert F_o\rvert)w^{1/2}]^d$	0.031	0.082	0.066

^{a} Background counts were measured before (BG1) and at the end (BG2) of the scan. Intensities were determined from the total scan (CT) and background (BG) counts by I = CT − TR(BG1 + BG2). σ_I = [CT + (TR)^2(BG1 + BG2)]$^{1/2}$; $F_o = (I/L_p)^{1/2}$, where L_p is the Lorentz and polarization correction. ^{b} Standard reflections were as follows. *cis*-$[Ni(C_{10}H_{24}N_4)(H_2O)_2]Cl_2{\cdot}2H_2O$: 10,0,0; 0,3,0; 0,0,8. $[Ni(C_{10}H_{24}N_4)]ZnCl_4$ (298 K): 0,0,12; 8,0,0; 0,8,0. $[Ni(C_{10}H_{24}N_4)]ZnCl_4$ (173 K): 0,8,0; 8,0,0; 0,0,−8. ^{c} No absorption corrections were applied. ^{d} $w = n/(\sigma_F^2 + mF^2)$. In the final cycle values of n and m were 1.99 and 2 × 10^{-4}, 1.89 and 2 × 10^{-3}, and 2.19 and 1 × 10^{-3} for $[Ni(C_{10}H_{24}N_4)(H_2O)_2]Cl_2{\cdot}2H_2O$, $[Ni(C_{10}H_{24}H_4)]ZnCl_4$ (298 K), and $[Ni(C_{10}H_{24}N_4)]ZnCl_4$ (173 K), respectively.

Table III. Final Positional Parameters (with Esd's) for Non-Hydrogen Atoms of $[Ni(C_{10}H_{24}N_4)(H_2O)_2]Cl_2{\cdot}2H_2O$

atom	x	y	z
Ni	0.26037 (2)	0.15958 (3)	0.24493 (3)
N1	0.1511 (2)	0.0481 (3)	0.3831 (2)
N4	0.3638 (1)	0.1011 (2)	0.3876 (2)
N8	0.3747 (1)	0.2494 (2)	0.1065 (2)
N11	0.2160 (1)	−0.0786 (2)	0.0797 (2)
C2	0.2040 (2)	−0.0243 (4)	0.4893 (3)
C3	0.3158 (2)	0.0910 (4)	0.5278 (3)
C5	0.4721 (2)	0.2240 (3)	0.4178 (3)
C6	0.5224 (2)	0.2391 (3)	0.2768 (3)
C7	0.4840 (2)	0.3403 (3)	0.1773 (3)
C9	0.3686 (2)	0.0951 (4)	−0.0168 (3)
C10	0.2568 (2)	−0.0254 (3)	−0.0577 (2)
C12	0.1050 (2)	−0.1853 (3)	0.0505 (3)
C13	0.0634 (2)	−0.2385 (4)	0.1880 (4)
C14	0.0508 (2)	−0.0852 (4)	0.3077 (4)
O1	0.1459 (1)	0.2334 (2)	0.1280 (2)
O2	0.3060 (1)	0.4231 (2)	0.3841 (2)
Cl1	0.37463 (5)	0.71193 (7)	0.19363 (7)
Cl2	0.83075 (5)	0.4921 (1)	0.37163 (7)
O3	0.0217 (2)	0.3348 (3)	0.3301 (2)
O4	0.2376 (2)	0.4224 (3)	−0.0738 (3)

without change in nitrogen stereochemistry. This was clearly demonstrated by the fact that dissolving this yellow planar complex in water produces a violet solution of the cis complex.

We now report an X-ray structural analysis of both the folded complex *cis-RRRR*-[Ni(cyclam)$(H_2O)_2]Cl_2{\cdot}2H_2O$ and the α-planar complex *RRRR*-[Ni(cyclam)]$ZnCl_4$. As well, we report the determination, by microcalorimetry, of the enthalpy of interconversion of *RRRR*-[Ni(cyclam)]$^{2+}$ to the β-planar isomer, *RRSS*-[Ni(cyclam)]$^{2+}$, both in the solid and in solution. These thermodynamic measurements were made in part by determining the heat of dissolution of the diastereomeric perchlorate salts and are, we believe, the first calorimetric results obtained for the ΔH of interconversion of nickel(II) macrocycle configurational isomers.

Experimental Section

Materials. *cis*-[Ni(cyclam)$(OH_2)_2]Cl_2{\cdot}2H_2O$. The complex was prepared as a blue powder as previously reported.[13] Crystals suitable for X-ray data collection were prepared in the following manner. A concentrated aqueous solution of the cis complex was prepared at pH 3, where the rate of isomerization is lowest. The filtered blue solution was concentrated at 0 °C under reduced pressure. After storage in the refrigerator for 10 days, crystals were isolated by filtration, washed with diethyl ether, and dried for several hours in a vacuum desiccator. The crystals consisted of a mixture of well-formed mauve crystals and much smaller blue crystals. Mauve crystals were separated from the mixture by hand for elemental analysis and for X-ray analysis. Anal. Calcd for $C_{10}H_{32}Cl_2N_4NiO_4$: C, 29.89; H, 7.97. Found: C, 30.09; H, 7.91.

***RRRR*-[Ni(cyclam)]$(ClO_4)_2$.** The complex was prepared either by the previously published method[14] or directly from the mixed-ligand complex [Ni(cyclam)(en)]$(ClO_4)_2$. (*Caution*: These perchlorates are potentially explosive.) The mixed-ligand complex (0.72 g) was suspended in 2 mL of water to which was added 6 mL of 70% $HClO_4$. The reaction mixture was cooled in the freezer for about 15 min and the orange product collected on a glass frit, washed with diethyl ether, and dried for several hours in a vacuum desiccator. The typical yield was 75%.

***RRRR*-[Ni(cyclam)]$ZnCl_4$.** *RRRR*-[Ni(cyclam)]$(ClO_4)_2$ (0.2 g) was dissolved in 2 mL of 10^{-3} M $HClO_4$, and the resulting blue solution was filtered. A 0.2-mL portion of 2 M $ZnCl_2$/4 M NH_4Cl was added, and the solution was allowed to stand overnight. The resulting orange crystals were filtered through a glass frit and washed with methanol and diethyl ether. The typical yield was 60%. Several such preparations were made before crystals suitable for X-ray analysis were obtained.

Crystal Data and Intensity Measurements. $[Ni(C_{10}H_{24}N_4)(H_2O)_2]Cl_2{\cdot}2H_2O$. A mauve crystal was selected from a mixture of mauve and blue crystals and was epoxied to a glass fiber with the longest crystal dimension approximately parallel to the fiber axis. Axial photographs indicated that the crystal belonged to the triclinic system. The absence of any systematic absences in the diffraction data was consistent only with space group $P1$ or $P\bar{1}$. $P\bar{1}$ was assumed, and successful refinement of the structure in this space group confirmed the choice. The structure was solved by standard heavy-atom methods. After the positions of all non-hydrogen atoms had been determined and subjected to isotropic refinement, a subsequent difference Fourier map revealed the locations of each of the hydrogen atoms. In subsequent cycles of least-squares refinement the hydrogen atom positional parameters were held constant and only their isotropic thermal parameters were allowed to vary. Both positional and anisotropic thermal parameters for non-hydrogen atoms were allowed to vary until convergence was achieved. Crystal data and additional

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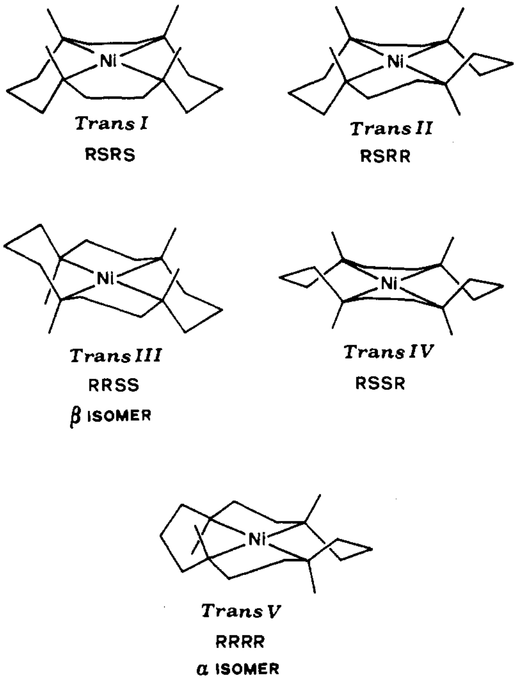

Trans I
RSRS

Trans II
RSRR

Trans III
RRSS
β ISOMER

Trans IV
RSSR

Trans V
RRRR
α ISOMER

Figure 1. Configurational isomers of planar [Ni(cyclam)]$^{2+}$.

Table IV. Final Positional Parameters (with Esd's) for Non-Hydrogen Atoms of [Ni($C_{10}H_{24}N_4$)]$ZnCl_4$

atom	*x*	*y*	*z*
Zn	0.0000	0.4931 (1)	0.0000
Cl1	0.1523 (2)	0.6235 (3)	0.0588 (1)
Cl2	0.1138 (2)	0.3670 (2)	−0.0842 (1)
Ni	−0.1121 (2)	0.5000	0.2500
N1	0.0242 (9)	0.3762 (8)	0.2792 (4)
N2	−0.2506 (8)	0.3663 (9)	0.2701 (4)
C1	−0.013 (2)	0.232 (1)	0.2703 (8)
C2	−0.107 (2)	0.186 (2)	0.318 (1)
C3	−0.221 (1)	0.276 (1)	0.3297 (7)
C4	−0.386 (2)	0.443 (1)	0.285 (1)
C5	0.165 (1)	0.420 (1)	0.2432 (8)

details of data collection and refinement are contained in Tables I and II, respectively. Non-hydrogen atom coordinates are given in Table III.

[Ni($C_{10}H_{24}N_4$)]$ZnCl_4$. Axial photographs of the orange, rectangular crystal indicated that it belonged to the orthorhombic system. Systematic absences in a data set collected at 298 K were consistent with the $P4_1$ and $P4_122$ space groups. Solution of the structure was initiated with use of $P4_122$. The coordinates of the Zn and Ni atoms were determined from a three-dimensional Patterson synthesis. The remaining non-hydrogen atoms were located from a difference Fourier after least-squares refinement of these atoms. Isotropic least-squares refinement of the non-hydrogen atoms revealed some unusual bond distances that were not resolved by refinement in the $P4_1$ space group. A second data set was collected at 173 K and refined with use of $P4_122$. Although there was some improvement in the *R* value, the C–C and C–N bond distances were still outside their normal range. Because of the large thermal parameters associated with the carbon atoms, hydrogen atom positions could not be determined. Positions of hydrogen atoms bonded to nitrogen were located and were refined isotropically. Crystal data and additional details of data collection and isotropic refinement at both 298 and 173 K are contained in Tables I and II, respectively. Table IV gives non-hydrogen atom coordinates for the 173 K determination.

Scattering factors for both determinations were taken from the usual source;[15] those for all atoms except hydrogen were corrected for real and imaginary anomalous dispersion components with use of the dispersion factors given by Cromer.[16] All computations were carried out with use of Sheldrick's SHELX-76 program package with minor local modifications.

Spectrophotometric Determination of $\Delta H°$ and $\Delta S°$ for *RRRR*-[Ni(cyclam)]$^{2+}$. The concentration of *RRRR*-[Ni(cyclam)]$^{2+}$ was monitored at 450 nm with a Cary 14 recording spectrophotometer and 10-cm quartz cells inserted into jacketed cell holders through which thermostated water was circulated. Temperature measurements were made with a thermocouple inserted directly into the cell. Solutions of 10 mM *RRRR*-[Ni(cyclam)]$(ClO_4)_2$ at pH 3 ($HClO_4$) were prepared; the total ionic strength was adjusted to 0.10 with $NaClO_4$. A molar absorptivity of 100 cm^{-1} M^{-1} was estimated from previous results.[14] When measurements were made after the sample was allowed to equilibrate at each temperature for approximately 30 min, nonlinear ln *K* vs. 1/*T* plots were obtained due to the competitive isomerization to the *RRSS* isomer. To minimize the time required to acquire temperature–absorbance data, absorbance measurements were taken as the temperature increased. The sample was then allowed to cool, and measurements were taken as the temperature decreased. Both plots of ln *K* vs. 1/*T* gave good linear fits with almost identical slopes and intercepts.

Table V. Interatomic Distances (Å) and Angles (deg) for [Ni($C_{10}H_{24}N_4$)(H_2O)$_2$]Cl_2·$2H_2O$

	Interatomic Distances (σ)		
Ni–N1	2.109 (0.002)	Ni–N4	2.093 (0.002)
Ni–N8	2.106 (0.002)	Ni–N11	2.092 (0.002)
Ni–O1	2.140 (0.001)	Ni–O2	2.130 (0.002)
N1–C2	1.488 (0.003)	N1–C14	1.487 (0.003)
N4–C3	1.479 (0.003)	N4–C5	1.479 (0.003)
N8–C7	1.491 (0.003)	N8–C9	1.482 (0.003)
N11–C10	1.490 (0.003)	N11–C12	1.473 (0.003)
C2–C3	1.503 (0.004)	C5–C6	1.504 (0.004)
C6–C7	1.507 (0.004)	C9–C10	1.515 (0.004)
C12–C13	1.494 (0.004)	C13–C14	1.538 (0.004)
	Angles (σ)		
N4–Ni–N1	83.4 (0.1)	N8–Ni–N1	174.4 (0.1)
N8–Ni–N4	92.7 (0.1)	N11–Ni–N1	92.9 (0.1)
N11–Ni–N4	99.4 (0.1)	N11–Ni–N8	83.8 (0.1)
O1–Ni–N1	90.5 (0.1)	O1–Ni–N4	171.7 (0.1)
O1–Ni–N8	93.7 (0.1)	O1–Ni–N11	86.5 (0.1)
O2–Ni–N1	93.9 (0.1)	O2–Ni–N4	87.6 (0.1)
O2–Ni–N8	89.9 (0.1)	O2–Ni–N11	170.8 (0.1)
O2–Ni–O1	87.2 (0.1)	C2–N1–Ni	107.7 (0.2)
C14–N1–Ni	117.1 (0.2)	C14–N1–C2	112.1 (0.2)
C3–N4–Ni	105.7 (0.1)	C5–N4–Ni	117.4 (0.1)
C5–N4–C3	111.0 (0.2)	C7–N8–Ni	118.1 (0.1)
C9–N8–Ni	107.9 (0.2)	C9–N8–C7	110.5 (0.2)
C10–N11–Ni	105.4 (0.1)	C12–N11–Ni	117.8 (0.1)
C12–N11–C10	111.4 (0.2)	C3–C2–N1	109.6 (0.2)
C2–C3–N4	108.6 (0.2)	C6–C5–N4	112.2 (0.2)
C7–C6–C5	116.1 (0.2)	C6–C7–N8	114.3 (0.2)
C10–C9–N8	109.6 (0.2)	C9–C10–N11	108.5 (0.2)
C13–C12–N11	111.7 (0.2)	C14–C13–C12	115.3 (0.2)
C13–C14–N1	113.6 (0.2)		

Microcalorimetric Measurements. Heats of dissolution of *RRRR*-[Ni(cyclam)]$(ClO_4)_2$ and of *RRSS*-[Ni(cyclam)]$(ClO_4)_2$ were determined by using an LKB 10700/2 batch microcalorimeter.

In a typical experiment about 4 mg of the complex was introduced by weight into one side of the calorimetric cell; 2 mL of 0.091 M $NaClO_4$ (Carlo Erba RPE grade) at pH 3 or 10 was introduced into the other side by a precision pipet (Pipetman). The concentration of $NaClO_4$ was chosen in order to obtain a final ClO_4^- concentration equal to 0.1 M.

The concentrations of the forms in the solution resulting from the calorimetric measurements were checked spectrophotometrically.

Results and Discussion

Description of the Structure of *cis*-[Ni($C_{10}H_{24}N_4$)(OH_2)$_2$]Cl_2·$2H_2O$. The crystal structure consists of *cis*-[Ni($C_{10}H_{24}N_4$)(OH_2)$_2$]$^{2+}$ cations, noninteracting chloride anions, and lattice water molecules. The cyclam ligand is folded (trans-V stereochemistry or *RRRR* set of nitrogen configurations) so that the water molecules can be accommodated in cis positions. A drawing of the cation is given in Figure 2. Table V lists selected interatomic distances and angles.

The axial and equatorial Ni–N distances are essentially the same (average 2.100 (9) Å). The Ni–O distances are slightly longer at 2.140 and 2.130 Å. The angles about the nickel ion are somewhat distorted from the ideal octahedral angles with N11–Ni–N4 expanded to 99.4° and N8–Ni–N1 reduced to 174.4 (1)°. The O2–Ni–O1 angle is 87.2 (1)°. There is a distortion of the equatorial plane such that there is an 8.6° dihedral angle between the N4, Ni, N11 and O1, Ni, O2 planes. In spite of these dis-

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(15) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, Table 2.2A.

(16) Cromer, D. T. *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, Table 2.3.1.

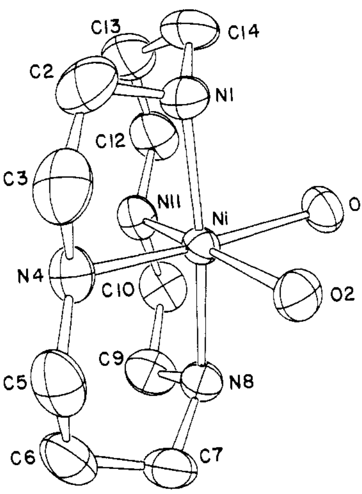

Figure 2. ORTEP drawing of the cation *cis*-$[Ni(C_{10}H_{24}N_4)(OH_2)_2]^{2+}$. Hydrogen atoms are not shown; probability ellipsoids are 50%.

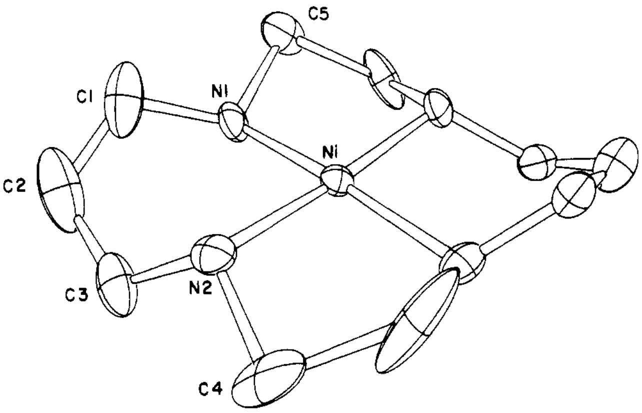

Figure 3. ORTEP drawing of the cation $[Ni(C_{10}H_{24}N_4)]^{2+}$. Hydrogen atoms are not shown; probability ellipsoids are 30%.

tortions there is an approximate twofold axis that bisects the O2-Ni-O1 and N11-Ni-N4 angles.

It should be noted that there are only small differences in a few of the bond angles between *cis*-$[Ni(C_{10}H_{24}N_4)(OH_2)_2]^{2+}$ and *trans-RRSS*-[Ni(cyclam)]Cl_2.[12] The N-C-C angles in the five-membered and six-membered chelate rings of the former complex are ca. 2 and 5–6° larger, respectively, than the corresponding angles in the latter. The N-Ni-N angles are about 2° smaller in *cis*-$[Ni(C_{10}H_{24}N_4)(OH_2)_2]^{2+}$ in both the five- and six-membered rings; all other angles are nearly the same.

Description of the Structure of $[Ni(C_{10}H_{24}N_4)]ZnCl_4$. The crystal structure consists of planar $[Ni(C_{10}H_{24}N_4)]^{2+}$ cations and noninteracting, approximately tetrahedral $ZnCl_4^{2-}$ anions. There are crystallographically imposed twofold axes for both the cation and the anion. The nitrogen donor configurations are the same as those in *cis*-$[Ni(C_{10}H_{24}N_4)(OH_2)_2]^{2+}$. A drawing of the cation is given in Figure 3. A listing of selected interatomic distances and angles is given in Table VI. The parameters for the $ZnCl_4^{2-}$ anion compare favorably with those in other structures.[17] However, the C-C and C-N distances in the five-membered chelate ring of the cation are anomalous although the Ni-N distances and N-Ni-N angles appear quite reasonable. The unusual appearance of the thermal ellipsoids for the carbon atoms indicates that there is some type of disorder associated with the chelate rings but which apparently does not greatly affect the nitrogen atoms. No attempt has been made to develop a model for the disorder as the primary aim of this structure determination was to establish the stereochemistry of the nitrogen donor set.

Table VI. Interatomic Distances (Å) and Angles (deg) for $[Ni(C_{10}H_{24}N_4)]ZnCl_4$

Interatomic Distances (σ)			
Zn–Cl1	2.254 (0.002)	Zn–Cl2	2.277 (0.002)
Ni–N1	1.896 (0.009)	Ni–N2	1.937 (0.008)
N1–C1	1.477 (0.015)	N1–C5	1.595 (0.014)
N2–C3	1.436 (0.015)	N2–C4	1.556 (0.017)
C1–C2	1.351 (0.022)	C2–C3	1.458 (0.022)
C4–C4	1.697 (0.042)	C5–C5	1.606 (0.028)
Angles (σ)			
Cl2–Zn–Cl1	107.8 (0.1)	Cl1–Zn–Cl1	110.3 (0.2)
Cl2–Zn–Cl2	113.7 (0.1)	N2–Ni–N1	90.5 (0.3)
C1–N1–Ni	114.3 (0.7)	C5–N1–Ni	109.2 (0.6)
C5–N1–C1	115.6 (1.0)	N1–Ni–N1	89.4 (0.5)
C3–N2–Ni	115.1 (0.7)	C4–N2–Ni	107.9 (0.7)
C4–N2–C3	110.2 (1.2)	N2–Ni–N2	90.1 (0.6)
C2–C1–N1	115.5 (1.5)	C3–C2–C1	114.6 (1.4)
C2–C3–N2	115.1 (1.3)		

Discussion of the Structural Results. The thermodynamically most stable diastereoisomer of both six-coordinate and four-coordinate nickel(II)–cyclam complexes (or other complexes having M-N distances in the range of ca. 1.9–2.1 Å) is the trans-III or *RRSS* isomer.[18] This isomer has both six-membered chelate rings in the chair form and both five-membered chelate rings in the gauche form and as a result has the lowest strain energy of the five possible planar isomers. The trans-V or *RRRR* diastereomer has a considerably higher strain energy and is unlikely to occur except under conditions of kinetic control. Of the five diastereomers, only the *RRRR* form should fold to produce a cis complex without an increase in ring strain and/or nonbonding interactions. Molecular mechanics calculations suggest that a six-coordinate cis-*RRRR* form should be comparable in stability to that of the six-coordinate, trans-*RRSS* isomer for M-N distances >ca. 2.09 Å.[18c] In this context it is interesting that the Ni-N distances in the *cis*-$[Ni(C_{10}H_{24}N_4)(OH_2)_2]^{2+}$ cation average 2.1 Å. The cis-diaqua complex is the predominant form that exists in aqueous solution except in the presence of high concentrations of perchlorate.[14] Approximately the same bonding interactions would be present in a trans-diaqua *RRRR* complex so that it is likely that the conversion to a cis complex is a result of a reduction in ligand strain energy.

Thermodynamic Measurements. The primary thermochemical data listed in Table VIIA were obtained from microcalorimetric measurements or from the temperature dependence of the blue to yellow equilibrium shown in eq 1. The conditions of the

$$\textit{cis-RRRR}\text{-}[Ni(cyclam)(H_2O)_2]^{2+} \overset{K}{\rightleftharpoons} \textit{trans-RRRR}\text{-}[Ni(cyclam)]^{2+} + 2H_2O \quad (1)$$

measurements were guided by information from previous kinetic studies.[13] (i) The *RRSS* complex, upon dissolution in water, yields a solution containing 71% yellow species (planar, low-spin *RRSS* isomer) and 29% blue species (octahedral, high-spin trans-*RRSS* diaqua isomer).[20] By combining the heat of dissolution of *RRSS*-[Ni(cyclam)]$(ClO_4)_2$ with the heat of blue-to-yellow interconversion ($\Delta H° = 5.4$ kcal mol^{-1}),[20] we obtain the heat of

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(17) For some representative examples of recently determined structures of compounds that contain the $ZnCl_4^{2-}$ anion see: Kubiak, M.; Głowiak, T. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1984**, *C40*, 2039. Zuniga, F. J.; Chapuis, G. *Acta Crystallogr., Sect. B: Struct. Sci.* **1983**, *B39*, 620. Borne, P. E.; Taylor, M. R. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1983**, *C39*, 430. Secco, A. S.; Trotter, J. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1983**, *C39*, 317. Bombieri, G.; Forsellini, E.; Del Pra, A.; Tobe, M. L. *Inorg. Chim. Acta* **1981**, *51*, 177. Bombieri, G.; Benetollo, F.; Del Pra, A.; Tobe, M. L.; House, D. A. *Inorg. Chim. Acta* **1981**, *50*, 89. Bloomquist, D. R.; Willett, R. D. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1981**, *B37*, 1353.

(18) In addition to the conclusions drawn in ref 3 a variety of other studies have reached similar ones. For examples see: (a) Whimp, P. O.; Bailey, M. F.; Curtis, N. F. *J. Chem. Soc. A* **1970**, 1956. (b) DeHayes, L. J. Ph.D. Thesis, The Ohio State University, 1972. (c) Thom, V. J.; Fox, C. C.; Boeyens, J. C. A.; Hancock, R. D. *J. Am. Chem. Soc.* **1984**, *106*, 5947.

(19) Billo, E. J. *Inorg. Chem.* **1984**, *23*, 2223.

(20) Anichini, A.; Fabbrizzi, L.; Paoletti, P.; Clay, R. M. *Inorg. Chim. Acta Lett.* **1977**, *24*, 21.

Table VII

(A) Microcalorimetric Data for the Dissolution of Solid Complexes[a,b]

complex	pH	final composition	ΔH_{diss}, kcal mol^{-1}
RRSS-[Ni(cyclam)](ClO$_4$)$_2$	3 or 10	71% yellow, 29% blue	9.46 ± 0.07
RRRR-[Ni(cyclam)](ClO$_4$)$_2$	3	100% cis	4.80 ± 0.08
RRRR-[Ni(cyclam)](ClO$_4$)$_2$	10	71% yellow, 29% blue	5.98 ± 0.08

(B) Spectrophotometric Data for High-Spin–Low-Spin Interconversion of [Ni(cyclam)]$^{2+}$ Complexes[a]

reacn	pH	ionic strength	$\Delta G°$, kcal mol^{-1}	$\Delta H°$, kcal mol^{-1}	$\Delta S°$, cal K^{-1} mol^{-1}
trans-*RRSS* → *RRSS*[c]		0.1	−0.53	5.4	20
cis-*RRRR* → *RRRR*	3	0.1	3.1 ± 0.1	3.2 ± 0.3	0.5 ± 0.5
cis-*RRRR* → *RRRR*	3	5.0	1.2 ± 0.1	2.6 ± 0.04	4.6 ± 0.1

[a] 25 °C. [b] 0.10 M NaClO$_4$. [c] Reference 20.

dissolution of *RRSS*-[Ni(cyclam)](ClO$_4$)$_2$ to give a solution either completely yellow or completely blue: $\Delta H°$ = 11.1 ± 0.1 kcal mol^{-1} (100% yellow) and $\Delta H°$ = 5.7 ± 0.1 kcal mol^{-1} (100% blue). (ii) The *RRRR* complex, upon dissolution in water, yields a solution essentially completely *cis-RRRR*-[Ni(cyclam)(H$_2$O)$_2$]$^{2+}$. The rate of cis-*RRRR* to trans-*RRSS* isomerization was determined previously; the reaction is acid- and base-catalyzed and has a rate minimum at pH 3, where the half-life of isomerization is approximately 250 days. Thus, microcalorimetric measurement at pH 3 provides the enthalpy change for the conversion

$$RRRR\text{-[Ni(cyclam)](ClO}_4)_2\text{(s)} \rightarrow cis\text{-}RRRR\text{-[Ni(cyclam)(H}_2\text{O)}_2]^{2+}\text{(aq)} + 2\text{ClO}_4\text{(aq)}$$

At pH 10 the isomerization reaction is rapid (half-life approximately 7 s) and the enthalpy change determined is

$$RRRR\text{-[Ni(cyclam)](ClO}_4)_2\text{(s)} \rightarrow RRSS\text{-[Ni(cyclam)]}^{2+}\text{(aq)} + 2\text{ClO}_4^-\text{(aq)}$$
$$\text{71\% yellow/29\% blue}$$

By calculations similar to those done in (i) above, we obtain the heat of dissolution of *RRRR*-[Ni(cyclam)](ClO$_4$)$_2$: $\Delta H°$ = 7.6 ± 0.1 kcal mol^{-1} to give 100% yellow species and 2.2 ± 0.1 kcal mol^{-1} to give 100% blue species. From these results we obtain a value of −3.5 ± 0.2 kcal mol^{-1} for the interconversion from *RRRR*-[Ni(cyclam)](ClO$_4$)$_2$ to *RRSS*-[Ni(cyclam)](ClO$_4$)$_2$ in the solid state and a value of −2.6 ± 0.2 kcal mol^{-1} for the interconversion from *cis-RRRR*-[Ni(cyclam)(H$_2$O)$_2$]$^{2+}$ to *trans-RRSS*-[Ni(cyclam)(H$_2$O)$_2$]$^{2+}$ in solution. (iii) The $\Delta G°$, $\Delta H°$, and $\Delta S°$ values for the interconversion of the *cis-RRRR* diaqua complex to the planar *RRRR* complex were determined spectrophotometrically. Except in solutions of relatively high perchlorate concentration, the solutions contain only small proportions of the low-spin complex, and the absorbance changes upon an increase of the temperature are small. In addition, the measurement is complicated by the slow isomerization of the *RRRR* complex to the thermodynamically more stable *RRSS* isomer. In order to minimize isomerization, the temperature range spanned was small and the experimental data were acquired in a short time period; both of these factors tend to make the error limits of the measurements larger. The $\Delta H°$ and $\Delta S°$ values were determined at 5 M NaClO$_4$ and at 0.1 M NaClO$_4$; the results are shown in Table VIIB, with, for comparison, the corresponding values for the *RRSS* form. The thermodynamic data are summarized in Figure 4.

The $\Delta H°$ and $\Delta S°$ values for the high-spin–low-spin interconversion (eq 1) are in agreement with the few values recorded for similar interconversions where the high-spin complex is known, from structural or spectral information, to be in the cis geometry (Table VIII).

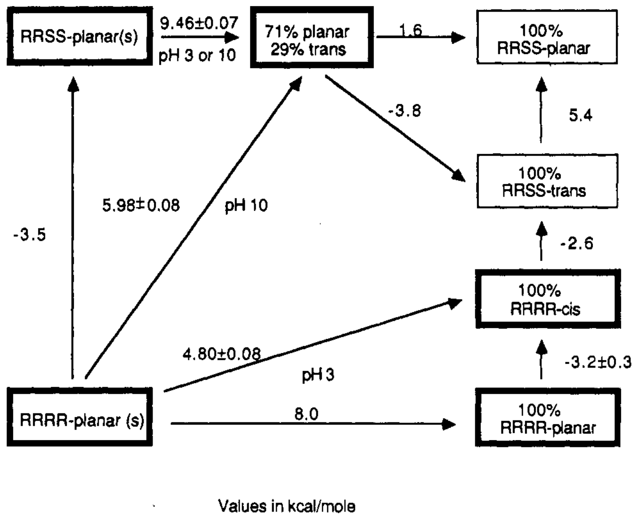

Figure 4. Thermochemical cycle for *RRRR* and *RRSS* isomers of nickel(II)–cyclam. The heavy boxes indicate species studied in the present work. Solid complexes are anhydrous perchlorates.

Table VIII. Thermodynamic Functions for the High-Spin–Low-Spin Interconversion of Some *cis*-Diaquanickel(II) Complexes with Tetraaza Ligands[a]

complex	ionic strength	$\Delta G°$, kcal mol^{-1}	$\Delta H°$, kcal mol^{-1}	$\Delta S°$, cal K^{-1} mol^{-1}
[Ni(tren)]$^{2+}$[b]	0.10	2.6	3.3	2.7
[Ni(12aneN$_4$)]$^{2+}$[c]	0.10	3.4	5.8 ± 0.2	8.1 ± 0.6
[Ni(12aneN$_4$)]$^{2+}$[c]	4.0	1.3	3.3 ± 0.1	6.7 ± 0.2
[Ni(12aneN$_4$)]$^{2+}$[d]	5.0	0.0	1.7	5.5
cis-[Ni(2,3,2-tet)]$^{2+}$[e]	0.10	0.4	3.1	9
cis-[Ni(cyclam)]$^{2+}$[f]	0.10	3.1 ± 0.1	3.2 ± 0.3	0.5 ± 0.5
cis-[Ni(cyclam)]$^{2+}$[f]	5.0	1.2 ± 0.1	2.6 ± 0.4	4.6 ± 0.1

[a] 25 °C. [b] Reference 22. [c] Coates, J. H.; Hadi, D. A.; Lincoln, S. F.; Dodgen, H. W.; Hunt, J. P. *Inorg. Chem.* **1981**, *20*, 707. [d] Plassman, W. H.; Swisher, R. G.; Blinn, E. L. *Inorg. Chem.* **1980**, *19*, 1101. [e] Calculated from ref 23. [f] This work.

Early studies of the thermodynamics of the high-spin–low-spin interconversion of nickel(II) complexes of tetraaza ligands assumed (implicitly) a trans-diaqua geometry for the high-spin complex. Both Fabbrizzi[21] and Margerum[22] estimated the entropy change for release of the two coordinated water molecules to be ca. 15–20 cal K^{-1} mol^{-1}. Yet for several nickel(II) complexes studied by these and other investigators, $\Delta S°$ was found to be significantly lower; for example, for Ni(2,3,2-tet)$^{2+}$, $\Delta S°$ was found to be 9 cal K^{-1} mol^{-1}.[22] It was suggested that for these complexes there was incomplete release of the water molecules. However, Vitiello and Billo[23] showed that the octahedral component of the 2,3,2-tet equilibrium contains both cis and trans isomers and that when the cis–trans and trans–planar equilibria are separately evaluated, the $\Delta S°$ value for the trans–planar equilibrium falls within the predicted range of 15–20 cal K^{-1} mol^{-1}.

The cis complexes in Table VIII have $\Delta S°$ values much lower than the 15–20 cal K^{-1} mol^{-1} observed for trans-diaqua complexes.

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(21) Sabatini, L.; Fabbrizzi, L. *Inorg. Chem.* **1979**, *18*, 438.

(22) Hinz, F. P.; Margerum, D. W. *Inorg. Chem.* **1974**, *13*, 2941.

(23) Vitiello, J. D.; Billo, E. J. *Inorg. Chem.* **1980**, *19*, 3477.

Table IX

(A) Thermodynamic Functions for Interconversion Reactions[a]

equilibrium	ΔG°, kcal mol^{-1}	ΔH°, kcal mol^{-1}	ΔS°, cal K^{-1} mol^{-1}
RRRR-planar(aq) → *RRSS*-planar(aq)	−5.3	−0.4	16.4
RRRR-planar(aq) → *trans-RRSS*-diaqua(aq)	−4.8	−5.8	−3.4
cis-RRRR-diaqua(aq) → *trans-RRSS*-diaqua(aq)	−1.7[b]	−2.6	−3.0

(B) Thermodynamic Functions for the Reactions of Formation of the Isomers of [Ni(cyclam)]$^{2+}$(aq) in Water Solution[a]

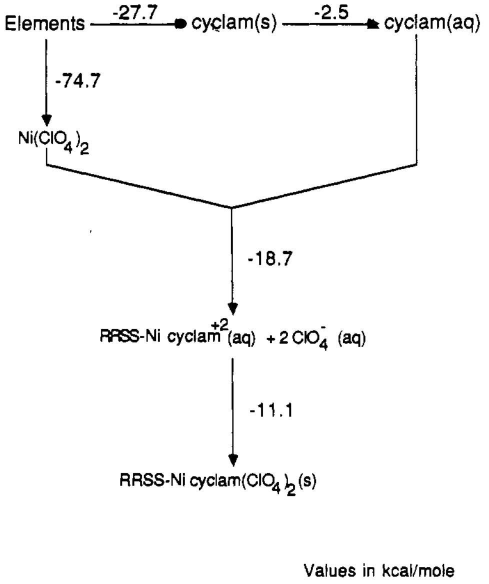
reacn	ΔG°, kcal mol^{-1}	ΔH°, kcal mol^{-1}	ΔS°, cal K^{-1} mol^{-1}
Ni^{2+}(aq) + cyclam(aq) → *RRSS*-planar(aq)	−30.1	−18.7	38.2
Ni^{2+}(aq) + cyclam(aq) → *trans-RRSS*-diaqua(aq)	−29.6	−24.1	18.4
Ni^{2+}(aq) + cyclam(aq) → *cis-RRRR*-diaqua(aq)	−27.9	−21.5	21.5
Ni^{2+}(aq) + cyclam(aq) → *RRRR*-planar(aq)	−24.8	−18.3	21.8

[a] 25 °C, 0.10 M $NaClO_4$. [b] Calculated from ref 19.

The cis–planar interconversion is composite, consisting of cis–trans isomerization and trans–planar interconversion. The overall entropy change for cis–planar interconversion appears to fall in the range 0–9 cal K^{-1} mol^{-1}. The decrease in ΔH with increasing ionic strength, observed in other cases, is seen here also.

From the thermochemical cycle of Figure 4 we calculate the overall ΔH° for the isomerization *RRRR*-planar → *RRSS*-planar, for which we obtain $\Delta H^\circ = -0.4 \pm 0.2$ kcal mol^{-1}. This value, corresponding to the inversion of two six-membered rings from twist-boat to chair conformation, is significantly smaller than the approximately −7 kcal mol^{-1} predicted by the suggestion of Whimp, Bailey, and Curtis,[24] who assumed energies of 3.5 kcal mol^{-1} for each six-membered ring in a twist-boat conformation and 2.0 kcal mol^{-1} for each five-membered ring in a strained asymmetrical gauche conformation, relative to the more stable chair and symmetrical gauche conformations. However, we note that Hambley,[25] by molecular mecanics calculations, obtained for the four-coordinate nickel(II)–tetramethylcyclam complexes the following strain energies: 131.3 kJ mol^{-1} (31.4 kcal mol^{-1}) for the *RSRS* isomer, 135.0 kJ mol^{-1} (32.3 kcal mol^{-1}) for the *RSRR* isomer, and 141.7 kJ mol^{-1} (33.9 kcal mol^{-1}) for the *RRSS* isomer. Using the data for the *RSRS* and *RSRR* isomers, we estimate a value of 138.7 kJ mol^{-1} (33.2 kcal mol^{-1}) for the strain energy of the *RRRR* isomer. On this basis we conclude that for the four-coordinate nickel(II)–tetramethylcyclam complex the *RRRR* isomer is more stable than the *RRSS* isomer by 0.7 kcal mol^{-1}. We expect a somewhat smaller energy difference in the unsubstituted macrocycle, and in view of the rather large experimental errors, our value is not unreasonable. This reaction is driven by a favorable entropic contribution ($\Delta S^\circ = 16.4$ cal K^{-1} mol^{-1}; Table IXA), which is too large to be explained only in terms of different values of internal entropy in the *RRRR*-planar and *RRSS*-planar species, but which gives strong evidence of different solute–solvent interactions. The *RRRR*-planar complex seems to be more strongly solvent organizing and interacting than does the *RRSS*-planar, to such a point that the entropic contribution to its formation is equal to that for the formation of the cis-diaqua complex (Table IXB), in which two molecules of water are retained. In the folded complex, the two nitrogen atoms N4 and N11 (see Figure 2) have hydrogen atoms directed toward one another, presumably decreasing solvation through hydrogen bonding and thus resulting in a liberation of water molecules relative to the planar complex. This entropic effect compensates that due to the addition of two molecules of water in cis positions.

With the value of the heat of solution of *RRSS*-[Ni(cyclam)]$(ClO_4)_2$ ($\Delta H^\circ = 11.1$ kcal mol^{-1}; see thermochemical cycle) and the enthalpy changes related to its formation from the elements in their standard state[26] it is possible to calculate the enthalpy of formation of the solid *RRSS*-[Ni(cyclam)]$(ClO_4)_2$ ($\Delta H^\circ = -134.7$ kcal mol^{-1}) according to the cycle



For *RRRR*-[Ni(cyclam)]$(ClO_4)_2$(s) the value is −131.2 kcal mol^{-1}.

Unfortunately data of this type are very scanty, and at this time there is no possibility for a useful comparison.

Registry No. *cis-RRRR*-[Ni(cyclam)$(OH_2)_2$]Cl_2·$2H_2O$, 104194-92-5; *RRRR*-[Ni(cyclam)]$ZnCl_4$, 104319-04-2; *RRRR*-[Ni(cyclam)]$(ClO_4)_2$, 104319-05-3; *RRSS*-[Ni(cyclam)]$(ClO_4)_2$, 57456-82-3; *cis-RRRR*-[Ni(cyclam)$(H_2O)_2$]$^{2+}$, 78684-35-2; *trans-RRSS*-[Ni(cyclam)$(H_2O)_2$]$^{2+}$, 64616-26-8.

Supplementary Material Available: Tables of anisotropic thermal parameters for non-hydrogen atoms and positional and isotropic parameters for hydrogen atoms (4 pages); tables of calculated and observed structure factors (26 pages). Ordering information is given on any current masthead page.

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[24] Whimp, P. O.; Bailey, M. F.; Curtis, N. F. *J. Chem. Soc. A* **1970**, 1956.

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[26] (a) Clay, R. M.; Micheloni, M.; Paoletti, P.; Steel, W. V. *J. Am. Chem. Soc.* **1979**, *101*, 4119. (b) *NBS Tech. Note (U.S.)* **1969**, *No. 270-4*, 45. (c) Fabbrizzi, L.; Paoletti, P.; Clay, R. M. *Inorg. Chem.* **1978**, *17*, 1042.