decomposition of $[(NH_3)_5Co(OClO)]^{2+}$ may reflect the smaller Franck–Condon barrier associated with the cobalt(III) center containing only monodentate ligands.[29,30] Finally, the observed ΔS^* values for the three IET reactions fall within a narrow range (3–15 eu) which indicates only little solvent reorganization in the transition state, a result which is entirely in harmony with intramolecular electron transfer.

Acknowledgment. Financial support by the National Science Foundation, Grant No. CHE 79-26497, is gratefully acknowledged. We also thank Mr. Robert Whittle for conducting the cobalt(II) experiments.

Registry No. $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$, 42901-32-6.

---

(30) Orgel, L. E. Report of the Tenth Solvay Conference, Brussels, Belguim, 1956.

Contribution from the Department of Chemistry,
Boston College, Chestnut Hill, Massachusetts 02167

Preparation and Kinetics of Isomerization of *cis*-Ni(cyclam)$(H_2O)_2^{2+}$

E. J. Billo

Received December 17, 1980

Complexes of macrocyclic tetraaza ligands commonly exhibit tetragonal stereochemistry with the four nitrogen atoms in the equatorial plane. The in-plane ligand field provided by the four nitrogen donors of the 14-membered-ring saturated macrocycle cyclam ([14]aneN_4, 1,4,8,11-tetraazacyclotetradecane) is sufficiently strong to stabilize low-spin nickel(II). The electronic spectrum of Ni(cyclam)$^{2+}$ exhibits a single band at 22 400 cm^{-1} characteristic of square-planar diamagnetic nickel(II) complexes. Recently Fabbrizzi[1] demonstrated that dilute aqueous solutions of Ni(cyclam)$^{2+}$ also contain 29% of the octahedral species Ni(cyclam)$(H_2O)_2^{2+}$, presumably the trans isomer.

There are few exceptions to coplanar coordination by cyclam, although smaller macrocycles tend to adopt the folded configuration upon coordination to nickel(II).[2] (Both cis and trans isomers of cyclam complexes of cobalt(III),[3] rhodium(III),[4] and ruthenium(III)[5] have been isolated.) The present paper describes the facile conversion of Ni(cyclam)$^{2+}$ to *cis*-Ni(cyclam)$(H_2O)_2^{2+}$ and reports some of its equilibrium and kinetic properties. In acidic solution, the cis isomer isomerizes to the trans isomer extremely slowly; the half-life at pH 3 is approximately 250 days.

Experimental Section

***cis*-Ni(cyclam)(en)$(ClO_4)_2$.** Ethylenediamine was added to an aqueous solution of Ni(cyclam)$(ClO_4)_2$ (e.g., 4 mM Ni(cyclam)$^{2+}$, 20 mM en). Sodium perchlorate was added to the resulting violet solution, whereupon violet *cis*-Ni(cyclam)(en)$(ClO_4)_2$ precipitated. Anal. Calcd for $NiC_{12}H_{32}N_6Cl_2O_8$: C, 27.82; H, 6.23; N, 16.23. Found: C, 27.79; H, 6.07; N, 16.16. *Warning: Perchlorate salts of similar complexes are explosive; they are heat and pressure sensitive. Only small amounts of this complex should be prepared and should be handled with care.*

Table I. Electronic Spectral Data of Some Nickel(II) Polyamine Complexes in Aqueous Solution

complex	λ_{max} $(\epsilon)^a$			
Ni(cyclam)(en)$^{2+}$	880 (10.8)	800 (sh)	535 (8.4)	343 (13.6)
Ni(2,3,2-tet)(en)$^{2+\,b}$	880 (7.5)	800 (sh)	535 (7.0)	342 (10.9)
cis-Ni(cyclam)-$(H_2O)_2^{2+}$	890 (14)		548 (8.3)	348 (14)
cis-Ni(2,3,2-tet)-$(H_2O)_2^{2+\,c}$	900 (9.5)		550 (5.5)	345 (11)
trans-Ni(3,2,3-tet)-$(H_2O)_2^{2+\,b,d}$	800 (4), 745 (4)		550 (5)	350 (9)

[a] λ_{max} given in nm, ϵ in M^{-1} cm^{-1}. [b] Reference 9. [c] Reference 7. [d] Reference 8.

***cis*-Ni(cyclam)Br_2.** A suspension of Ni(cyclam)(en)$(ClO_4)_2$ in boiling methanol was acidified with concentrated HBr, yielding blue *cis*-Ni(cyclam)Br_2.

Kinetic Measurements. The cis to trans isomerization was followed at 450 nm (appearance of planar Ni(cyclam)$^{2+}$). The majority of the rate constants were determined by the initial rate method; an effective molar absorptivity of 50 M^{-1} cm^{-1} was used for Ni(cyclam)$^{2+}$ at $I = 0.1$, $NaClO_4$. The faster reactions were followed to completion, and rate constants were obtained from plots of ln $(A_\infty - A)$ vs. t. All rates were measured at 25 °C with $I = 0.1$, $NaClO_4$. Reaction pH was adjusted by the addition of perchloric acid (pH 1–3), 0.10 M boric acid (pH 5), 0.01 M borate buffer (pH 7–9), or sodium hydroxide (pH 10). There was no detectable rate enhancement caused by boric acid–borate buffer, but an experiment using acetic acid to obtain a pH near 3 resulted in relatively rapid (overnight) isomerization. Rates were measured beginning either with acidified solutions of Ni(cyclam)(en)$^{2+}$ or with solutions of Ni(cyclam)Br_2. Rates in basic solution were measured with use of only the latter complex. Hydronium and hydroxide ion concentrations were obtained from $-\log [H^+] = \text{pH} - 0.11$ and $\log K_w = -13.78$, for 25 °C and $I = 0.10$.

Results and Discussion

Addition of ethylenediamine to a yellow aqueous solution of Ni(cyclam)$^{2+}$ yields in a few minutes a violet solution from which Ni(cyclam)(en)$^{2+}$ can be isolated. Since en can only coordinate to cis positions, the cyclam ligand must adopt the folded configuration (*cis*-β).[6] Acidification of the violet solution to, e.g., pH 3 yields a blue-violet solution of *cis*-Ni(cyclam)$(H_2O)_2^{2+}$ (eq 1). The spectrum of this complex is

$$cis\text{-Ni(cyclam)(en)}^{2+} + 2H_3O^+ \rightarrow cis\text{-Ni(cyclam)}(H_2O)_2^{2+} + H_2en^{2+} \quad (1)$$

typical of *cis*-$Ni^{II}N_4O_2$ (see Table I). The ν_1 band in the near-infrared spectrum is diagnostic of cis or trans coordination.[7,8] Solutions of *cis*-Ni(cyclam)Br_2 in water have identical spectra with those of acidified *cis*-Ni(cyclam)(en)$^{2+}$.

Violet solutions of *cis*-Ni(cyclam)$(H_2O)_2^{2+}$ isomerize slowly to yellow Ni(cyclam)$^{2+}$. In contrast, addition of ammonia also produces a violet octahedral complex, but the yellow color of Ni(cyclam)$^{2+}$ is regenerated immediately upon acidification; the ligand has remained in the planar configuration.

Depending on the concentration of en added, a small amount of planar Ni(cyclam)$^{2+}$ remains. Spectrophotometric measurements at 450 nm were used to determine the equilibrium constant for reaction 2. Because of the very low solubility

$$\text{Ni(cyclam)}^{2+} + \text{en} \rightleftharpoons \text{Ni(cyclam)(en)}^{2+} \quad (2)$$

of the mixed-ligand complex in the presence of appreciable

---

(1) Fabbrizzi, L. *Inorg. Chim. Acta* **1977**, *24*, L21–L23.
(2) Fabbrizzi, L. *Inorg. Chem.* **1977**, *16*, 2667–2668.
(3) Bosnich, B.; Poon, C. K.; Tobe, M. L. *Inorg. Chem.* **1965**, *4*, 1102–1108.
(4) Hay, R. W.; Norman, P. R. *J. Chem. Soc. Dalton Trans.* **1979**, 1441–1445.
(5) Isied, S. S. *Inorg. Chem.* **1980**, *19*, 911–914.
(6) Hawkins, C. M. "Absolute Configuration of Metal Complexes"; Wiley-Interscience: New York, 1971; p 5.
(7) Vitiello, J. D.; Billo, E. J. *Inorg. Chem.* **1980**, *19*, 3477–3481.
(8) Cook D. F.; McKenzie, E. D. *Inorg. Chim. Acta* **1978**, *31*, 59–68.
(9) Spetnagel, W. J. Ph.D. Dissertation, New Mexico State University, 1973.

0020-1669/81/1320-4019$01.25/0

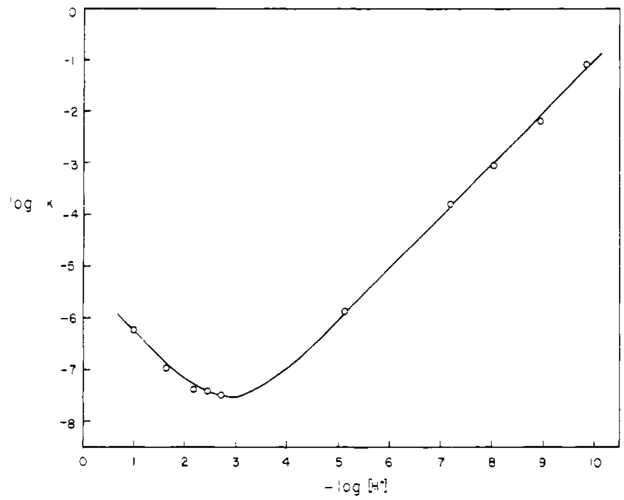

Figure 1. Hydrogen ion dependence of the observed rate of cis–trans isomerization of *cis*-$Ni(cyclam)(H_2O)_2^{2+}$ (T = 25 °C, $[ClO_4^-]$ = 0.1 M).

concentrations of perchlorate ion, the equilibrium constant was determined without the usual background electrolyte. A value of log K for eq 2 of 2.6 ± 0.1 was obtained.

The K value for reaction of en with $Ni(cyclam)^{2+}$ is much smaller than for en reacting with either $Ni(en)_2(H_2O)_2^{2+}$ (log K = 4.3)[10] or with $Ni(trien)(H_2O)_2^{2+}$ (log K = 5.3 ± 0.1).[7] The latter complex is nearly 100% cis and thus provides a model for reaction of en with a *cis*-tetramine complex. In the absence of interligand repulsions, a lower stability constant for en binding is indicative of the extent of trans isomer. We used the decrease in log K for en binding to $Ni(2,3,2\text{-tet})(H_2O)_2^{2+}$ to calculate the fraction of cis isomer[7] and found excellent agreement with the equilibrium constant determined by an independent method. The fraction of the complex in the form of the cis isomer is given by $\alpha_{cis} = K_{NiLen}/K_{Ni(trien)(en)}$; for L = cyclam, $\alpha_{cis} = 10^{-2.7}$. This value, less than 1% in the cis form, must be taken as a lower limit since interligand repulsions may be important in the case of the macrocyclic ligand. However, there is good agreement in the case of the nickel(II) complex of 3,2,3-tet between the fraction of cis form estimated from the binding constant of en (approximately 3%)[11] and from an independent spectrophotometric method (less than 5%).[8] Interligand steric interactions should be similar for en reacting with *cis*-$Ni(cyclam)(H_2O)_2^{2+}$ and *cis*-$Ni(3,2,3\text{-tet})(H_2O)_2^{2+}$.

Cis–Trans Isomerization. The isomerization of *cis*-$Ni(cyclam)(H_2O)_2^{2+}$ to *trans*-$Ni(cyclam)(H_2O)_2^{2+}$ was determined over the pH range 1–10. The trans isomer is in rapid equilibrium with planar $Ni(cyclam)^{2+}$, and the appearance of the latter was monitored at 450 nm. The pH profile of the reaction is shown in Figure 1. In acid solution the reaction is acid catalyzed, reaching a minimum at pH values around 3. At this pH the half-life for isomerization is approximately 250 days at 25 °C. The reaction is base catalyzed from pH 4 to at least pH 10. The rate data from pH 5 to 10 describe a straight line (log k vs. $-\log [H^+]$) with least-squares slope of 0.99 ± 0.03. The rate law for isomerization is eq 3; the rate constants are listed in Table II.

$$k_{obsd} = k_0 + k_H[H_3O^+] + k_{OH}[OH^-] \qquad (3)$$

A similar pH profile was observed in the cis–trans isomerization of $Ni(2,3,2\text{-tet})^{2+}$, although the reactions were relatively much faster. The acid-catalyzed and pH-independent

Table II. Rate Constants for the Cis–Trans Isomerization of *cis*-$Ni(cyclam)(H_2O)_2^{2+}$ and *cis*-$Ni(2,3,2\text{-tet})(H_2O)_2^{2+}$ [a]

	cis-Ni(cyclam)-$(H_2O)_2^{2+}$	*cis*-Ni(2,3,2-tet)-$(H_2O)_2^{2+}$ [b]
k_0	1.5×10^{-8}	1.1×10^{-4}
k_H, $M^{-1}\,s^{-1}$	5.8×10^{-6}	1.9×10^{3}
k_{OH}, $M^{-1}\,s^{-1}$	560	450

[a] 25 °C, I = 0.10 ($NaClO_4$). [b] Reference 7.

isomerization rates of *cis*-$Ni(cyclam)(H_2O)_2^{2+}$ are much slower than the corresponding rates for *cis*-$Ni(2,3,2\text{-tet})(H_2O)_2^{2+}$. Surprisingly, however, the base-catalyzed rate constant is essentially identical for the two complexes.

Although the two complexes have similar pH profiles, it is unlikely that they have identical mechanisms, at least for acid-catalyzed isomerization. The mechanism suggested[7] for the acid isomerization of *cis*-$Ni(2,3,2\text{-tet})(H_2O)_2^{2+}$ involves dissociation of a terminal nitrogen donor and rapid proton equilibration of the amino group. Ring closure ultimately leads to the trans isomer. Similar proton dependence has also been observed in the dissociation of nickel(II) complexes of linear polyamines, in the pH region corresponding to the protonation constant of the free terminal amino group, i.e., around pH 7. At higher acidities, typically below pH 4, the free amino group is rapidly and completely protonated, the rate step then becoming the pH-independent rate of nickel–nitrogen bond breaking.

In the present case, however, dissociation of a coordinated nitrogen to form a complex in which cyclam is tridentate is unlikely. The cyclic structure of the ligand makes dissociation of a single nitrogen donor difficult. Margerum and coworkers[12] have suggested that the rate acceleration observed in the dissociation of some nickel(II) polyamine complexes at high acidities (≥0.1 M) arises from the association of a proton with the amino group, after the metal–nitrogen bond is broken but before solvation of the metal ion. This mechanism may be particularly applicable to complexes of relatively rigid ligands which cannot dissociate easily by the normal stepwise unwrapping mechanism. Zompa[13] proposed a similar mechanism for the acid dissociation of nickel(II) complexes of cyclic triamine ligands.

The base-catalyzed isomerization likely proceeds by an internal conjugate base mechanism, in which hydroxide ion deprotonates an amine and generates an intermediate which rearranges rapidly. This rearrangement, from the folded to the planar form, must involve inversion of nitrogen configuration if, as suggested by Bosnich, Poon, and Tobe,[3] the nitrogen configurations of the most stable forms of the folded and planar complexes are not the same.

Base-catalyzed isomerization is surprisingly rapid. In the pH range 8–10, the isomerization of the cyclam complex is as fast as that of the 2,3,2-tet complex. In contrast, the rate constant for pH-independent isomerization is 10^4 times slower in the case of the cyclic ligand. It is not clear why the base-catalyzed isomerization of the cyclam complex is so uncharacteristically rapid, whereas other rate processes involving the dissociation or rearrangement of complexes of macrocyclic ligands are slow.

cis-$Ni(cyclam)(H_2O)_2^{2+}$ is a likely intermediate of both formation and dissociation reactions of $Ni(cyclam)^{2+}$. The formation reaction would be expected to proceed by initial coordination of the ligand in a folded configuration, so as to permit sequential replacement of coordinated water molecules. In the case of Cu^{2+} + teta (teta = *rac*-5,7,7,12,14,14-hexa-

---

(10) Sillen, L. G., Martell, A. E., Eds. *Spec. Publ.—Chem. Soc.* **1964**, *No. 17*.

(11) Billo, E. J., unpublished results.

(12) Margerum, D. W.; Weatherburn, D. C.; Cayley, G.; Pagenkopf, G. K. *ACS Monogr.* **1978**, *No. 168*.

(13) Murphy, L. J., Jr.; Zompa, L. J. *Inorg. Chem.* **1979**, *18*, 3278–3281.

methyl-1,4,8,11-tetraazacyclotetradecane), an unstable complex containing teta in the folded configuration is initially formed and slowly converts to a planar red complex.[14]

In a kinetic study by Kaden[15] of the formation of Ni(cyclam)$^{2+}$, no intermediates were reported. The rate of formation was second order, first order in nickel ion and first order in cyclam. In order for an intermediate such as *cis*-Ni(cyclam)$(H_2O)_2^{2+}$ to be undetected, the rate of isomerization of the folded complex to the planar form would have to be more rapid than the rate of formation. Although slow, the isomerization rates observed here are indeed faster than the rates of formation measured by Kaden. Thus it is possible that the formation of Ni(cyclam)$^{2+}$ proceeds through the proposed folded intermediate. In order for the intermediate to accumulate in detectable amount during the formation reaction, much higher concentrations of metal ion and of ligand would be necessary.

It is also expected that acid dissociation of Ni(cyclam)$^{2+}$ proceeds through a succession of folded intermediates, of which *cis*-Ni(cyclam)$(H_2O)_2^{2+}$ is the first. Linear polydentate ligands generally dissociate via a stepwise unwrapping mechanism; although this mechanism is not available for complexes of macrocyclic ligands, a comparable mechanism would begin with the folding of the planar macrocycle. It is unlikely that the folded isomer could be detected in the acid dissociation of Ni(cyclam)$^{2+}$, an extremely slow process.[16]

Registry No. *cis*-Ni(cyclam)(en)$(ClO_4)_2$, 78638-51-4; *cis*-Ni(cyclam)Br_2, 78684-34-1; Ni(cyclam)$(ClO_4)_2$, 15220-72-1; *cis*-Ni(cyclam)$(H_2O)_2^{2+}$, 78684-35-2.

---

(14) Cabbiness, D. K.; Margerum, D. W. *J. Am. Chem. Soc.* **1969**, *91*, 6540–6541.
(15) Kaden, T. *Helv. Chim. Acta* **1970**, *53*, 617–622.
(16) Busch, D. H. *Acc. Chem. Res.* **1978**, *11*, 392–400.

Contribution from the Department of Chemistry,
Stanford University, Stanford, California 94305

(4-Aminopyridine)pentaammineruthenium(II) and -(III)

James E. Sutton and Henry Taube*

Received January 20, 1981

The investigations of binuclear bis(pentaammineruthenium) complexes bridged by ligands of the 4,4′-dipyridyl type revealed that the properties of the 4,4′-dipyridylamine analogue were in certain respects distinctly different from those of the other complexes in the series.[1] These differences included a greater instability toward aquation for the fully reduced complex and the appearance of a new electronic transition in the visible region of the spectrum for the fully oxidized complex.

This study was undertaken to gain further insight into these differences. Absorption characteristics of (4-aminopyridine)pentaammineruthenium(II) and -(III) and the aquation kinetics of the reduced form as a function of the acidity of the medium used are reported here.

Experimental Section

Materials. 4-Aminopyridine was purchased from Aldrich, ammonium hexafluorophosphate from Ozark-Mahoning, and hexaammineruthenium chloride from Matthey-Bishop, all used without further purification. Europium(III) oxide was obtained from Research Chemicals and reduced to Eu(II) in acidic medium with use of zinc amalgam.

Table I. Absorption Maxima in the UV-Visible Spectra of (4-Aminopyridine)pentaammineruthenium(II) and -(III)[a]

Ru(II)		Ru(III)	
λ, nm	log ε	λ, nm	log ε
239	3.95	253	4.05
359	3.78	321	3.68
388	sh[b]	505	3.51

[a] Obtained in pH pH 8 phosphate buffer. Ru(II) complex prepared by reduction of the Ru(III) complex with Eu^{2+}. [b] sh = shoulder.

Argon (99.995%) and chlorine gases were purchased from Liquid Carbonic. The argon was freed of oxygen by passing it through a scrubbing tower charged with 0.25 M chromium(II) in 0.5 M perchloric acid over zinc amalgam. The chlorine was used as supplied.

House line distilled water was purified by redistillation from alkaline permanganate in an all-glass still.

Ruthenium Complexes. The hexaammineruthenium chloride was converted to chloropentaamminerutheniun(III) chloride by following the literature procedure.[2]

(4-Aminopyridine)pentaammineruthenium(III) Hexafluorophosphate. A 100-mg sample of finely powdered $[Ru(NH_3)_5Cl]Cl_2$ was suspended in 5 mL of water and purged with argon before reducing over zinc amalgam for 1 h. Excess 4-aminopyridine was added and allowed to react for 15 min before oxidizing the product by bubbling chlorine gas through the solution. A crude sample was precipitated by adding the solution to 150 mL of rapidly stirred acetone. The solid was collected and redissolved in 10 mL of water, and solid NH_4PF_6 was added to bring $[PF_6^-]$ to about 5 M. The resulting solution was stored in the refrigerator overnight, producing purple crystals, which were filtered, washed with ethanol and ether, and dried in a vacuum desiccator; yield 85 mg (35%). Anal. Calcd for $[Ru(NH_3)_5(4\text{-}NH_2py)](PF_6)_3$: C, 8.39; H, 2.96; N, 13.71. Found: C, 8.30; H, 3.26; N, 13.79.[3]

Instrumentation. Electronic Spectra. Spectra in the ultraviolet and visible regions were recorded with use of matched quartz cells in a Beckman Model 5270 spectrophotometer.

Electrochemistry. Electrochemical measurements were made on a Princeton Applied Research Model 173 potentiostat and Model 175 universal programmer system. Formal potentials ($E_{1/2}$) were measured by cyclic voltammetry using a carbon-paste electrode. Carbon paste was purchased from Bio-Rad, Inc., packed into the cavity of a Teflon plug fitted with a copper wire to form a lead, and held in a glass tube. Potentials were measured against a saturated calomel electrode (SCE, Beckman Model 39190) at 20 °C and are uncorrected for junction potentials. They were corrected to the hydrogen scale by adding 0.244 V. The voltammetric measurements were made in a standard H-cell with the test solution compartment separated from the reference electrode compartment by a fine-porosity glass frit. A platinum wire was used as an auxiliary electrode.

Temperature Control. Constant temperatures (±0.2 °C) were maintained with a Haake Model FK2 constant-temperature bath connected to a thermostated cell holder in the spectrophotometer. The temperature of the cell was monitored with a Digitic Model 5810 digital thermometer.

Kinetics. The rate of aquation of (4-aminopyridine)pentaammineruthenium(II) to produce the corresponding aquopentaammine ion was followed spectrophotometrically by monitoring the disappearance of the visible transition of the rutheniun(II) complex associated with coordination of 4-aminopyridine.

A solution of the corresponding ruthenium(III) complex was prepared in the appropriate concentration of hydrochloric acid (ionic strength adjusted to 2 M with NaCl), placed in a spectrophotometer cell, degassed, and allowed to equilibrate thermally in the spectrophotometer. Ruthenium(III) was reduced to ruthenium(II) by syringing a stoichiometric amount of europous ion into the cell. The absorbance was then monitored at a fixed wavelength as a function of time. The data were plotted as log $(A_t - A_\infty)$ vs. time where A_t and A_∞ represent the absorbances at time t and at completion of the reaction, respectively. These plots were linear over at least 4 half-lives,

---

(1) Sutton, J. E.; Taube, H. *Inorg. Chem.* **1981**, *20*, 3125.
(2) Vogt, L.; Katz, J.; Wiberly, S. *Inorg. Chem.* **1965**, *4*, 1157.
(3) Microanalysis performed by the Stanford Microanalytical Laboratory.
(4) Shepherd, R. E.; Taube, H. *Inorg. Chem.* **1973**, *12*, 1392.

0020-1669/81/1320-4021$01.25/0